# Investigations on 1,2-oxaphosphetane complexes

Dissertation

zur

Erlangung des Doktorgrades (Dr. rer. nat.)

der

Mathematisch-Naturwissenschaftlichen Fakultät

der

Rheinischen Friedrich-Wilhelms-Universität Bonn

vorgelegt von

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aus

Bonn

Bonn, 2017

Angefertigt mit Genehmigung der Mathematisch-Naturwissenschaftlichen Fakultät
der Rheinischen Friedrich-Wilhelms-Universität Bonn

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Tag der Promotion: 16.10.2017

Erscheinungsjahr: 2017

Der Unterschied zwischen Genie und Wahnsinn definiert sich lediglich aus dem Erfolg.

*James Bond 007 – Der Morgen stirbt nie*

Teilergebnisse aus dieser Arbeit wurden mit Genehmigung der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Bonn vorab veröffentlicht.

(1) “Synthesis of Li/OR phosphinidenoid complexes: on the evidence for intramolecular O-Li donation and the effect of cation encapsulation” R. Streubel, A. W. Kyri, L. Duan, G. Schnakenburg, *Dalton Trans.* **2014**, 43, 2088 - 2097.

(2) “Synthesis and Reaction of the First 1,2-Oxaphosphetane Complexes“ A. W. Kyri, V. Nesterov, G. Schnakenburg, R. Streubel *Angew. Chem. Int. Ed.* **2014**, *53*, 10809 - 10812.

(3) “*C*-Trifluoromethyl-Substituted 1,2-Oxaphosphetane Complexes: Synthetic and Structural Study“ A. W. Kyri, G. Schnakenburg, R. Streubel, *Organometallics* **2016**, *35*, 563 - 568.

(4) “A novel route to C-unsubstituted 1,2-oxaphosphetane and 1,2-oxaphospholane complexes“ A. W. Kyri, G. Schnakenburg, R. Streubel, *Chem. Commun.* **2016**, *52*, 8593 - 8595.

(5) “Synthesis of a monomolecular anionic FLP complex” A. W. Kyri, R. Kunzmann, G. Schnakenburg, Z.–W. Qu, S. Grimme, R. Streubel, *Chem Commun.* **2016**, *52*, 13361 - 13364.

(6) “Synthesis and Deprotonation of Aminophosphane Complexes: First K/N(H)R Phosphinidenoid Complexes and Access to a Complex with a $P_2N$-Ring Ligand“ P. Kumar Majhi, A. W. Kyri, A. Schmer, G. Schnakenburg, R. Streubel, *Chem. Eur. J.* **2016**, *22*,15413 - 15419.

(7) “Ring opening of a sterically crowded 1,2-oxaphosphetane complex” A. W. Kyri, P. Brehm, G. Schnakenburg, R. Streubel, *Dalton Trans.* **2017**, *46*, 2904 - 2909.

(8) “1,1´-Bifunctional Aminophosphane Complexes via N-H Bond Insertion of a Li/Cl Phosphinidenoid Complex and First Studies on N/P Mono Functionalizations” R. Streubel, A. Schmer, A. W. Kyri, G. Schnakenburg, *Organometallics* **2017**, *36*, 1488 - 1495.

**Tagungsbeiträge:**

(1) A. Kyri, T. Heurich, R. Streubel, 10th European Workshop on Phosphorus Chemistry, Regensburg/Germany, March 18th - 20th, **2013**: *"Searching for phosphanyl and phosphoxyl complexes"* (poster contribution).

(2) A. Kyri, R. Streubel, MHC-6 PhD Workshop, Bonn/Germany, April 5th – 7th, **2013**: *"Synthesis and reactions of new Li/OR phosphinidenoid complexes"* (oral contribution).

(3) T. Heurich, A. Kyri, R. Streubel, Z.-W. Qu, S. Grimme, S. Saeidpour, O. Schiemann SFB 813 Workshop, Trier/Germany, September 25th – 27th, **2013**: *"Targeting Phosphoxyl and Phosphanyl Complexes"* (poster contribution).

(4) A. Kyri, R. Streubel, 15. Aniversary of the Tokitoh workgroup, Kyoto/Japan, June 7th, **2014**: *"First synthesis and reactions of 1,2-oxaphosphetane complexes "* (poster contribution) and *"Synthetic chemistry using Li/Cl phosphinidenoid complexes" (*poster contribution).

(5) A. Kyri, R. Streubel, 9th International Conference on Inorganic Chemistry (AGICHEM) Edinburgh/ Scotland, July 30th – August 1st, **2014**: *"First synthesis and reactions of 1,2-oxaphosphetane complexes "* (poster contribution).

(6) A. Kyri, R. Streubel, MHC-7 PhD Workshop, Freiberg/Germany, September 19th - 21st, **2014**: *"Synthesis and reactions of the first 1,2-oxaphosphetane complexes "* (oral contribution).

(7) A. W. Kyri, R. Streubel, 12th European Workshop on Phosphorus Chemistry, Kassel/Germany, March 16th – 18th, **2015**: *"Insertion reactions of phosphinidenoid complexes"* (oral contribution).

(8) A. W. Kyri, R. Streubel, 10th Organoelement Chemistry Seminar, Kyoto University, Kyoto, Japan, June 8th, **2015**: *"Synthesis of 1,2-Oxaphosphetane Complexes and Reactions with Brønsted acids"* (poster contribution).

(9) V. Nesterov, A. Kyri, T. Heurich, T. Wasano, T. Agou, T. Sasamori, N. Tokitoh, R. Streubel, 11th International Conference on Heteroatom Chemistry, Caen, France, June 14th – 19th, **2015** "*Attempted synthesis of silyl substituted phosphasilenes*" (poster contribution).

(10) A. W. Kyri, R. Streubel, 50th Meeting of Young Chemists, Hiroshima/Japan, July 29th - 31st, **2015**: *"Synthesis and reactions of 1,2-oxaphosphetane complexes – New building blocks"* (poster contribution).

(11) R. Kunzmann, A. W. Kyri, R. Streubel, 13th European Workshop on Phosphorus Chemistry, March 7th - 9th, **2016**: Berlin, Germany, *"Synthesis of polyfunctional phosphane complexes having a P-O-E bonding motif"* (poster Contribution).

(12) A. Kyri, R. Streubel, 13th European Workshop on Phosphorus Chemistry, March 7th - 9th, **2016**: Berlin-Germany, *"1,2-Oxaphosphetane complexes: first reactivity studies"* (poster Contribution).

(13) A. Kyri, R. Streubel, MHC-8 PhD Workshop, Kassel/Germany, March 11th - 13st, **2016**: *"Synthesis and first reactions of 1,2-oxaphosphetane complexes"* (oral contribution).

(14) P. K. Mahji, T. Sasamori, A. Kyri, T. Agou, Y. Mizuhata, J.-D. Guo, S. Nagase, V. Nesterov, R. Streubel, N. Tokitoh 96th Annual Meeting of the Chemical Society of Japan, Kyoto, Japan, March 24th – 27th **2016**: *"Synthesis of 2-Chlorophosphasilene coordinated by an N-Heterocyclic Carbene"* (poster contribution).

(15) R. Kunzmann, A. W. Kyri, R. Streubel, 21st International Conference on Phosphorus Chemistry, June 5th - 10th, **2016**: Kazan, Russia, *"Polyfunctional phosphane complexes containing P-O-E motifs as potential precursors for novel strained three-membered P-ligands"* (poster contribution).

(16) A. W. Kyri, R. Streubel, 21st International Conference on Phosphorus Chemistry, June 5th-10th, **2016**: Kazan, Russia, *"1,2-Oxaphosphetane complexes: syntheses and reactions"* (oral contribution).

(17) A. Kyri, P. Brehm, R. Streubel, 3rd European Conference on Smart Inorganic Polymers, Porto, Portugal, September 12th - 14th, **2016**: *"1,2-Oxaphosphetane complexes: novel precursors for P-containing polymers?"* (poster contribution).

Die vorliegende Arbeit wurde im Zeitraum von November 2012 bis Mai 2017 im Arbeitskreis von Prof. Dr. R. Streubel am Institut für Anorganische Chemie der Rheinischen Friedrich Wilhelms-Universität in Bonn angefertigt.

Hiermit versichere ich, dass ich diese Arbeit selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

Bonn, den 11. Mai 2017

**Danksagung:**

An dieser Stelle möchte ich mich bei all jenen bedanken die mich während der letzten Jahre in meinem Werdegang begleitet und mir zur Seite gestanden haben.

Vor allem **Prof. Dr. Rainer Streubel** danke ich, nicht nur für die Möglichkeit diese Arbeit in seiner Forschungsgruppe durchzuführen, sondern auch für die vielen fruchtbaren Gespräche, die Möglichkeiten der aktiven Teilnahme an viele Konferenzen und das Ermöglichen zweier Auslandsaufenthalte.

**Prof. Dr. Robert Glaum** danke ich für die Übernahme der Aufgabe des Zweitgutachters. Zudem danke ich sowohl **Prof. Dr. Dirk Menche** als fachnahem als auch **Prof. Dr. Diana Imhof** als fachfremdem Mitglied der Prüfungskommission.

**Prof. Dr. Norihiro Tokitoh** und **Prof. Dr. Takahiro Sasamori** von der Universität Kyoto (Japan) danke ich für die Aufnahme in die Forschungsgruppe während meiner zwei Forschungsaufenthalte dort in den Jahren 2014 und 2015. Hierbei möchte ich auch allen aktuellen und ehemaligen Mitarbeitern der Forschungsgruppe Tokitoh für die herzliche Aufnahme und deren große Hilfe danken. Vor allem **Dr. Tomohiro Agou** bedarf hier einer extra Nennung für die viele Hilfe im Labor und für die vielen Orte in Japan die ich durch ihn gesehen habe.

Bedanken will ich mich bei den Mitarbeitern der Analytikabteilung der Universität Bonn ohne deren Hilfe diese Arbeit nicht möglich gewesen wäre. Hierbei will ich vor allem **Dr. Gregor Schnakenburg** und **Charlotte Rödde** für das Vermessen und Lösen der zahlreichen Einkristallstrukturen namentlich erwähnen. **Frau Karin Prochnicki** danke ich für die Aufnahme der zahlreichen NMR-Spektren und der Durchführung der NMR-Sondermessungen, sowie Frau **Dr. Senada Nozinovic** für die fruchtbaren Diskussionen. Ebenso danke ich Frau Hannelore Spitz und Frau Ulrike Weynand für die Aufnahme von NMR Spektren. Für die Aufnahme von MS Spektren danke ich Frau Christine Sondag, Frau Karin Peters-Pflaumbaum, Frau Nora Schocher und **Frau Dr. Marianne Engeser**. Frau Anna Martens danke ich für die Durchführung der Elementaranalysen sowie Frau Kerstin Kühnel-Lysek für die Vorbereitung der empfindlichen Proben.

Des Weiteren möchte ich mich ganz herzlich bei **Dr. Melina Klein** bedanken, für die anregenden Diskussionen, die gute Atmosphäre in Labor 1.013 und die morgendlichen Kaffeerunden, ebenso **Jan Faßbender** für dies alles. Dann **Dr. Maren Bode** und **Dr. Carolin Albrecht** für die gute Atmosphäre im Labor und all diesen für die Diskussionen und das was ich von ihnen gelernt habe.

Für Betreuung und sehr gute Hinweise zum Arbeiten im Labor danke ich **Dr. Vitaly Nesterov**. Und **Abhishek Koner** vor allem für abendliche Diskussionen.

Für Unterstützung im Labor danke ich noch all denen die mit mir und unter meiner Leitung im Labor den Anfang ihrer beruflichen Laufbahn gestartet haben:

Mein Dank geht daher an die Studenten die ich während ihrer Abschlussarbeiten im Rahmen des Masterstudiums oder Diplomstudiums (**Niklas Künemund, Robert Kunzmann, Alexander Schmer, Philip Junker**) sowie Bachelorstudiums (**Philipp Brehm, Florian Gleim**) mitbetreuen durfte. Ich habe ihnen hoffentlich nicht nur einiges beibringen können sondern auch immer selber von ihnen gelernt.

Als Auszubildenden, den ich in der letzten Phase seiner Ausbildung betreuen durfte, danke ich **Christof Grimmling** für seine Unterstützung bei den alltäglichen Aufgaben im Labor und vor allem der Hilfe bei der Synthese etlicher Ausgangsverbindungen für die Gruppe.

Zudem danke ich Johanna Salz für ihr Vertrauen in mich als Betreuer für ihr Schülerpraktikum.

Und zuletzt danke ich meiner Familie: meinen Eltern, meinen beiden Schwestern und meinem Zwillingsbruder. Ihnen allen habe ich in den schweren Zeiten der letzten Jahre viel zu verdanken und ohne sie würde ich heute nicht da stehen wo ich nun bin.

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# Numbering and abbreviations

Due to the huge amount of derivatives, especially in case of the metal complexes, a specific numbering scheme was developed for clarity.

$$\mathbf{X.Ya_M^n}$$

The numbering consists of the following parts:

- X a consecutive number describing the type of compound
- Y a number describing the substituents at phosphorus:
  - 1 for $CH(SiMe_3)_2$ (bis(trimethylsilyl)methyl)
  - 2 for $C_5Me_5$ (1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)
  - 3 for $CPh_3$ (triphenylmethyl)
- a alphabetic character for further organic substituents at the complex (for each case a closer description is given in the corresponding schemes)
- M element symbol of the metal in the pentacarbonyl substituent (not given if only the tungsten complex was prepared)
  - W for tungsten
  - Mo for molybdenum
  - Cr for chromium
- n denotes the presence of isomers for the compound and is given as number for each one, starting from the one with the strongest deshielded signal in the $^{31}P$ NMR spectrum (not given if only one isomer was observed)

| | | | |
|---|---|---|---|
| Å | Ångström ($1 \cdot 10^{-10}$ m) | T | temperature |
| ° | angle in degree | $^{t}$Bu | *tert*-butyl |
| Ar | aromatic substituent | t/tert | tertiary |
| ATR | Attenual Total Reflexion | ESI | electrospray ionization |
| au | Atomic unit | $Et_2O$ | diethyl ether |
| br | broad signal | Et | ethyl |
| calc. | calculated | eV | electron volt |
| °C | degree Celsius | FWHM | full width at half maximum |
| cat | catechol | g | gram |
| $C_6D_6$ | deuerated benzene | h | height or hour |
| $CDCl_3$ | deuterated chloroform | HMBC | Heteronuclear Multiple Bond Correlation |
| cm | centimeter | HMDS | hexamethyldisilazide |
| $C_5Me_5$ | 1,2,3,4,5-pentamethyl-cyclopenta-2,4-dien-1-yl | HMPT | hexamethylphosphoramide |
| CSD | Cambridge Structural Database | HMQC | Heteronuclear Multiple Quantum Correlation |
| Cy | cyclohexyl ($C_6H_{11}$) | Hz | Hertz |
| Cp | cyclopenta-2,4-dien-1-yl | $^{i}$Pr | iso-propyl |
| 12-crown-4 | 1,4,7,10-tetraoxacyclododecane | IR | infrared |
| d | days | $^{n}J_{X,Y}$ | coupling constant (between the elements X,Y over n bonds) in Hz |
| $\delta$ | chemical shift in ppm | K | Kelvin |
| $\Delta$ | thermal reaction | L | ligand |
| ø | diameter | m | medium |
| $\Delta\delta$ | chemical shift difference | m | multiplett |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene | M | metal or molar weight in g/mol |
| dec. | decomposition | *m*-CPBA | meta-chloroperoxybenzoic acid |
| DEPT | Distortionless Enhancement by Polarization | Me | methyl ($CH_3$) |
| EA | elemental analysis | mg | milligram |

| | | | |
|---|---|---|---|
| EI | electron impact ionization | min | minutes |
| eq. | equivalent | mL | millilitre |
| $ML_n$ | transition metal fragment bearing n ligands | THF | tetrahydrofuran |
| mmol | millimol | TfOH | trifluoromethanesulfonic acid |
| MS | mass spectrometry | THF-$d_8$ | deuterated tetrahydrofuran |
| m/z | mass to charge ratio | TMEDA | Tetramethylethylenediamine |
| *n* | normal | toluene-$d_8$ | deuterated toluene |
| $^n$Bu | *n*-butyl | $\tilde{\nu}$ | wave number |
| nm | nanometre | vs | very strong |
| NMR | nuclear magnetic resonance | VT-NMR | Variable Temperature NMR |
| % | percent | w | weak |
| PE | petroleum ether | X | halogen or leaving group |
| Ph | phenyl ($C_6H_5$) | | |
| ppm | parts per million | | |
| q | quartet | | |
| quin | quintet | | |
| R, R´, R´´ | organic substituent | | |
| r.t. | room temperature | | |
| s | singlet | | |
| sat | satellites | | |
| solv | solvent | | |
| t | triplett or time | | |

# 1 General introduction - from phosphorus to phosphinidenoid complexes

## 1.1 Phosphorus, the precious element

Regarding the recent developments around the world, *i.e.* a higher living standard, and with this the higher consumption of resources, it is necessary for chemistry to concentrate on novel synthetic strategies. These novel strategies should help to preserve the priceless resources of our planet for future generations.

One of the most precious elements, which is often one of the first referred to in discussions about our resources, is phosphorus.[1] The biggest suppliers today are China, Africa and the USA, but their stocks are not endless. There is indeed a lot of phosphorus dissolved in the surface water on earth, either deriving from soil erosion or from sewage but this can, to date, not be mined efficiently.[2]

The high value of phosphorus for humanity is hereby not only based on its limited resources but also on the scope of its high-end applications, *e.g.* in ligands for enantioselective catalysis[3] or in flame retardant materials,[4,5] besides its basic use as fertilizer.[6]

Phosphorus,[7] as 15$^{th}$ element of the periodic system, is one of the essential elements for all life on earth and found in the living nature in form of phosphorus esters or phosphates. As ATP and ADP it forms parts of the DNA and is essential for the energy cycle of cells. Additionally it can be found as hydroxyl- or fluoroapatite ($Ca_5X(PO_4)_3$, X = OH, F) in the bones and teeth of mammals.

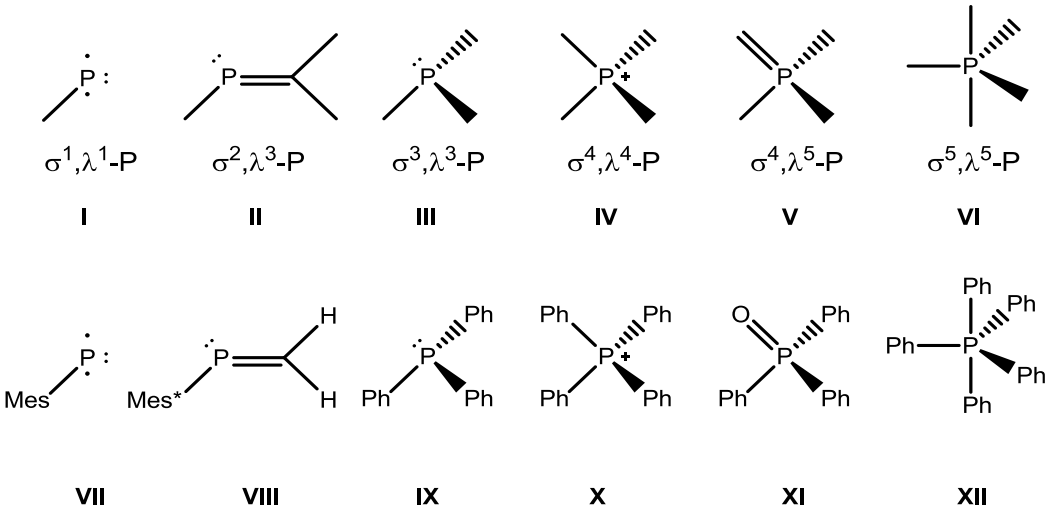
For phosphorus, all oxidation states between -III (*e.g.* in $PH_3$) and +V (*e.g.* in $H_3PO_4$, phosphorus acid) are known. $P^V$ compounds play a substantial role in nature, but the “true” synthetic potential of phosphorus is based on compounds bearing a free electron pair at the phosphorus centre. These, mainly $P^{III}$, compounds, *e.g.* $Ph_3P$, can be used widely, for example as ligands in organic catalysis or as starting materials for the Wittig reaction.

Due to its high reactivity, especially towards oxygen, all phosphorus compounds found in nature are in oxidation state +V. Usually phosphorus is obtained in form of apatites, less common is the mining of other phosphates (*e.g.* iron- or aluminium phosphate). After reduction of phosphates with carbon, the phosphorus is obtained as $P_4$ molecules (formed by condensation of $P_2$ molecule containing gas). $P_4$, the so called white phosphorus, is the most reactive allotrope and, despite being starting point of all phosphorus chemistry, only one of

several allotropic modifications. If white phosphorus is heated under exclusion of oxygen it yields red phosphorus with a polymeric structure. The transformation can be catalysed by iodine. Other allotropic forms are for example violet phosphorus (Hittorf´s phosphorus, obtained from red phosphorus by prolonged heating above 550 °C, composed of polymeric phosphorus chains) and black phosphorus (obtained by heating white phosphorus under high pressures (about 1.2 giga pascals)), which contains of layers of corrugated $P_6$-rings, connected in a manner similar to graphene.

Most phosphorus is subsequently oxidized with air to produce phosphorus pentoxide and from this hydrolysed to give phosphoric acid. Some part of the synthesized phosphorus is first oxidized by Chlorine to $PCl_3$, the most common starting point for phosphorus organic chemistry.

Several descriptors were developed due to the variety of different bonding situations that phosphorus can adopt. While the $\sigma^n$-descriptor gives the number of $\sigma$ bonds and with this the coordination number of the phosphorus atom, the $\lambda^n$-descriptor gives (implicitly) information about the number of all bonds ($\sigma$ and $\pi$).[8] Metal fragments coordinated by the free electron pair of a phosphorus atom are not taken into account with these descriptors.




***Scheme 1.1:*** Important bonding motifs of phosphorus in different chemical environments (**I-VI**) and some examples (**VII-XII**).[8]

The $\kappa$-descriptor specifies the atom of a ligand that is coordinating to the metal centre as illustrated in **XIII** (figure 1.1).[9]

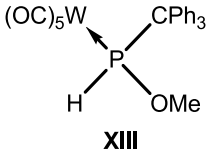
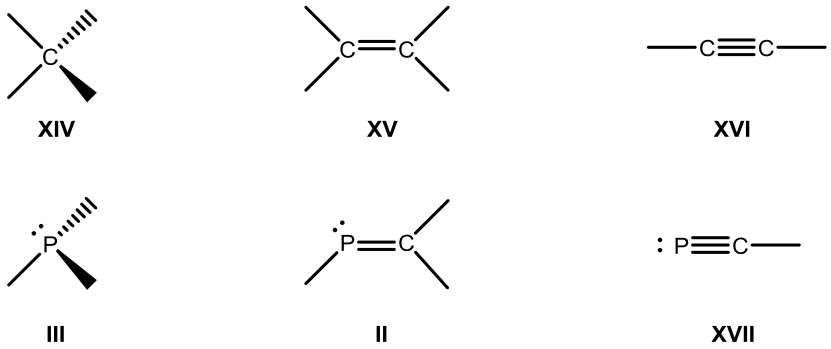



***Figure 1.1:*** Pentacarbonyl[$\sigma^3$,$\lambda^3$-methoxy(triphenylmethyl)phosphane-$\kappa P$]tungsten(0)[10]

Phosphorus shows a diagonal relationship to carbon. This relation means that an element is, in specific reactions and structures, closer to an element of a different group and period than to its heavier and lighter homologues. For phosphorus and carbon many similar structural motifs and reactions are known. Important examples can be found especially in modern synthesis and use of phosphorus or carbon in low coordination states. Therefore, phosphorus was also referred to as “the carbon copy”.[11] The known phosphaalkenes **II** and phosphaalkines **XVII** can be mentioned as examples of such similar behaviour (scheme 1.2).




***Scheme 1.2:*** Generalized examples of carbon compounds and their isolobal $P^{III}$ analogues.[11]

## 1.2 Development of novel building blocks: From carbenes to phosphinidenoid complexes

A breakthrough in carbon chemistry was the development of a special kind of highly reactive low-coordinated carbon compounds, the so called carbenes, which can be used as versatile building blocks, either as transient species or as stable derivatives.[12] In general carbenes, carbon compounds possessing an electron sextet at the C-centre, show a broad reactivity.[13] For example, insertion reactions into different $\sigma$-bonds or addition reactions to $\pi$-systems are known. Depending on the electronic nature of the substituents as well as on the generation method, carbenes can be formed in two different electronic states. They are classified as singlet (having both electrons paired, most often in the same orbital as well as one empty p-orbital) or triplet (having two unpaired electrons in different orbitals) carbenes.[13] Methods to synthesize carbenes involve, to just name two, the decomposition of chloro(organo)mercury compounds[3] or the $N_2$-release from diazo compounds, e.g from $CH_2N_2$.[14] Several such reactions were investigated over the last decades and allow the use of carbenes, as such as well as in transition metal-catalysed reactions.

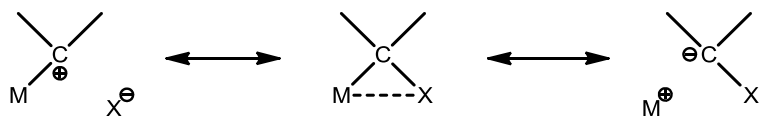
A second breakthrough was the synthesis of some of the first stable heterocyclic carbenes by Arduengo in 1991 and the first structural verification by an X-ray diffraction study.[15] These N-heterocyclic carbenes (NHCs, singlet carbenes) can be isolated, stored and have

subsequently been used to stabilize many novel structural motifs or as ligands in catalysis. Earlier, push-pull-substituted derivatives were described by Bertrand. The true nature of these carbenes was strongly discussed as the P-C bond showed multiple bond character, but these compounds showed also typical carbene type reactivity (*e.g.* cyclopropanation reaction with alkenes or epoxide formation with aldehydes).[16] Since that time, several more stable derivatives could be synthesized, *e.g.* the mixed substituted cyclic alkyl amino carbenes (CAACs).[17]

In contrast to NHCs and other acyclic, donor-substituted carbenes, stabilization of carbenes can also be achieved by coordination to a transition metal centre.[18,19] Due to the high variability of possible coordination modes, only terminal carbene complexes shall be briefly mentioned. Again the reactivity is strongly influenced by the electronic nature of the carbene ligand and the complexes can be separated into two types. The first ones are known as Fisher-type carbene complexes[18] (electrophilic carbene complexes, that can be formally described as composed of a singlet-singlet combination of the carbene fragment and the metal fragment[20]) and the latter ones as Schrock-type carbene complexes[19] (nucleophilic carbene complexes, having a triplet-triplet combination[20]). Both types of complexes have been used in novel synthetic strategies, catalytically as well as stoichiometric.[20] Carbene complexes, unfortunately, show (very often) a different reactivity than free carbenes but could be used as carbene transfer reagents.[20]

Due to their extremely high reactivity, non-stabilized carbenes are in most cases problematic to handle. Therefore, a new strategy was necessary to achieve carbene-like reactions. One strategy is the synthesis and use of so called carbenoids **XVIII**. Carbenoids[21,22] feature an electropositive metal (M) and a good leaving group (most often a halogen atom X) at the same carbon atom, so that under formal elimination of MX a carbene could be formed. As the reaction mechanism usually does not involve free carbenes, this often leads to a high(er) selectivity by reducing the number of side reactions.

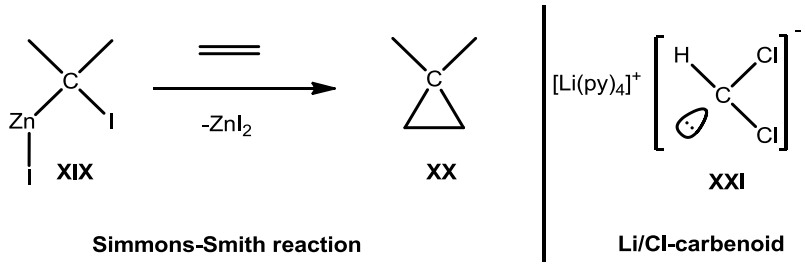
Noteworthy is, that carbenoids can show several different types of reactivity, based on their ambiphilic nature (scheme 1.4). This means that, besides allowing addition or insertion reactions (in analogy to carbenes), they also allow electrophilic and nucleophilic substitution, as can be illustrated by their electronic resonance structures (scheme 1.3).[21]




electrophilic **XVIII´** carbene-like **XVIII´´** nucleophilic **XVIII´´´**

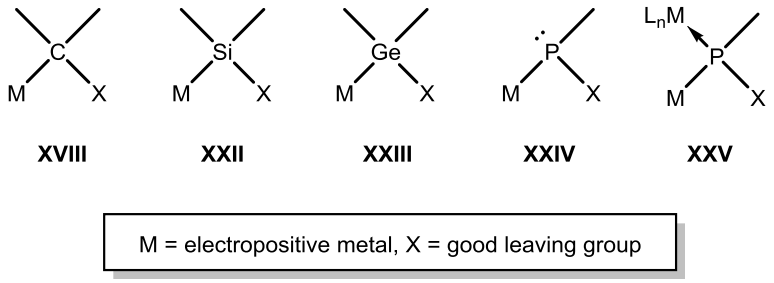
***Scheme 1.3:*** Simplified canonical electronic resonance structures of carbenoids.

One of the best described examples for carbenoid chemistry is the Simmons-Smith reaction (scheme 1.4), where, starting from alkenes, a zink/iodine carbenoid **XIX** is used in cycloaddition reactions to yield cyclopropanes **XX**.[23] A second well known example of carbenoid formation is the reaction between dichloromethane and strong bases to form a dichlorocarbenoid, which could even be isolated by separating the cation with pyridine ligands (**XXI**, scheme 1.4).[24]



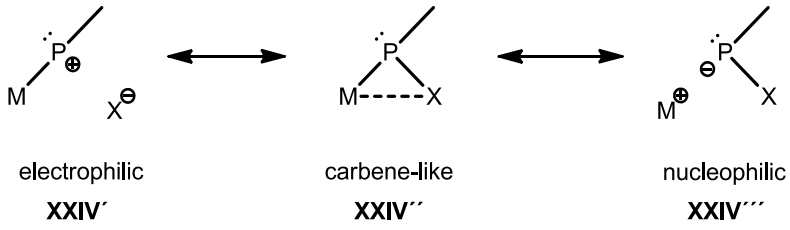

***Scheme 1.4:*** Zn/I-carbenoid in the Simmons-Smith reaction[23] (left) and an example for an isolated Li/Cl carbenoid[24] (right).

Over the last years, beside carbenoids[25] **XVIII** also silylenoids[26] **XXII** and germylidenoids[27] **XXIII** were described, broadening the scope of possible group 14 "-enoid" chemistry.




***Scheme 1.5:*** Generalized structures of a carbenoid **XVIII**, silylenoid **XXII**, germylidenoid **XXIII**, phosphinidenoid **XXIV** and phosphinidenoid complex **XXV**

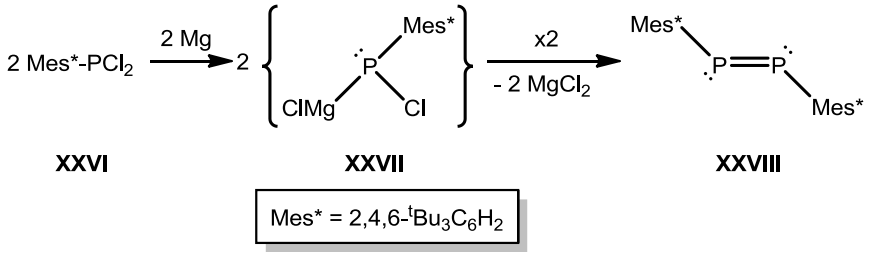
A priori, the phosphinidenoids, being related to carbenoids, should show similar ambiphilic behaviour and similar electronic resonance structures (scheme 1.6).




***Scheme 1.6:*** Generalized electronic resonance structures of phosphinidenoids.

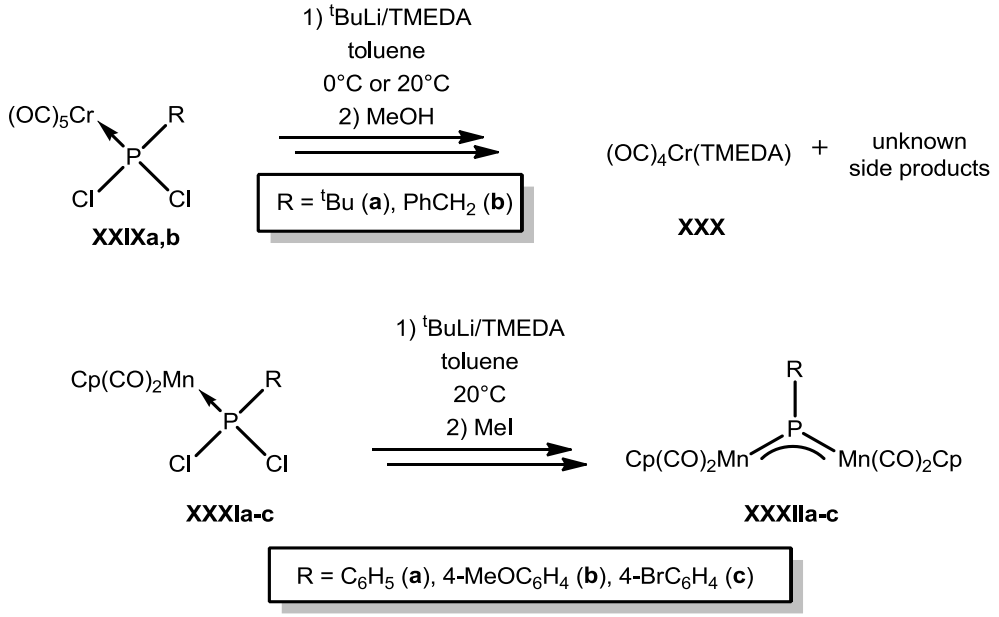
The existence of phosphinidenoids **XXIV**, being examples of group 15 "-enoids", has not been proven to date. They were proposed as plausible intermediates in several reactions but

never detected by spectroscopic means: Yoshifuji reported the reduction of dichloro-(organo)phosphane **XXVI** with magnesium to form the first *E*-diphosphene **XXVIII** (scheme 1.7).[28] Yoshifuji also suggested formation of the intermediate **XXVII** and proposed the name "phosphinidenoid" for the first time.[29]




***Scheme 1.7:*** Synthesis of diphosphene **XXVIII** via a proposed Mg/Cl phosphinidenoid by Yoshifuji.[29]

If the lone pair of the phosphorus atom is coordinated to a transition metal fragment (*e.g.* $W(CO)_5$), phosphanido complexes can be synthesized that should show close similarity to carbenoids, structurally and in their reactivity. A first attempt to create these so called M/X phosphinidenoid complexes (**XXV**) was published by Huttner *et al* in 1985.[30] Yet, after the (assumed) Li/halogen exchange in dichlorophosphane complexes, only decomposition products of **XXIXa,b** or, in case of **XXXIa-c**, bridged dinuclear phosphinidene complexes (**XXXIIa-c**) were isolated (scheme 1.8).

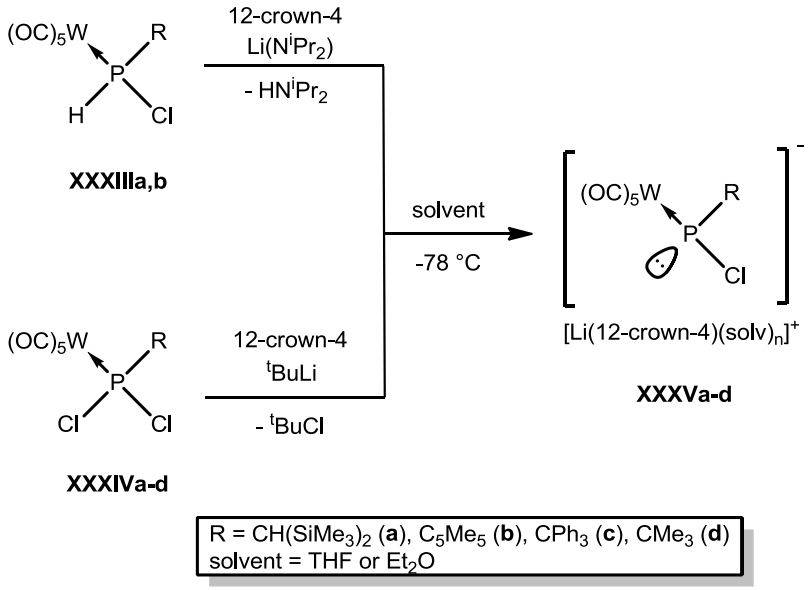



***Scheme 1.8:*** First attempts to obtain Li/Cl phosphinidenoid complexes by Huttner.[30]

A solution to the problem was presented by Streubel in 2007,[31] when the first characterised derivative of the class of phosphinidenoid complexes was stabilized by separation of the cation from the anion using a crown ether (12-crown-4) (scheme 1.9). The ion separation was essential for thermal stabilization and, hence, allowed for their synthetic

use at low temperature. During the following years, investigations revealed the potential of the Li/Cl phosphinidenoid complexes as interesting building blocks as well as several similarities to the carbenoid chemistry (scheme 1.10 and 1.11).

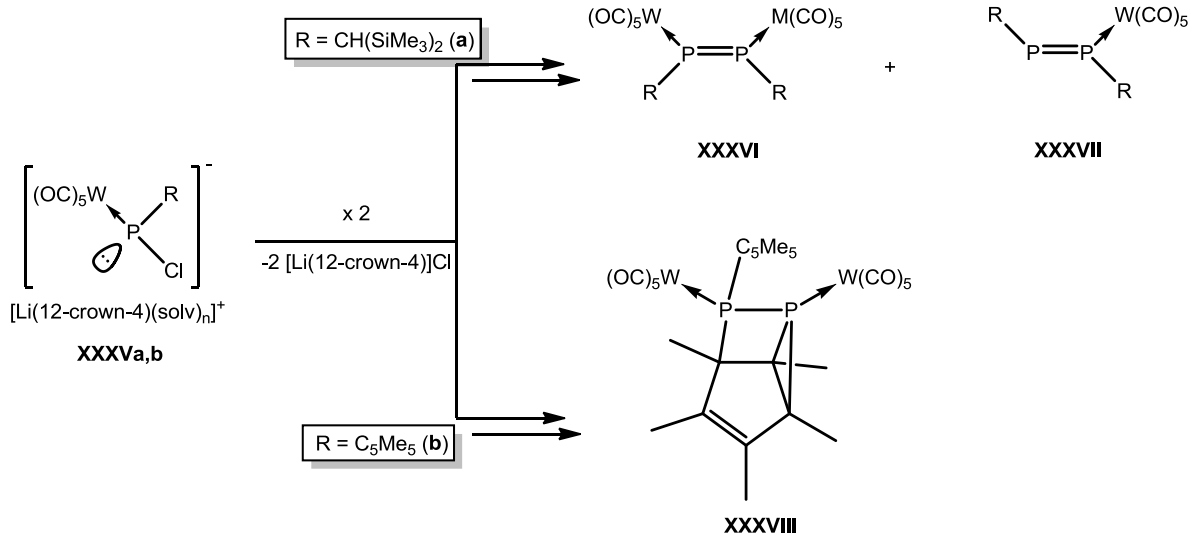
The synthesis of Li/X phosphinidenoid complexes **XXXVa-d** was performed by deprotonation of chloro(organo)phosphane complexes **XXXIIIa,b** using LDA or by Li/Cl exchange starting from the corresponding dichloro(organo)phosphane complexes **XXXIVa-d** using $^{t}$BuLi (scheme 1.9) in the presence of 12-crown-4.[31–33] Due to the high reactivity and, in most cases, the decomposition below ambient temperature, the complexes are normally generated and reacted *in situ* at low temperature. The solid state molecular structures were obtained for **XXXVa**[34] and **XXXVc**,[35] showing well separated ion pairs having a [Li(12-crown-4)$_2$] cation.[34,35] In case of a more stable Li/F phosphinidenoid complex, which is even stable at ambient temperature for several hours, a molecular structure was presented having only one molecule of crown ether coordinated to lithium, but also an additional diethyl ether molecule. Studies revealed separated ions also in solution.[36]




***Scheme 1.9:*** Generation of Li/Cl phosphinidenoid complexes **XXXVa-d** by Streubel. [31–33]

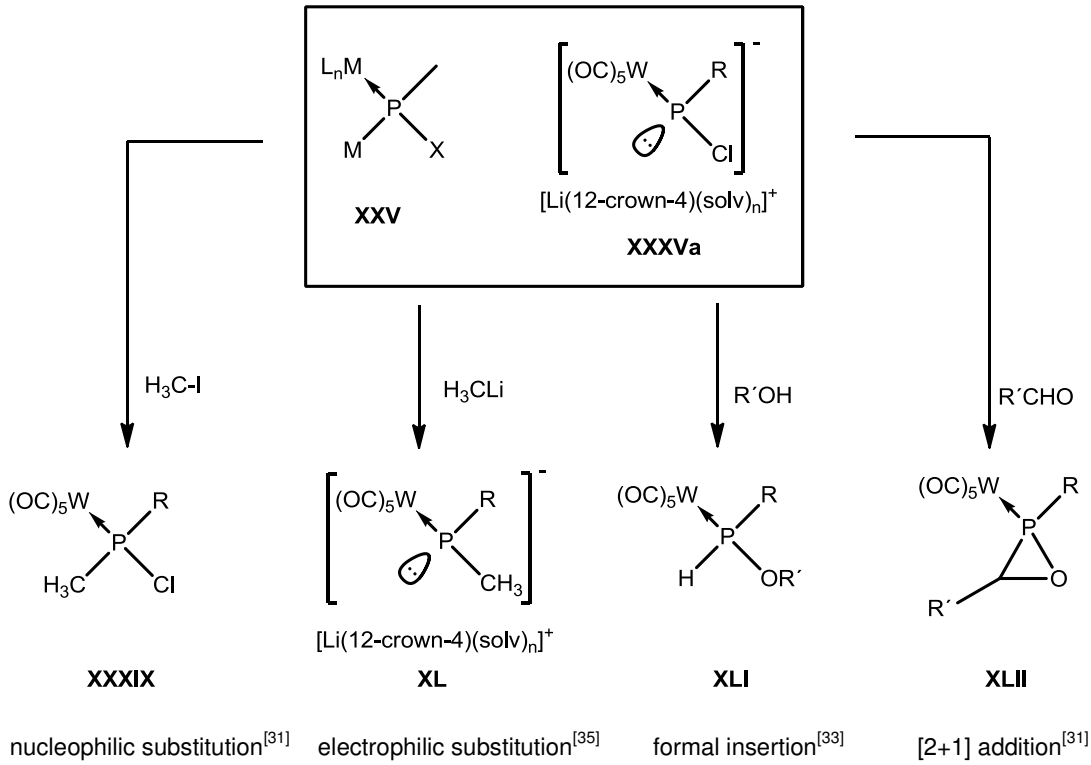
Nowadays the synthesis starting from the chloro(organo)phosphane complexes **XXXIIIa,b** is not used anymore due to the more time-efficient synthetic protocol using the dichloro-(organo)phosphane complexes **XXXIVa-d.** In addition, the deprotonation protocol formed diisopropyl amine which was found to influence the reaction outcome in several cases. *I.e.* it can lead to subsequent reactions such as protonation or deprotonation of other reactive intermediates.[31,37,38]

A set of Li/Cl phosphinidenoid complexes was described by Streubel *et al*. having different group 6 metal fragments (*P*-M(CO)$_5$ with M = Cr, Mo, W).[39,40] as well as different *P*-R groups, ranging from extremely reactive complexes with small substituents (R = $^t$Bu)[41] to complexes with moderate (R = $C_5Me_5$,[32] $CH(SiMe_3)_2$[31]) and sterically demanding substituents (R = $CPh_3$).[33] The stabilisation by the bulky $CPh_3$ substituent was remarkable as it led to a phosphinidenoid complex which was even stable for about one day at ambient temperature, while all other Li/Cl derivatives started to decompose at significant lower temperatures (normally above -50 °C). Especially for the *P*-$CH(SiMe_3)_2$ and the *P*-$C_5Me_5$ derivatives these decomposition pathways were well investigated (scheme 1.10), allowing often qualitative and semi-quantitative evaluations of the reactions due to the specific $^{31}$P NMR data of the side products.




***Scheme 1.10:*** Decomposition reactions of Li/Cl phosphinidenoid complexes **XXXVa**[31] and **XXXVb**.[32]

Extensive studies over the past decade by the research group of Streubel demonstrated that phosphinidenoid complexes are very useful building blocks in phosphorus chemistry, comparable to carbenoids in carbon chemistry (scheme 1.11) The Li/Cl phosphinidenoid complexes show nucleophilic reactions[31], electrophilic reactions[35] as well as formal insertion into OH bonds[10,33] and 1,2-addition to different π-systems,[31,42] the latter being comparable to the cyclopropanation reaction of carbenoids.

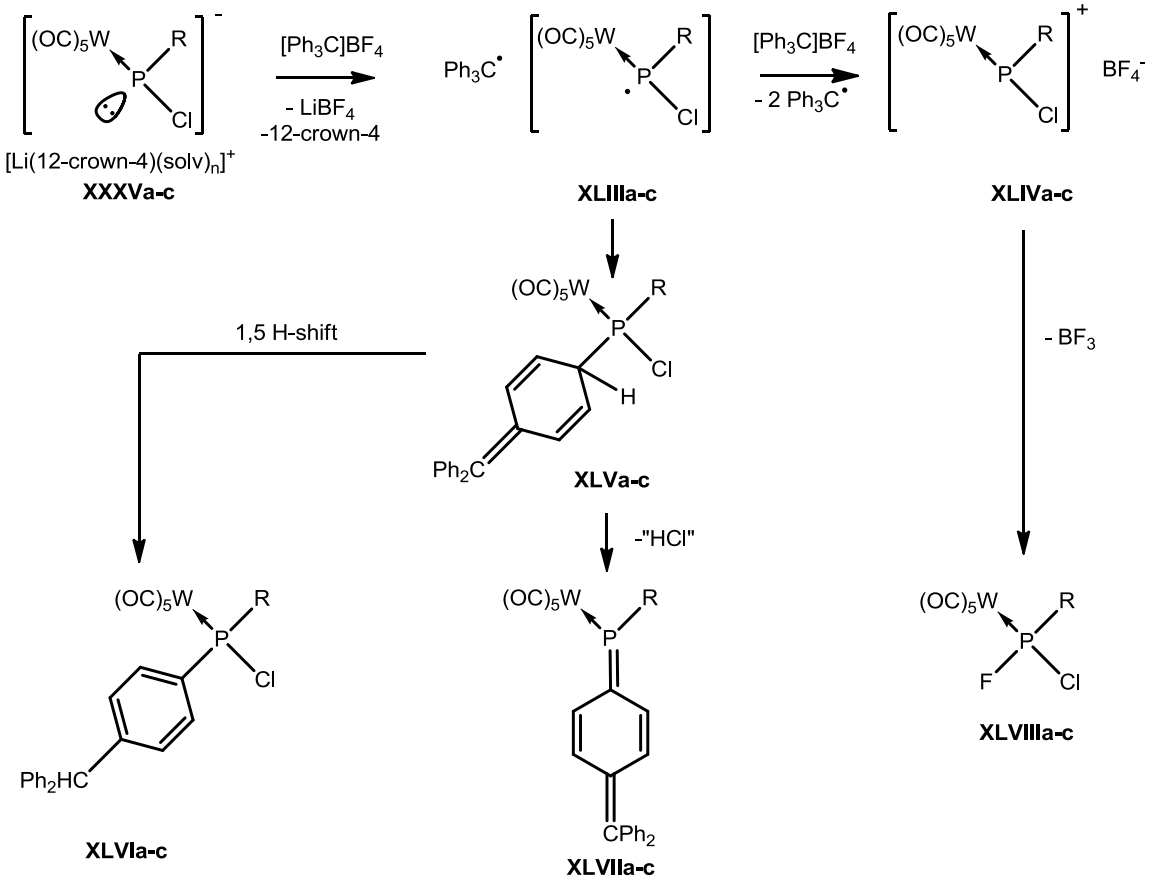



***Scheme 1.11:*** Examples for the reactivity of Li/Cl phosphinidenoid complexes (R = $CH(SiMe_3)_2$, R´= variable organic substituent).

The last type of reaction that shall be mentioned is the oxidative single electron transfer (SET) reaction of Li/Cl phosphinidenoid complexes **XXXVa-c** (scheme 1.12). In case of $[Ph_3C]BF_4$ as the oxidant two important steps were identified.[43] The first step consists of the formation of solvent-caged (close) radical pairs **XLIIIa-c** which can recombine to form "hetero-Gomberg" dimers **XLVa-c**. Depending on the nature of the substituent at phosphorus and the conditions, hydrogen shift to give complexes **XLVIa-c**, or HCl elimination to yield *para*-phosphachinomethane complexes **XLVIIa-c** were observed.

While in the beginning complexes **XLVa-c** were proposed only as intermediates, they could be isolated and unambiguously identified just recently.[44] It was shown that moderately strong N-bases induce a 1,5-hydrogen shift, thus enabling rearomatisation. In contrast, addition of stronger bases such as KHMDS led to formal HCl abstraction and formation of the *para*-phosphaquinomethane complex derivative.

A second oxidation step may occur, as well, requiring excess of the oxidant $Ph_3C^+$ and yielding the P-F derivatives **XLVIIIa-c** as final products. The reaction may involve phosphonium complexes **XLIVa-c** as reactive intermediates that, due to their high Lewis acidity, abstract fluoride from the $BF_4^-$ anion.[43]




***Scheme 1.12:*** Examples for oxidative SET reactions of Li/Cl phosphinidenoid complexes **XXXVa-c**.[43]

# 2 Objective of the thesis

The research in this PhD work was focused on reactions of Li/Cl phosphinidenoid complexes with a variety of different substrates having N-H bonds or strained heterocyclic rings, to study the hitherto scarcely investigated formal insertion reactions of a $P_1$-fragment into different polar E-E´-bonds. In case of the strained rings, the focus was on epoxides.

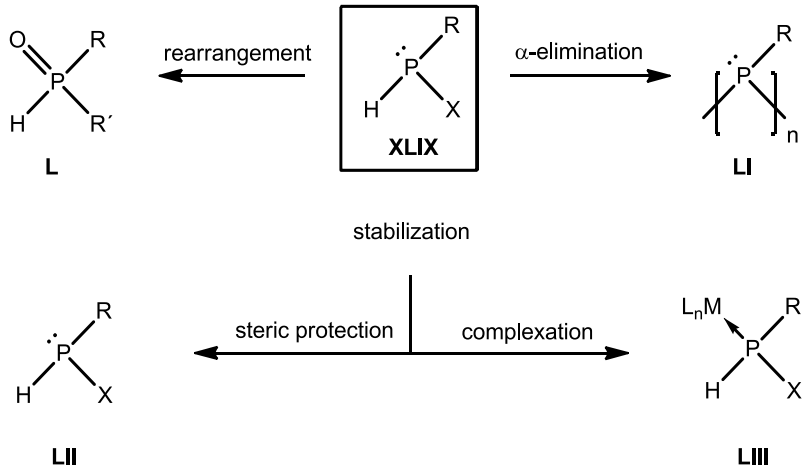
Furthermore, the chemistry of the new product complexes was to be investigated towards their own potential as molecular building blocks to form novel P-ligands.

# 3 Insertion reactions into N-H bonds

## 3.1 Introduction to aminophosphane complexes

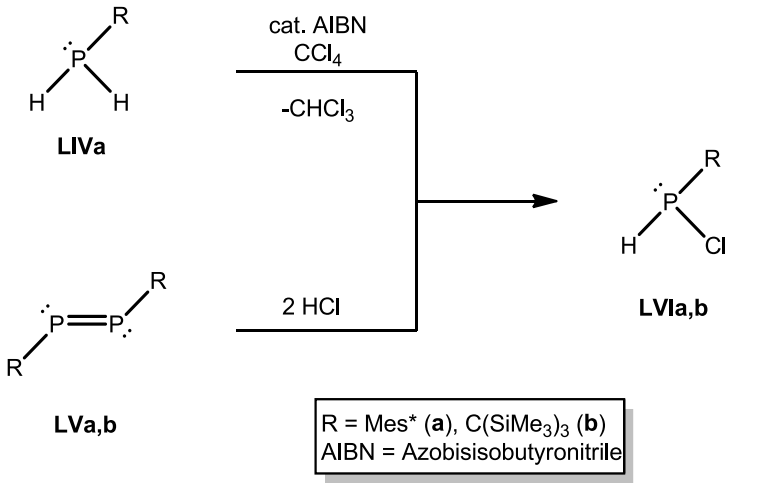
Phosphanes bearing a hydrogen atom together with an electronegative substituent (**XLIX**, X = OR, NHR, $NR_2$, halogen) on the same phosphorus atom are scarce. On one hand they can undergo rearrangement reactions, *e.g.* to yield phosphane oxides (**L**),[45,46] on the other hand they can undergo formal $\alpha$-elimination[47][48] to initiate rearrangement reactions, dimerizations, oligomerizations or insertion reactions, thus yielding products of transient (or formal) phosphinidenes, *e.g.* **LI**. Therefore they are complicated to synthesize.

Stabilization of compounds **XLIX** was mainly achieved in two ways: the kinetic protection by applying sterically demanding *P*-substituents (**LIIa,b** (*e.g.* R = Mes*[49] or $CPh_3$[50])) or the complexation to a transition metal fragment (**LIII**).[48]



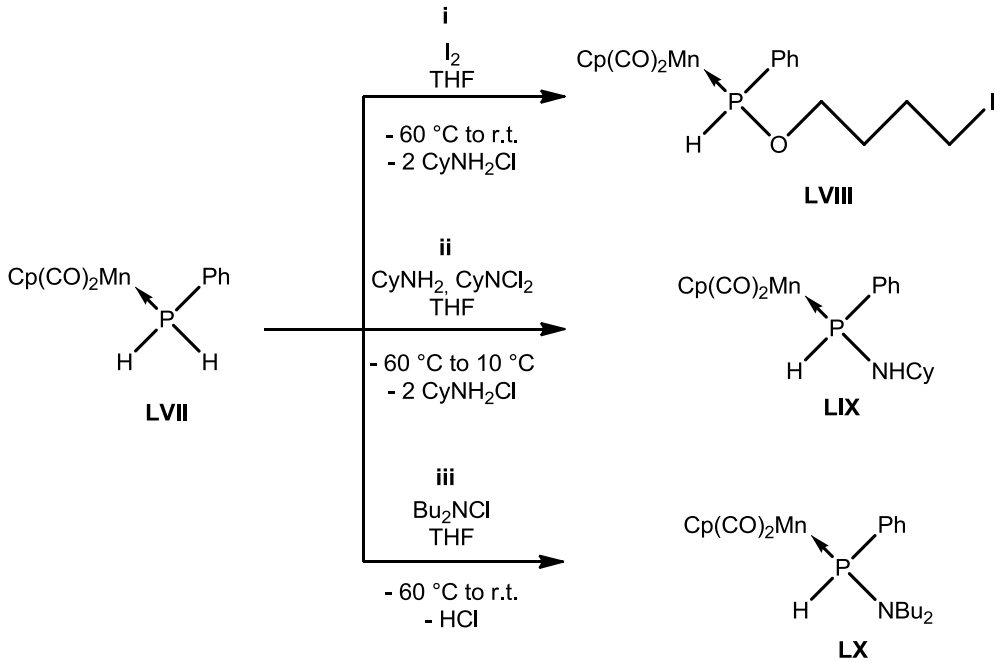

***Scheme 3.1:*** Typical reactions and stabilisation of secondary phosphanes bearing electronegative substituents (X = OR, NHR, $NR_2$, halogen, $L_nM$ = transition metal fragment).

An example for steric protection is the Mes*P(H)Cl **LVIa**. This compound was synthesized via different routes, namely the radical mediated chlorination of the corresponding phosphane **LIV**[49] or the splitting of a diphosphene **LVa** with $HCl_{(g)}$,[51,52] reported by Cowley *et al.* in 1983. The second route was later expanded to another diphosphene derivative bearing the $C(SiMe_3)_3$ substituent **LVb**.[52]



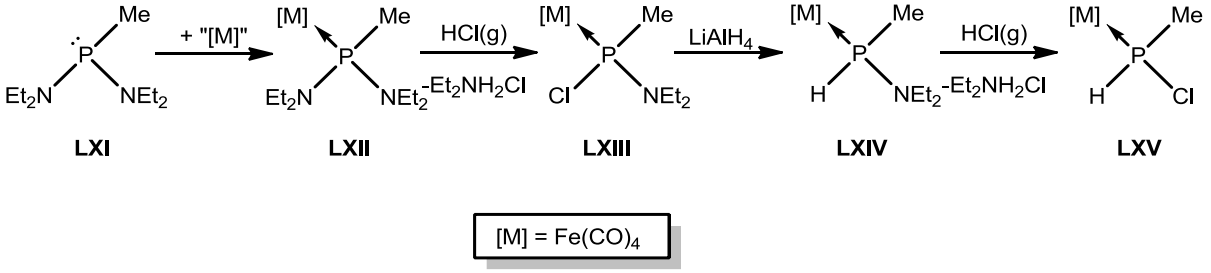

***Scheme 3.2:*** Synthetic strategies to the unligated chlorophosphanes **LVIa,b**[49],[51,52] (Mes* = 2,4,6-$^{t}Bu_3C_6H_2$).

The stabilization by complexation was described first by Huttner *et al.* for phosphinite complex **LVIII** and the aminophosphane complexes **LIX** and **LX,** all having the combination of a PX and PH motif.[48] They were obtained by oxidation of the corresponding primary phosphane complex **LVII** with iodine in the presence of THF (**i**), the reaction of **LVII** with a mixture of cyclohexylamine and *N,N*-dichlorocyclohexylamine (**ii**) or the reaction with $Bu_2NCl$ (**iii**). All three complexes are air stable at ambient temperature and no $\alpha$-elimination was observed, even under harsh conditions.



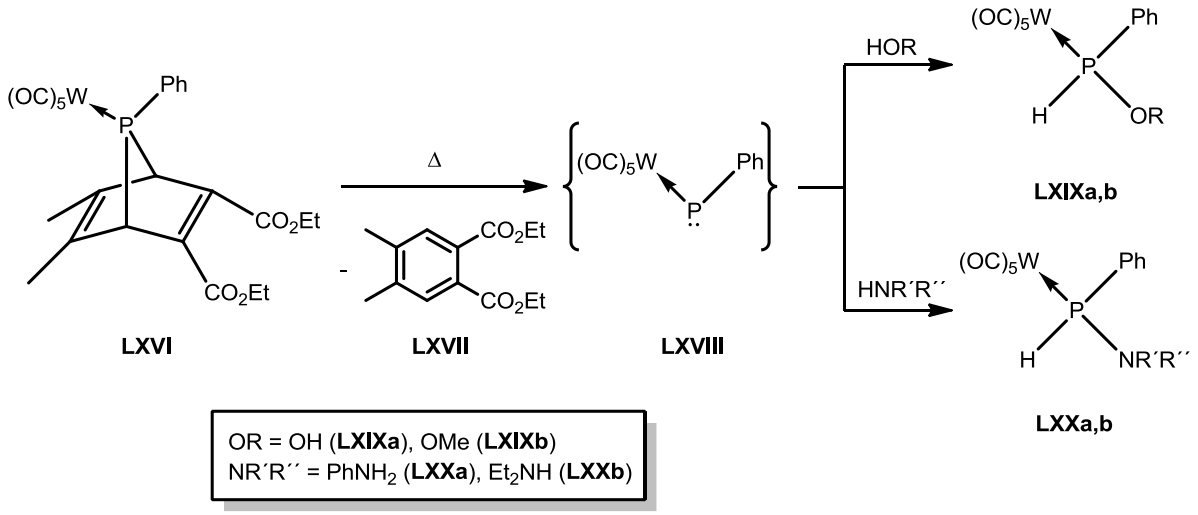

***Scheme 3.3:*** Syntheses of the first phosphinite complex **LVIII** and the first aminophosphane complexes **LIX** and **LX** by Huttner.[48]

Due to the problematic synthesis of suitable precursors, the complexation of free H/X phosphanes is usually not feasible and/or advantagous. Therefore, a step-wise *P*-ligand conversion including protection and deprotection of the phosphorus centre was developed by Vahrenkamp in 1983[53] for an iron tetracarbonyl complex bearing a diethylamino-(organo)phosphane ligand. The reaction sequence was investigated for a broader set of group 6 metal complexes ([M] = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$) and P substituents (R = $^t$Bu, Cy, Ph, (-)Men) by Lorenzen *et al.* in 1990.[46] In the first step, diamino(organo)phosphan **LXI** was coordinated and then converted with $HCl_{(g)}$ to the asymmetrically substituted amino(chloro)phosphane complex **LXIII**. Subsequent reduction with $LiAlH_4$, yielded the aminophosphane complex **LXIV**. The exchange of the amino by a chloro substituent could again be achieved using $HCl_{(g)}$ (**LXV**).



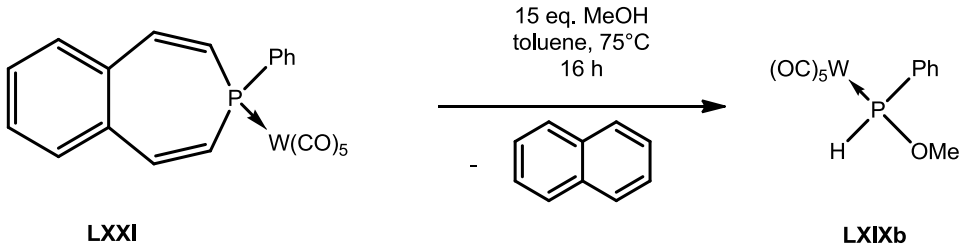

***Scheme 3.4:*** Step wise synthesis of aminophosphane complexes **LXV** by Vahrenkamp[53].

A different route was presented in 1982 by Mathey *et al.* showing that phosphinite complexes **LXIXa,b** and aminophosphane complexes **LXXa,b** can be synthesized via thermal decomposition of phosphanorbornadiene complex **LXVI** in the presence of the respective amine or alcohol.[47] Here the insertion reaction of an *in situ* formed electrophilic terminal phosphinidene complex **LXVIII** into the NH or OH bonds led to the desired products. A drawback of these syntheses are especially the reaction conditions, while NH functional substrates reacted already in boiling toluene, temperatures above 120 °C in a high pressure vessel were necessary for most OH functional substrates. In addition, the syntheses of phosphanorbornadiene complexes bearing sterically demanding substituents at P (*e.g.* 9-fluorenyl[54]) are quite complicated. The necessary Diels-Alder reaction for the formation of the norbornadiene motif can be supressed by the steric demand so that these complexes usually need several more reaction steps in the synthesis than those bearing smaller substituents like Me or Ph.



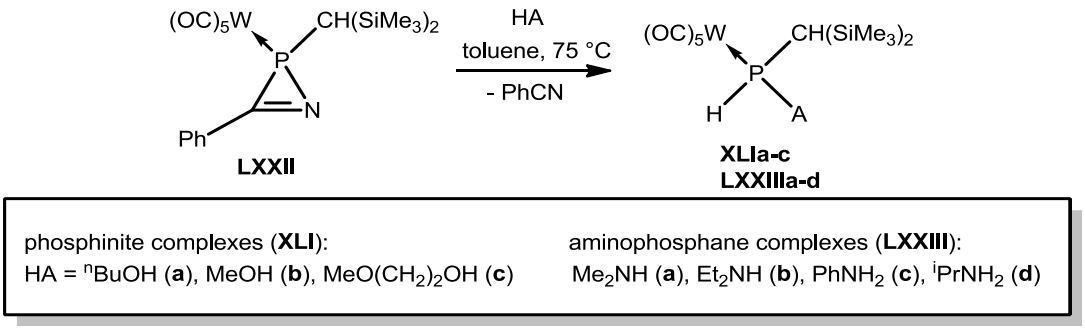

***Scheme 3.5:*** Thermal synthesis of PH functional phosphane complexes **LXIXa,b** and **LXXa,b** using 7-phosphornorbornadiene complex **LXVI** by Mathey.[47,54]

A somewhat similar route to phosphinite complexes was described by Lammertsma, who started from a phosphepine complex, but only the reaction of complex **LXXI** with methanol has been described so far (scheme 3.6).[55]



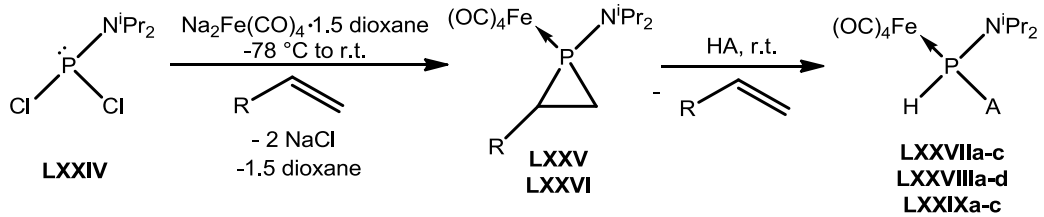

***Scheme 3.6:*** Synthesis of phosphinite complex **LXIXb** by Lammertsma.[55]

The third thermal route was presented by Streubel in 2010. Here, the decomposition of 2*H*-azaphosphirene complex **LXXII** at elevated temperature was used to generate the transient electrophilic phosphinidene complex that subsequently reacted either with alcohols to form phosphinite complexes **XLIa-c**[56] or with different primary or secondary amines to form aminophosphane complexes **LXXIII-c**.[57]




***Scheme 3.7:*** Syntheses of phosphinite and amino phosphane complexes by Streubel.[56,57]

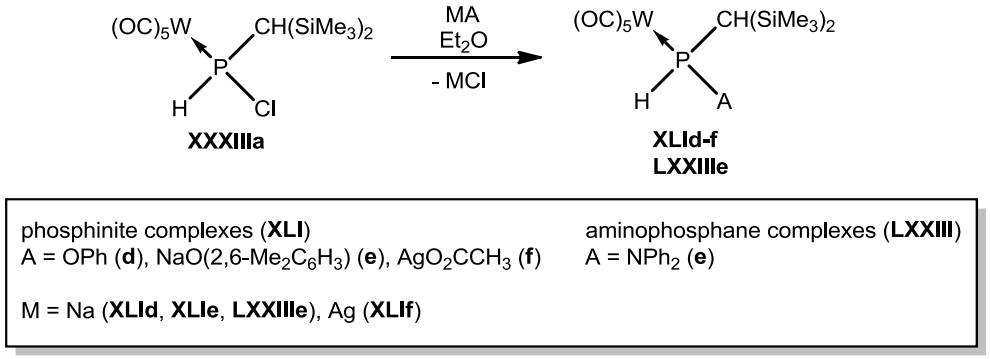
The most recent published reaction sequence, involving again a terminal electrophilic phosphinidene complex, was presented by Lammertsma.[58] Starting from dichloro-(diisopropylamino)phosphane **LXXIV** and Collman´s reagent ($Na_2Fe(CO)_4$ · 1.5-dioxane), a phosphinidene complex was generated in a double salt elimination reaction. This phosphinidene complex is, in 1-pentene or 1-hexene as solvent, in an equilibrium with the corresponding phosphiranes **LXXV** or **LXXVI**, respectively, and the term "bottled phosphinidene complex" was used by Lammertsma to emphasize its reactivity. In the presence of protic compounds (such as amines or alcohols), a clean conversion to the corresponding aminophosphane **LXXVIIa-c** or phosphinite complexes **LXXVIIIa-d** was observed. This reaction has the advantage to yield amino-substituted Fe complexes. The latter can easily be further functionalized at phosphorus and the iron centre at ambient temperature, meaning that possible thermal decomposition of the products is suppressed.




R = $^n$Pr (**LXXV**), $^n$Bu (**LXXVI**)
HA = $R^1NH_2$ ($R^1$ = allyl (**LXXVIIa**), Ph (**LXXVIIb**), cyclopropanyl (**LXXVIIc**))
$R^2OH$ ($R^2$ = Me (**LXXVIIIa**), $CH_2Ph$ (**LXXVIIIb**), $CH_2CH_2Cl$ (**LXXVIIIc**), $CH_2CCH$ (**LXXVIIId**))
$R^3CO_2H$ ($R^3$ = Me (**LXXIXa**), o-pyridyl (**LXXIXb**), 2-thiophen (**LXXIXc**))

***Scheme 3.8:*** Syntheses of tetracarbonyliron-substituted phosphinite and aminophosphane complexes by Lammertsma.[58]

Another route to phosphinite [56] and aminophosphane[57] complexes was presented by Streubel using a post-functionalization strategy, *i.e.* using chloro(organo)phosphane complex **XXXIIIa** and sodium alkoxides or sodium amides in salt elimination reactions (scheme 3.9). A drawback in these reactions were the possible deprotonation of the starting chloro(organo)-phosphane complex, leading in the end to the formation of diphosphene complexes (**XXXVI** and **XXXVII**) via transient phosphinidenoid complexes (for more information on the diphosphene complexes see chapter 1.2) and the laborious multi-step synthesis of the chloro(organo)phosphane complex **XXXIIIa**.

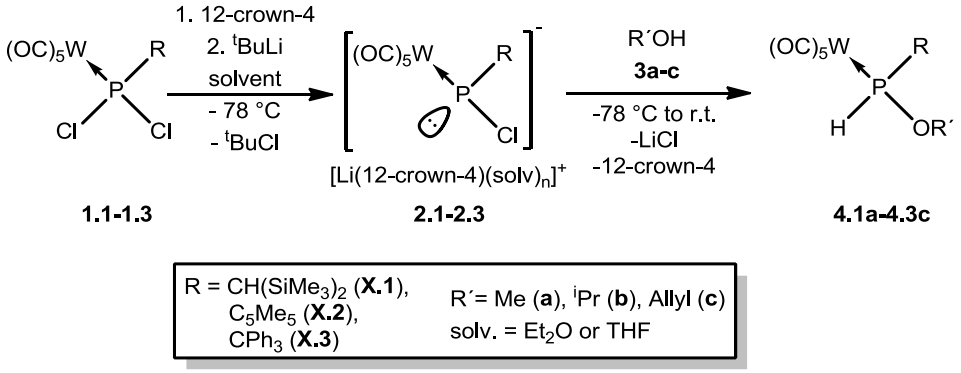



***Scheme 3.9:*** Syntheses of phosphane complexes via salt elimination reactions by Streubel.[56,57]

The analogous reactions in main-group "-enoid" chemistry have attracted considerable attention in the past owing to the versatile construction of useful building blocks. Those are the insertion reactions of metallocarbenoids, which are derived from diazocarbonyl compounds, into X-H bonds of main-group compounds (X = C, N, P, O, S, etc.).[59,60] A similar reactivity for phosphinidenoid complexes would be of high interest for the synthesis of P-containing building blocks.

## 3.2 Insertion reactions using $R_2NH$

Although being similar to electrophilic phosphinidene complexes in their reactivity, the true potential of Li/Cl phosphinidenoid complexes was not fully unveiled, yet. First investigations towards the formal insertion reactions of the Li/Cl phosphinidenoid complexes into the OH-bond of alcohols were just recently presented by Streubel.[10,33] *E.g.* warming up a *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complex **2.3** containing solution in the presence of isopropanol **3b** selectively yielded the phosphinite complex **4.3b**.[33]

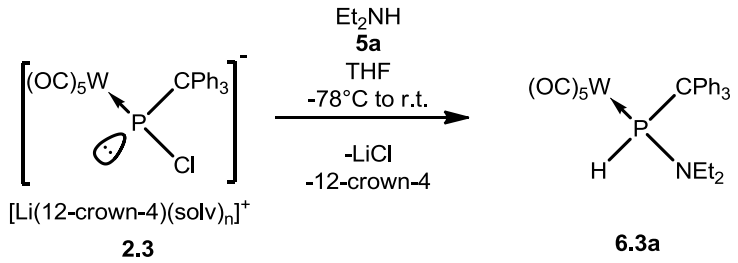



***Scheme 3.10:*** Synthesis of phosphinite complexes **4.1a-4.3c** by formal insertion of phosphinidenoid complexes **2.1-2.3** in OH-bonds of different alcohols **3a-c**.[33]

To broaden the scope of such formal insertion reactions the reagents were changed to the easiest accessible pentel analogues of the alcohols, the amines. In this research field, problems depending on the different reactivity (especially the lower acidity of the proton) as

well as the steric influence of a second organic substituent and, in this regard, the possibility of double insertion reactions due to more hydrogen-nitrogen bonds in the primary amines were of great interest. To avoid possible problems by such multiple insertion reactions, the investigation was started with secondary amines.

A first successful product formation was observed for the reaction of **2.3** with diethylamine **5a** (scheme 3.11). The aminophosphane complex showed a resonance signal at 74.4 ppm with a doublet splitting in the $^{31}P$ NMR spectrum due to the directly bonded hydrogen atom, thus having a $^{1}J_{P,H}$ coupling constant of 352.2 Hz; satellite signals from the coupling to the $^{183}W$ nucleus ($^{1}J_{W,P}$ = 252.1 Hz, natural abundance of $^{183}W$ = 14.3 %) were also observed.




***Scheme 3.11:*** Synthesis of aminophosphane complex **6.3a** using diethylamine **5a** and the *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complex **2.3**.

Using other substrates, the reaction was found to be strongly dependent on the steric demand of the amine substituents. When the steric demand is too high, the reaction is slowed down significantly and no product formation is observed, *i.e.* the reactions with diisopropylamine (**5b**) as well as dicyclohexylamine (**5c**) were unselective. These unselective reactions showed several side products, of which the phosphinidenoid complex **2.3** at 252.1 ppm ($^{1}J_{W,P}$ = 77.6 Hz)[33], and a product at 12 ppm, that corresponds to a formal insertion reaction of the phosphinidenoid complex into a *para*-CH bond of $Ph_3CH$ [$(OC)_5W\{P(CPh_3)(para\text{-}(CHPh_2)C_2H_4)H\}$], could be identified as not substrate specific product.[61] The mechanism to yield the second product is so far not clear. A reaction between Li/Cl phosphinidenoid complex **2.3** and $Ph_3CH$ did not show a clean conversion.

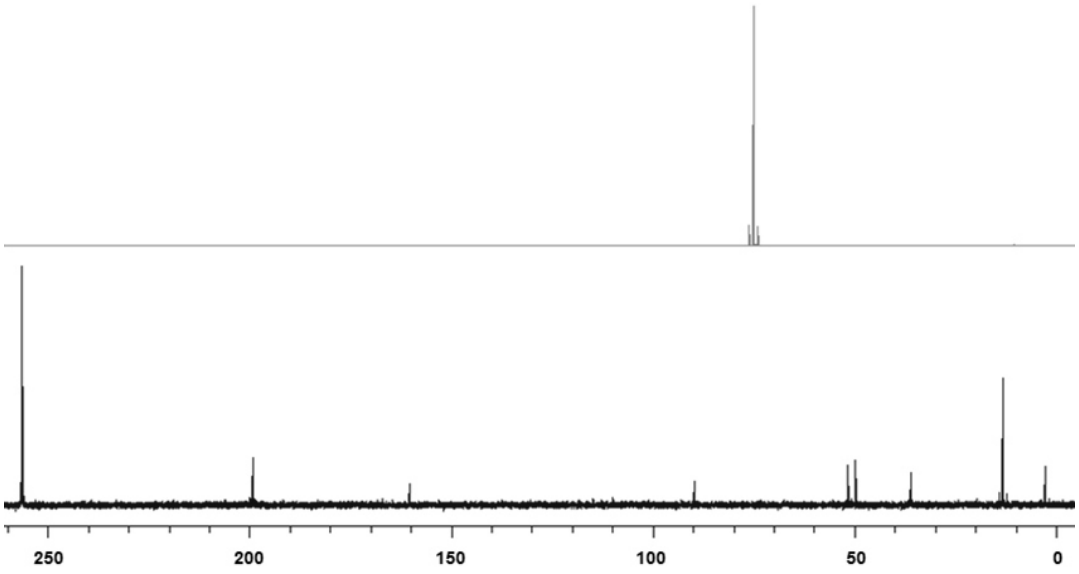



***Figure 3.1:*** $^{31}P\{^{1}H\}$ NMR spectra for the reaction solution of Li/Cl phosphinidenoid complex **2.3** with diethylamine (**5a,** top) and diisopropylamine (**5b**, bottom).

Based on the results presented herein, Schmer could show in his MSc thesis that the reaction was found to yield aminophosphane complexes only when the $\alpha$-C atom is bearing just one *C*-substituent, *e.g.* the reaction with dibenzylamine (**5d**) was possible. A set of acyclic (dimethylamine (**5e**)**,** dibenzylamine (**5d**)) and cyclic (piperidine (**5f**)**,** pyrrolidine (**5g**)) secondary amines was used by Schmer and the prepared complexes were completely characterised, including $^{1}H$, $^{13}C\{^{1}H\}$ and $^{31}P$ NMR, mass spectrometry, elemental analysis and single crystal diffraction studies.[62]

The biggest advantages of this novel route were found especially in the yields and the easy work-up by simple filtration over $SiO_2$ in most cases. Previous routes gave lower yields according to Duan (10-50 %)[57], while in the present cases they were moderate and good (45 – 82 %) and starting from the easier accessible dichloro(organo)phosphane complexes as starting materials.

***Table 3.1:*** $^{31}P$ NMR data (in $CDCl_3$) and yields of complexes **6.3a-e**.

| | $R_2$ | $\delta^{31}P$ [ppm] | $^{1}J_{W,P}$ [Hz] | $^{1}J_{P,H}$ [Hz] | yield [%] |
|---|---|---|---|---|---|
| **6.3a** | $Et_2$ | 74.4 | 252.1 | 352.2 | 81 |
| **6.3d** | $(PhCH_2)_2$[62] | 77.3 | 254.5 | 354.6 | 52 |
| **6.3e** | $Me_2$[62] | 82.6 | 254.9 | 349.8 | 82 |
| **6.3f** | $(CH_2)_5$[62] | 58.4 | 254.5 | 346.1 | 62 |
| **6.3g** | $(CH_2)_4$[62] | 81.9 | 254.6 | 345.9 | 45 |

Single crystals of **6.3a**, suitable for X-ray diffraction studies, were obtained from a saturated diethyl ether solution. The complex shows a planar geometry at the nitrogen atom with a sum of bond angles of 359° and 359.6° (for two independent molecules), presumably due to steric effects of the bulky $CPh_3$ and $W(CO)_5$ groups. All other structural parameters are in good accordance with the ones found for complexes **9.3a-f** (cf. chapter 3.3) and similar to those described in the literature[57] and shall therefore not be discussed further.

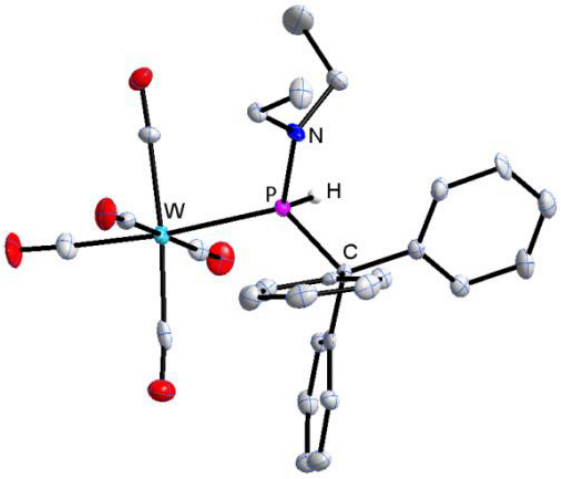
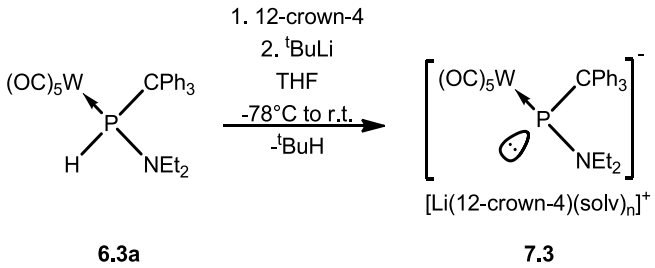



***Figure 3.2:*** DIAMOND plot of the molecular structure of complex **6.3a** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at phosphorus are omitted for clarity. Only one of two independent molecules in the unit cell is shown for clarity. Both sets of data for the two independent molecules are given (molecule 1/molecule2), selected bond lengths in Å and angles in °: P-W 2.5540(18)/2.5509(17), P-N 1.673(6)/1.678(6), P-C 1.957(7)/1.954(6), W-P-C 123.1(2)/123.1(2), W-P-N 115.9(2)/115.6(2), C-P-N 109.7(3)/110.3(3).

For aminophosphane complex **6.3a**, bearing two organic substituents at N, a deprotonation at the PH functionality could be achieved by the addition of $^{t}$BuLi. This deprotonation led selectively to the *P*-amino-substituted phosphinidenoid complex **7.3** (scheme 3.12).




***Scheme 3.12:*** Synthesis of Li/$NEt_2$ phosphinidenoid complex **7.3.**

The successful formation of phosphinidenoid complex **7.3** could be deduced from the $^{31}$P NMR spectrum, and no side-products were observed. This outcome is in stark contrast to the one for the corresponding *P*-$CH(SiMe_3)_2$-substituted complex, where a deprotonation led to a fast decomposition of the complex with partial decomposition to unknown products, even below ambient temperature.[57] A low field shifted resonance signal was observed for

complex **7.3** at $\delta^{31}P$ = 160.3 ppm with a small coupling constant between phosphorus and tungsten ($^1J_{W,P}$ = 102.6 Hz), both are typical for known phosphinidenoid complexes.[31][10,33] Unfortunately, the complex decomposed after a short time at ambient temperature, yielding mainly the starting material **6.3a** as well as a small amount of un-identified products (figure 3.3).

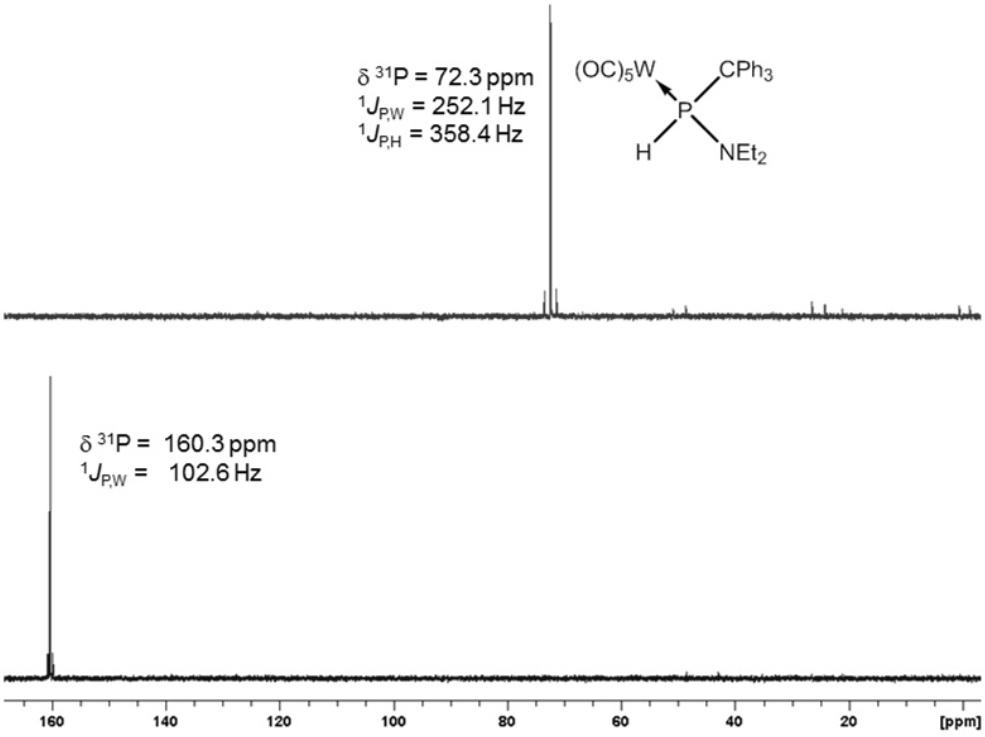
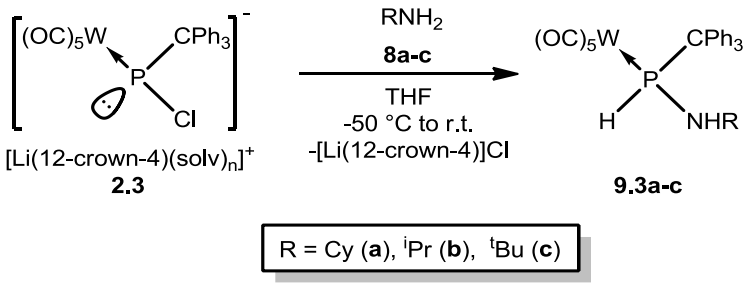



***Figure 3.3:*** $^{31}P\{^1H\}$ NMR of Li/$NEt_2$ phosphinidenoid complex **7.3** in the reaction mixture after 20 minutes (bottom) and after one day at ambient temperature (top).

## 3.3 Insertion reactions using $RNH_2$

The reaction of phosphinidenoid complexes **2.1-2.3** with primary amines might in principle be problematic due to the possibility to form products from mono-insertion and bis-insertion reactions.

Nevertheless a selective reaction to 1,1´-bifunctional aminophosphane complexes was achieved using the *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complex **2.3**. The observation of only one signal in the $^{31}P\{^1H\}$ NMR spectrum for each complex proved that only the mono-insertion product is formed, presumably due to the high steric demand of the *P*-$CPh_3$ substituent.




***Scheme 3.13:*** Syntheses of aminophosphane complexes **9.3a-c** using the formal $P_1$-insertion reaction of Li/Cl phosphinidenoid complex **2.3** in the presence of primary amines **8a-c**.

A set of reactions using primary amines, having slightly different steric demand for the substituents at the N-centre ($CyNH_2$ (**8a**), $^iPrNH_2$ (**8b**) and $^tBuNH_2$ (**8c**), scheme 3.13), was performed and the obtained aminophosphane complexes **9.3a-c** were unambiguously characterised by multinuclear NMR, IR and MS measurements as well as elemental analysis and single crystal X-ray diffraction studies.

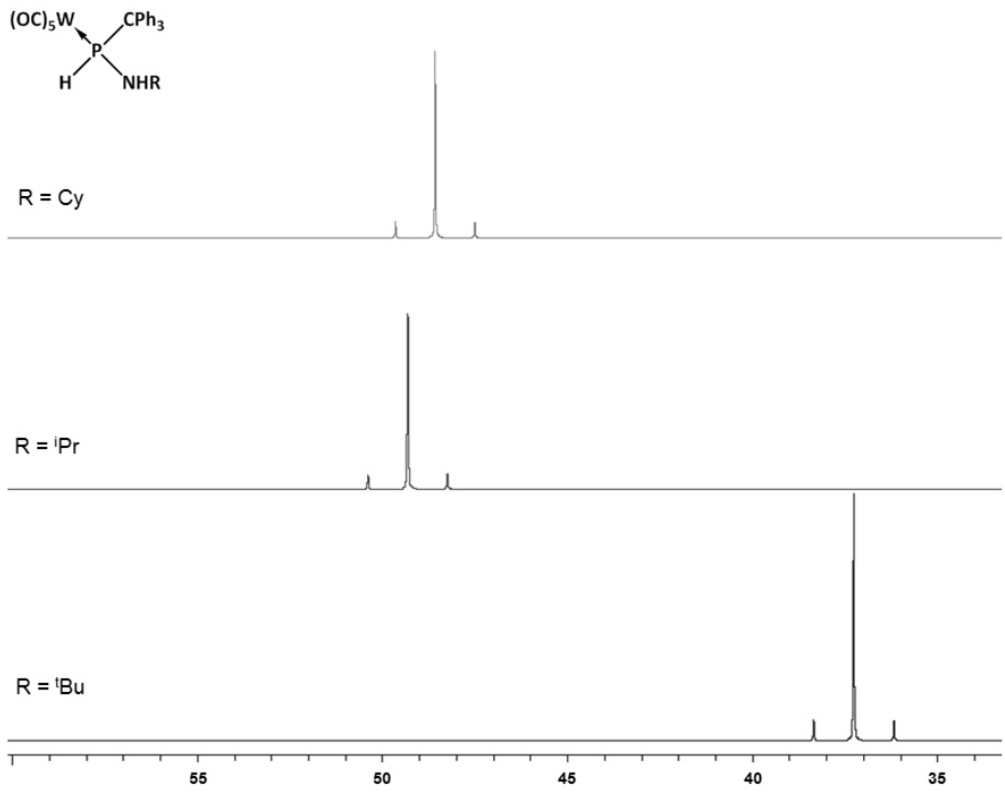



***Figure 3.4:*** $^{31}P\{^{1}H\}$ NMR spectra of aminophosphane complexes **9.3a-c**.

Around the same time, several other derivatives were prepared by Mahji[63] (R = Me (**9.3d**), Ph (**9.3e**) and Schmer[62] (R = Et (**9.3f**)) using this strategy. It is also worthwhile to mention that Schmer could observe a selective reaction with ammonia under the same conditions, leading to the *P*-$NH_2$-substituted organophosphane complex, the second known derivative having this substitution pattern.[47]

Complexes **9.3a-f** displayed resonances in the range of 37 to 58 ppm ($^{1}J_{W,P}$ = 258.4 - 264.5 Hz and $^{1}J_{P,H}$ = 332.6 - 346.5 Hz, selected NMR spectroscopic data are given in table 3.2). The resonance signals are significantly shifted towards lower field, compared to the resonance signals of complexes bearing the *P*-$CH(SiMe_3)_2$ substituent which were described by Duan ($\delta^{31}P$ = 5.3 - 46.1 ppm, $^{1}J_{W,P}$ = 249.2 - 263.2 Hz, $^{1}J_{P,H}$ = 320.2 - 357.7 Hz).[57]

***Table 3.2:*** $^{31}P$ NMR data (in $CDCl_3$) and yields of complexes **9a-f**.

| | R | $\delta^{31}P$ [ppm] | $^{1}J_{W,P}$ [Hz] | $^{1}J_{P,H}$ [Hz] | yield [%] |
|---|---|---|---|---|---|
| **9.3a** | Cy | 48.6 | 260.4 | 333.0 | 77 |
| **9.3b** | $^{i}$Pr | 49.4 | 260.5 | 332.6 | 71 |
| **9.3c** | $^{t}$Bu | 37.3 | 263.7 | 342.3 | 84 |
| **9.3d** | Me[63] | 57.4 | 258.4 | 346.1 | 83 |
| **9.3e** | Ph[63] | 54.6 | 264.5 | 342.0 | 79 |
| **9.3f** | Et[62] | 53.7 | 258.8 | 346.5 | 84 |

Comparison of **9.3a-f** to complexes **6.3a-e**, shows that *N,N*-disubstituted complexes possess smaller $^{1}J_{P,H}$ coupling constants (approximately 7 Hz) and smaller $^{1}J_{W,P}$ coupling constants (approximately 5 Hz). The $^{31}$P resonance signals are also significantly low-field shifted (*e.g.* $\delta^{31}$P = 74.4 ppm for complex **6.3a**) in comparison to those of complexes obtained with primary amines (*e.g.* $\delta^{31}$P = 53.7 ppm for complex **9.3f**). The stronger shielding by introducing more hydrogen substituents at the N-centre was also described by Duan for *P*-CH(SiMe$_3$)$_2$-substituted aminophosphane complexes[57].

High-field shifted resonances were observed with increase of the steric demand of the amino group ($\delta^{31}$P for Me>$^{i}$Pr>$^{t}$Bu), consistent with the trend observed for phosphinite complexes.[56] The P-H bond stretching vibrations are in line with reported values, being between 2310 and 2370 cm$^{-1}$ in the IR spectra of complexes **9.3a-f**.

Single crystals of **9.3a-c** suitable for X-ray diffraction studies could be obtained from saturated diethyl ether solutions. Complexes **9.3a** and **9.3c** crystallized in the space group P2$_1$/c and complex **9.3b** in P$\bar{1}$. The molecular structures are displayed in figure 3.5.

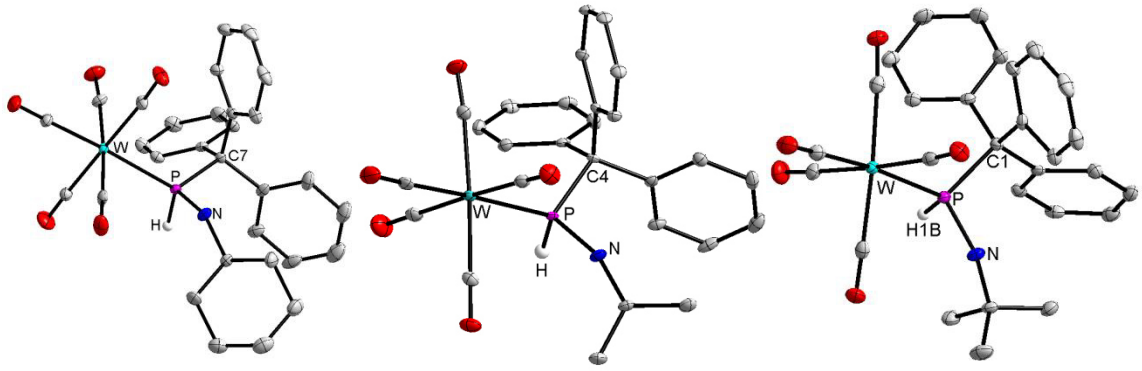


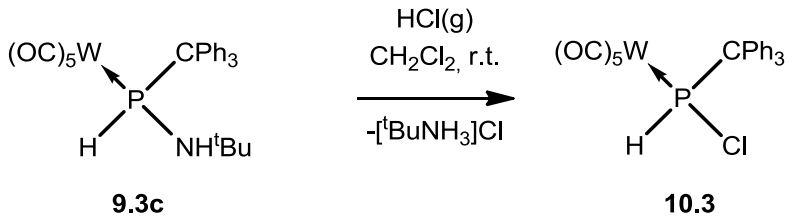

***Figure 3.5.*** DIAMOND plot of the molecular structures of complexes **9.3a-c** (from left to right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at phosphorus are omitted for clarity. In case of **9.3b** only one of two independent molecules in the unit cell is shown for clarity.

The phosphorus centres, including the W(CO)$_5$ fragment and not the P-H unit, display a trigonal geometry with a bond angle sum of about 340°, similar to those found in phosphinite complexes.[10] All complexes show a significant bond elongation for the P-C bonds and P-W bond lengths similar compared to the ones found for *P*-CH(SiMe$_3$)$_2$-substituted aminophosphane complexes.[57] The P-C bond elongation has been reported as a feature of all *P*-CPh$_3$-substituted phosphane complexes as well as unligated *P*-CPh$_3$-substituted phosphanes. In the past it was often attributed to the repulsive interaction induced by the bulky triphenylmethyl group. This explanation is rather questionable as no further elongation could be observed by complexation to the bulky W(CO)$_5$ group and it still demands to be seen by calculation what causes this effect.

***Table 3.3:*** Selected bond lengths in Å and angles in ° for complexes **9.3a-c**. Both sets of data for the independent molecules are given for **9.3b** (molecule 1/molecule 2).

| | P-W | P-C | P-N | C-P-N | C-P-W |
|---|---|---|---|---|---|
| **9.3a** | 2.5210(5) | 1.912(2) | 1.6652(18) | 106.64(9) | 121.53(6) |
| **9.3b** | 2.5361(8)/ 2.5344(8) | 1.924(3)/ 1.927(3) | 1.663(3)/ 1.674(3) | 104.13(13)/ 107.54(13) | 116.54(10)/ 122.75(9) |
| **9.3c** | 2.5324(6) | 1.918(2) | 1.670(2) | 110.24(10) | 110.99(7) |

To gain access to the *P*-$CPh_3$-substituted chlorophosphane complex **10.3**, representing an interesting molecular building block, aminophosphane complex **9.3c** was reacted with $HCl_{(g)}$ in dichloromethane (scheme 3.14). The reaction showed a clean conversion of the starting material to the desired product, whereas neither a reaction with $HCl_{(g)}$ in $Et_2O$ nor a reaction with $PCl_3$ in $CH_2Cl_2$ led to any significant exchange reaction.




**9.3c** **10.3**

***Scheme 3.14:*** Synthesis of the *P*-$CPh_3$-substituted chlorophosphane complex **10.3**.

Isolation of complex **10.3** was performed by removal of all volatiles and subsequent extraction with diethyl ether to separate the product from the formed ammonium salt. The resonance signal shows typical values for chloro(organo)phosphane complexes in the $^{31}P$ NMR spectrum (in $CDCl_3$) with 70.7 ppm, $^1J_{W,P}$ = 270.8 Hz and a P-H coupling ($^1J_{P,H}$ = 343.7 Hz) as well as an absorption in the IR spectrum due to the P-H bond vibration at 2351 $cm^{-1}$. A small splitting of the resonance signal was observed, *i.e.* two signals in a ratio of 2:1 were assigned to the $^{35}Cl$ and $^{37}Cl$ isotopomers ($^{35}Cl$: $\delta^{31}P$ = 71.22 ppm, $^1J_{W,P}$ = 270.95 Hz, $^{37}Cl$: $\delta^{31}P$ = 71.20 ppm, $^1J_{W,P}$ = 270.93 Hz).These $^{31}P$ NMR data are similar to the ones observed for the corresponding *P*-$C_5Me_5$-substituted derivative **10.2**[64] ($^{35}Cl$: $\delta^{31}P$ = 76.75 ppm, $^1J_{W,P}$ = 274.2 Hz; $^{37}Cl$: $\delta^{31}P$ = 76.73 ppm, $^1J_{W,P}$ = 273.9 Hz). The ratio of the two isotopomers represents the natural abundance of the $^{35}Cl$ and $^{37}Cl$ isotopes and their electronic influence in the P-Cl bond exerts a small effect on the shielding of the phosphorus nucleus, but the effect is quite small and no other data of complex **10.3** are influenced by this effect.

A molecular structure in the single crystal could be determined, too, showing the constitutional P(H)Cl motif (figure 3.6).

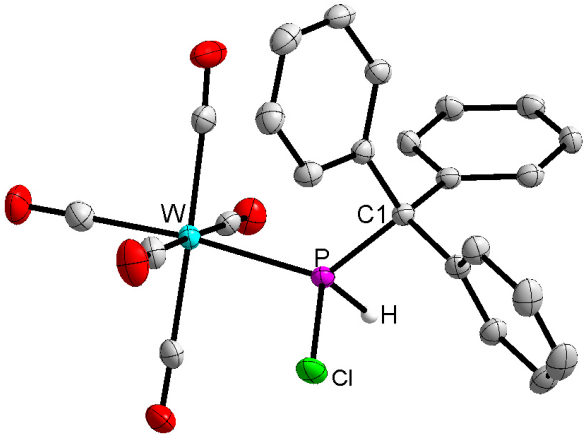
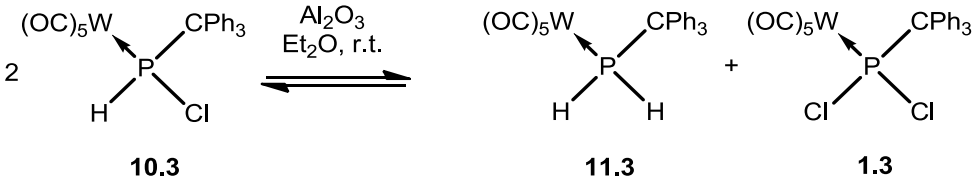



***Figure 3.6:*** DIAMOND plot of the molecular structure of complex **10.3** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at phosphorus are omitted for clarity. Selected bond lengths in Å and angles in °: P-W 2.4868(9), P-C1 1.917(3), P-Cl 2.0596(11), Cl-P-W 107.55(5), C1-P-Cl 104.19(10), C1-P-W 128.54(10).

The molecular structure of **10.3** shows a slight shortening of the P-C bond compared to the corresponding *P*-$CPh_3$-substituted dichlorophosphane complex **1.3**[33] (1.917(3) Å vs 1.955(2) Å in **1.3**) as well as a slight elongation of the P-W bond (2.4868(9) Å vs 2.4685(6) Å in **1.3**).

Research performed with derivatives of chlorophosphane complex **10.3** bearing the $CH(SiMe_3)_2$ group (**10.1**) or $C_5Me_5$ group (**10.2**), had already shown that deprotonation with weakly nucleophilic bases like LDA leads to Li/Cl phosphinidenoid complexes **2.1**[31] or **2.2.**[32] Also substitution reactions of the chloride were performed, to yield for example phosphinite complexes[56] or aminophosphane complexes.[57] Therefore, bearing the sterically more demanding $CPh_3$ substituent, **10.3** could lead to a variety of new applications in the future.

An interesting observation was made when a diethyl ether solution of complex **10.3** was treated with aluminium oxide, or when work-up procedures involving aluminium oxide as solid phase material for filtration or column chromatography were tried (scheme 3.15). Both conditions led to an H/Cl exchange between two molecules of **10.3** (“scrambling” or “dismutation”), forming the dichloro(organo)phosphane complex **1.3** and the primary phosphane complex **11.3**, which could easily be identified due to their literature known $^{31}P$ resonance signals at 166.2 ppm ($^1J_{W,P}$ = 319.7 Hz) for dichloro(organo)phosphane complex **1.3**[33] and -41.2 ppm ($^1J_{P,H}$ = 329.3 Hz, $^1J_{W,P}$ = 225.1 Hz) for the phosphane complex **11.3**[33]. No complete conversion was found even after prolonged reaction time (ratio (**1.3** : **10.3** : **11.3**) after 1 day: 3:88:9, ratio after 7 days 6:78:16), indicating an equilibrium between the three complexes.




**10.3** **11.3** **1.3**

***Scheme 3.15:*** Dismutation reaction of **10.3** in the presence of $Al_2O_3$.

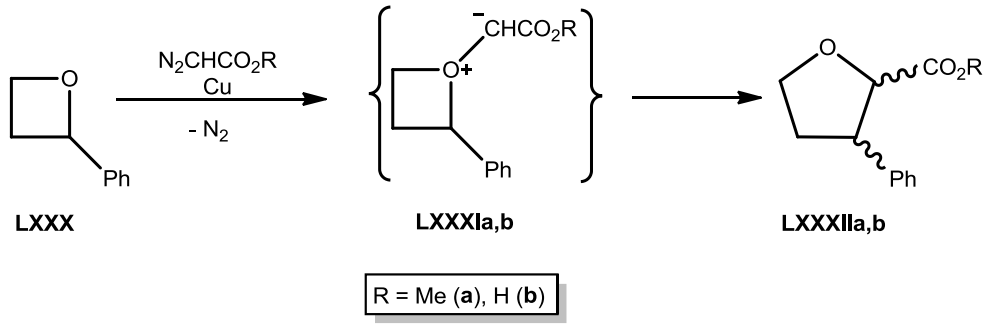
A similar dismutation reaction was described previously by Mathey for the *P*-Ph-substituted derivative of **10**; the stronger Lewis acid $AlCl_3$ catalysed the reaction in dichloromethane and led to an almost quantitative conversion to the corresponding dichloro- and primary phosphane complexes.[47] No such dismutation was described for the *P*-$CH(SiMe_3)_2$ or *P*-$C_5Me_5$-substituted derivatives (**10.1** and **10.2**), yet.

While the obtained aminophosphane complexes are of great interest as building blocks for further phosphane complexes due to the presence of the P-H and the N-H functionalities, the problem with decomposition and reprotonation hampered further research (c.f. scheme 3.12 and figure 3.3). A solution to this problem was found by the group of Streubel, *i.e.* Majhi showed that the stability of such phosphinidenoid complexes is significantly enhanced when the cation is changed to $[K(18\text{-crown-}6)]^+$.[63] First reactivity studies on the K/N(H)R phosphinidenoid complexes were done by Majhi and Schmer.[62] Majhi could prove that under double deprotonation conditions a reaction with $PhPCl_2$ led to an azadiphosphiridine complex. Schmer could additionally show that a selective functionalization either at the P or the N centre is possible.[62]

# 4 Insertion reactions into strained heterocycles

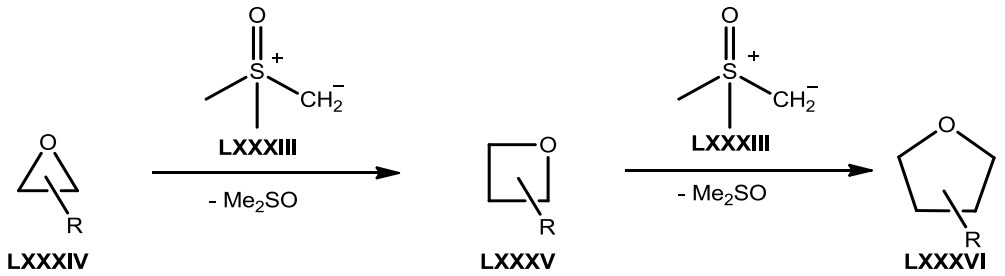
## 4.1 Introduction

To overcome problems observed for carbenes, due to their high reactivity and therefore often low selectivity, several carbene transfer reagents were developed and subsequently used for ring expansion and insertion reactions. Examples for these reagents are diazo organo compounds in the presence of transition metals, which can mimic carbene reactivity in ring expansion reactions.[59] This was presented for example by Nozaki and *co*-workers in 1986 in the reactions of phenyloxetane **LXXX** to give substituted tetrahydrofuranes **LXXXIIa,b**.[65] Formation of oxonium-ylides **LXXXIa,b** from the oxetane with diazoalkanes in the presence of copper and a subsequent [1,2]-*C*-shift was proposed as mechanism for the ring expansion reaction (scheme 4.1).




***Scheme 4.1:*** Cupper catalysed ring expansion reaction of an oxetane by Nozaki *et al.*[65]

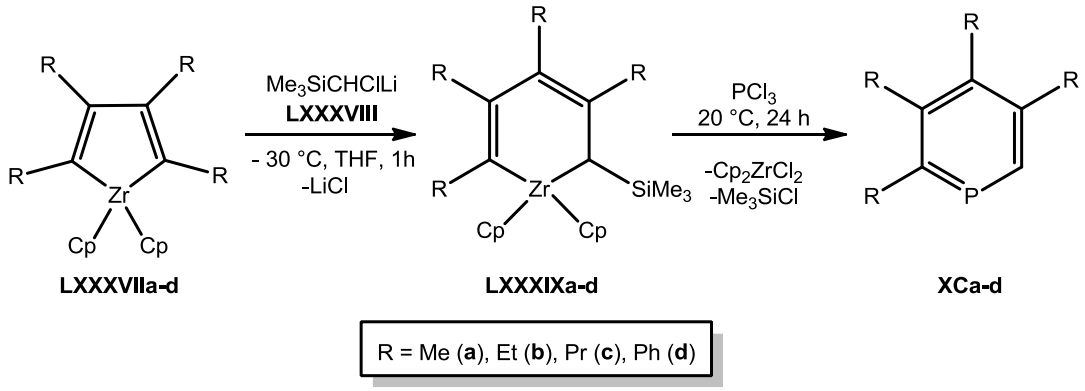
To avoid the use of reactive carbenes or explosive and toxic diazoalkanes, several more systems to transfer carbene fragments, *e.g.* methylene ($CH_2$), were developed. One of these systems is a mixture of trimethylsulfoxonium iodide ([$Me_3SO$]I) and KO$^t$Bu in $^t$BuOH as solvent.[66] Similarly, a deprotonation of the trimethylsulfoxonium iodide with NaH can be used to generate the reactive dimethylsulfoxoniummethylid **LXXXIV**.[67] These systems, using sulfur-ylides, allow easy access to epoxides **LXXXIV** from ketones, oxetanes **LXXXV** from epoxides and tetrahydrofuranes **LXXXVI** from oxetanes (scheme 4.2).[68]




***Scheme 4.2:*** Stepwise heterocyclic ring expansion reactions using dimethylsulfoxonium-methylid as methylene source (Johnson-Corey-Chaykovsky reaction, R = variable substituents).[68]

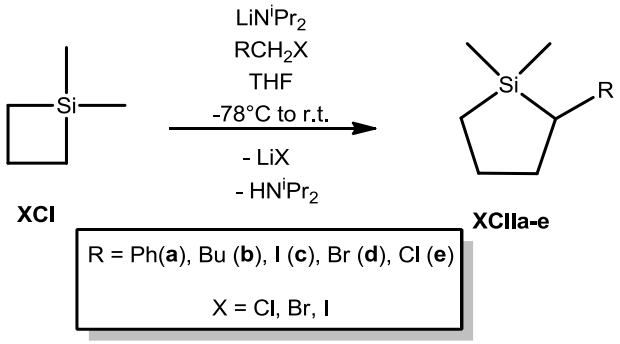
The implementation of non-transition metal carbenoids to mimic the reactivity of carbenes in the preparation of heterocyles is still extremely scarce. The Simmons-Smith reaction, which can efficiently be used in cyclopropanation reactions or epoxide formation reactions,[23] was rarely used in ring expansion reactions, so far. To the best of my knowledge (SciFinder search from 10th of May 2017), reactions of zink carbenoids with epoxides have not been described.

Newer developments involve the use of Li/Cl carbenoids, easily accessible by deprotonation of the corresponding halo alkanes with strong bases (*e.g.* LDA), for the ring expansion of different heterocycles.[69–71] Three of those reactions shall be shown exemplarily. The reaction of zirkonacycles **LXXXVIIa-d** with the sila-neopentyl Li/Cl carbenoid **LXXXVIII** led to valuable precursors (**LXXXIXa-d**) for the synthesis of phosphinines **XCa-d**.[69]



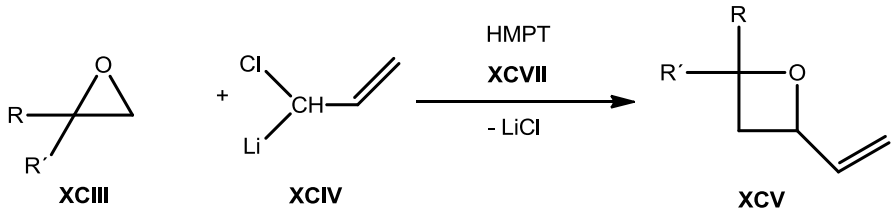

***Scheme 4.3:*** Carbenoid ring expansion and subsequent phosphinine formation using zircona-cyclopentadienes **LXXXVIIa-d**.[69]

The second example is the ring expansion reaction of silacyclobutane **XCI** with Li/X carbenoids to yield silacyclopentanes **XCIIa-e**.[70]




***Scheme 4.4:*** Ring expansion of 1,1-dimethylsilacyclopropane **XCIII** with different Li/halogen carbenoids.[70]

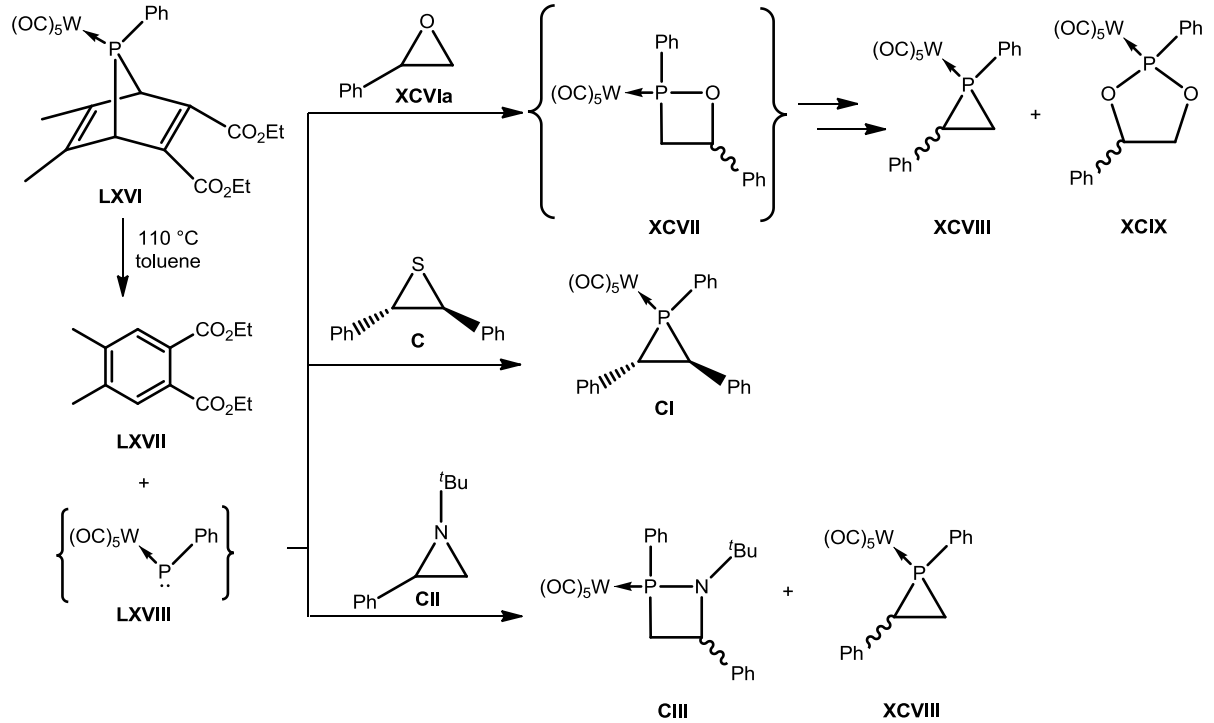
Li/Cl carbenoid **XCIV** was used in ring expansion reactions of different 1,1´-disubstituted epoxides **XCIII**, which was described by Migniac in 1985.[71]




***Scheme 4.5:*** Ring expansion reaction of epoxides using Li/Cl carbenoids **XCIV** (R, R´= various organic substituents).[71]

In contrast to the insertion reactions of carbene equivalents in carbon chemistry, only two attempts towards ring expansion reactions of epoxides utilizing terminal phosphinidene complexes being isolobal to carbenes were published prior to this work.[72][73]

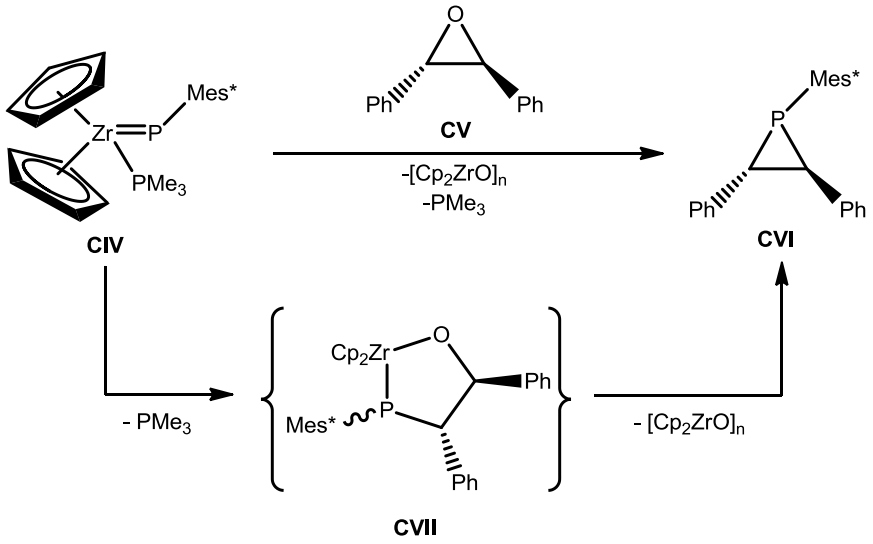
The first such ring expansion reaction to a 1,2-oxaphosphetane complex **XCVII** was proposed by Mathey *et al.* 1987 to occur in the thermal reaction of a 7-phosphanorbornadiene complex (**LXVI**) with styrene oxide **XCVIa** (scheme 4.6)[72] but only a mixture of a phosphirane (**XCVIII**, 9 % isolated yield) and a 1,3-dioxaphospholane complex (**XCIX**, 46 % isolated yield) was obtained. It should be emphasized here that, while the comparable reaction with a thiirane (**C**) only led to the corresponding phosphirane complex **CI**, the reaction with an aziridine derivative (**CII**) gave a 1,2-azaphosphetane complex as insertion product (**CIII**, 40 % isolated yield, obtained as mixture of isomers).




***Scheme 4.6:*** Reactions of a transient, terminal electrophilic phosphinidene complex **LXVIII** with different three membered heterocycles, published by Mathey *et al.* in 1987.[72]

Because the reaction of the terminal electrophilic phosphinidene complex developed by Mathey was only performed at elevated temperatures, it is worthwhile to compare it to the described reaction of *trans*-stilbene oxide (**CV**) with the isolable, terminal nucleophilic phosphinidene complex **CIV** (scheme 4.7). This comparison illustrates several problems, *e.g.* the nature of the metal complex fragment coordinated to the phosphorus centre which has to be tuned accordingly.

The reaction reported by Stephan *et al.* showed, that the nucleophilic terminal phosphinidene complex **CIV** does not yield the product of an insertion reaction but phosphirane **CVI** in a formal exchange of the O atom for a PR unit.[73] This formal exchange proves the close relation between nucleophilic phosphinidene complexes and the electronically comparable and similarly reacting Schrock-type carbene complexes.

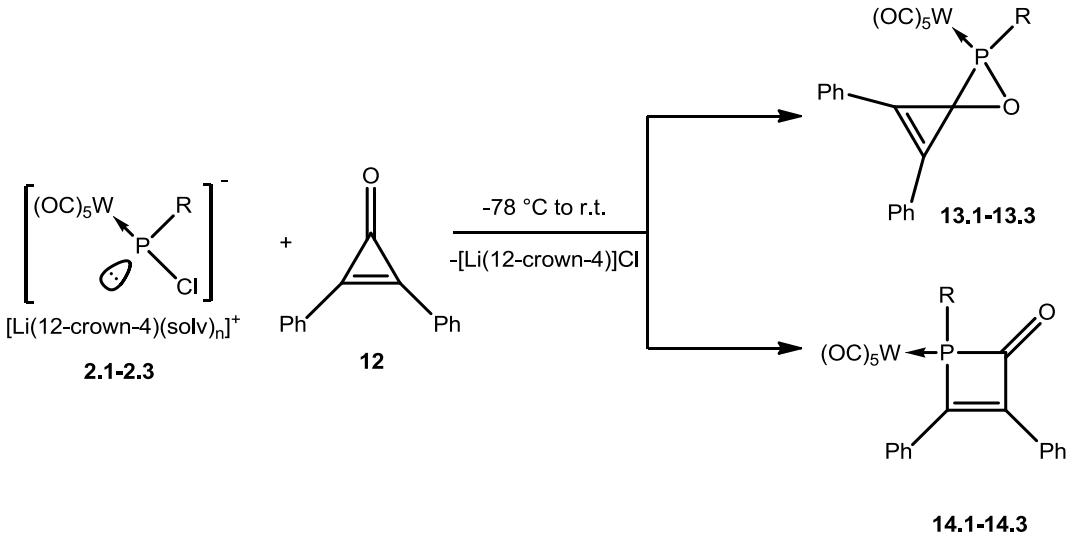



***Scheme 4.7:*** Reactions of transient terminal nucleophilic phosphinidene complex **CIV** with *trans*-stilbene oxide (**CV**) by Stephan *et al.*[73]

In comparison to the well-established carbene transfer reagents, it would be of interest to have a phosphinidene-transfer reagent that is able to perform ring expansion reactions. In this regard, a good alternative to the only transiently formed electrophilic phosphinidene complexes are often Li/Cl phosphinidenoid complexes (see chapter 1.2), allowing for a better control of the reaction while preserving the reactivity. Advantageous is that these complexes can be generated and used at low temperature, so that Lewis acid or thermally induced follow-up reactions are suppressed.

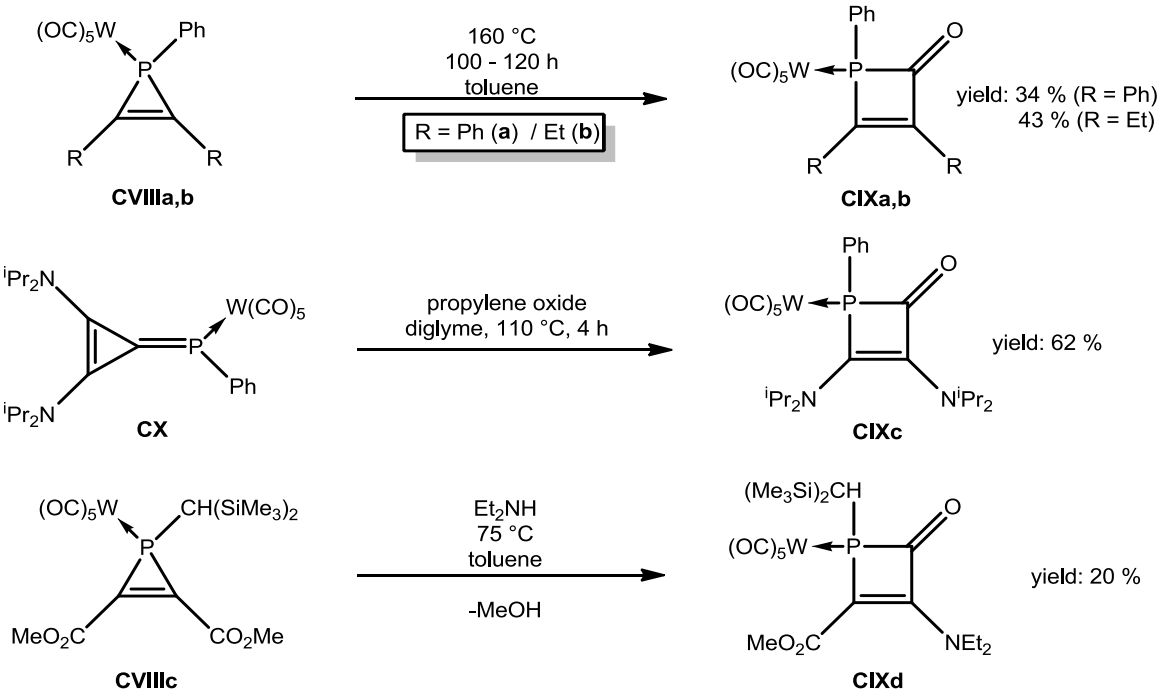
## 4.2 Insertion reactions of Li/Cl phosphinidenoid complexes into cyclopropenone

Previous work in the research group of Streubel only provided one example of a formal insertion of a $P_1$ fragment, originating from Li/Cl phosphinidenoid complexes, into a strained heterocycle:[74] the reaction of Li/Cl phosphinidenoid complex **2.1** with diphenylcyclopropenone **12** did not yield the expected spirocyclic oxaphosphirane complex **13.1**. Instead, 1,2-dihydrophosphet-2-one complex **14.1**, a phosphorus analogue of unsaturated $\beta$-lactams was formed by the formal insertion of a phosphinidene fragment into a C-C bond of the three-membered ring, was obtained (scheme 4.8).




***Scheme 4.8:*** Ring expansion reaction of diphenylcyclopropenone to 1,2-dihydrophosphet-2-one complexes **14.1-14.3** using different Li/Cl phosphinidenoid complexes.

It should be noted that such 1,2-dihydrophosphet-2-one complexes (**ClXa-d**) have been prepared previously by three other methodologies (scheme 4.9): The intramolecular ring expansion of 1*H*-phosphirene complexes **CVIIIa,b** with carbon monoxide,[75] the oxidation of phosphaalkene complex **CX** with propylene oxide,[76] and the ring expansion of 1*H*-phosphirene complex **CVIIIc** in combination with an aminolysis.[77] All three methodologies required tediously prepared starting materials and, especially in the first two cases, harsh reaction conditions. Despite the multi-step preparation of these complexes, a first reactivity study was presented by Mathey in 1985 showing the synthetic potential of these complexes by oxidative decomplexation,[75] hydrolysis under basic conditions, aminolysis and the reduction of the C=O unit with $NaBH_4$ or $LiAlH_4$.[78]




***Scheme 4.9:*** Previously described syntheses of 1,2-dihydrophosphet-2-one complexes **CIXa,b**,[75] **CIXc**[76] and **CIXd**.[77]

To exploit and compare the results obtained by Klein, the reaction of diphenyl-cyclopropenone **12** with the *P*-$C_5Me_5$-substituted Li/Cl phosphinidenoid complex **2.2** was performed.

The reaction yielded selectively one complex that could be isolated by extraction from the reaction mixture with *n*-pentane and assigned to the corresponding 1,2-dihydrophosphet-2-one complex **14.2**. The resonance signal in the $^{31}P$ NMR spectra at 111.0 ppm as well as the $^1J_{W,P}$ coupling constant of 233.5 Hz are in good accordance to the ones described before by Klein ($\delta^{31}P$ = 91.5 ppm, $^1J_{W,P}$ = 230.2 Hz) and a second derivative prepared by Mathey showed similar values (*e.g.* R = R´ = R´´ = Ph, M = W, $\delta^{31}P$ = 86.9, $^1J_{W,P}$ = 231.9 Hz).[75]

Finally, support for the proposed molecular structure of **14.2** could be obtained from a single crystal diffraction study (figure 4.1).

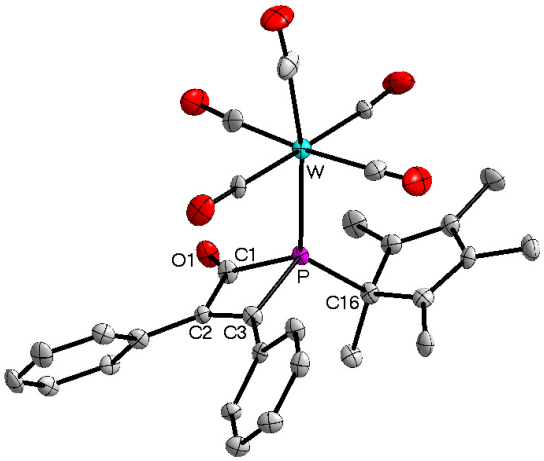



***Figure 4.1:*** DIAMOND plot of the molecular structures of 1,2-dihydrophosphet-2-one complexes **14.2** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. Selected bond lengths in Å and angles in °: W-P 2.5004(17), P-C1 1.905(7), P-C3 1.857(6), P-C16 1.877(7), C2-C3 1.362(9), C3-P-C1 70.9(3).

The data for the molecular structure (figure 4.1) show consistency compared to the complex obtained by Klein.[74] The ring system is characterized by the C2-C3 bond length of 1.362(9) Å.

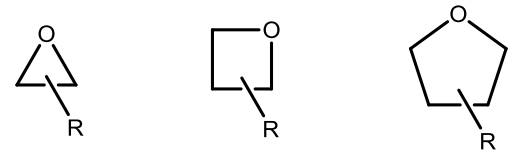
The corresponding complex, bearing the *P*-$CPh_3$ substituent was synthesized recently by Junker, showing similar NMR and bonding parameters.[79]

The observations made for these first insertion reactions gave rise to the fundamental question, if strained heterocycles in general can be used in such ring expansion reactions and, hence, providing access to novel four-membered E,P-heterocyclic ligands. The results of these investigations will be presented and discussed in the following chapters.

# 5 Synthesis of 1,2-oxaphosphetane complexes by insertion into epoxides

## 5.1 Introduction to small-sized O,P-heterocycles

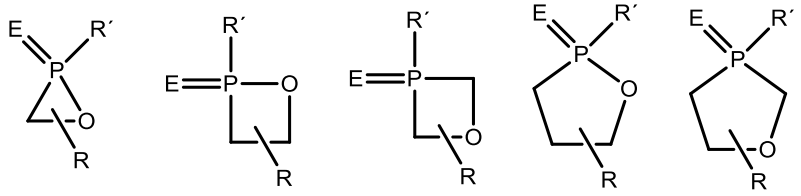
Ethylene oxide (oxirane, R = H), as the most important single derivativeof the oxiranes (**LXXXIV**, scheme 5.1), and other small-sized O-heterocycles are amongst the most useful building blocks in organic chemistry and material science.[80] Therefore, oxiranes are fine chemicals produced in a scale of several million tons per year. Activation and polymerization reactions can not only be used for oxiranes but also for the less reactive, larger heterocycles such as oxetanes **LXXXV** and tetrahydrofuranes **LXXXVI** (scheme 5.1).[81]




**LXXXIV** **LXXXV** **LXXXVI**

***Scheme 5.1*:** Oxiranes **LXXXIV**, oxetanes **LXXXV** and tetrahydrofuranes **LXXXVI** (R = various substituents).

Similar to those rings, phosphorus- and oxygen-containing heterocycles gained more and more interest over the last years due to their industrial use in several high-end applications, *e.g.* the use as additives in flame retardant materials.[4,5] Therefore the search for new heterocyclic phosphorus-containing building blocks became a desirable task.



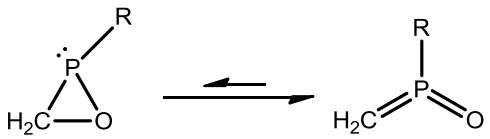

**CXIa-e** **CXIIa-e** **CXIIIa-e** **CXIVa-e** **CXVa-e**

e.g. E = $W(CO)_5$ (**a**), O (**b**), NR´ (**c**), lone pair (**d**) or $R´_2$ (**e**)

**Scheme 5.2:** Oxaphosphiranes **CXIa-e**,1,2-oxaphosphetanes **CXIIa-e, 1,3-**oxaphosphetanes **CXIIIa-e,** 1,2-oxaphospholanes **CXIVa-e** and 1,3-oxaphospholanes **CXVa-e** (R, R´= variable organic substituents).

Based on the high importance of the small oxygen-containing saturated heterocycles in carbon chemistry it surprises that most $\sigma^4,\lambda^5$-P and $\sigma^5,\lambda^5$-P derivatives of the O,P-heterocycles are still poorly investigated and almost no $\sigma^3,\lambda^3$-P derivatives are known. Several problems for the syntheses of such ring systems were described in the literature, but also some stable derivatives thereof. For the $\sigma^3,\lambda^3$-oxaphosphiranes (**CXId**), problems in the

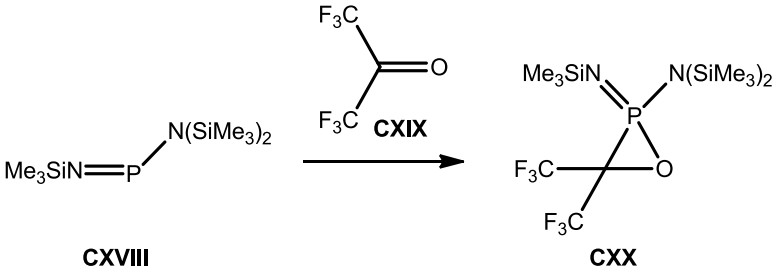
syntheses of suitable precursors and in adaption of the reactions used for the syntheses of oxiranes were hampering research for a long time. For example oxidation of unligated phosphaalkenes with *m*-CPBA does not yield oxaphosphiranes but the corresponding phosphaalkene *P*-oxides (= alkylidene(oxo)phosphoranes).[82,83] In addition, the three-membered $\sigma^3,\lambda^3$-phosphorus heterocycles are prone to ring opening under valence isomerization. First such predictions, based on theoretical calculations of ring systems having a symmetric $PA_2$ constitution, led to the assumption that the equilibrium for oxaphosphiranes is on the side of the open form isomer (scheme 5.3).[84] Very recently, a new theoretical study provided first insights into the situation of oxaphosphiranes and transition metal complexes thereof.[85]




**CXVI** **CXVII**

***Scheme 5.3:*** Postulated valence isomerization of $\sigma^3,\lambda^3$-oxaphosphiranes (R = H, $CH_3$, F, $NH_2$) [84]

Only very few derivatives of $P^v$-oxaphosphiranes were reported so far.[86,87] In one case an equilibrium between the oxaphosphirane and its dimer was found,[88] making further investigations of its specific reactivity impossible. An isolable $\sigma^4,\lambda^5$-oxaphosphirane (**CXX**) was presented by Röschenthaler and Schmutzler in 1978, obtained from the reaction of iminophosphane **CXVIII** with hexafluoroacetone **CXIX** (scheme 5.4). The rearrangement is prevented by the double bonded P-substituent and dimerization is suppressed by introduction of sterically demanding substituents.

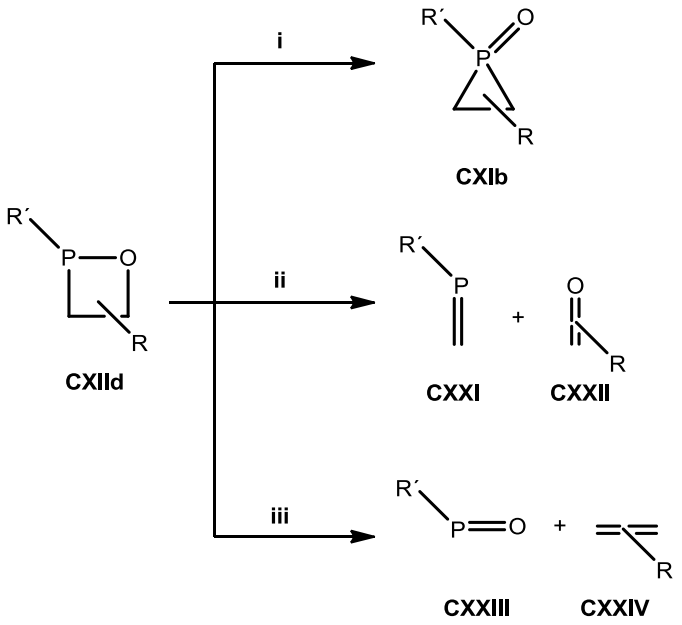



**CXVIII** **CXX**

***Scheme 5.4:*** Synthesis of the first $\sigma^4,\lambda^5$-oxaphosphirane derivative[86]

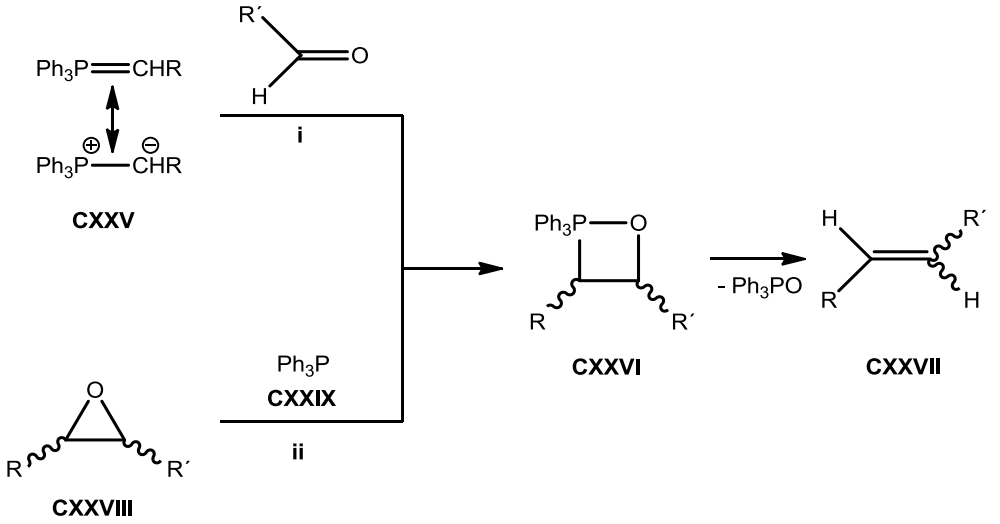
No $\sigma^3,\lambda^3$-oxaphosphetanes are known to date which is somewhat surprising. A retro-synthetic analysis leads to various scenarios (scheme 5.5): an isomerization to a three-membered $\sigma^4,\lambda^5$-phosphirane oxide **CXIb** (**i**) could occur, which, due to the existence of such a phosphirane oxide,[89] seems to be feasible (but isomerization is unknown). Other possibilities would be [2+2] retroaddition reactions forming phosphaalkenes **CXXI** and carbonyl derivatives **CXXII** (**ii**) or to form phosphinidene oxides **CXXIII** and corresponding

alkene derivatives **CXXIV** (**iii**). Both types of reactions have not been described, but the inverse reaction of **ii** was tried and in the reaction of hexafluoroacetone with a phosphaalkene in a ratio of 2:1, a 1,3,2-dioxaphospholane was formed.[90]



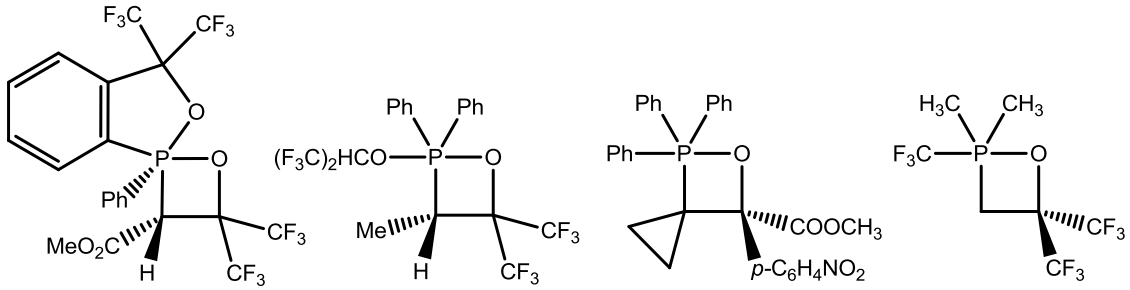

***Scheme 5.5:*** Hypothetical rearrangement and decomposition pathways of 1,2$\sigma^3$,$\lambda^3$-oxaphosphetanes.

In contrast, 1,2$\sigma^5$,$\lambda^5$-oxaphosphetanes already had a great impact on phosphorus chemistry in the past and were investigated in great detail. The reaction between aldehydes or ketones and phosphonium ylides **CXXV** which led to alkene formation was first presented by Wittig in 1953,[91,92] representing a fundamental breakthrough in the use of strained phosphorus heterocycles in organic synthesis.[93] Great effort was invested to clarify the reaction mechanism and 1,2$\sigma^5$,$\lambda^5$-oxaphosphetanes **CXXVI** were proposed as key intermediates in the reaction (scheme 5.6),[94] and their formation was verified by $^{31}$P NMR measurements. During the past decades several derivatives could be isolated and characterized, including single crystal X-ray results (scheme 5.7).[95–97] Nevertheless, also betaines and several equilibria between stereoisomers of the 1,2-oxaphosphetanes are involved in the reaction mechanism proposed today.[13]



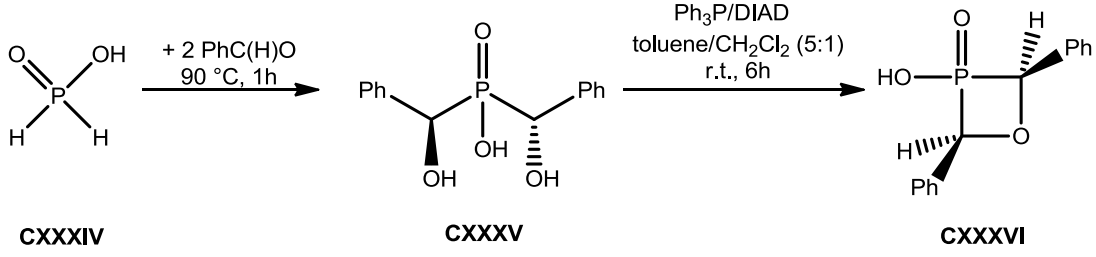

***Scheme 5.6:*** 1,2$\sigma^5$,$\lambda^5$-oxaphosphetane rings in the simplified mechanism for the Wittig reaction (**i**)[91,92] and in the the deoxygenation of epoxides with triphenylphosphane (**ii**).[98]

Interestingly, such 1,2$\sigma^5$,$\lambda^5$-oxaphosphetanes were also proposed as intermediates in the deoxygenation reactions of epoxides using $\sigma^3$,$\lambda^3$-phosphanes.[98] This would be a remarkable similarity to the formal ring expansion reaction by insertion of carbenes into epoxides.




***Scheme 5.7:*** Examples of by single crystal X-ray diffraction studies characterized 1,2$\sigma^5$,$\lambda^5$-oxaphosphetanes (**CXXX**[95], **CXXXI**[97], **CXXXII**[96], **CXXXIII**[99]).

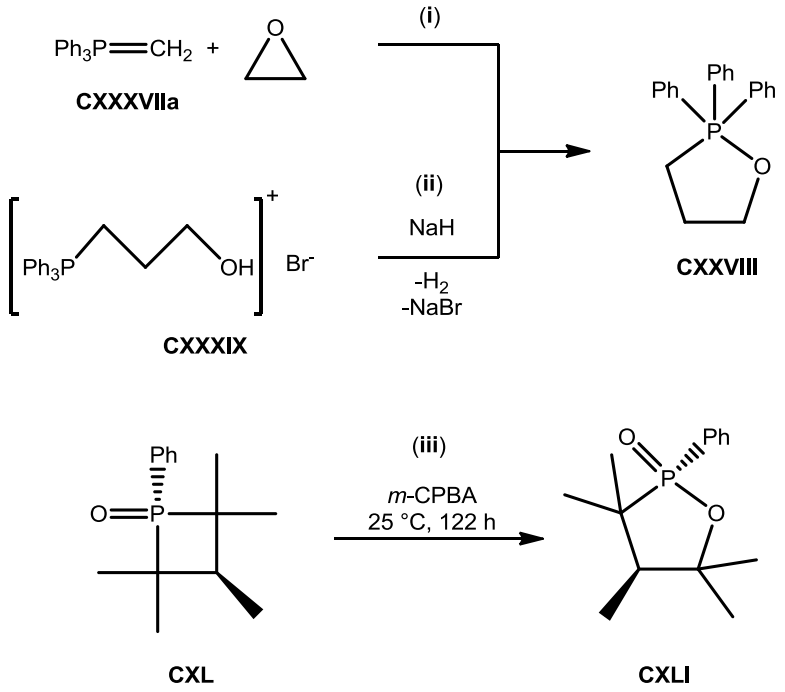
It is also noteworthy that regioisomeric 1,3$\sigma^5$,$\lambda^5$-oxaphosphetanes, e.g. **CXXXVI**, were synthesized by an intramolecular Mitsunobu reaction (scheme 5.8).[100]




***Scheme 5.8:*** Example of the synthesis of 1,3$\sigma^4$,$\lambda^5$-oxaphosphetanes[100] (DIAD = diisopropyl azodicarboxylate)

Similar to the situation of oxaphosphetanes, 1,2- as well as 1,3-oxaphospholanes are possible regioisomers for this five-membered ring system. Several synthetic strategies were developed for the synthesis of 1,2$\sigma^5$,$\lambda^5$-oxaphospholanes **CXXXVIII**. These involve insertions of ylides (e.g. **CXXXVII**) into epoxides (**i**, scheme 5.9),[101] the reaction of triphenylphosphane with 3-bromopropanole and ring closing by subsequent dehydrohalogenation from the phosphonium salt **CXXXIX** (**ii**, scheme 5.9)[102] or the oxidation of a phosphetane-oxide (**CXL**) with *m*-CPBA to the corresponding Bayer-Villiger product **CXLI** (**iii**, scheme 5.9).[103]

In contrast to the three- and four-membered heterocycles, also 1,2$\sigma^3$,$\lambda^3$-oxaphospholane derivatives are known.[104] Surprisingly, the 1,3-oxaphospholanes are even less investigated, which might be due to their missing synthetic accessibility, as only very few multi-step syntheses were described so far.[105]




***Scheme 5.9:*** Synthetic routes to 1,2$\sigma^5$,$\lambda^5$-oxaphospholane (**CXXXVIII**)[101][102] and a 1,2$\sigma^4$,$\lambda^5$-oxaphospholane (**CXLI**).[103]

Of special interest for further functionalization are the derivatives containing a P-O bond, as rings containing only C-O or P-C bonds (1,3-oxaphosphetanes and 1,3-oxaphospholanes) are reacting very similar to their carbon derivatives, while the phosphorus atom mainly plays a spectator role. Therefore focus of this work was placed on the P-O containing ring systems.

As the background picture suggested, blocking of the phosphorus lone pair could suppress decomposition and, hence, allow for the synthesis and isolation of the first derivatives of 1,2$\sigma^3$,$\lambda^3$-oxaphosphetanes, *e.g.* by coordination to a transition metal. In particular, as there is

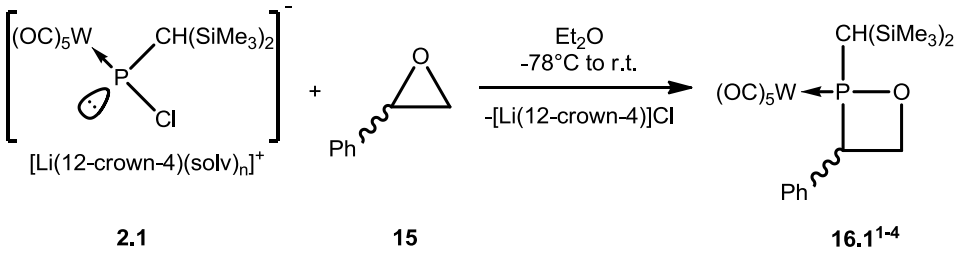
ample precedence from oxaphosphirane chemistry as research by Mathey[82] and Streubel[31][106] has revealed. The development of synthetic strategies to and investigation of the reactivity of oxaphosphirane complexes **CXIa** have been longstanding areas of research.[107–110] In contrast, no 1,2-oxaphosphetane complexes **CXIIa** and only two examples of 1,2-oxaphospholane complexes **CXIVa** were described so far.[111,112]

## 5.2 Synthesis of *P*-bis(trimethylsilyl)methyl-substituted 1,2-oxaphosphetane derivatives

### 5.2.1 The reactions with monosubstituted epoxides

As discussed before (see chapter 4.1), formal ring expansion reaction of epoxides using a terminal phosphinidene complex fragment ($P_1$ fragment) could lead to 1,2-oxaphosphetane complexes, but only one unsuccessful attempt has been described so far.[113] Based on the previous successful ring expansion reaction of a cyclopropenone derivative (see chapter 4),[74] a novel method for the synthesis of 1,2-oxaphosphetane complexes was envisaged: the reaction of Li/Cl phosphinidenoid complexes with oxirane derivatives.

In an early study, Bode has speculated that in the thermal reaction of a *P*-$CH(SiMe_3)_2$-substituted 2*H*-azaphosphirene complex with styrene oxide or propylene oxide 1,2-oxaphosphetane complexes are formed, besides several other products.[113] More recently, Nesterov gained further evidence for the targeted complexes using **2.1** and styrene oxide **15** (scheme 5.4) and, although these reaction showed a significantly increased selectivity compared to the one previously described by Bode, isolation and full characterization of the products was not achieved; furthermore, the assignment of the unusual $^{31}P$ chemical shift of the products could not be asserted. Nevertheless, the continued progress in Li/Cl phosphinidenoid complex chemistry provided further stimulus to start a detailed investigation.




**2.1** **15** **16.1[1-4]**

***Scheme 5.10:*** Reaction of Li/Cl phosphinidenoid complex **2.1** with styrene oxide (**15**).

Hereafter, the in-depth study on the formation of 1,2-oxaphosphetane complexes will be presented. Firstly, the reaction from Nesterov was repeated under different conditions (figure 5.1). Changing the solvent from THF to $Et_2O$ showed a first slight increase in selectivity. A little excess of the epoxide (up to 2.8 equivalents) could be effectively used to suppress the formation of diphosphene complexes (derived from self-reactions of **2.1**) in most cases.[31] Addition of Cu(I)Cl (1 equivalent) as additional Lewis acid, to activate the epoxide via a proposed Cu-O coordination, showed only a negligible influence on the selectivity. The highest selectivity was observed if an excess of 12-crown-4 was employed, but unfortunately the excess crown ether was extremely difficult to separate during further work-up. Therefore,

the isolation of the complex was attempted using standard reaction conditions (one equivalent $^{t}$BuLi, one equivalent 12-crown-4 and diethyl ether as solvent, figure 5.1).

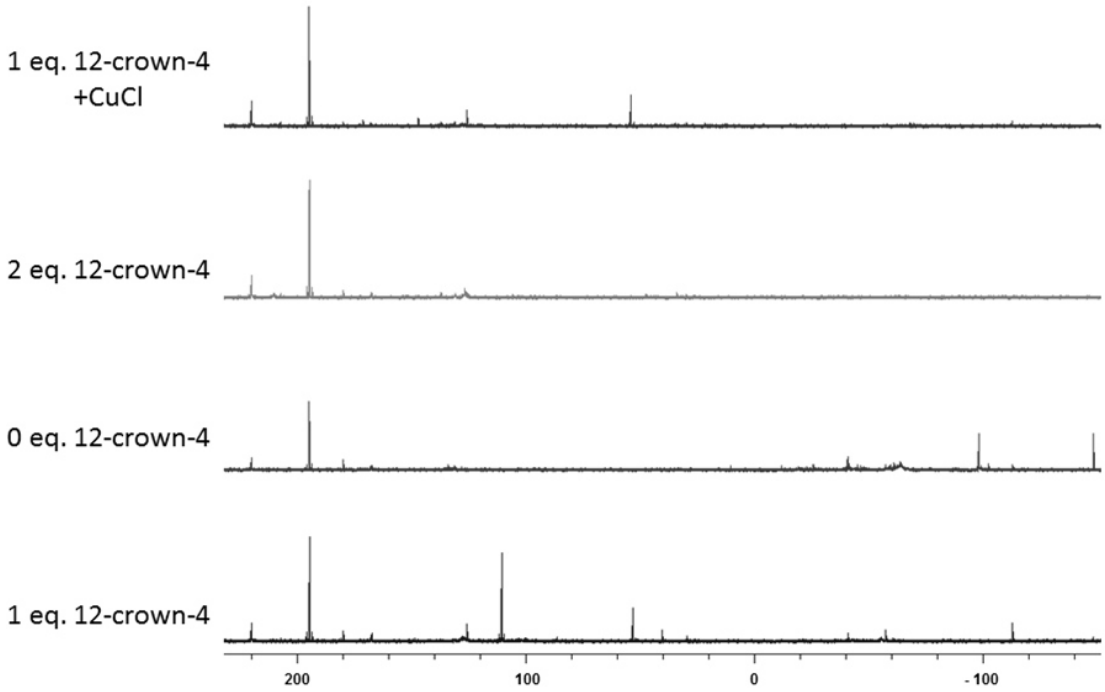



***Figure 5.1:*** $^{31}P\{^{1}H\}$ NMR spectra for the reaction mixtures of Li/Cl phosphinidenoid complex **2.1** and styrene oxide in $Et_2O$ under different reaction conditions.

After optimization of the conditions, it was achieved to obtain complexes **16.1** as mixture of isomers. The complexes showed a surprisingly high thermal stability, *i.e.* a very slow, unselective decomposition of a mixture of isomers (ratio 40:4:53:3) was observed starting at 100 °C.

Four signals with similar $^{31}P\{^{1}H\}$ NMR spectroscopic parameters were observed (Figure 5.2 and table 5.1).

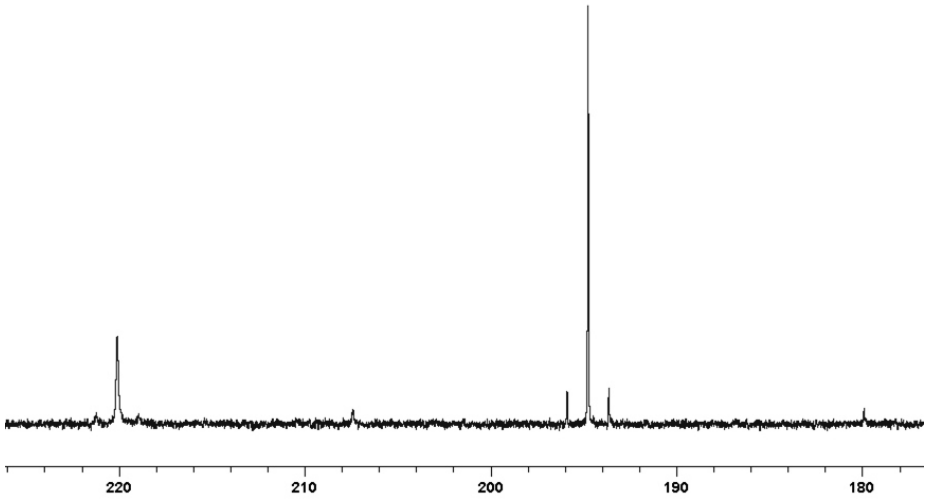
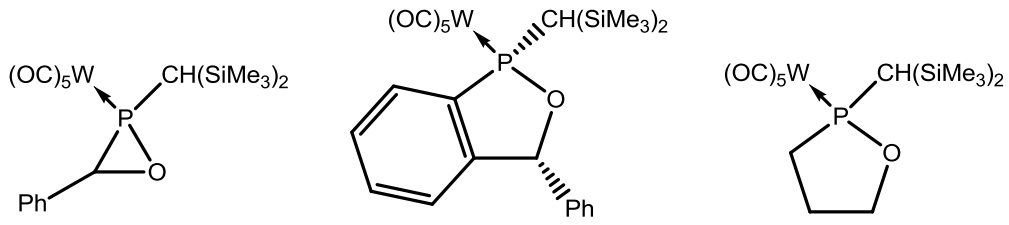



***Figure 5.2:*** $^{31}P\{^{1}H\}$ NMR spectrum for complexes **16.1**$^{1-4}$ after isolation from the reaction mixture (in $CDCl_3$).

NMR spectroscopic measurements revealed that the four signals could be assigned to four isomers of the corresponding 1,2-oxaphosphetane complexes **16.1**[1-4], showing $^{31}$P resonance signals at much lower field than it would be anticipated based on data of oxaphosphirane complexes **17.1**[1][106] and **17.1**[2][114] and 1,2-oxaphospholene complex **18.1**[115,116] or 1,2-oxaphospholane complex **19.1**[1] (scheme 5.11, for complex **19.1**[1] see chapter 6).




| **17.1**[1] | **17.1**[2] | **18.1** | **19.1**[1] |
|---|---|---|---|
| *s-cis* | *s-trans* | | |
| $\delta^{31}$P = 38.2 ppm | $\delta^{31}$P = 31.0 ppm | $\delta^{31}$P = 140 ppm | $\delta^{31}$P = 139.5 ppm |
| $^{1}J_{W,P}$ = 307.7 Hz | $^{1}J_{W,P}$ = 292.3 Hz | $^{1}J_{W,P}$ = 278 Hz | $^{1}J_{W,P}$ = 275.5 Hz |
| $^{2}J_{P,H}$ = < 1Hz | $^{2}J_{P,H}$ = 17.2 Hz | $^{2}J_{P,H}$ = 6.3 Hz | $^{2}J_{P,H}$ = 12.8 Hz |

***Scheme 5.11:*** Examples of different O,P-heterocyclic ligands, $^{31}$P NMR data as well as the exocyclic $^{2}J_{P,H}$ couplings for oxaphosphirane complexes **17.1**[106] and **17.1**[114], oxaphospholene complex **18.1**[115,116] and 1,2-oxaphospholane complex **19.1**[1] (all measured in $CDCl_3$).

The most interesting NMR feature is the magnitude of the exocyclic $^{2}J_{P,H}$ coupling constant. Two of the isomers (**16.1**[3,4]) showed coupling constants of approximately 19.5 Hz while the other two (**16.1**[1,2]) showed far lower coupling constant magnitudes of approximately 5 Hz. This is an indication that the mixture contains two types of atropisomers, one in which the CH-proton of the $CH(SiMe_3)_2$ substituent is oriented towards the metal fragment (s-*cis*) and one in which the proton is oriented in the opposite direction (s-*trans*). This dependency was observed several times before in oxaphosphirane complex chemistry and the correlation between the orientation and coupling constant was proven by Peréz via independent synthesis of the two atropisomeric complexes **17.1**[1][106] and **17.1**[2].[114] Complex **16.1**[1] was obtained in almost pure form (98% of **16.1**[1]) by extraction of the other isomers with *n*-pentane and recrystallization from diethyl ether, containing only small amounts of **16.1**[3].

***Table 5.1:*** Selected NMR characteristics of the isomers of the first isolated 1,2-oxaphosphetane complexes.(measured in $CDCl_3$, [a] broadened signal, [b] not observed due to low signal/noise ratio)

| | $^{31}P\{^1H\}$ NMR | | $^1H$ NMR (P-C*H*$(SiMe_3)_2$) | | ratio |
|---|---|---|---|---|---|
| | $\delta$ [ppm] | $^1J_{W,P}$ [Hz] | $\delta$ [ppm] | $^2J_{P,H}$ | 1:2:3:4 |
| **16.1**[1] | 220.2 | 275.4 | 2.25 | 6.4 | 40 |
| **16.1**[2] | 210.7[a] | -[b] | 1.70 | 4.0 | 4 |
| **16.1**[3] | 195.1 | 273.1 | 2.59 | 19.4 | 53 |
| **16.1**[4] | 179.7 | 281.1 | 2.29 | 19.5 | 3 |

Mass spectrometric measurements confirmed the molecular composition of the mixture of **16.1**[1-4] as $C_{20}H_{27}O_6PSi_2W$ and an elemental analysis using the isomer mixture was performed, and the result was in accordance with the elemental composition. Based on this, the successful insertion of the $P_1$-fragment into the epoxide was proposed and the ring constitution was finally confirmed by a single crystal X-ray diffraction study (Figure 5.3).

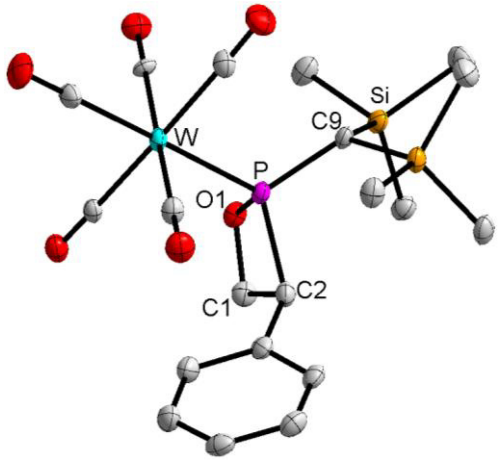
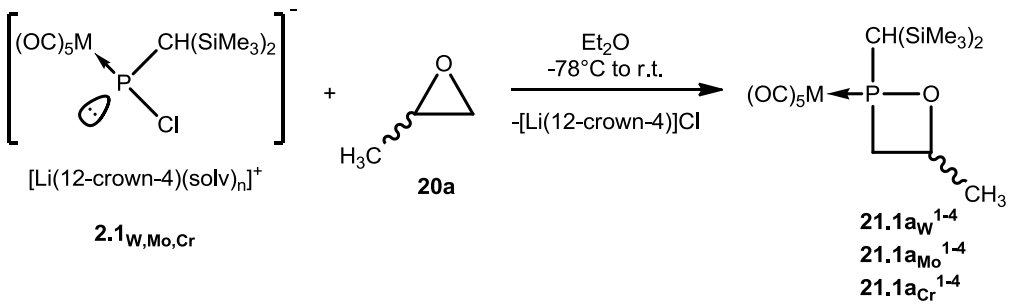



***Figure 5.3:*** DIAMOND plot of the molecular structure of 1,2-oxaphosphetane complex **16.1** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. Selected bond lengths in Å and angles in °: W-P 2.4749(11), P-O1 1.677(3), P-C2 1.894(5), P-C9 1.820(4), C1-C2 1.537(6), C1-O1 1.458(5), C2-P-O1 79.20 (18), P-C2-C1 84.5(3), C2-C1-O1 99.2(3), C1-O1-P 95.3(3), C9-P-O1 107.28, C2-P-C9 109.76(19), O1-P-W 111.47(11), C2-P-W 124.78(14), C9-P-W 116.91(15).

The molecular structure of **16.1** shows the non-planar four-membered POCC-ring as main ligand motif and proves that the reaction took place at the benzylic position of the styrene oxide, yielding the corresponding 3-regioisomer of the 1,2-oxaphosphetane complex. This is in contrast to the expected attack at the least hindered side of the epoxide, but typical for styrene oxide as the benzylic position is the most electrophilic one.[117]

All bond lengths, also for the bonds in the ring, are in the expected range for single bonds and show neither a significant elongation nor shortening. The bond angles in the ring represent the four membered heterocycle with the sum of all four ring angles equals 358.2° being almost exactly the geometrically expected, but bond angles between 79.2 and 99.2° were found. In addition, the ring shows a slight folding with a folding angle of 14.2°.

Surprisingly, the selectivity of the reactions increased drastically when alkyl-substituted epoxides were used. For example, the reaction of the *P*-$CH(SiMe_3)_2$-substituted Li/Cl phosphinidenoid complex **2.1** with propylene oxide (**20a**) in diethyl ether led to a mixture of four isomers of the 1,2-oxaphosphetane complex **21.1a$_W$** in high selectivity (ratio see table 5.2). A minor side-product with a resonance signal at 103 ppm (less than 1 % by $^{31}P$ NMR-integration) was observed; the nature of the side product and its formation will be discussed in chapter 5.2.2.




***Scheme 5.12:*** The reaction of Li/Cl phosphinidenoid complexes **2.1$_W$**, **2.1$_{Mo}$** and **2.1$_{Cr}$** with propylene oxide **20a**.

To broaden the scope of the reaction, a set of 1,2-oxaphosphetane complexes was synthesized using the homologous Li/Cl phosphinidenoid complexes **2.1$_W$**, **2.1$_{Mo}$** and **2.1$_{Cr}$**, bearing the different group 6 metal pentacarbonyl fragments. A selective reaction was observed in all cases, but a drop in yield for the Mo and Cr complexes was found, compared to **21.1a$_W$** (table 5.2).

Complexes **21.1a$_{W\text{-}Cr}$** showed similar analytic characteristics and only a small influence of the metal fragment on the isomeric ratio was observed. The amount of **21.1a$_{Cr}^1$** and **21.1a$_{Cr}^3$** is slightly reduced (about 10 %) in favour of isomer **21.1a$_{Cr}^4$** (table 5.2). A typical shift of the resonance signal to lower field is observed when comparing the W, Mo and the Cr derivatives ($\Delta\delta$ W/Mo ~ 32 ppm, $\Delta\delta$ Mo/Cr ~ 25 ppm).

***Table 5.2:*** $^{31}P\{^1H\}$ NMR data ($CDCl_3$) and yields for the *C*-Me-substituted 1,2-oxaphosphetane complexes **21a$_W$-21a$_{Cr}$** ([a] not determined due to low signal/noise ratio).

| | $\delta^{31}P$ [ppm] ($^1J_{W,P}$ [Hz]) | | | | ratio [1:2:3:4] | yield [%] |
|---|---|---|---|---|---|---|
| | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | | |
| **21.1a$_W^{1-4}$** | 176.4 (273.4) | 169.2 - [a] | 164.5 (267.8) | 164.4 (268.7) | 30:4:19:47 | 58 |
| **21.1a$_{Mo}^{1-4}$** | 209.8 | 201.0 | 196.2 | 195.7 | 30:6:46:18 | 27 |
| **21.1a$_{Cr}^{1-4}$** | 233.1 | 226.7 | 222.6 | 221.0 | 23:3:14:60 | 11 |

A similar, typical influence was observed for the CO resonance signals in the $^{13}C\{^1H\}$ NMR spectra, *i.e.* the resonance signals are shifted towards lower field in going from W to Mo and Cr ($\Delta\delta$ W/Mo ~ 8 ppm (*cis*-CO) and ~ 11 ppm (*trans*-CO), $\Delta\delta$ Mo/Cr ~ 11 ppm (*cis*-CO) and ~ 11ppm (*trans*-CO)). A typical influence on the magnitude of the $^2J_{P,C}$ coupling constant was also observed, in which the coupling constants are quite similar for W and Mo complexes ($^2J_{P,C}$(*cis*-CO) ~ 8 Hz (W) / 10 Hz (Mo), $^2J_{P,C}$ (*trans*-CO) ~ 24 Hz (W) / 27 Hz (Mo)) and the coupling constants for Cr complexes are significantly different ($^2J_{P,C}$(*cis*-CO) ~ 15 Hz (Cr), $^2J_{P,C}$ (*trans*-CO) ~ 7 Hz (Cr)). While most signals for the ligand systems are similar, a slight influence on the magnitude of the $^1J_{P,C}$ coupling constants for the P-$CH_2$ group was observed: in contrast to the data found for the $M(CO)_5$ unit, the Cr and Mo complexes are quite similar and only the W complexes show slightly higher coupling constants ($\Delta^1J_{P,C}$ ~ 3-7 Hz).

While the $^1$H NMR data are almost identical, a small but significant influence was found for the *P*-C*H*$(SiMe_3)_2$ proton, which experienced a slight highfield-shift in going from W to Cr to Mo ($\Delta\delta$ ~ 0.1 ppm per each derivative) with the magnitudes of the $^2J_{P,H}$ coupling constants being similar for Cr and W and being significantly smaller for Mo ($\Delta^2J_{P,H}$ ~ 2-3 Hz, table 5.3). The signals for the W complex are magnified in figure 5.4 to show the observable difference in the coupling constants for the s-*cis* and s-*trans* configurated complexes.

***Table 5.3:*** Selected $^1$H NMR data ($CDCl_3$) for the P-C*H*$(SiMe_3)_2$ proton of the *C*-Me-substituted 1,2-oxaphosphetane complexes **21.1a$_W$-21.1a$_{Cr}$** ([a] very weak signal, [b] not determined due to low signal/noise ratio).

| | $\delta^1$H [ppm] ($^2J_{P,H}$ [Hz]) | | | |
|---|---|---|---|---|
| | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 |
| **21.1a$_W$$^{1-4}$** | 1.99 (6.2) | 2.46 (~ 19)[a] | 2.24 (19.5) | 1.93 (6.0) |
| **21.1a$_{Mo}$$^{1-4}$** | 1.78 (3.8) | -[b] | 1.72 (3.3) | 1.96 (18.1) |
| **21.1a$_{Cr}$$^{1-4}$** | 1.88 (6.8) | 2.30 (20.3) | 2.09 (20.0) | 1.84 (6.1) |

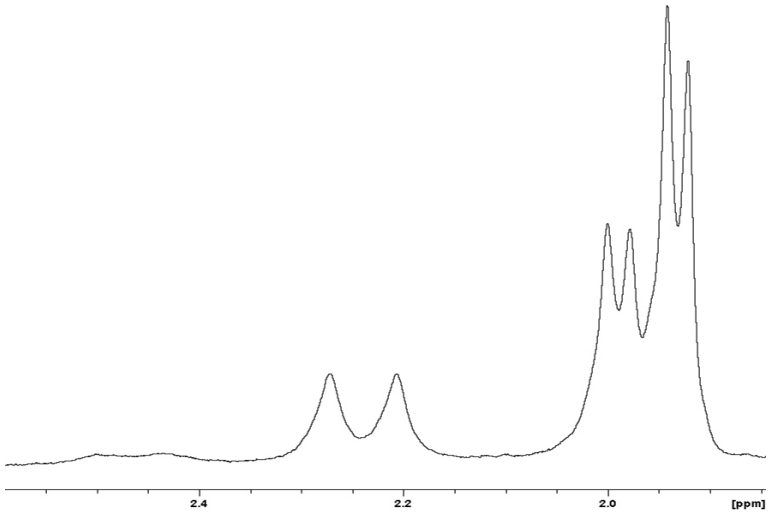



***Figure 5.4:*** Zoom in on the *P*-C*H*($SiMe_3$)$_2$ signals in the $^1$H NMR spectrum of complexes **21.1a$_W$**[1-4] as example of the signal pattern.

Single crystals that were suitable for X-ray diffraction studies could be obtained for the three complexes from saturated *n*-pentane solutions. All three complexes crystallized in the space group $P2_12_12_1$. The three molecular structures (figure 5.5) show the heterocyclic ligands and similar data for the bond lengths and angles.

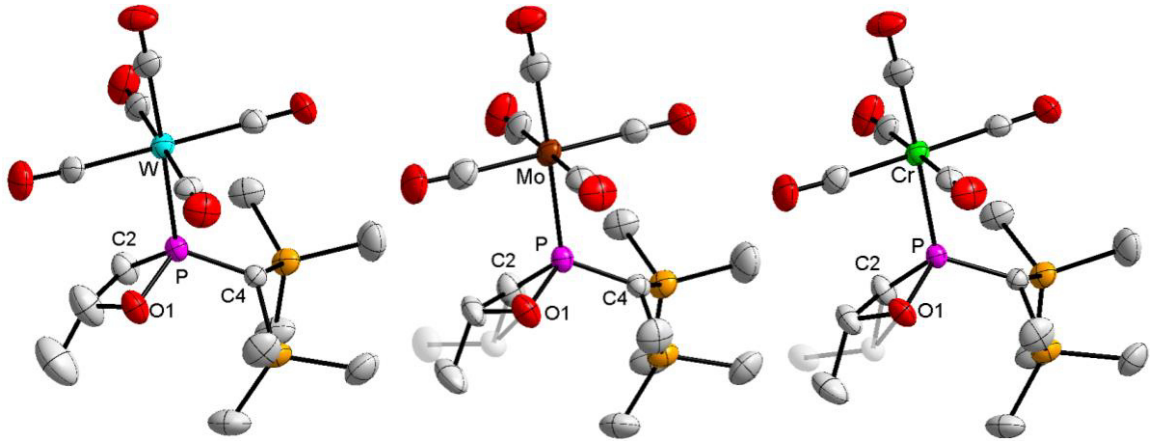



***Figure 5.5:*** DIAMOND plot of the molecular structures of 1,2-oxaphosphetane complexes **21.1a$_W$, 21.1a$_{Mo}$** and **21.1a$_{Cr}$** (from left to right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. The split-site (1:1) for the Me-C unit is represented using a transparent mode for clarity.

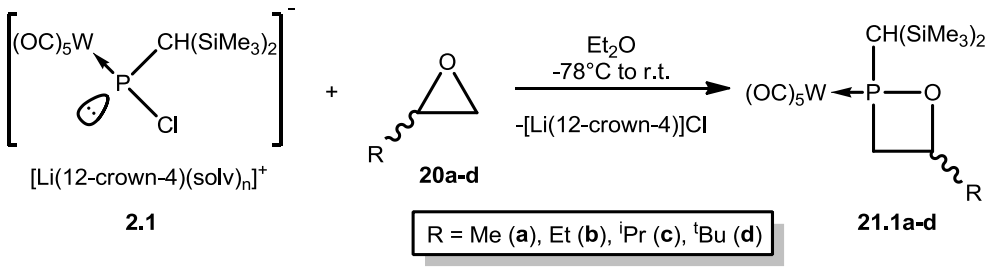
The three molecular structures are isostructural and only the P-M bond for the case M = Cr is slightly shorter due to the smaller Cr atom. Of special interest are the molecular structures of **21.1a$_{Cr}$** and **21.1a$_{Mo}$** as they show that two isomers co-crystallized (substituent at the ring oriented towards or away from the $M(CO)_5$ fragment). Depending on the orientation of the

C-substituent of the isomer, the ring folds in the opposite direction to reduce the steric interaction of the *C*-substituent and the *P*-substituent or the metal fragment (table 5.4).

***Table 5.4:*** Selected bond lengths in Å and angles in ° for 1,2-oxaphosphetane complexes **21.1a$_W$**-**21.1a$_{Cr}$** (folding angles are given for solid/transparent part of the splitting).

| | P-C2 | P-C4 | P-M | C2-P-O1 | folding angle |
|---|---|---|---|---|---|
| **21.1a$_W$** | 1.827(5) | 1.800(5) | 2.4846(14) | 79.7(2) | 21.9 |
| **21.1a$_{Mo}$** | 1.817(3) | 1.806(3) | 2.4883(8) | 80.03(14) | 33.09/16.2 |
| **21.1a$_{Cr}$** | 1.830(3) | 1.807(3) | 2.3412(8) | 79.90(13) | 27.3/20.6 |

To obtain further insight into the effect of different substituents and the scope of the ring forming reaction, the specifics including the steric demand of the *C*-substituent at the epoxide was changed stepwise. Therefore the reaction of **2.1** was performed with butylene oxide **20b**, 1,2-epoxy-3-methylbutane **20c** and 3,3-dimethylbutylene oxide **20d** (scheme 5.13).




***Scheme 5.13:*** Syntheses of 1,2-oxaphosphetane complexes **21.1a-d** bearing different sterically demanding *C*-substituents.

While the reaction was very selective using propylene oxide **20a**, and still quite selective in case of butylene oxide **20b**, first problems were observed in case of 1,2-epoxy-3-methylbutane **20c**. Finally, the reaction with 3,3-dimethylbutylene oxide **20d** led mainly to the diphosphene complexes **22** and **23** and, besides some unknown side products, only in traces to the 1,2-oxaphosphetane complexes **21.1d**[1-4]. Direct comparison of the four reaction spectra clearly shows how the selectivity is influenced by the steric demand of the substituent R at the epoxide ring (figure 5.6).

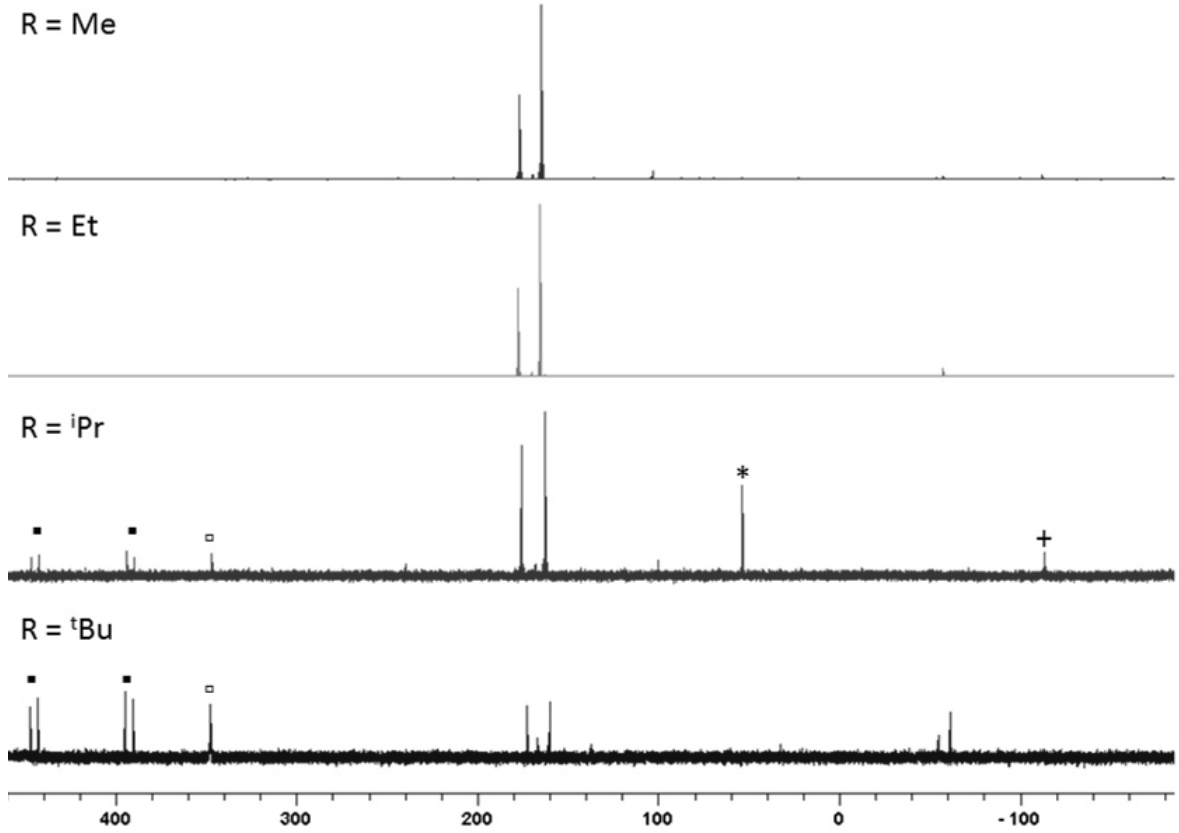
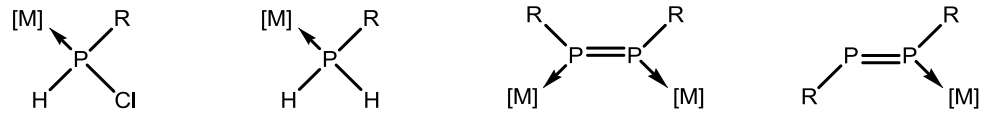



***Figure 5.6:*** $^{31}P\{^{1}H\}$ NMR spectra for the reaction mixtures of the syntheses of 1,2-oxaphosphetane complexes with different steric demanding *C*-substituents R.

The formation of diphosphene complexes (**22** ▫, **23** ▪), formed due to decomposition of the Li/Cl phosphinidenoid complex as a competing reaction pathway, as well as small amounts of the chloro(organo)phosphane complex (**10.1**, *) and phosphane complex (**11.1**, $^{+}$) were observed. They were assigned using their typical NMR data (scheme 5.14).



**10.1**
$\delta\ ^{31}P$ = 54 ppm
$^{1}J_{W,P}$ = 268.3 Hz
$^{1}J_{P,H}$ = 348.4 Hz

**11.1**
$\delta\ ^{31}P$ = - 116.5 ppm
$^{1}J_{W,P}$ = 219 Hz
$^{1}J_{P,H}$ = 333 Hz

**22**
$\delta\ ^{31}P$ = 347.7 ppm
$J_{W,P}$ = 143.7/ 103.0 Hz

**23**
$\delta\ ^{31}P$ = 443.8 / 388.1 ppm
$^{1}J_{W,P}$ = 232 Hz
$^{1}J_{P,P}$ = 514 Hz

***Scheme 5.14:*** $^{31}P$ NMR data for the chlorophosphane complex **10.1**[118] ($CDCl_3$), phosphane complex **11.1**[119] ($C_6D_6$) and the diphosphene complexes **22**[31] and **23**[120] (R = $CH(SiMe_3)_2$ and [M] = $W(CO)_5$).

While these reactions showed a clear trend with regard to reactivity, no significant influence was observed on the isomeric ratio (table 5.5). A good comparison for the case R = $^{t}$Bu is not possible due to the low amount of 1,2-oxaphosphetane complexes formed (9.5% of the reaction mixture by $^{31}P$ NMR integration) and, therefore, the bad signal to noise ratio in the $^{31}P\{^{1}H\}$ NMR spectrum and a larger error in the $^{31}P$ NMR integration.

***Table 5.5:*** $^{31}P\{^{1}H\}$ NMR data ($CDCl_3$) and yields for the *C*$^4$-R-substituted 1,2-oxaphosphetane complexes **21.1a$_W$-21.1d** and their isomers ([a] not determined due to low signal to noise ratio, measurement in $Et_2O$).

| | R (yield [%]) | $\delta^{31}P$ [ppm] ($^{1}J_{W,P}$ [Hz]) | | | | ratio [1:2:3:4] |
|---|---|---|---|---|---|---|
| | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | |
| **21.1a$_W$**$^{1-4}$ | **Me** (58 %) | 176.4 (273.4) | 169.2 - [a] | 164.5 (267.8) | 164.4 (268.7) | 30:4:19:47 |
| **21.1b**$^{1-4}$ | **Et** (31 %) | 177.1 (274.8) | 169.8 (271) | 165.1 (268.4) | 165.0 (268.8) | 29:4:23:44 |
| **21.1c**$^{1-4}$ | **$^{i}$Pr** (20 %) | 174.7 (274.8) | 167.1 (274) | 162.6 (268.6) | 161.7 (268.7) | 29:5:24:42 |
| **21.1d**$^{1-4}$ | **$^{t}$Bu** (not isolated) | 172.2 -[a] | 166.5 -[a] | not observed -[a] | 159.8 -[a] | 35:21:0:43 |

Complexes **21.1b**$^{1-4}$ and **21.1c**$^{1-4}$ could be isolated and characterized by all means necessary. The yield of complexes **21.1c**$^{1-4}$ was quite low (20 %) due to the formation of the side-products. No further discussion of the NMR or IR data will be done as there are no significant differences to the previously described complexes.

Single crystals suitable for X-ray diffraction studies could be obtained for complexes **21.1b** and **21.1c** from saturated *n*-pentane solutions. Both complexes show two co-crystallized isomers by a split-site of the ring, due to the relative orientation of the *C*-substituent to the metal fragment (figure 5.7). No significant influence of the *C*-substituent could be observed on the bond lengths and angles when comparing the three complexes bearing the Me, Et and $^{i}$Pr substituents (table 5.6).

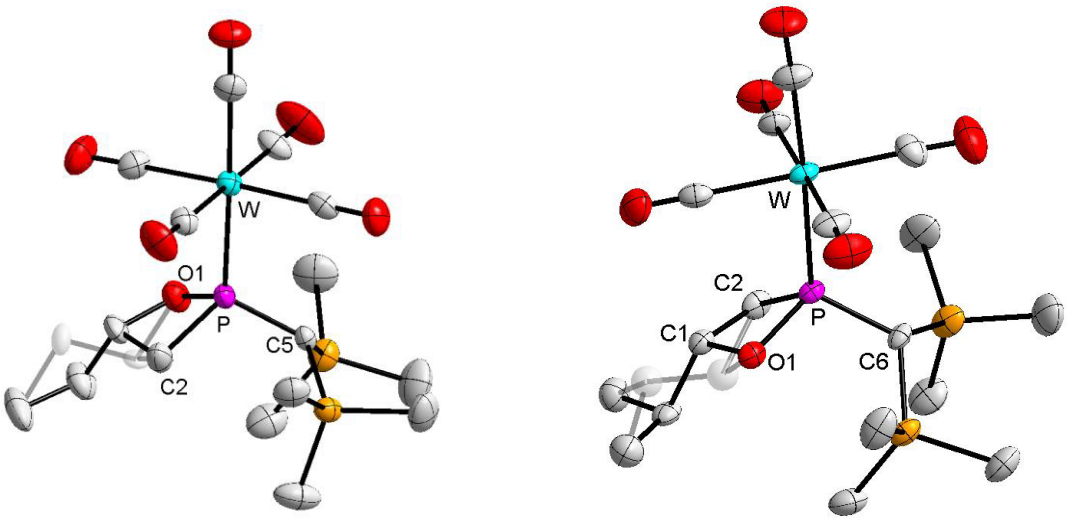
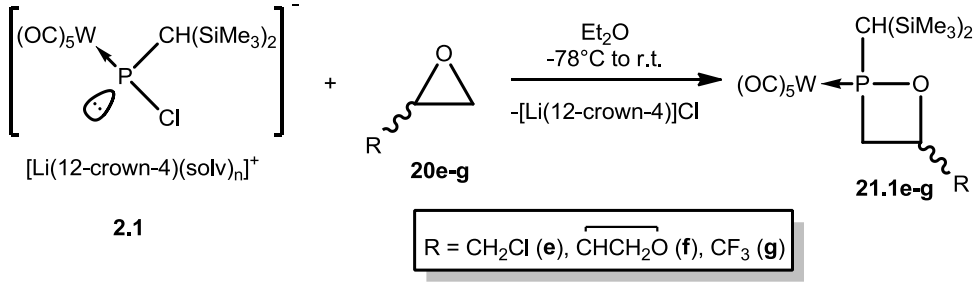



***Figure 5.7.*** DIAMOND plot of the molecular structures of 1,2-oxaphosphetane complexes **21.1b** (left) and **21.1c** (right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. The split-sites (1:1) for the R-C units are represented using a transparent mode for clarity.

***Table 5.6:*** Selected bond lengths in Å and angles in ° for 1,2-oxaphosphetane complexes **21.1a$_W$-21.1c** (folding angles are given for solid/transparent part of the splitting).

| | P-$CH_2$ | P-CH | P-W | P-O | $CH_2$-P-O1 | folding angle |
|---|---|---|---|---|---|---|
| **21.1a$_W$** | 1.827(5) | 1.800(5) | 2.4846(14) | 1.672(4) | 79.7(2) | 21.9 |
| **21.1b** | 1.800(5) | 1.809(4) | 2.4789(12) | 1.668(3) | 79.7(2) | 26.5 /19.7 |
| **21.1c** | 1.846(6) | 1.808(6) | 2.4818(15) | 1.668(5) | 79.6(3) | 24.3/19.1 |

The next part of the investigations using complex **2.1** focused on the quest of functional group tolerance, as functional groups in the epoxide could lead to side reactions or might even activate the epoxide for the reaction. Especially the last aspect could provide further insight into the possible reaction mechanism. Also the influence of the substitution on the spectroscopic data, like the NMR chemical shifts or the magnitudes of the different coupling constants as well as the isomeric ratio should be checked.




***Scheme 5.15:*** Reaction of Li/Cl phosphinidenoid complex **2.1** with different functionalized epoxides (**20e-g**).

Using epichlorohydrin (**20e**) it could be shown that the reaction is not disturbed by the presence of an additional halogen atom at the epoxide substituent. Employing 1,3-butadiene diepoxide (**20f**) it could further be proven that not even an additional epoxy substituent changes the reaction outcome (scheme 5.15). In case of **21.1f** more than the typical four signals for the isomers were observed in the reaction mixture, but all additional signals in less than 1% (figure 5.8). These signals might correspond to complexes where a subsequent reaction took place at the second epoxy-ring, as they are found in larger amounts if the reaction was performed with an excess of the Li/Cl phosphinidenoid complex (cf. chapter 5.3.3). Nevertheless the formation of only four isomers is counter-intuitive as one more stereogenic centre is introduced in the molecule with the epoxy substituent.

To increase the reactivity while maintaining a steric demand of the substituent similar to the $^t$Bu group, the reaction with the $CF_3$-substituted epoxide (**20g**) was performed, leading to 1,2-oxaphosphetane complexes **21.1g$^{1-4}$** in a selective reaction.

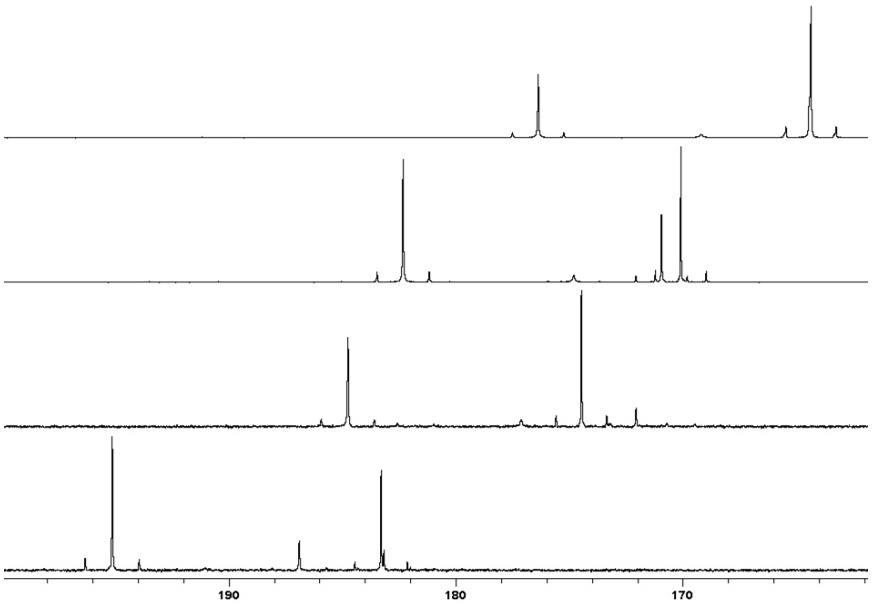



***Figure 5.8:*** $^{31}P\{^{1}H\}$ NMR spectra for the reactions of Li/Cl phosphinidenoid complex **2.1** with propylene oxide (**20a**), epichlorohydrin (**20e**), 1,3-butadiene diepoxide (**20f**) and 1,1,1-trifluoro-2,3-propylene oxide (**20g**) (from top to bottom).

All products could be isolated in moderate to good yields (35 – 61 %). A strong influence of the substituent was found especially on the $^{31}P$ NMR data if the electronic nature of the C-substituent is changed stepwise from weakly electron-donating ($CH_3$) to strongly electron-withdrawing ($CF_3$). Not only do the signals show a deshielding of the phosphorus nucleus but also an increase in the magnitude of the $^{1}J_{W,P}$ coupling constant (table 5.7). This is unexpected, as in other heterocyclic phosphane complexes, *e.g.* oxaphosphirane complexes, *C*-substituents only showed a rather small influence on the NMR spectroscopic data, especially the $^{1}J_{W,P}$ couplings. Nevertheless a comparable effect of electron withdrawing substituents at phosphorus on the chemical shift and the coupling to tungsten was described before.[121]

The ratio of isomers seems to be only slightly influenced by the introduction of the electron-withdrawing groups. Formation of the isomer with the resonance signal at lowest field is more favoured than in case of the Me, Et and $^{i}$Pr-substituted complexes, but no further trend could be observed by changing the substituent.

***Table 5.7:*** $^{31}P\{^{1}H\}$ NMR data, yields and isomeric ratios for complexes **21.1a$_W$** and **21.1e-g**.

| | R (yield [%]) | $\delta^{31}P$ [ppm] ($^{1}J_{W,P}$ [Hz]) | | | | ratio [1:2:3:4] |
|---|---|---|---|---|---|---|
| | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | |
| **21.1a$_W$**$^{1-4}$ | **$CH_3$** (58 %) | 176.4 (273.4) | 169.2 - [a] | 164.5 (267.8) | 164.4 (268.7) | 30:4:19:47 |
| **21.1e**$^{1-4}$ | **$CH_2Cl$** (61 %) | 182.4 (278.6) | 174.8 (281.0) | 171.0 (274.4) | 170.1 (271.3) | 44:7:19:30 |
| **21.1f**$^{1-4}$ | **Epoxy** (49 %) | 184.8 (283.9) | 177.1 - [a] | 174.5 (271.4) | 172.1 (273.9) | 41:7:44:8 |
| **21.1g**$^{1-4}$ | **$CF_3$** (35 %) | 195.1 (289.5) | 186.9 (292.5) | 183.3 (279.6) | 183.2 (283.2) | 49:14:31:6 |

Single crystals of the three new derivatives could be obtained from saturated *n*-pentane solutions at 4 °C, and the molecular structures prove the constitution of all three 1,2-oxaphosphetane complexes including unchanged *C*-substituents at the rings (figure 5.9).

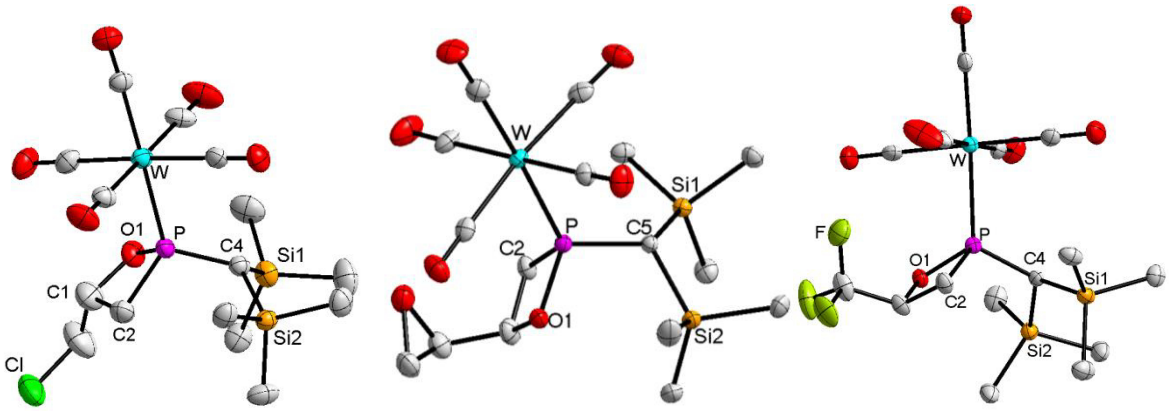



***Figure 5.9:*** DIAMOND plot of the molecular structures of 1,2-oxaphosphetane complexes **21.1e, 21.1f** and **21.1g** (from left to right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity.

All data for the bond lengths and angles are in the expected range, similar to other 1,2-oxaphosphetane complexes and they show only small differences that can be neglected (table 5.8).

***Table 5.8:*** Selected bond lengths in Å and angles in ° for 1,2-oxaphosphetane complexes **21.1a** and **21.1e-g**.

| | P-$CH_2$ | P-CH | P-W | P-O | $CH_2$-P-O1 | folding angle |
|---|---|---|---|---|---|---|
| **21.1a$_W$** | 1.827(5) | 1.800(5) | 2.4846(14) | 1.672(4) | 79.7(2) | 21.9 |
| **21.1e** | 1.835(4) | 1.813(4) | 2.4726(10) | 1.693(3) | 80.35(18) | 22.3 |
| **21.1f** | 1.841(4) | 1.809(4) | 2.4914(10) | 1.679(3) | 79.79(16) | 2.2 |
| **21.1g** | 1.858(4) | 1.802(4) | 2.4672(11) | 1.687(3) | 78.83(17) | 1.9 |

An especially interesting feature of the 1,2-oxaphosphetane complexes was found: the ring geometry of complexes **21.1** was highly flexible with respect to the folding angle (figure 5.10), describing a range from almost planar (**21.1g**, folding angle: 1.9°) to strong folded, with almost 25° folding (**21.1e**, folding angle 22.3°).

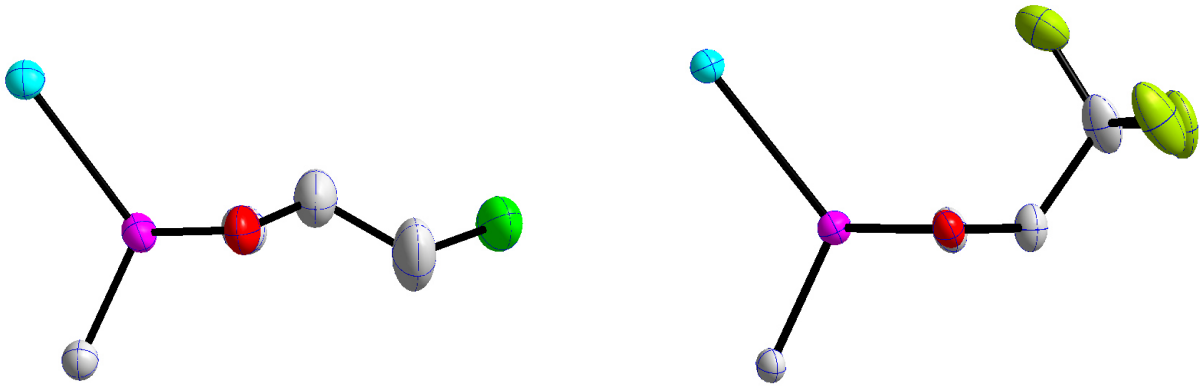
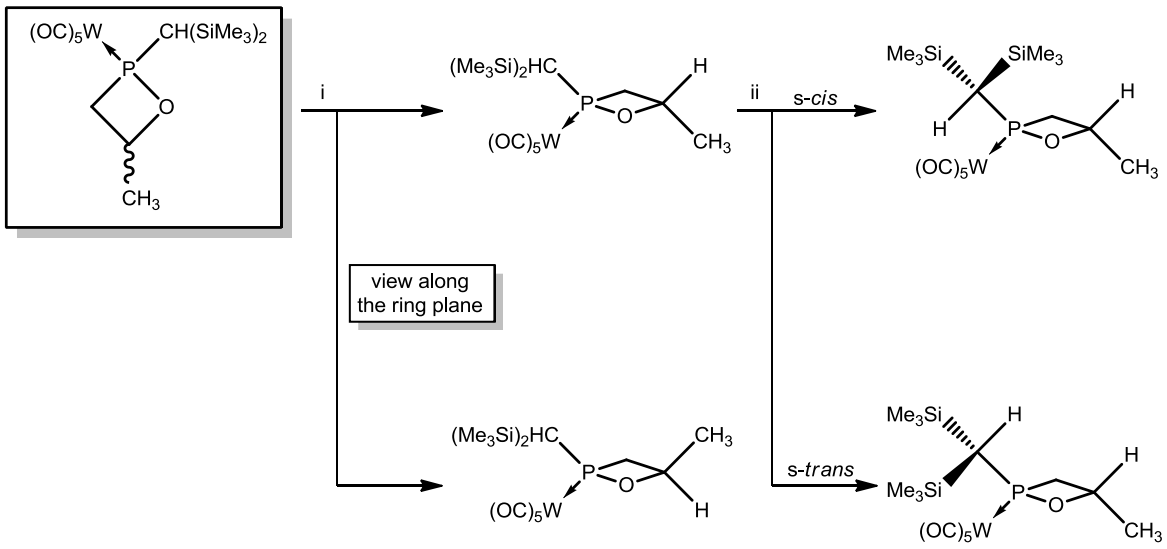


***Figure 5.10:*** Side view along the 1,2-oxaphosphetane rings in the molecular structures of complexes **21.1e** (left) and **21.1g** (right) (the thermal ellipsoids are set at 50 % probability level, hydrogen atoms as well as the CO and $SiMe_3$ groups are omitted for clarity).

As no influence of the steric demand on the folding angle was found in case of the Me, Et and $^{i}$Pr-substituted complexes (**21.1a-c**), it can be proposed that the change in the electronic structure plays the dominant role here. But the statistical platform comprising only a small number of derivatives doesn't allow for a final conclusion, yet. A theoretical study could provide further insights.

### 5.2.2 Discussion of the origins of isomerisms

As in all studies described above four isomers of 1,2-oxaphosphetane complexes were found, a more detailed study on the origins of the isomerisms deemed necessary, although molecular structures and the NMR characteristics of complexes **21.1a**-**21.1g** had provided first hints to one origin: the orientation of the *C*-substituent relative to the metal fragment (**i**, scheme 5.16) and the additional problem of the orientation of the CH-proton of the $CH(SiMe_3)_2$ group (**ii**, scheme 5.16) pointing to (s-*cis*) or away (s-*trans*) from the $W(CO)_5$ fragment. This was already proposed for the *C*-Ph-substituted 1,2-oxaphosphetane complex **16.1**, and was envisaged as reason for the formation of four isomers (scheme 5.16). The possible formation of different regioisomers (*C*-substitution in 3- or 4-position) was neglected due to the usually very high regioselectivity found in nucleophilic reactions of epoxides and phosphanides[122] alongside the clear-cut assignment of all ring-$CH_2$ groups as part of *P*-$CH_2$ units by $^{13}C\{^1H\}$ NMR, except for **16.1**.




***Scheme 5.16:*** Illustration of the proposed situations for the isomerism in 1,2-oxaphosphetane complexes.

So far, all reactions were performed using racemic mixtures of epoxides which was done mainly for cost efficiency as the enantiomerically pure epoxides are quite expensive. Therefore, it was necessary to rule out an influence of the initial stereochemical information on the reaction outcome. Using enantiomerically pure R(+)-propylene oxide, no significant change on the reaction selectivity or the ratio of the formed isomers was observed (figure 5.11), proving that the formation of the isomers is independent from the configuration of the epoxide used. An enantiomeric excess was not determined as separation of the isomers was considered to be of minor interest for the problem investigated herein.

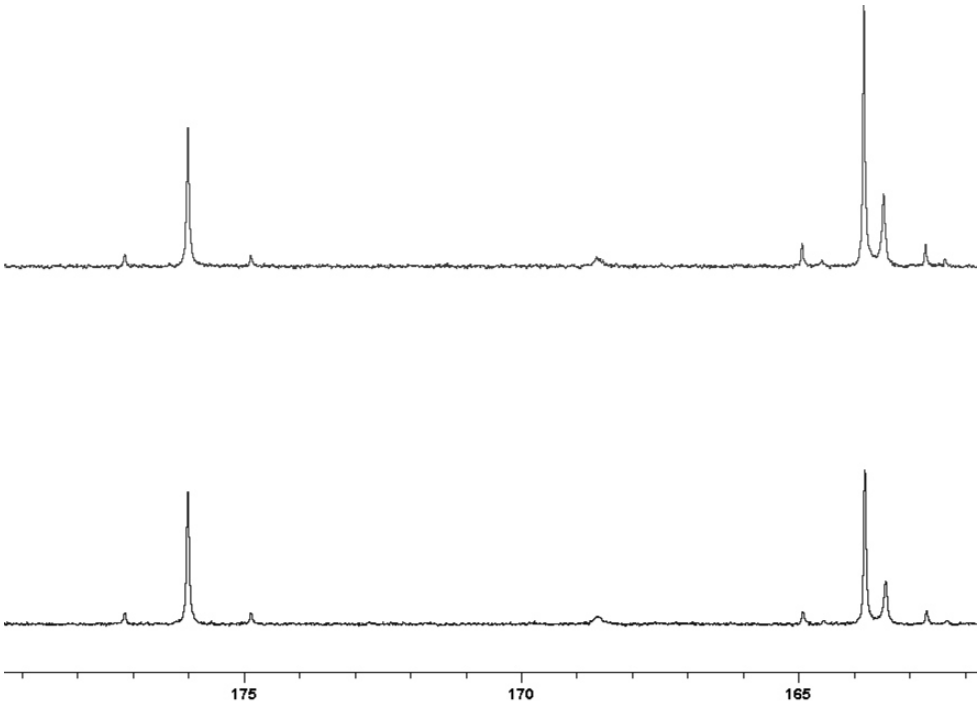
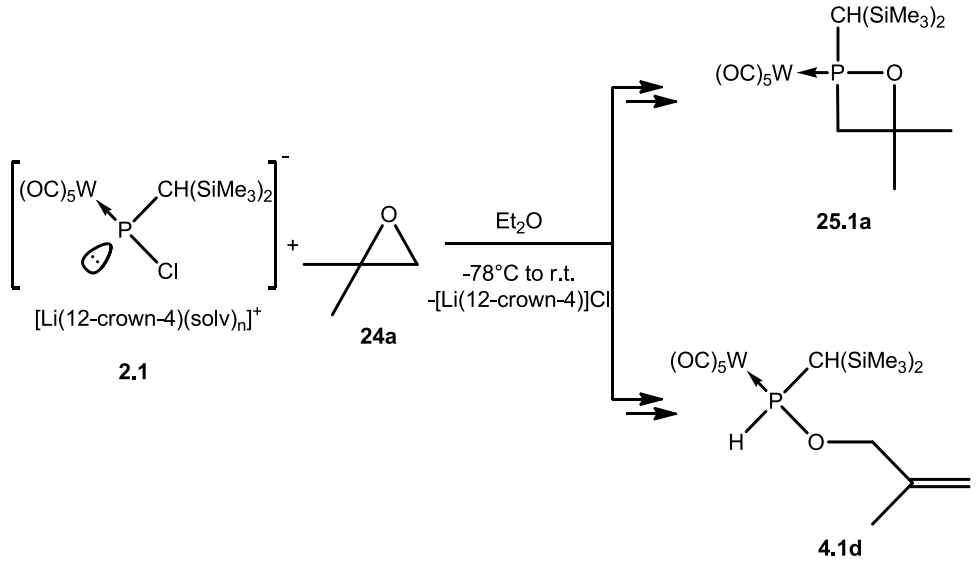



***Figure 5.11:*** $^{31}P\{^{1}H\}$ NMR spectra from the reaction mixtures of the reactions of **2.1** and propylene oxide, as racemic mixture (top) and enantiomerically pure R(+)-propylene oxide (bottom).

After steric and electronic effects on the isomeric ratio were studied, further investigations on a stepwise conceptual elimination of stereogenic centres in the rings were started.

As first step the "removal" of the stereogenic carbon centre was envisaged via employment of symmetrically 1,1-disubstituted epoxides while preserving all other reaction conditions.

Using the simplest 1,1-disubstituted epoxide, namely the 1,1-dimethyloxirane **24a**, a reaction was observed that did not only lead to the isomeric 1,2-oxaphosphetane complexes **25.1a**[1-2], but also to a novel side-product (**4.1d**) in significant amounts (ratio (**25.1a** : **4.1d**): 47:53, scheme 5.17). This side-product contained a P-H bond, as evidenced through the coupling in the $^{31}P$ NMR spectrum ($^{1}J_{P,H}$ = 322.3 Hz). Furthermore, the resonance signal of **4.1d** at 103.6 ppm ($^{1}J_{W,P}$ = 268.1 Hz) appeared in the range of phosphinite complexes, obtained via formal insertion of a phosphinidene fragment into OH bonds (compare chapter 1.2).[10]




***Scheme 5.17:*** Reaction of Li/Cl phosphinidenoid complex **2.1** with 1,1-dimethyloxirane **24a**.

While the formation of complex **4.1d** as side product was unexpected, the reduction of stereogenic centres in the epoxide led to the proposed reduction of the number of isomers observed for 1,2-oxaphosphetane complex **25.1a**. Only two isomers were observed instead of four, formed in a ratio of almost 1:2 (table 5.9). In addition the typical dependency of the $^2J_{P,H}$ coupling constants for two orientations of the $CH(SiMe_3)_2$ proton was observed ($^2J_{P,H}$ (Isomer 1) = 4.6 Hz, $^2J_{P,H}$ (Isomer 2) = 18.9 Hz).

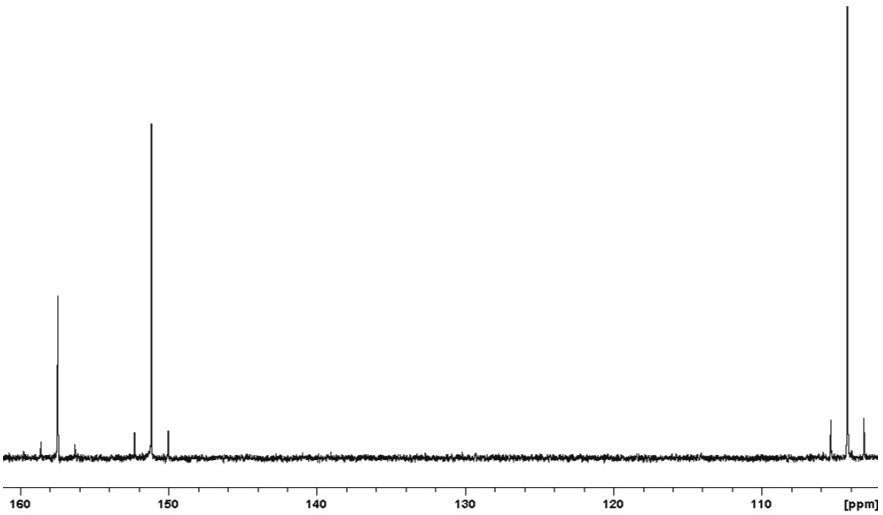



***Figure 5.12:*** $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture from Li/Cl phosphinidenoid complex **2.1** and 1,2-dimethylepoxide **24a**, measured in diethyl ether**.**

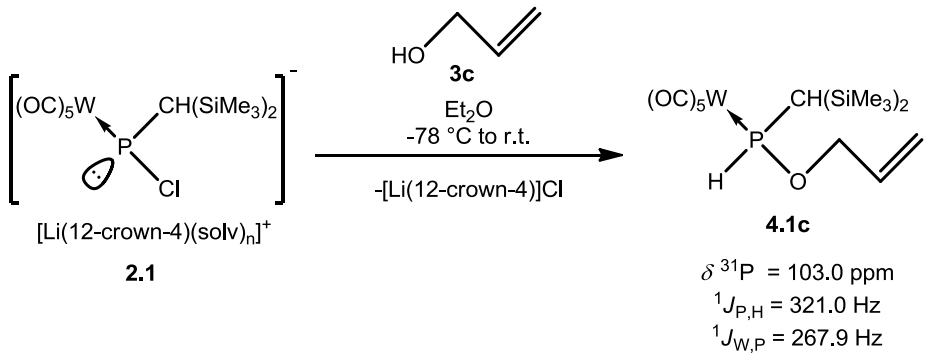
Both isomers display comparable NMR data sets for all other atoms, also the chemical shifts for the resonances of the quaternary $C(CH_3)_2$ carbon atoms in the $^{13}C\{^1H\}$ NMR are nearly identical for both isomers (85.5 and 85.6 ppm). This strong deshielding proves the C-O connection, so that the presence of two different regioisomers (substitution in 3 and 4 position) can again be ruled out.

***Table 5.9:*** $^{31}$P NMR data and yields for complexes **25.1a**[1-2] and **4.1d**.

| | $\delta^{31}$P [ppm] | $^1J_{W,P}$ [Hz] | $^1J_{P,H}$ [Hz] | yield [%] | ratio |
|---|---|---|---|---|---|
| **25.1a**[1] | 157.5 | 277.5 | - | 17 | 36 |
| **25.1a**[2] | 151.1 | 276.0 | - | | 64 |
| **4.1d** | 103.6 | 268.1 | 322.3 | 7 | - |

The $^{31}$P NMR data show some interesting features compared to those observed for *C*-mono-substituted 1,2-oxaphosphetane complexes. The resonance signals showed a significant highfield-shift which is just the opposite effect to the situation found for oxaphosphirane complexes. The $^1J_{W,P}$ coupling constant shows only a slightly higher magnitude than the one for the *C*-methyl-substituted complex **21.1a$_W$**.

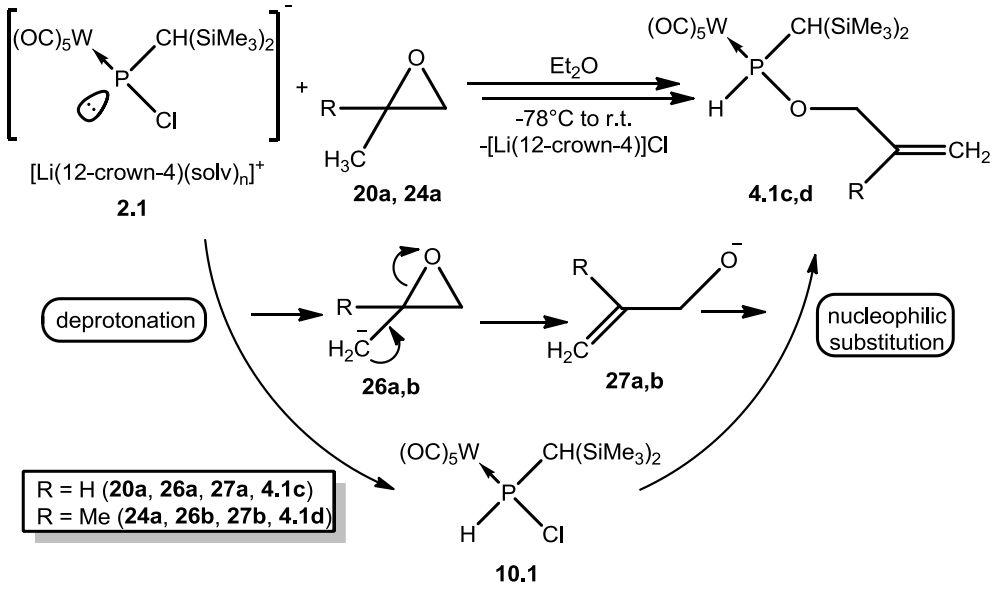
Renewed inspection of the $^{31}$P NMR reaction spectra of the reaction solution of complex **21.1a$_W$** (chapter 5.2.1) revealed that a side product, similar to **4.1d**, was already observed when propylene oxide was used. Despite being less than 1 % of the reaction mixture, by integration of the signals in the $^{31}$P NMR, the resonance signal could easily be assigned to the allyl-substituted phosphinite complex **4.1c**.[10] This complex was already prepared and characterized using the formal insertion reaction of Li/Cl phosphinidenoid complex **2.1** in the OH bond of allyl alcohol **3c** (scheme 5.18) and, hence, could be employed here as authentic sample to prove the identity of the resonance signal.




***Scheme 5.18:*** Synthesis and $^{31}$P NMR data ($CDCl_3$) for complex **4.1c**.[10]

The formation of complexes **4.1c** and **4.1d** can be explained by a different initial reaction step (scheme 5.19). While the first step for the formation of 1,2-oxaphosphetane complexes **21.1a$_W$** and **25.1a** is supposed to be a nucleophilic attack on the epoxide ring, a deprotonation at the C$^\alpha$-position could lead to chloro(organo)phosphane complex **10.1** and carbanions **26a,b** which can rearrange in a ring opening reaction to give the unsaturated alkoxides **27a,b**. This deprotonation and rearrangement is a well-known reaction sequence for $CH_3$-substituted epoxides,[123] *e.g.* as first step in the anionic polymerization of propylene

oxide initiated by strong bases.[124] A nucleophilic substitution yields the complexes **4.1c,d** in a reaction similar to the synthesis of phosphinito complexes described by Duan.[56]




***Scheme 5.19:*** Formation of phosphinite complexes **4.1c,d** by deprotonation and rearrangement of the $CH_3$-substituted epoxides **20a** and **24a**.

Complex **4.1d** and a mixture of isomeric complexes **25.1a**$^1$ and **25.1a**$^2$ were separated by low temperature column chromatography. The formation of phosphinite complex **4.1d** and the 1,2-oxaphosphetane complexes **25.1a**$^{1\text{-}2}$ was also proven by single crystal X-ray diffraction studies (figure 5.13).

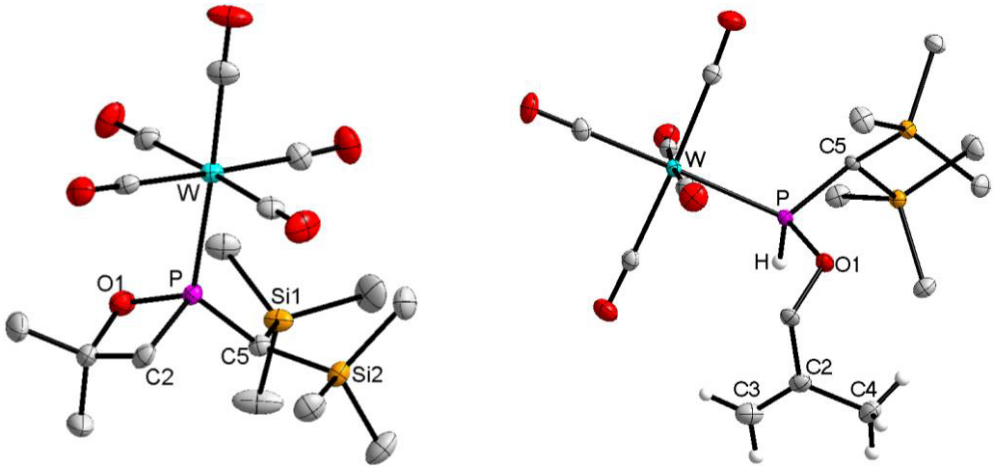



***Figure 5.13:*** DIAMOND plot of the molecular structures of complexes **25.1a** (left) and **4.1d** (right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at phosphorus and at the $H_2C$=C-$CH_3$ subunit are omitted for clarity.

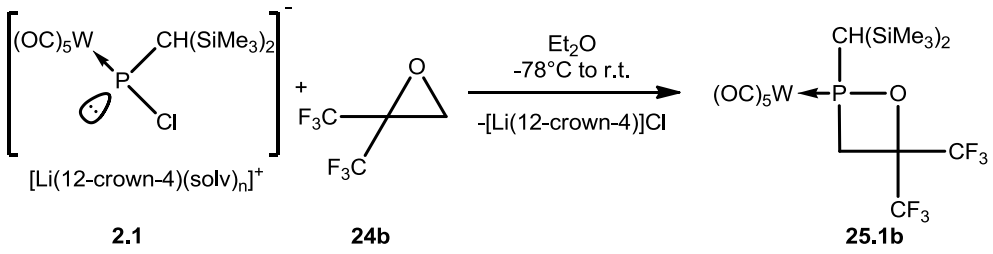
Except for a shortening of the P-$CH_2$ bond, compared to the 4-mono and other 4,4-disubstituted 1,2-oxaphosphetane complexes, all data obtained were close to previously described derivatives of both classes of compounds. Interestingly, the molecular structure of

complex **25.1a** showed the s-*trans* conformation of the W-P-C-H motif for the first time for an 1,2-oxaphosphetane complex. This could explain the small differences in the structural data, but is of special interest as it proves the existence of the two relative orientations of the *P*-$CH(SiMe_3)_2$ group for this ligand system. The ring folding angle of complex **25.1a** is quite small (folding angle 2.2°), presumably due to the missing option to avoid steric interactions between the *C*-methyl groups and the bulky substituents at the phosphorus centre (the $W(CO)_5$ and $CH(SiMe_3)_2$ groups). The latter was discussed to be the reason for the strong ring folding in the case of *C*-mono-substitution, *e.g.* **21.1a$_W$**.

***Table 5.10:*** Selected bond lengths in Å for complexes **21.1a**, **25.1a** and **4.1c,d.**

| | *P-CH$_2$* | *P-CH* | *P-W* | *C=C* | *P-O* |
|---|---|---|---|---|---|
| **21.1a$_W$** | 1.827(5) | 1.800(5) | 2.4846(14) | - | 1.672(4) |
| **25.1a** | 1.804(3) | 1.809(3) | 2.4879(7) | - | 1.664(2) |
| **4.1d** | - | 1.8087(18) | 2.4849(4) | 1.323(3) | 1.6242(13) |
| **4.1c**[10] | - | 1.804(3) | 2.4750(7) | 1.309(6) | 1.626(2) |

To avoid the side reactions, described for the 1,1-dimethylepoxide **24a**, the bis-$CF_3$-substituted epoxide **24b** was employed (scheme 5.20).




***Scheme 5.20:*** Synthesis of 1,2-oxaphosphetane complex **25.1b**.

Surprisingly, the reaction proceeded fast, despite having two bulky $CF_3$ substituents (compare chapter 5.2.1), and a very selective reaction occurred leading to (only) two isomers of the 1,2-oxaphosphetane complex **25.1b**[1,2]; the formation of one isomer was largely preferred (ratio 96:4). This clearly serves as an impressive example of electronic substrate activation for Li/Cl phosphinidenoid complex reactions.

***Table 5.11:*** $^{31}P\{^{1}H\}$ and selected $^{1}H$ NMR data for complexes **25.1b$^{1}$** and **25.1b$^{2}$** (**25.1b$^{1}$** in $CDCl_3$, **25.1b$^{2}$** in toluene-$d_8$).

| | $^{31}P\{^{1}H\}$ NMR | $^{1}H$ NMR (P-C*H*) | ratio | |
|---|---|---|---|---|
| | $\delta$ [ppm] ($^{1}J_{W,P}$ [Hz]) | $\delta$ [ppm] ($^{2}J_{P,H}$[Hz]) | initial | after heating* |
| **25.1b$^{1}$** | 198.2 (297.6) | 2.25(4.0) | 96 | 7 |
| **25.1b$^{2}$** | 191.5 (295.0) | 2.70(19.5) | 4 | 93 |

* 85 °C, 3 days

Interestingly, the $^{2}J_{P,H}$ coupling constants revealed the typical values for the s-*cis* and s-*trans* isomers ($^{2}J_{P,H}$ (**25.1b$^{1}$**) = 4.0 Hz, $^{2}J_{P,H}$ (**25.1b$^{2}$**) = 19.5 Hz), and the isomer ratio was changed by heating the product in toluene-$d_8$ at 85 °C for three days (the ratio changed from 96:4 to 7:93). This is a clear indication that the present case is due to atropisomerism caused by the hindered rotation around the exo-P-C bond. Unfortunately, also slight decomposition occurred over time, so that the second isomer was only characterized from the mixture by multinuclear NMR spectroscopy.

The molecular structure of **25.1b** (figure 5.14), obtained from a single crystal X-ray diffraction study using crystals obtained from a saturated *n*-pentane solution, proofs the 1,2-oxaphosphetane ligand ring motif, but it was also strongly disordered in several atoms and groups. Therefore, it just serves as constitutional proof, but the data will not be discussed further (see appendix, chapter 12.17 for further details on the disordering).

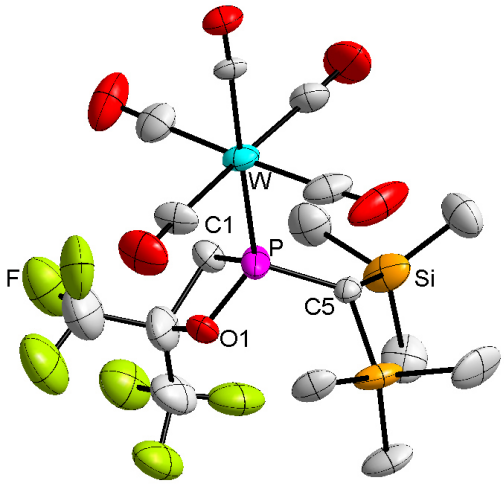


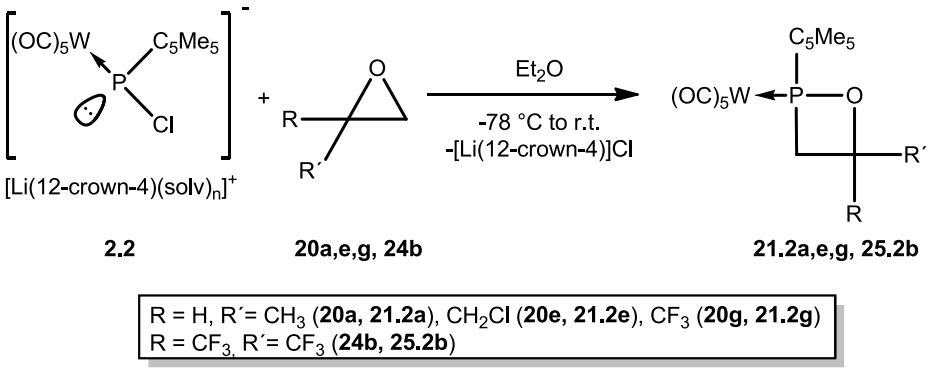

***Figure 5.14:*** DIAMOND plot of the molecular structure of 1,2-oxaphosphetane complex **25.1b** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. The disordering of several groups is not shown for clarity. Selected bond lengths in Å and angles in °: P-W 2.4562(19), P-O1 1.568(12), P-C1 2.04(2), P-C5 1.805(7), C1-P-O1 76.5(7).

## 5.3 Synthesis of *P*-$C_5Me_5$ and *P*-$CPh_3$-substituted 1,2-oxaphosphetane complexes

In the past years, two more substituents were implemented in phosphinidenoid chemistry, the $CPh_3$[33] and the $C_5Me_5$[32] substituent. The *P*-$C_5Me_5$-substituted complexes offered new reactivity by involvement of the ring system in follow-up reactions whereas the *P*-$CPh_3$ substituent introduces more steric bulk into the molecule, allowing to access other novel structural motifs, *e.g.* chloroformylphosphane complexes.[37] Another advantage of these substituents is the suppression of atropisomers that were found in case of the *P*-$CH(SiMe_3)_2$-substituted derivatives.

### 5.3.1 *P*-$C_5Me_5$-substituted derivatives

The *P*-$C_5Me_5$-substituted Li/Cl phosphinidenoid complex is slightly less thermally stable (decomposition starts at -40 °C in solution)[125] than the *P*-$CH(SiMe_3)_2$-substituted one (decomposition starts at -30 °C)[126] and the influence of this was observed especially in the reaction with propylene oxide (scheme 5.21). The reaction could be performed in small scale to obtain the $^{31}P$ NMR data, but the product could not be obtained in large amounts due to faster thermal decomposition of the Li/Cl phosphinidenoid complex. The subsequent formation of several inseparable side products (especially complex **XXXVIII**) made isolation impossible, especially when the size of the reaction was scaled-up. Nevertheless, using *C*-$CF_3$-substituted epoxides the isolation of *P*-$C_5Me_5$-substituted 1,2-oxaphosphetane complexes (**21.1g** and **25.2b**) was possible.




***Scheme 5.21:*** Syntheses of *P*-$C_5Me_5$-substituted 1,2-oxaphosphetane complexes.

As proposed, and in contrast to the reactions observed for the *P*-$CH(SiMe_3)_2$-substituted complex, formation of only two isomers was observed when using mono-substituted epoxides (propylene oxide **20a**, epichlorohydrin **20e** and 1,1,1-trifluoro-2,3-propylene oxide **20g**, figure 5.15). A small influence on the isomeric ratio was observed by introducing the

steric more demanding $CF_3$ substituent (table 5.12), changing the ratio from around 1:1 to almost 2:1.

The reaction with hexafluoro isobutene oxide led to only one observable signal for complex **25.2b** in the $^{31}P\{^1H\}$ NMR spectrum, proving the proposed diminishing of the isomers by elimination of all stereogenic centres, besides at the phosphorus atom itself.

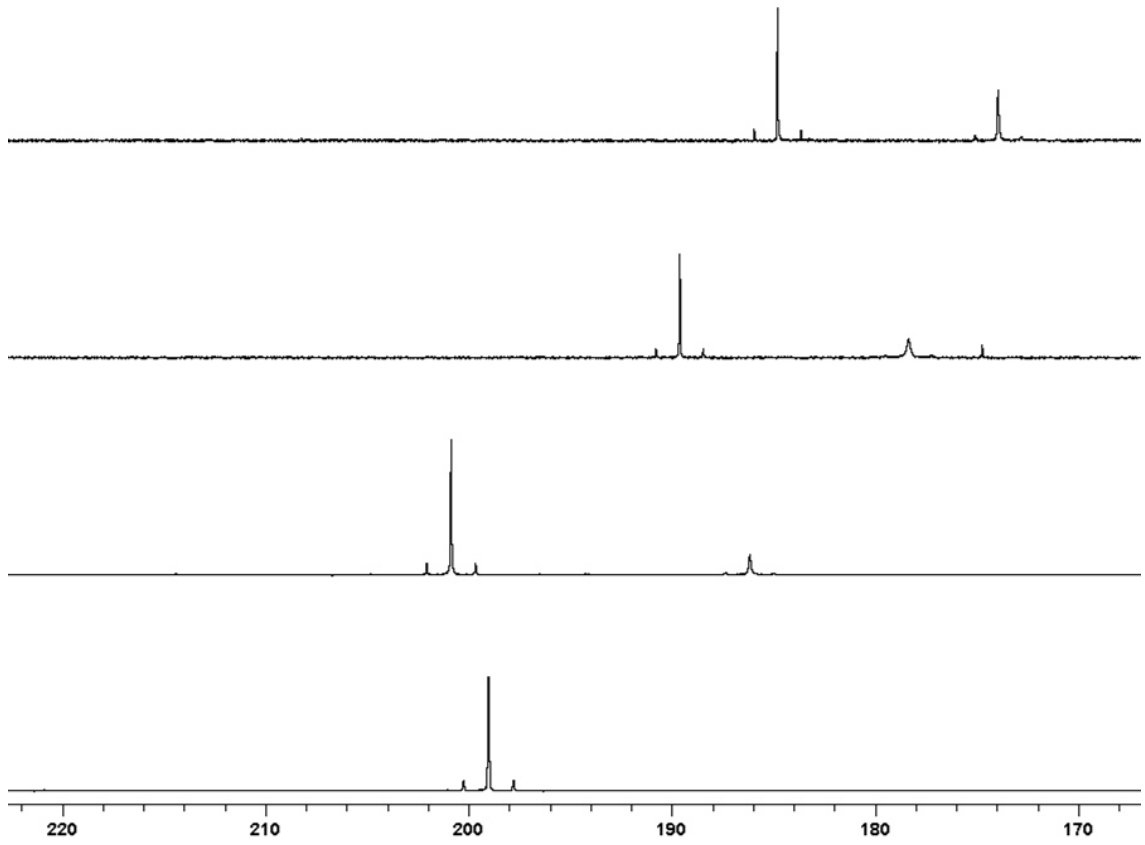



***Figure 5.15:*** $^{31}P\{^1H\}$ NMR spectra for the reaction mixtures of Li/Cl phosphinidenoid complex **2.2** and propylene oxide (**20a**), epichlorohydrin (**20e**), 1,1,1-trifluoro-2,3-propylene oxide (**20g**) and hexafluoroisobutene oxide (**24b**) (from top to bottom).

The $^{31}P\{^1H\}$ NMR data of all *P*-$C_5Me_5$-substituted 1,2-oxaphosphetane complexes are in a similar range as those found for the *P*-$CH(SiMe_3)_2$-substituted complexes. Nevertheless a slight shift to lower field was observed, that is common when comparing complexes bearing these two *P*-substituents.

***Table 5.12:*** $^{31}P\{^{1}H\}$ NMR data and yields for complexes **21.2a, 21.2e, 21.2g** and **25.2b** ([a] not isolated).

| | R, R´ | $\delta^{31}P$ [ppm] ($^{1}J_{P,W}$ [Hz]) | | ratio [1:2] | yield [%] |
|---|---|---|---|---|---|
| | | Isomer 1 | Isomer 2 | | |
| **21.2a**[1-2] | Me, H | 184.8 (279.5) | 174.0 (273.6) | 53:47 | -[a] |
| **21.2e**[1-2] | $CH_2Cl$, H | 189.6 (283.6) | 178.4 (280.0) | 53:47 | -[a] |
| **21.2g**[1-2] | $CF_3$, H | 200.8 (292.3) | 186.1 (284.0) | 73:27 | 36 % |
| **25.2b** | $CF_3$, $CF_3$ | 199.0 (295.1) | | - | 45 % |

Single crystals suitable for X-ray diffraction studies were obtained from saturated *n*-pentane solutions for complexes **21.2g** and **25.2b** (figure 5.16).

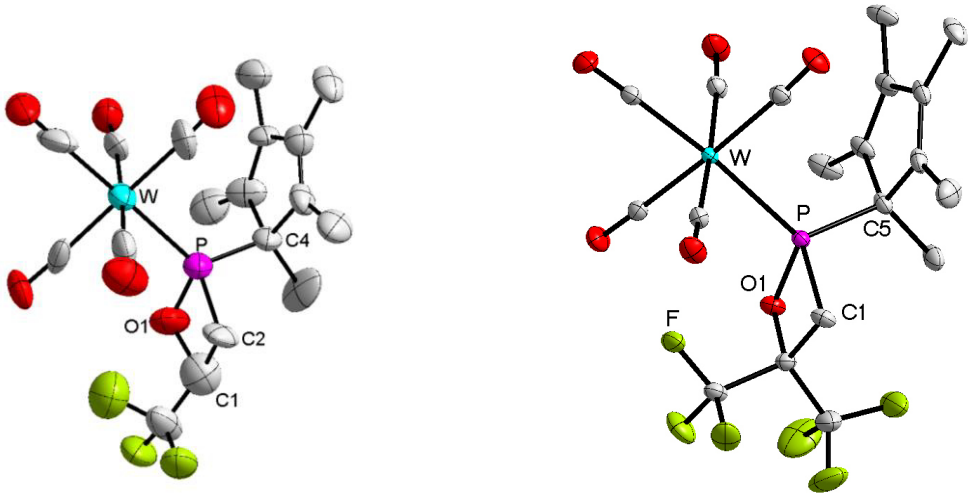



***Figure 5.16:*** DIAMOND plot of the molecular structures of complexes **21.2g** (left) and **25.2b** (right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity.

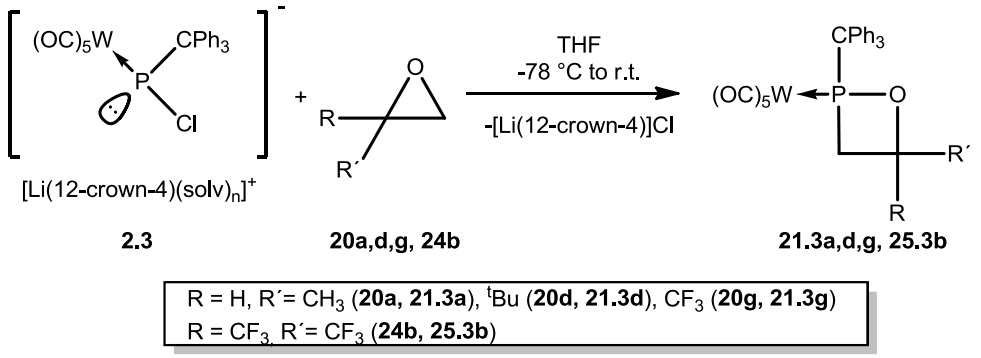
The data showed typical values for the bond lengths and angles, compared to previously presented 1,2-oxaphosphetane complexes. Unfortunately the structure of complex **21.2g** was of low quality, so that a further discussion based on direct comparison of the data for both complexes is not possible.

***Table 5.13.*** Selected bond lengths in Å and angles in ° for complexes **21.2g** and **25.2b**.

| | P-$CH_2$ | P-C4 | P-W | $CH_2$-P-O1 | folding angle |
|---|---|---|---|---|---|
| **21.2g** | 1.95(2) | 1.96(2) | 2.554(7) | 79.1(8) | 14.2 |
| **25.2b** | 1.835(2) | 1.849(2) | 2.4768(6) | 77.70(9) | 10.1 |

### 5.3.2 *P*-$CPh_3$-substituted derivatives

With the *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complex **2.3**,[33] being stable up to ambient temperature, no problems were found in most reactions with mono-substituted epoxides (scheme 5.22 and figure 5.17).




***Scheme 5.22:*** Reaction of Li/Cl phosphinidenoid complex **2.3** with different epoxides.

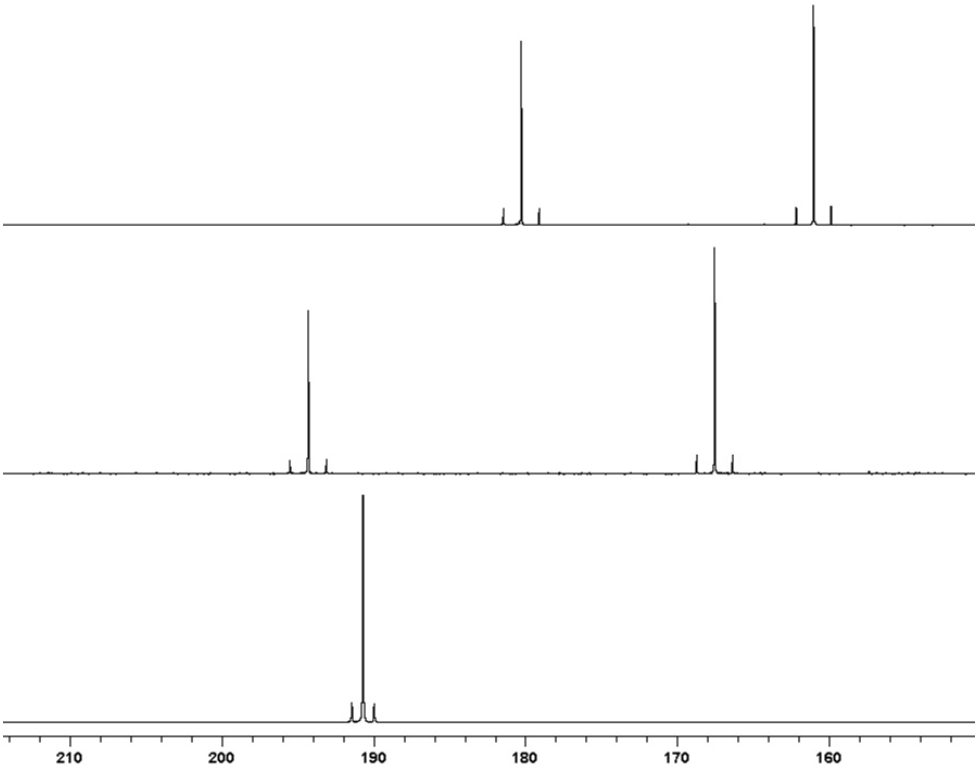



***Figure 5.17:*** $^{31}P\{^1H\}$ NMR spectra for the reactions of Li/Cl phosphinidenoid complex **2.3** with propylene oxide (**20a**, top), 11,1,1-trifluoro-2,3-propylene oxide (**20g**, middle) and hexafluoroisobutene oxide (**24b**, bottom), measured in $CDCl_3$.

Similar to the reactions using the *P*-$C_5Me_5$-substituted Li/Cl phosphinidenoid complex, only two isomers were found for the mono-substituted epoxides and only one isomer for the bis-$CF_3$-substituted derivative **25.3b**.

***Table 5.14:*** $^{31}P\{^{1}H\}$ NMR data and yields for complexes **21.3a,g** and **25.3b**.

| | R, R´ | $\delta^{31}P$ [ppm] ($^{1}J_{P,W}$ [Hz]) | | ratio | yield [%] |
|---|---|---|---|---|---|
| | | Isomer 1 | Isomer 2 | | |
| **21.3a**[1,2] | Me, H | 180.2 (283.1) | 161.0 (278.3) | 47:53 | 46 % |
| **21.3g**[1,2] | $CF_3$, H | 194.3 (295.3) | 167.5 (287.1) | 42:58 | 32 % |
| **25.3b** | $CF_3$, $CF_3$ | 190.7 (299.0) | - | - | 32 % |

The reactions using propylene oxide and 1,1,1-trifluoro-2,3-propylene oxide showed selective conversions to the 1,2-oxaphosphetane complexes. As expected, only two isomers were observed for these two cases, **21.3a**[1,2] in a ratio of 47:53 and **21.3g**[1,2] in a ratio of 42:58 (table 5.14).

All resonance signals show similarities to the ones found for the *P*-$C_5Me_5$ and *P*-$CH(SiMe_3)_2$-substituted complexes as far as chemical shift and coupling constants are concerned. While only a small influence of the *P*-substituent was found on most NMR data, the sterically demanding *P*-$CPh_3$ substituent leads to a stronger differentiation of the two isomers in the $^{31}P$ NMR spectra: a $\Delta\delta$ value of about 20-30 ppm for the *P*-$CPh_3$-substituted complexes, but only about 10-15 ppm for the derivatives bearing the other two *P*-substituents was found.

The reaction with hexafluoro isobutene oxide was still very selective but the work-up had to be done under complete exclusion of water, as long as the Lewis acidic salt [Li(12-crown-4)]Cl[127] was present. This is in stark contrast to previously described 1,2-oxaphosphetane complexes, which showed no significant tendency to react with water under similar conditions. A surprisingly high stability was found when complex **25.3b** was in a salt free solution. No reaction with water could be observed in THF, even at elevated temperature (T = 60 °C).

The resonance signal of complex **25.3b** in the $^{31}P\{^{1}H\}$ NMR spectrum (190.7 ppm, $^{1}J_{W,P}$ = 299.0 Hz) is in the range found for similar 1,2-oxaphosphetane complexes (191.5 – 199.0 ppm, $^{1}J_{W,P}$ = 295.1 – 297.6 Hz). All NMR characteristics are in accordance with the ones for *P*-$C_5Me_5$ and *P*-$CH(SiMe_3)_2$-substituted ring systems.

Single-crystal X-ray diffraction studies confirmed the 1,2-oxaphosphetane ring structure as the important feature of complexes **21.3a,g** and **25.3b** (Figure 5.18).

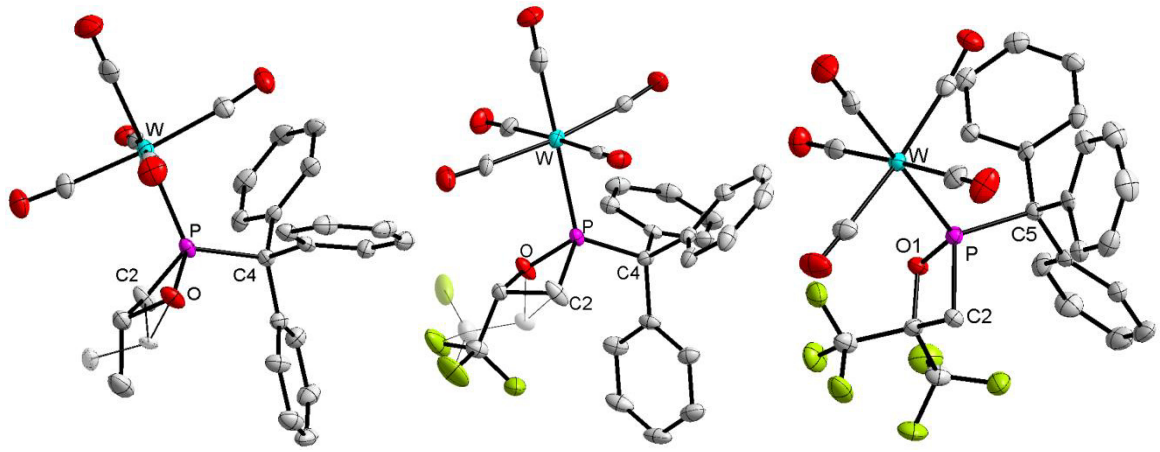



***Figure 5.18:*** DIAMOND plot of the molecular structures of the *P*-$CPh_3$-substituted 1,2-oxaphosphetane complexes **21.3a** (left), **21.3g** (middle) and **25.3b** (right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. The split-sites (1:1) for the Me-C and $F_3C$-C units are represented using a transparent mode for clarity.

For the three complexes all structural parameters are in the expected range, but an elongation of the exocyclic bonds was observed, compared to similar complexes bearing the *P*-$C_5Me_5$ (**25.2b**: P-W: 2.4768(6) Å, P-C: 1.849(2) Å) or the *P*-$CH(SiMe_3)_2$ substituent (**25.1b:** P-W: 2.4562(19) Å, P-C: 1.805(7) Å).

***Table 5.15:*** Selected bond lengths in Å and angles in ° for the *P*-$CPh_3$-substituted 1,2-oxaphosphetane complexes **21.3a**, **21.3g** and two independent molecules of **25.3b** (folding angles are given for solid/transparent part of the splitting).

| | P-$CH_2$ | P-$C^{exo}$ | P-W | P-O | $CH_2$-P-O1 | folding angle |
|---|---|---|---|---|---|---|
| **21.3a** | 1.843(4) | 1.905(4) | 2.4926(12) | 1.656(3) | 80.49(18) | 30.7/14.9 |
| **21.3g** | 1.841(4) | 1.885(4) | 2.4695(9) | 1.681(2) | 79.20(14) | 34.4/21.1 |
| **25.3b** | 1.843(4)/ 1.800(4) | 1.914(4)/ 1.913(4) | 2.5017(11)/ 2.4915(11) | 1.706(3)/ 1.713(3) | 78.41(15)/ 77.60(16) | 10.2/ 10.5 |

The higher thermal stability of the Li/Cl phosphinidenoid complex, compared to the ones bearing the $CH(SiMe_3)_2$ and $C_5Me_5$ substituents, allowed the reaction with the $^t$Bu-substituted epoxide. Remarkable is, that no reaction was observed below ambient temperature. After warming up the Li/Cl phosphinidenoid complex was found as main product, first, but a slow and selective reaction was observed over time at ambient temperature. The data for complexes **21.3d$^{1,2}$** are in the expected range (**21.3d$^1$**: $\delta^{31}$P = 181.0 ppm ($^1J_{W,P}$ = 285.2 Hz), **21.3d$^2$** $\delta^{31}$P = 155.2 ppm ($^1J_{W,P}$ = 279.9 Hz)) and the two isomers are formed in a ratio of 52 : 48 (figure 5.19).

Unfortunately no isolation was possible due to decomposition of the complexes during work up.

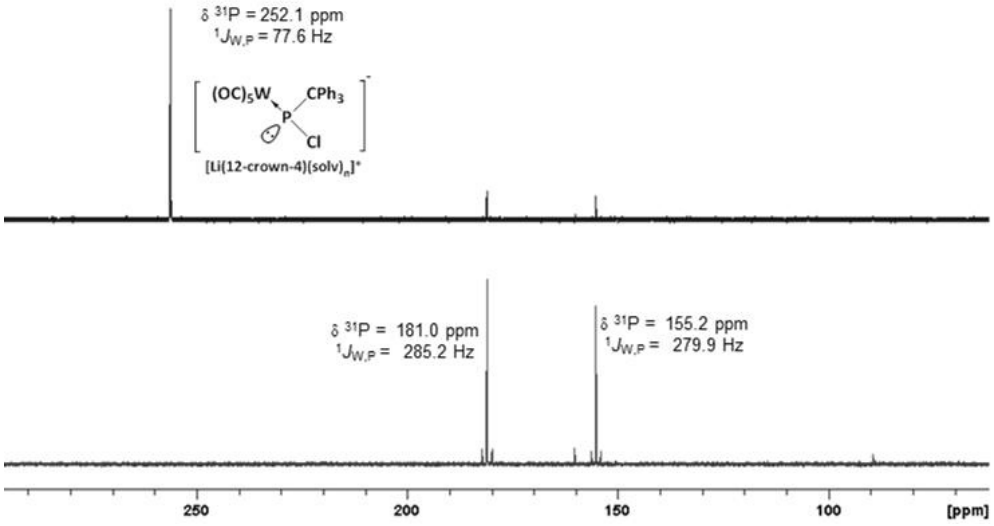
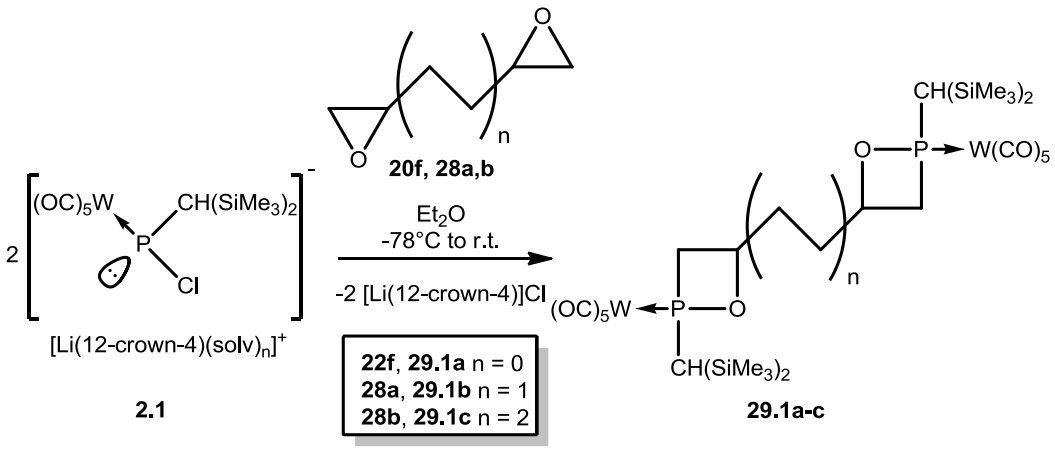



**Figure 5.19.** $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture of **2.3** with $^{t}$Bu-substituted epoxide (**20d**) (measured in THF) after 30 minutes at ambient temperature (top) and after 24 h at ambient temperature (bottom).

### 5.3.3 Attempts to synthezise bis-1,2-oxaphosphetane complexes

Polymers made from small heterocycles, *i.e.* oxiranes, oxetanes or tetrahydrofuranes, play a vital role in material science.[81] Therefore, future research might be focused on the target to obtain similar polymers from related phosphorus ligands such as oxaphosphiranes, oxaphosphetanes or oxaphospholanes. In general, polymers can be prepared from two types of monomers: mono- or bifunctional monomers like alkenes, alkynes and epoxides. In the second case two possibilities exist: the combination of two (same or different) functional groups in one monomer and a second component having also two functional groups which are added for the polymerization.

Therefore, the fundamental question for the present case was: is a bis-1,2-oxaphosphetane complex accessible using the new protocol? To study this Li/Cl phosphinidenoid complex **2.1** and symmetric diepoxides (**20f, 28a,b**) were applied. Taking into account that the stoichiometric reaction of 1,3-butadiene diepoxide was already explored (see chapter 5.2.1), *i.e.*, the mono ring expansion was clearly preferred but also significant amounts of side products (up to 50 % per integration in the $^{31}P\{^{1}H\}$ NMR spectra) were observed in case of the reaction with **20f**.




***Scheme 5.23:*** Strategy for the synthesis of bis-1,2-oxaphosphetane complexes **29.1a-c**.

Therefore, reaction of **2.1** and two other bis-epoxides having a variable chain length in-between the two epoxide rings, namely 1,5-hexadiene diepoxide (**28a**) and 1,7-octadiene diepoxide (**28b**), was studied (scheme 5.23). In case of 1,5-hexadiene diepoxide reaction to 1,2-oxaphosphetane complexes was only observed as minor reaction pathway, and the main products were the diphosphene complexes **22** and **23** (figure 5.20, middle). In contrast a selective reaction was observed for 1,7-octadiene diepoxide. Here, besides 6 % of diphosphene complexes (presumably due to the weight measuring error in such a small scale reaction), several resonance signals in the typical range of 1,2-oxaphosphetane

complexes were observed. As expected not only four but a larger number of different isomers were observed. Nevertheless, it was found that even in this case the typical signal pattern for 3-4 sets of isomers could be observed that was found for all mono-substituted 1,2-oxaphosphetane complexes bearing the *P*-$CH(SiMe_3)_2$ group (see chapter 5.2.1).

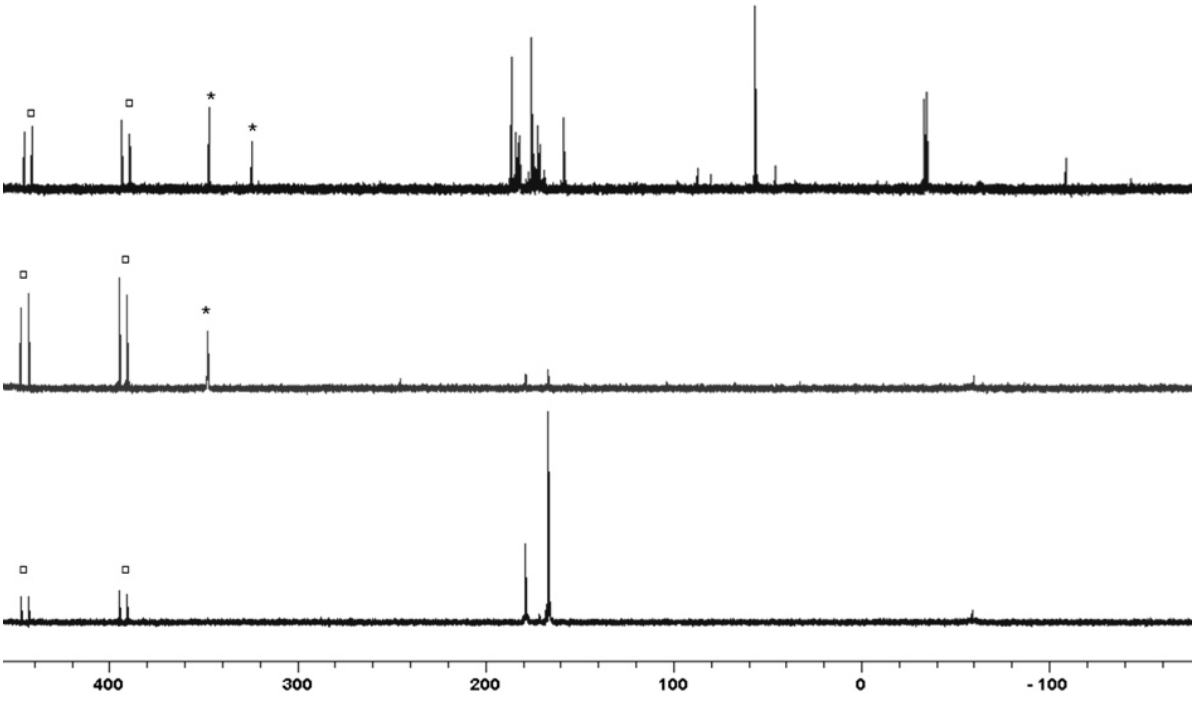



***Figure 5.20:*** $^{31}P\{^1H\}$ NMR spectra for the performed test reactions using 1,3-butadiene diepoxide (**20f**, top), 1,5-hexadiene diepoxide (**28a**, middle) and 1,7-octadiene diepoxide (**28b**, bottom) (* and ▫ describe diphosphene complexes with two (*, **22**) and one $W(CO)_5$ unit (▫, **23**)).

Due to the large number of isomers (figure 5.21) –the number of isomers could not be determined – no further NMR spectroscopic characterization could be performed. But the nature of the products was proven by other techniques, *i.e.* the MS experiment (EI, 70 eV) showed the signal for the molecular ion of **29.1c** (calc. for $C_{32}H_{52}O_{12}P_2Si_4W_2$) at m/z 1170.1; the subsequent loss of 10 CO molecules was found to be the preferred fragmentation pathway in this case.

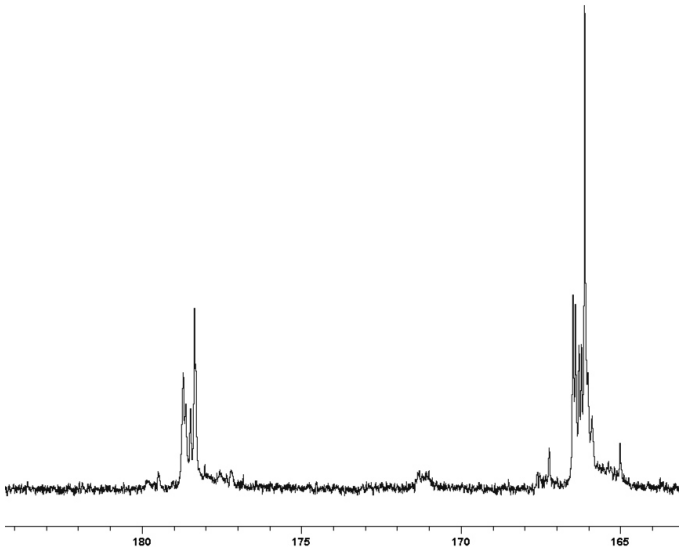



***Figure 5.21:*** $^{31}P\{^{1}H\}$ NMR spectrum of the isolated complex **29.1c**. Visible are groups of the different isomer signals and the typical isomeric pattern found also for other *C*-mono-substituted 1,2-oxaphosphetane complexes.

The elemental analysis of the mixture of **29.1c** (calc. for $C_{32}H_{52}O_{12}P_2Si_4W_2$: C 32.83 %, H 4.48 %; found C 33.08 %, H 4.56 %) lend further support to the proposed molecular composition of the products. Finally, a single crystal suitable for an X-ray diffraction study could be obtained from a saturated *n*-pentane solution at 4 °C thus confirming the proposed ligand structure (figure 5.22).

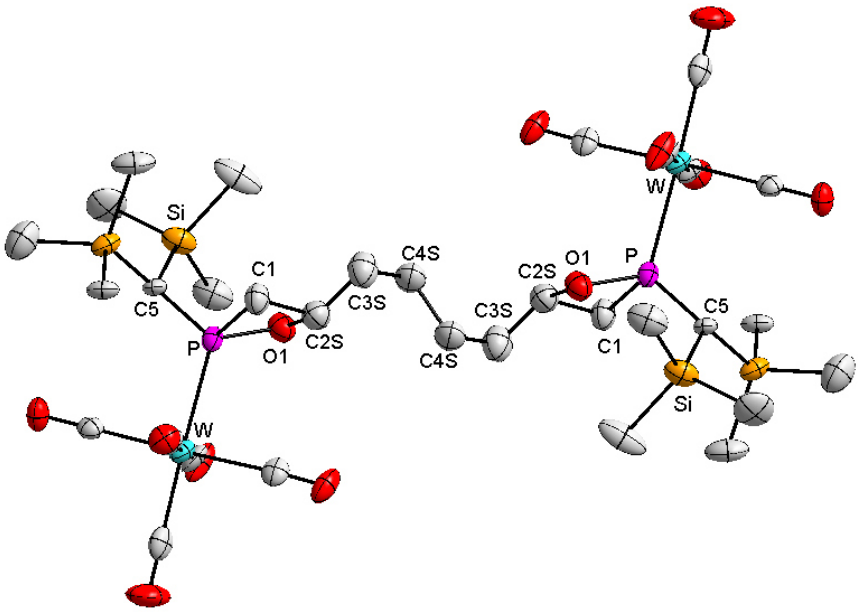



***Figure 5.22:*** DIAMOND plot of the molecular structure of complex **29.1c** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogens are omitted for clarity. Only the main orientation of the bridging $C_4$-unit and the ring folding is shown for clarity (split ratio 82:18). Selected bond lengths in Å and angles in °: W-P 2.480(3), P-C5 1.809(12), P-C1 1.824(14), P-O1 1.689(9), O1-P-C1 79.1(5), C5-P-W 116.7(4).

## 5.4 Some conclusions on 1,2-oxaphosphetane complexes

Comparison of the newly synthesized 1,2-oxaphosphetane complexes led to the following noteworthy aspects:

Most reactions proceeded with high selectivity and the formation of regioisomers was rarely observed, *i.e.* complex **16.1** represents the only 3-substituted 1,2-oxaphosphetane complex, so far. The reactivity of epoxides bearing sterically demanding substituents could be significantly enhanced by the introduction of strongly electron-withdrawing groups at the ring *C*-atom; *e.g.*, reaction of *P*-$CH(SiMe_3)_2$-substituted Li/Cl phosphinidenoid complex **2.1** with *C*-$CF_3$-substituted epoxides (**20g** or **24b**) was possible while the corresponding *C*-$^t$Bu derivative (**20d**) showed almost no reaction.

All isolated 1,2-oxaphosphetane complexes showed a high thermal stability, so that no or only slow decomposition was found in boiling toluene (111 °C). In several cases, even the transition to the gas phase could be performed without problems, *i.e.* complex **34.2** (cf. chapter 6) could even be evaporated for the purpose of purification without decomposition. In addition, a very low sensitivity towards water and oxygen was observed for the purified complexes. Of high interest for the purification was the solubility of the complexes: those complexes bearing the *P*-$C_5Me_5$ and the *P*-$CH(SiMe_3)_2$ substituent showed a good solubility in *n*-pentane or petroleum ether at ambient temperature. In contrast, the *P*-$CPh_3$-substituted derivatives were almost insoluble under similar conditions and significantly better soluble in diethyl ether and chlorinated solvents ($CHCl_3$, $CH_2Cl_2$).

Problems appeared due to the relative orientation of the *C*-substituent, either facing towards the $M(CO)_5$ substituent or away from it, therefore at least two isomers were formed for all *C*-monosubstituted derivatives. In addition, atropisomerism was found for *P*-$CH(SiMe_3)_2$-substituted complexes, giving rise to the problem of proper signal assignments in case of the minor isomers due to a bad signal-to-noise ratio. Consequently, further comparison of analytical data was hampered and, therefore, these 1,2-oxaphosphetane complexes were discussed separately in chapters 5.2 and 5.3.

Especially the $^{31}P\{^1H\}$ NMR data were found to be strongly influenced by the C-substituents. If for easier comparison between the derivatives the mean values of the isomers are taken a clear trend towards lower field shifted signals as well as higher $^1J_{W,P}$ coupling constants was observered when electron withdrawing *C*-substituents were introduced. A change of the *P*-substituent only resulted in small changes of below 20 ppm, dependent on the derivatives that are compared. The strongest shielding was observed for

*P*-CH(SiMe$_3$)$_2$-substituted complexes and the strongest deshielding for the *P*-C$_5$Me$_5$-substituted derivatives.

Comparison of the molecular structures obtained from X-ray diffraction studies were also hampered by problems due to the isomerism. Here, some structures were determined possessing either two isomers (co-crystallized) or only one of the possible isomers. Most structures were obtained showing the s-*cis* conformation for the *P*-CH(SiMe$_3$)$_2$ substituent, but also one example for the s-*trans* conformation could be observed (**25.1a**). No significant changes of the ring bond lengths and angles were observed upon changes of the *P*-substituents and no clear-cut trend was observed for electronical or sterical effects of the *C*-substituent.

Comparison of 16 structures led to the observation that the ring itself is almost invariant to the substitution pattern and mean values are given in figure 5.23. The structure of the 3-substituted derivative **16.1** as well as **29.1c** and the structures of **21.2g** and **25.1b**, having low quality, were not taken into account for this comparison. Also split layers were not taken into account due to significantly higher standard deviations and only one of two independent molecules of **25.3b**.

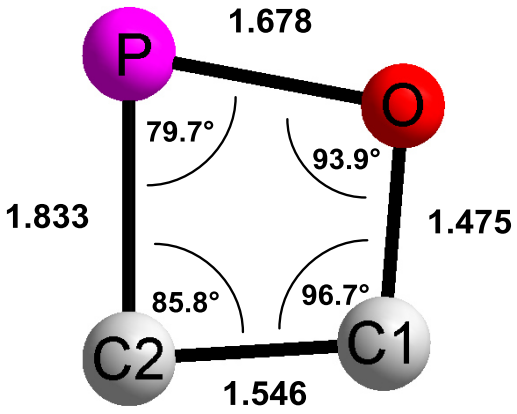



***Figure 5.23:*** Average bond lengths and angles for the ring system in 1,2-oxaphosphetane complexes.

Surprisingly no significant influence was found by the changed relative orientation of the C-R group and the metal fragment in case of complexes **21.1g** and **21.1f**.

A small influence was observed on the P-O bond length by introducing CF$_3$ groups in the molecules. Going from the *C*-Me to the *C*-CF$_3$ and *C*(CF$_3$)$_2$-substituted derivatives a slight elongation of this bond was observed, while the other bonds show no significant difference. This is observable especially in case of the *P*-CPh$_3$-substituted derivatives with values for the bond lengths of 1.656(3)Å (**21.3a**) < 1.681(2)Å (**21.3g**) < 1.706(3)/1.713(3) (**25.3b**) and could be either due to the steric demand of the CF$_3$ groups or their electronic influence.

***Table 5.16:*** Ranges for bond lengths in Å and angles in ° for 1,2-oxaphosphetane complexes and $\sigma^5,\lambda^5$-oxaphosphetanes (**CXXX**[95], **CXXXI**[97], **CXXXII**[96], **CXXXIII**[99]).

| | 1,2-oxaphosphetane complexes | **CXXX-CXXXIII** |
|---|---|---|
| **P-O** | 1.663(2) - 1.7272(17) | 1.781(6) - 1.851(1) |
| **P-C2** | 1.800(5) - 1.858(4) | 1.822(2) - 1.831(3) |
| **O-C1** | 1.433(4) - 1.527(6) | 1.36(2) - 1.404(3) |
| **C1-C2** | 1.518(3) - 1.603(7) | 1.520(5) - 1.55(1) |
| **C2-P-O** | 77.70(9) - 81.08(12) | 73.30(9) - 75.5(6) |
| **P-O-C1** | 91.8(3) - 96.1(2) | 94.7(2) - 97.0(5) |
| **O-C1-C2** | 94.4(4) - 98.5(3) | 97.0(7) - 100.5(14) |
| **C1-C2-P** | 82.7(3) - 88.44(15) | 88.1(11) - 93.0(1) |

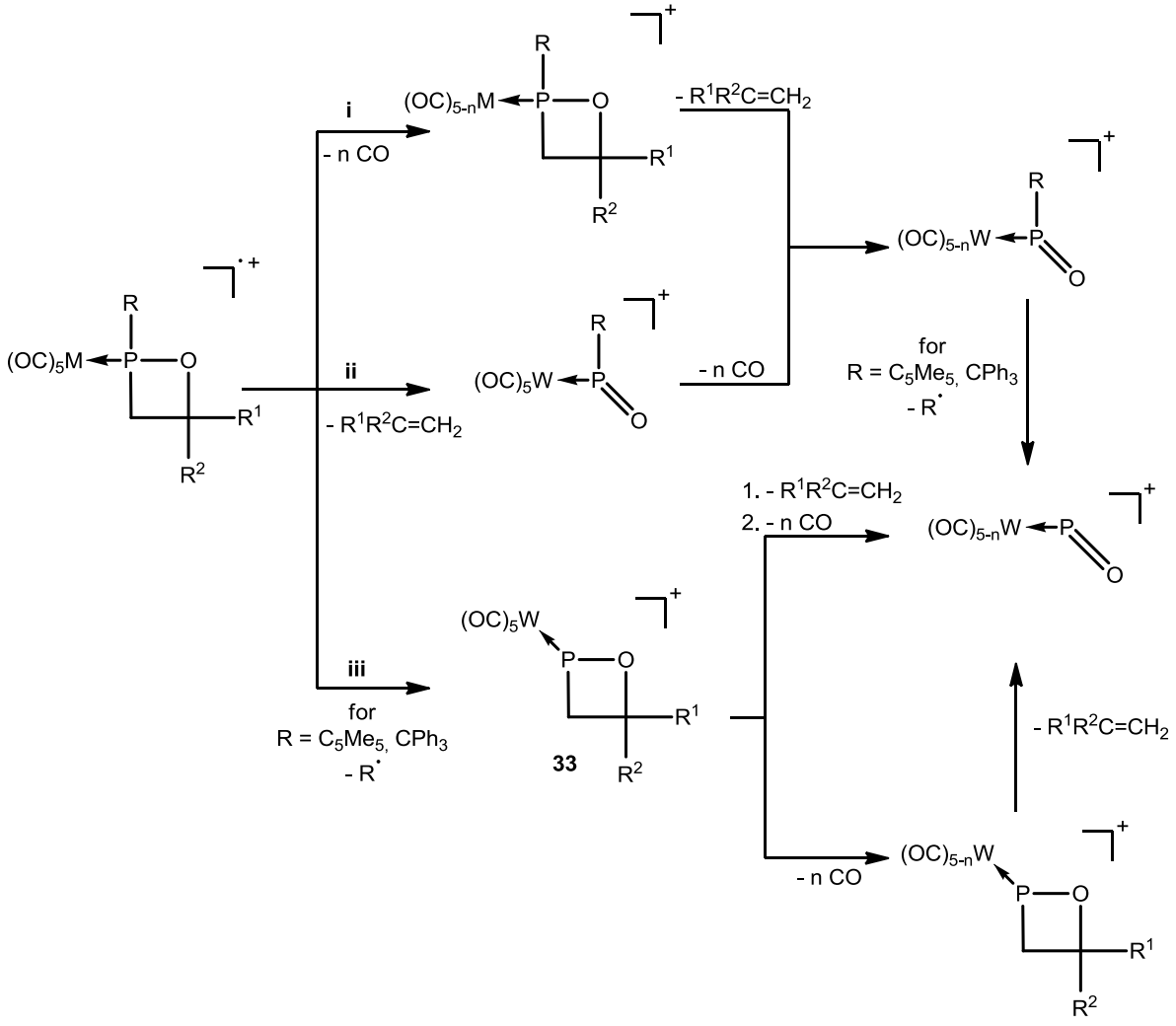
Comparison to the $\sigma^5,\lambda^5$-P derivatives, known in the literature, revealed several significant differences for bond lengths and angles (table 5.16): The P-O bond length is shortened in the complexes and the O-C bond is elongated. In contrast neither the P-C nor the C-C bonds show any significant difference. Although the O-P-C angle is increased in the complexes by an average of approximately 4.5° all other angles are smaller so that the overall sum of bond angles is not varying much.

In addition, a stronger influence of the substitution pattern was found on the folding angle of the ring, *i.e.* some derivatives with *P*-$CH(SiMe_3)_2$ substituents have almost planar rings while most possess strongly folded rings with folding angles between 10° and 30° (cf. chapter 5.2.1 and figure 5.10).

The IR spectra of the complexes showed three absorption bands for the carbonyl groups, as expected for an $M(CO)_5L$ fragment,[128] stemming from two $A_1$ and an E symmetric vibration. The signals are almost the same for all complexes, independent of the substitution pattern. An almost negligible influence was observed showing a slight shift to higher wave numbers for all three absorption bands with introduction of electron withdrawing substituents as well as by comparison of the *C*-mono-substituted and *C*-disubstituted complexes.

Especially the mass spectrometric data allow a closer comparison between all the obtained derivatives. All 1,2-oxaphosphetane complexes showed mass spectrometric fragmentation (EI, 70 eV) which can be divided into three typical decomposition pathways, mainly depending on the substituent at phosphorus. The first step was in most cases either found to be the splitting of a metal carbon bond with loss of different numbers of CO (**i**) or, to a minor part, the loss of an alkene unit (**ii**), similar to the oxaphosphetane decomposition in the Wittig reaction. The two pathways **i** and **ii** can happen in different order until all CO groups and the alkene are lost. For complexes where R = $C_5Me_5$ or $CPh_3$, a third pathway was found (**iii**),

which, in case of $C_5Me_5$, was even the preferred one. Here, splitting of the exocyclic P-C bond with loss of the *P*-substituent was found, either before or after loss of CO and the alkene unit, in the latter case, complexes of the type $[(OC)_{5-n}W\{PO\}]$[129] are formed. For most 1,2-oxaphosphetane complexes bearing the *P*-$CH(SiMe_3)_2$ substituent the formation of a phosphinidene oxide complex ($[(Me_3Si)_2HCRP(O)W]$) after complete loss of all five CO and the alkene was found.

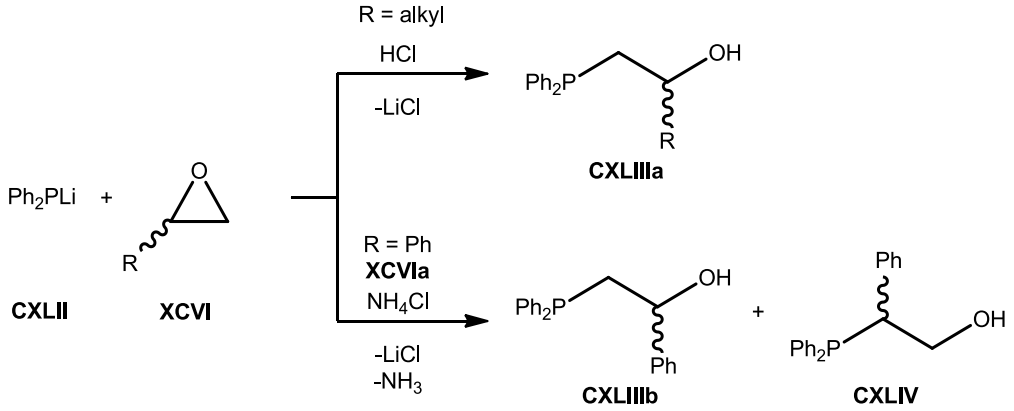



**Scheme 5.24:** Main mass spectrometric fragmentation pathways of 1,2-oxaphosphetane complexes under EI conditions (70 eV).

## 5.5 Proposed mechanism for the 1,2-oxaphosphetane complex formation

A proposal for a reaction mechanism was developed based on investigations on the reactivity of Li/Cl phosphinidenoid complexes towards epoxides.

Earlier studies on ring opening reactions of epoxides **XCVI** with alkali metal phosphanides **CXLII** have shown a preference for nucleophilic attack at the least hindered side of the epoxide ring, yielding 1,2-phosphanyl alcohols **CXLIII** as final products (scheme 5.25).[122] Further studies showed that, in case of aryl substituents, a mixture of two regioisomeric products can be observed, resulting from the reaction either at the benzylic position or the least hindered side (*e.g.* R = Ph, ratio (**CXLIIIb**: **CXLIV**) 70:30).[117]

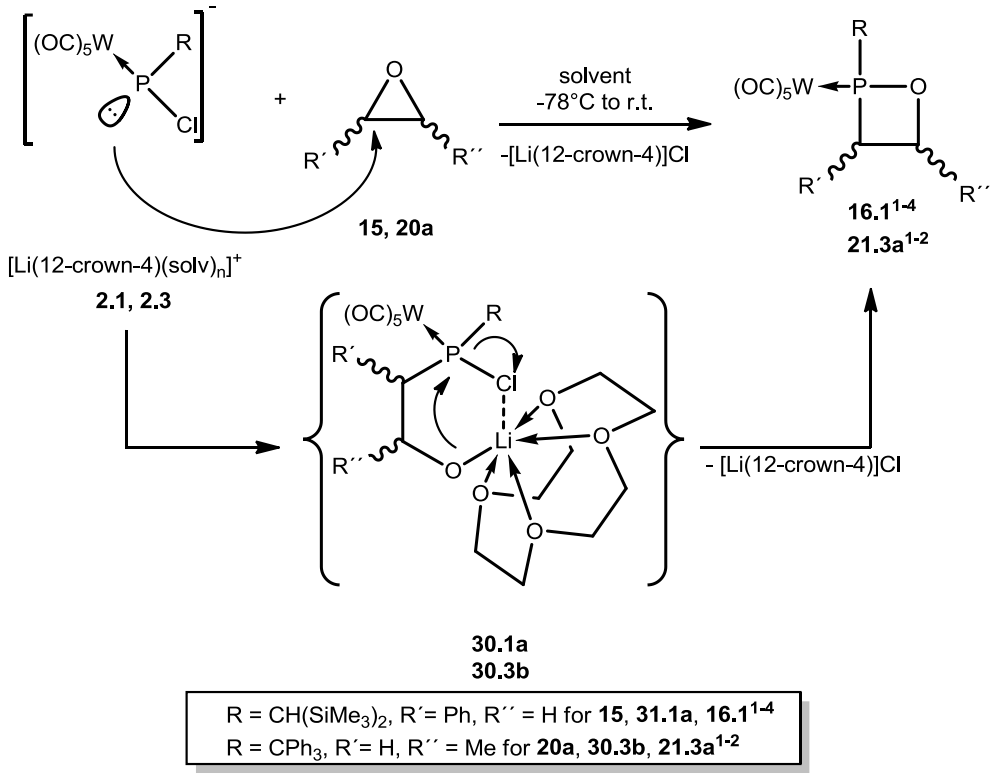



***Scheme 5.25:*** Ring opening reactions of mono-substituted epoxides with lithium diphenylphosphanide.[122][117]

The observed reaction of alkyl-substituted epoxides and Li/Cl phosphinidenoid complexes at the least hindered side as well as the activation of epoxides by electron-withdrawing substituents increasing the electrophilicity support this interpretation. Of special interest and, hence, crucial for the understanding of the mechanism is the regiochemical differentiation that was observed in case of styrene oxide (chapter 5.2.1). In aryl-substituted epoxides, the ring carbon atom that is located at the benzylic position is the most electrophilic one and, therefore, often the preferred site of attack in nucleophilic ring opening reactions. In contrast to this, a reaction of a terminal electrophilic phosphinidene complex would be expected to take place preferable at the least hindered side.

Here an ionic mechanism was proposed based on these observations (scheme 5.26). The acyclic intermediate **30** is formed after an initial nucleophilic ring opening by the Li/Cl phosphinidenoid complex **2**, followed by an intramolecular nucleophilic substitution that is facilitated by the close proximity of both reactive centres. A preorientation of the ring because of a Li/Cl interaction might also be assumed. Similar interactions were described previously, *e.g.* in the decomposition of alkoxyphosphinidenoid complexes.[10] Somewhat similar

intermediates were proposed for the formation of oxaphosphirane complexes by Klein,[34] which were also supported by DFT calculations performed by Espinosa.[130]




***Scheme 5.26:*** Proposed reaction mechanism for the formation of 1,2-oxaphosphetane complexes, examples are given for the formation of **16.1**$^{1-4}$ and **21.3a**$^{1-2}$.

To obtain additional evidence for the formation of intermediates, a variable temperature $^{31}P\{^{1}H\}$ NMR study (-60 °C to 25 °C in steps of 10 °C, figure 5.24) was performed to investigate the reaction of *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complex **2.3** and propylene oxide **20a**.

The reaction starts at -60 °C and is finished after reaching -10 °C. This observation again supports the ionic mechanism, as no decomposition of the *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complex can be observed up to ambient temperature in the absence of a substrate.[33] An intermediate formation and subsequent reaction of a terminal phosphinidene complex can therefore be excluded.

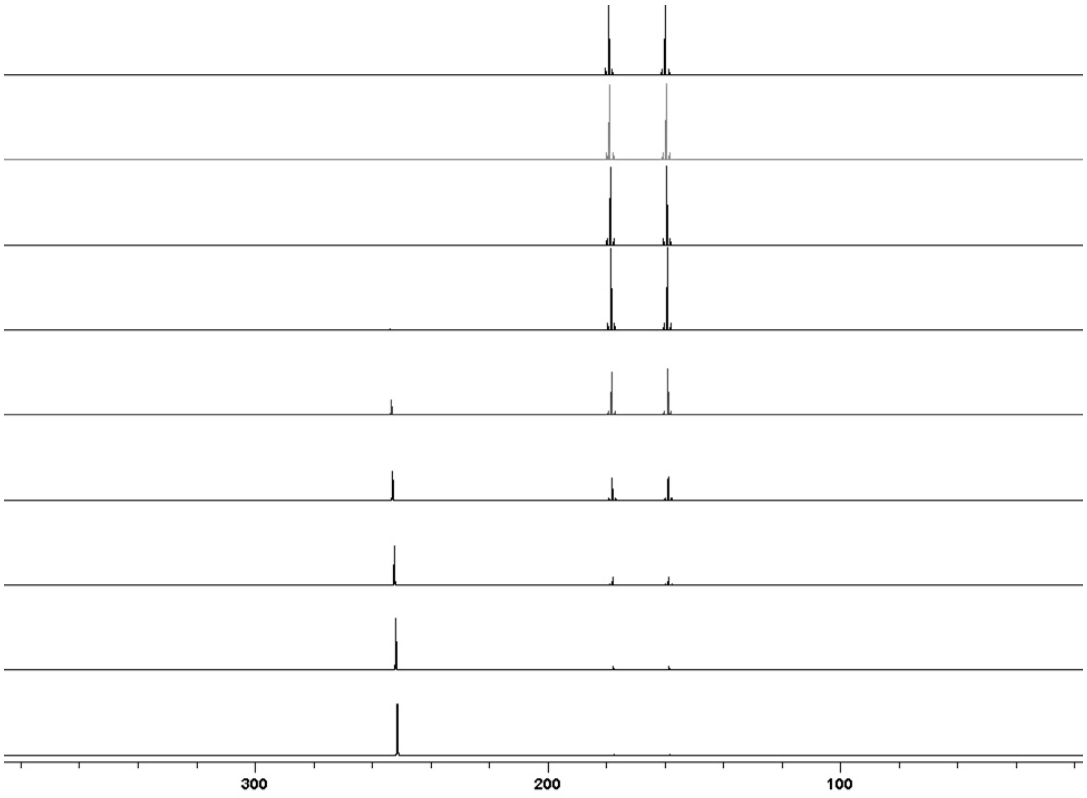



***Figure 5.24:*** Low temperature $^{31}P\{^{1}H\}$ NMR monitoring of the reaction between **2.1** and propylene oxide **20a** in THF. Shown are the spectra obtained from – 60 °C (bottom) to 20 °C (top) in steps of 10 °C difference.

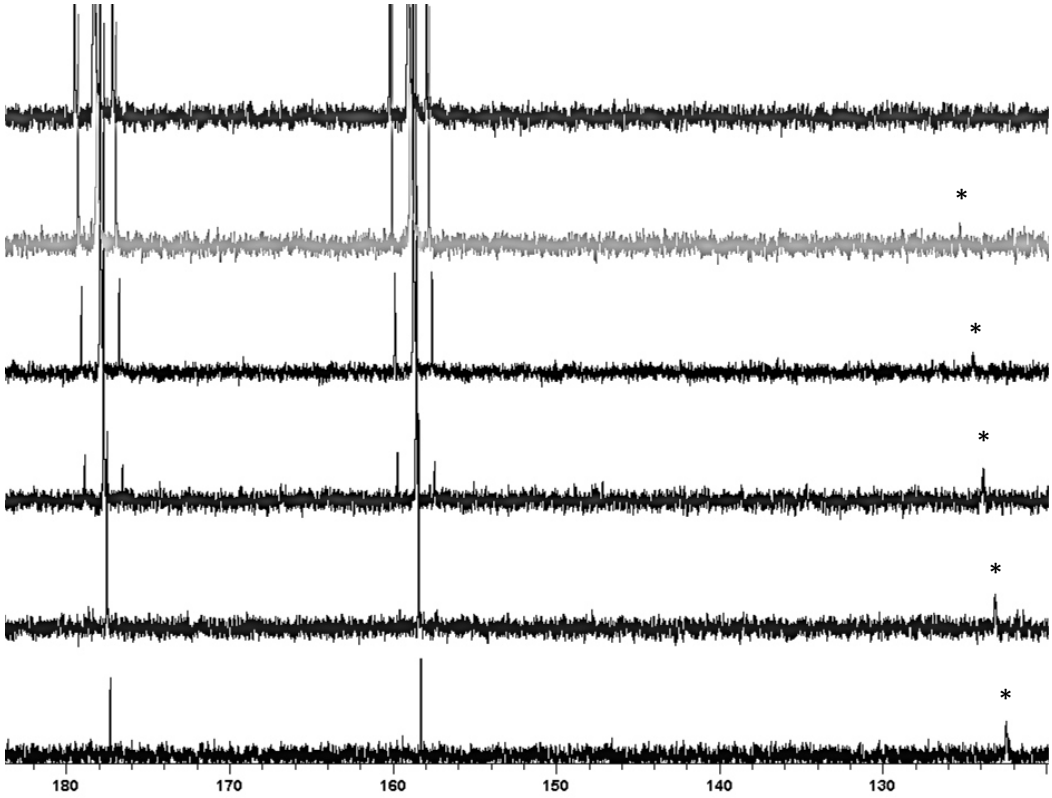



***Figure 5.25:*** Zoom in on the low temperature $^{31}P\{^{1}H\}$ NMR monitoring of the reaction between **2.3** and propylene oxide **20a**. Shown are the spectra obtained from -60 °C (bottom) to -10 °C (top) (steps of 10 °C).

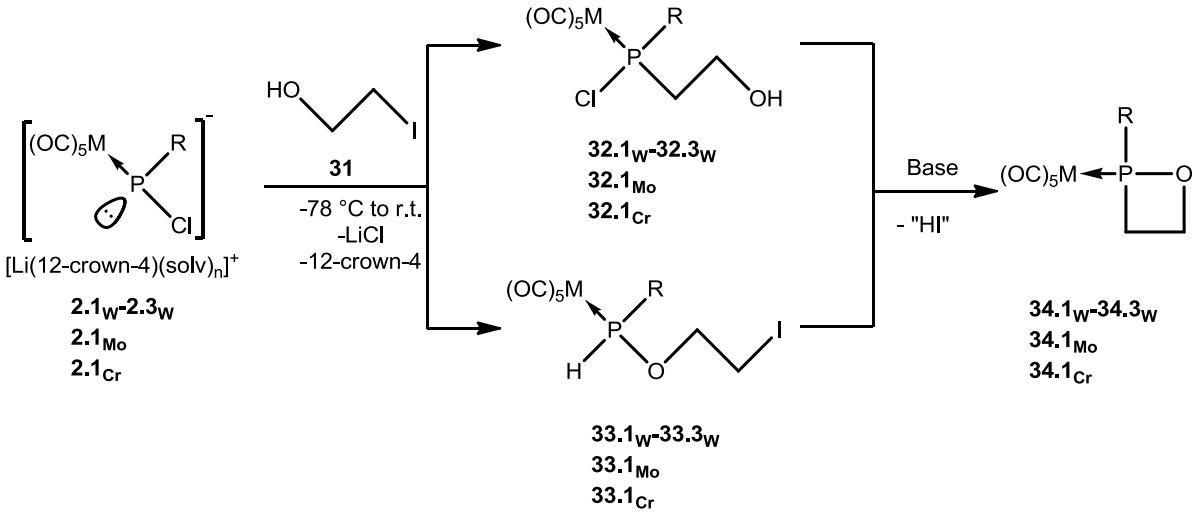
The $^{31}P\{^{1}H\}$ NMR spectra of the low temperature monitoring (figure 5.24) show mainly the resonance signals for the Li/Cl phosphinidenoid complex at 252.1 ppm with a typical small magnitude for the $^{1}J_{W,P}$ coupling constant (77.6 Hz) and two signals for the isomeric 1,2-oxaphosphetane complexes at 180.2 ppm ($^{1}J_{W,P}$ = 283.1 Hz) and 161.0 ppm ($^{1}J_{W,P}$ = 278.3 Hz). Nevertheless, closer inspection of the area between 100 and 200 ppm at low temperature revealed an additional resonance signal at approximately 125 ppm that is present as long as the reaction proceeds (*, figure 5.25). Assuming the nucleophilic ring opening reaction to be the rate determining step thus leading to a small and quasi-stationary concentration of the intermediate **30.3b** would explain the low intensity of the resonance signal.

A *P*-$CH(SiMe_3)_2$-substituted chloro(2-hydroxypropyl)phosphane complex **47.1b**[1-2] that is structurally closely related to the proposed intermediate could be synthesized (see later on chapter 8.2) and shows a similar shift in the $^{31}P$ NMR spectrum to the observed resonance signal (**47.1b**[1]: $\delta^{31}P$ = 119.8 ppm, $^{1}J_{W,P}$ = 276.0 Hz, **47.1b**[2]: $\delta^{31}P$ = 115.1 ppm, $^{1}J_{W,P}$ = 274.2 Hz). Deprotonation of this complex, formally leading to a similar intermediate, and the subsequent formation of 1,2-oxaphosphetane complexes further support the proposed mechanism (see chapter 8.2).

# 6 A novel route to C-unsubstituted O,P-containing heterocycles

A novel synthetic strategy to O,P-containing heterocycles was developed in order to clarify if substitution at the ring carbon atoms is crucial for the $^{31}$P NMR spectroscopic characteristics as well as for the thermal stability of these complexes.

The proposed synthetic strategy was the formation of an acyclic intermediate followed by a ring closing reaction in the second step. The first reaction step, the reaction of Li/Cl phosphinidenoid complexes with α,ω-halogenoalcohols (*e.g.* 2-iodoethanol, **31**), could lead to two types of products: the one formed by formal insertion into the OH bond of the alcohol (*e.g.* **33**) or the product of the nucleophilic substitution at the C-halogen centre (*e.g.* **32**) (scheme 6.1). Examples for both reactions, using only non-functionalized alcohols (methanol, *iso*-propanol, allylalcohol) or electrophiles (methyl iodide), are known from previous studies. The knowledge about reactions with alcohols profits from results previously obtained in my MSc thesis, *i.e.* from the experience obtained for non-functionalized alcohols (chapter 1.2). Apart from that the envisaged study would also examine the functional group tolerance of the formal $P_1$ insertion reaction into an O-H bond.

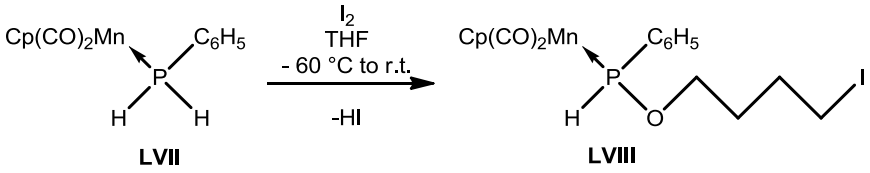



***Scheme 6.1:*** Proposed synthetic strategy to different C-unsubstituted 1,2-oxaphosphetane complexes.

Both initially formed complexes could lead to the desired ring systems via an intramolecular nucleophilic substitution after deprotonation by a suitable base. This reaction sequence offers several advantages to the previously described one: the probable elimination of regio- and stereoisomers due to loss of the C-substitution (chapter 5), the avoidance of toxic heterocycles like ethylene oxide gas by substituting them with α,ω-halogenoalcohols, *e.g.* 2-iodoethanol, as synthetic equivalents.

It is remarkable that no similar ring closing reaction has been described to date, especially as Huttner had already reported in 1975 on the formation of an α,ω-substituted phosphinite

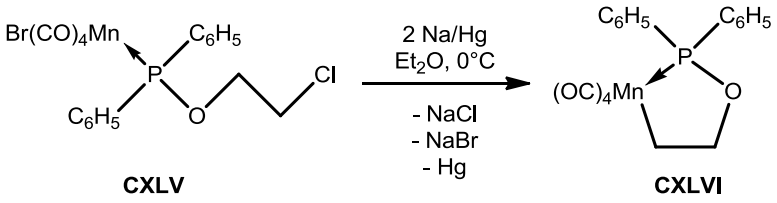
complex, representing the first stable derivative of this class of compounds. The alkoxy substituent in **LVIII** was hereby formed by ring opening of THF with *in situ* generated HI (scheme 6.2).[48]




LVII LVIII

***Scheme 6.2:*** Synthesis of the first phosphinite complex by Huttner.[48]

One more related reaction has to be mentioned. Lindner utilized a similar reaction procedure to form metallacycle **CXLVI**,[131] although no ring closing reaction to a heterocyclic phosphane ligand was described (scheme 6.3).




CXLV CXLVI

***Scheme 6.3:*** Ring closing reaction of a chloroethoxyphosphane complex.[131]

The first attempted reaction sequence with α,ω-halogenoalcohols was aiming at the synthesis of a *C*-unsubstituted 1,2-oxaphosphetane complexes **34**.

The reaction between **2.1** and 2-iodoethanol (**31**) led selectively to the 2-iodoethyl-phosphinite complex **33.1$_W$**, as the $^{31}$P NMR spectrum of the reaction mixture showed only one signal at 106.7 ppm with a direct coupling to one hydrogen atom ($^1J_{P,H}$ = 321.4 Hz) and satellites due to the coupling to the $^{183}$W nucleus ($^1J_{W,P}$ = 270.3 Hz) and thus a quantitative conversion. These parameters are in good accordance and lie within the range of known phosphinite complexes bearing the *P*-CH(SiMe$_3$)$_2$ substituent ($\delta^{31}$P = 91 - 109 ppm, $^1J_{W,P}$ = 266 - 274 Hz.

Complex **33.1$_W$** was obtained as yellow oil via extraction from the reaction mixture with *n*-pentane which partially solidified while standing at 4 °C. Tiny single-crystals could be obtained after several weeks, so that, in addition to multinuclear NMR and MS measurements, the molecular structure of the product could be confirmed by single crystal X-ray diffraction studies (Figure 6.1).

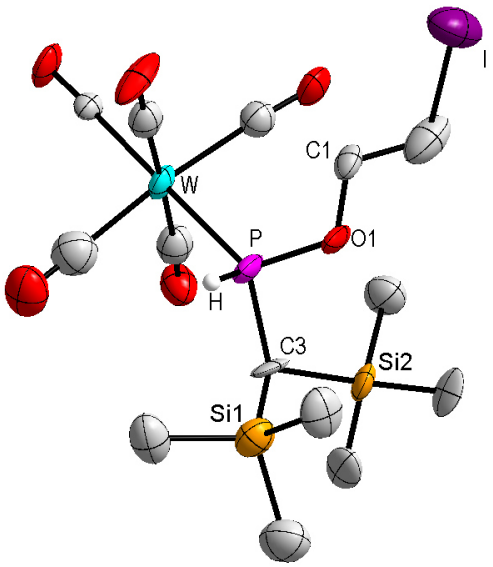
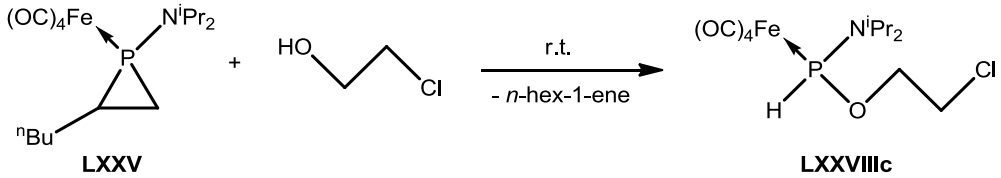



***Figure 6.1:*** DIAMOND plot of the molecular structure of 2-iodoethylphosphinite-complex **33.1$_W$** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at phosphorus are omitted for clarity.

A related result was reported by Lammertsma at the time this research was performed. Iron complex **LXXVIIIc** was obtained by insertion of tetracarbonyl-[(diisopropylamino)phosphinidene]iron(0) into the OH bond of 2-chloroethanol (scheme 6.4),[58] showing a similar shift for the resonance signal in the $^{31}$P NMR spectrum ($\delta^{31}$P = 136.5 ppm) and structural similarities to **33.1$_W$**. But no further investigations on its reactivity have been described, yet.

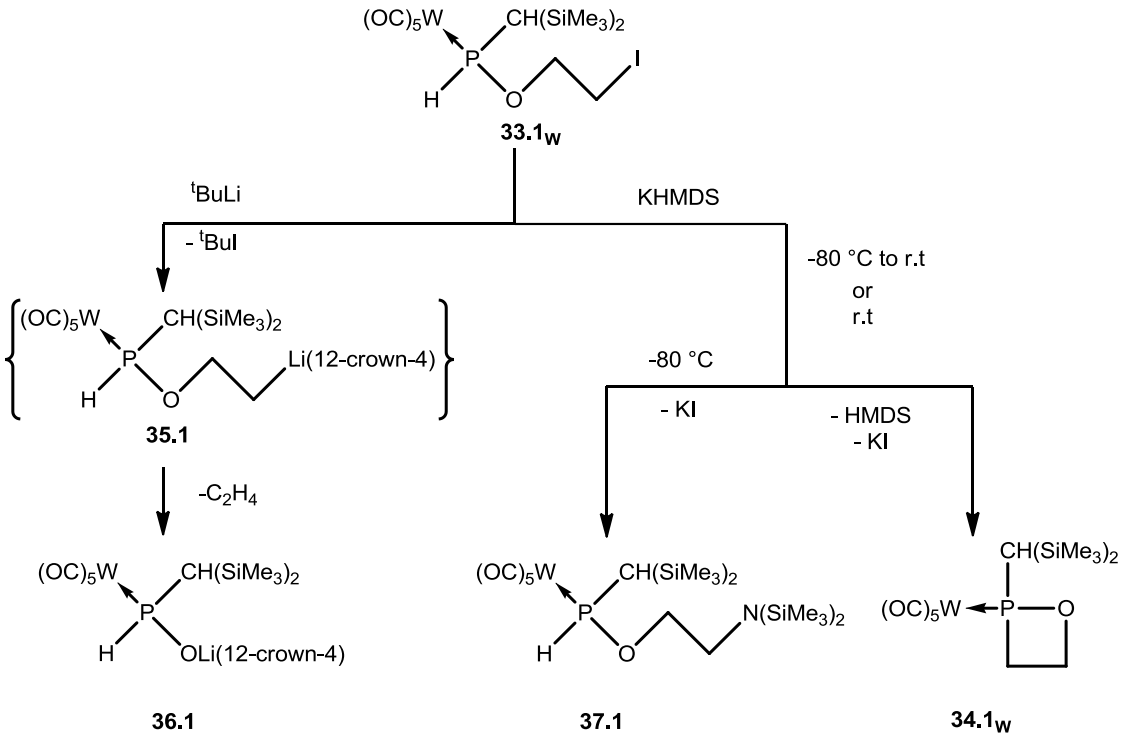



***Scheme 6.4:*** Synthesis of **LXXVIIIc** by Lammertsma.[58]

Surprisingly, complex **33.1$_W$** showed several base- and temperature-dependent reaction pathways, not only the proposed formal HCl elimination and cyclization. When *tert*-butyl-lithium in the presence of 12-crown-4 was used, an interesting result was obtained: not the expected 1,2-oxaphosphetane, but a phosphinito complex was formed (**36.1**, scheme 6.5). A selective lithium/iodine exchange, as typical reaction for lithium organic reagents, took place instead of the expected P-deprotonation, yielding **35.1**, followed by an elimination of ethylene to yield phosphinito complex **36.1** as final product (scheme 6.5).

Complex **36.1** was described before, and for the first time by Duan in 2011.[132] However, the novel synthetic access is superior due to the fact that the previous route was more time-consuming and more expensive as silver acetate had to be used. Starting from

dichloro(organo)phosphane complex **1.1** (isolated yield up to 75 %) this new route enabled easy access towards synthetic studies of phosphinito complex **36.1** as building block for novel phosphane ligands bearing a POE motif. First reactions and results using this building block will be discussed at the end of this chapter.




***Scheme 6.5**:* Base- and temperature-dependent reactions of 2-iodoethylphosphinite complex **33.1W**.

Two different reaction pathways were observed when the less nucleophilic base $KN(SiMe_3)_2$ (KHMDS for short) was used for the deprotonation (scheme 6.5). When the reaction was performed at low temperature (-80 °C), even with an excess of KHMDS (molar ratio 1 : 1.25) a mixture of two compounds was observed by $^{31}P$ NMR spectroscopy; both could be separated via low temperature column chromatography.

One product showed a resonance signal at 105.2 ppm with a direct coupling to the P-bound hydrogen atom ($^1J_{P,H}$ = 320 Hz) and satellites from the coupling to the $^{183}W$ nucleus ($^1J_{W,P}$ = 267.6 Hz); this is similar to the data obtained for the starting material **33.1W** (106.7 ppm, $^1J_{P,H}$ = 321.4 Hz, $^1J_{W,P}$ = 270.3 Hz). The small influence on the $^{31}P$ NMR characteristics for this first reaction product implies a change in the molecular structure further away from the phosphorus centre; therefore, complex **37.1** can be proposed as product of a nucleophilic substitution. The isolation of this complex was unfortunately not possible due to decomposition during column chromatography.

The second compound (complex **34.1W**) showed a resonance signal in the $^{31}P$ NMR spectrum at 190.3 ppm with a $^1J_{W,P}$ coupling constant of 267.7 Hz and no direct coupling to a proton. These data are in the typical range found for other 1,2-oxaphosphetane complexes

(see chapter 5). Isolation from the mixture, obtained at low temperature, was possible via low temperature column chromatography, but only in low yields (29 %).

When the reaction was performed at ambient temperature, a significant increase in selectivity was observed, yielding 1,2-oxaphosphetane complex **34.1$_W$** via an intramolecular nucleophilic substitution reaction (scheme 6.5) in good overall yields (up to 60 % starting from dichlorophosphane complex **1.1**).

Surprisingly, no isomerism due to the orientation of the CH group of the $CH(SiMe_3)_2$ substituent, that presented a significant problem in the characterization of other derivatives, was observed for complex **34.1$_W$**. A similar observation, regarding the selective formation of only one isomer, was found for the class of oxaphosphirane complexes by Peréz.[114] There, the ring opening reaction with HCl, followed by a base-induced ring closing reaction, only led to the formation of only one of two possible isomers.

For further comparison the reaction was repeated using the $Mo(CO)_5$ and $Cr(CO)_5$-substituted 2-iodoethyl phosphinite complexes **33.1$_{Mo}$** and **33.1$_{Cr}$** under otherwise identical conditions and the corresponding 1,2-oxaphosphetane complexes **34.1$_{Mo}$** and **34.1$_{Cr}$** could be isolated in reasonable yields via column chromatography and subsequent recrystallization or precipitation from *n*-pentane (see table 6.1).

***Table 6.1:*** Selected NMR data ($CDCl_3$) and yields for the *C*-unsubstituted 1,2-oxaphosphetane complexes **34.1$_{W\text{-}Cr}$**.

| | $^{31}$P NMR | $^{13}$C{$^1$H} NMR (P-*C*H) | $^1$H NMR (P-C*H*) | yield [%] |
|---|---|---|---|---|
| | $\delta$ [ppm] ($^1J_{M,P}$ [Hz]) | $\delta$ [ppm] ($^1J_{P,C}$ [Hz]) | $\delta$ [ppm] ($^2J_{P,H}$ [Hz]) | |
| **34.1$_{Cr}$** | 250.2 | 39.0 (18.6) | 1.99 (8.2) | 32 |
| **34.1$_{Mo}$** | 225.6 (151.7) | 38.7 (19.9) | 1.96 (7.3) | 27 |
| **34.1$_W$** | 191.4 (268.5) | 38.7 (14.2) | 2.10 (8.7) | 65 |

An outstanding feature, found for all 1,2-oxaphosphetane complexes, is the electronic differentiation of the ring-$CH_2$ protons, leading to quite complicated coupling patterns (figure 6.2).

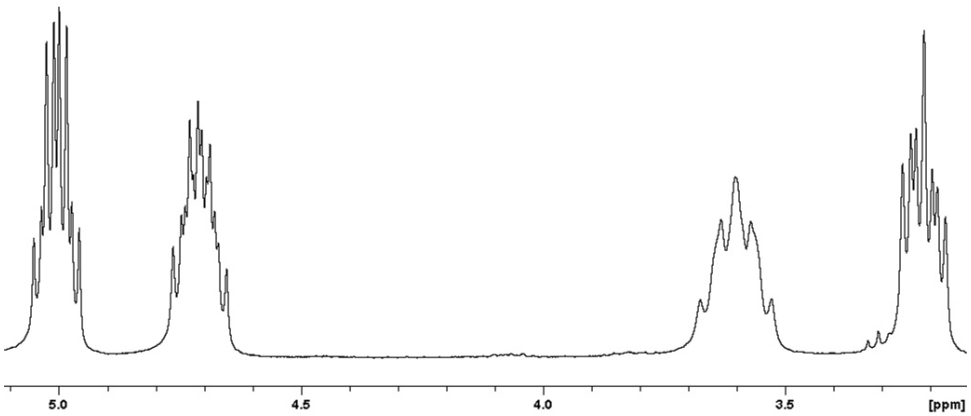



***Figure 6.2:*** Zoom in on a part of the $^{1}$H NMR spectrum of the $W(CO)_5$-1,2-oxaphosphetane complex **34.1$_W$**. The region for the resonance signals of the ring protons is shown exemplarily.

All three complexes crystallized well from *n*-pentane and the molecular structures in single crystals could be obtained by X-ray diffraction studies, proving again the formation of the C-unsubstituted complexes (figure 6.3).

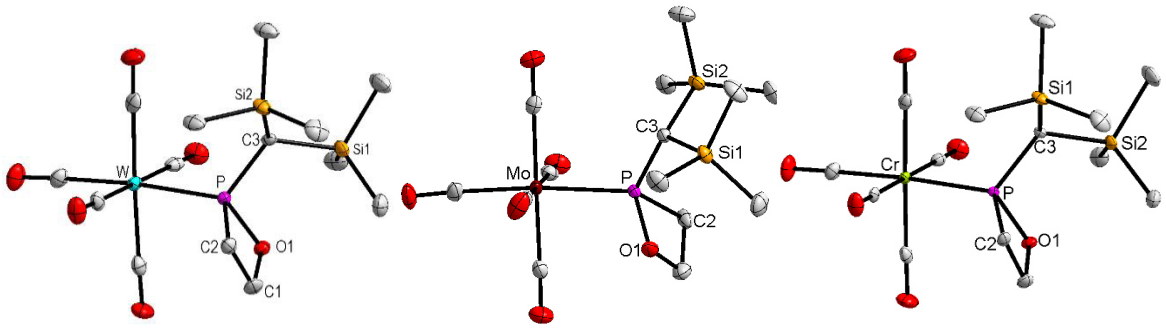


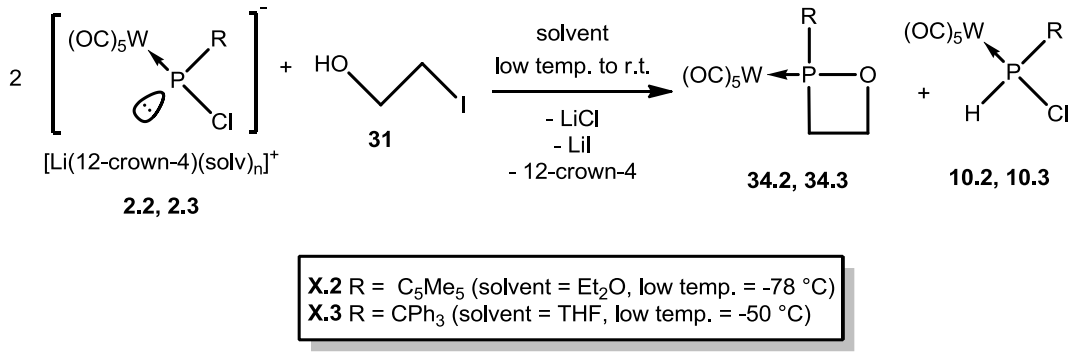

***Figure 6.3:*** DIAMOND plot of the molecular structures of 1,2-oxaphosphetane complexes **34.1$_W$** (left), **34.1$_{Mo}$** (middle) and **34.1$_{Cr}$** (right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity.

All three complexes **34.1$_W$, 34.1$_{Mo}$** and **34.1$_{Cr}$** are isostructural but the structure of the Mo complex showes the other enantiomer. It has to be noted that while the flack parameters were 0.126(5) for **34.1$_W$** and 0.05(3) for **34.1$_{Cr}$**, it was 0.52(3) for **34.1$_{Mo}$**. This indicates that the W and Mo-derivative crystallized as racemic twins, containing 12.6 % of the second enantiomer in case of **34.1$_W$** and an almost 1:1 ratio for the enantiomers of **34.1$_{Mo}$**. The single crystal data show no significant difference between the three complexes. Just the typical differences for the M-P bond were observed in going from Cr to W. Comparison to the *C*-Me derivatives shows an additional shortening of the P-M bond lengths, presumably due to the reduced steric demand of the ring; the folding angles were also significantly smaller.

***Table 6.2:*** Selected bond lengths in Å and angles in ° for 1,2-oxaphosphetane complexes **34.1$_W$, 34.1$_{Mo}$** and **34.1$_{Cr}$**.

| | P-C3 | P-C2 | P-M | C2-P-O1 | folding angle |
|---|---|---|---|---|---|
| **34.1$_{Cr}$** | 1.808(3) | 1.838(3) | 2.3183(8) | 80.11(11) | 15.1 |
| **34.1$_{Mo}$** | 1.809(2) | 1.833(2) | 2.4768(6) | 80.40(11) | 14.1 |
| **34.1$_W$** | 1.810(4) | 1.830(5) | 2.4654(13) | 80.5(2) | 15.4 |

In sharp contrast to the straightforward reaction and the observations for the *P*-CH(SiMe$_3$)$_2$-substituted complexes, the reactions of the *P*-C$_5$Me$_5$ and *P*-CPh$_3$-substituted phosphinidenoid complexes **2.2** and **2.3** with 2-iodoethanol **31** did not yield 2-iodoethylphosphinite complexes. In both reactions, performed under typical Li/Cl phosphinidenoid complex conditions, an almost 1:1 mixture of the 1,2-oxaphosphetane complexes **34.2** or **34.3** and the chloro(organo)phosphane complexes **10.2** or **10.3**, respectively, was formed (see scheme 6.6 and figure 6.4). Based on this observation, a reaction sequence can be assumed, in which one equivalent of the Li/Cl phosphinidenoid complex *in-situ* acts as a base towards the initially formed phosphinite complex and, hence, induces ring closure to **34.2** or **34.3**, while forming the chloro(organo)phosphane complex **10.2** or **10.3** as side-products.




***Scheme 6.6:*** Reaction of the *P*-CPh$_3$ and *P*-C$_5$Me$_5$-substituted phosphinidenoid complexes **2.2** and **2.3** with 2-iodoethanol (**31**).

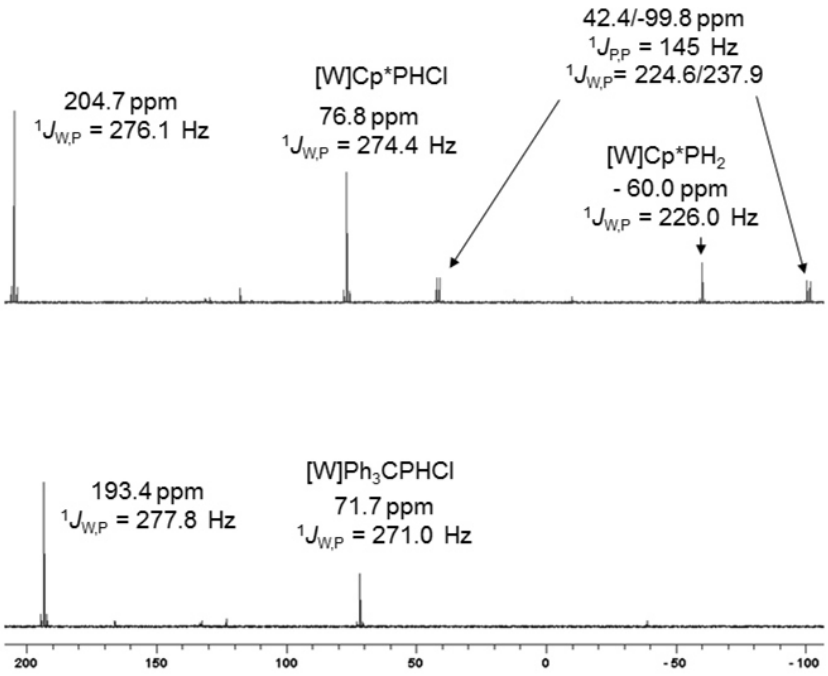


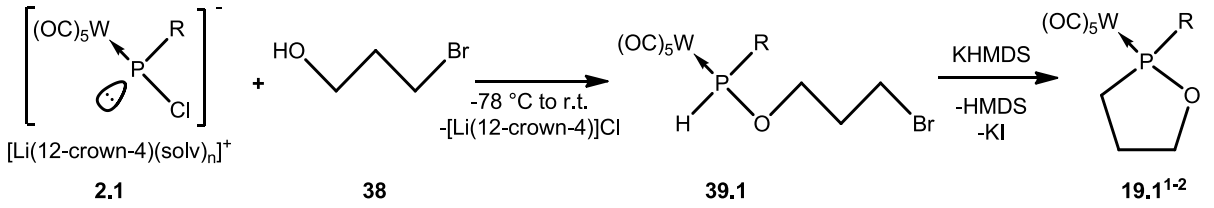

***Figure 6.4:*** $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures of **2.2** (top) and **2.3** (bottom) with 2-iodoethanol **31**.

Isolation of the *P*-$CPh_3$-substituted derivative was not possible due to the similar solubility and column chromatography retention times of the two reaction products (the 1,2-oxaphosphetane complex **34.3** and chlorophosphane complex **10.3**).

In contrast, a somewhat troublesome separation via low temperature column chromatography and an additional sublimation of the 1,2-oxaphosphetane complex **34.2** rendered the isolation of the *P*-$C_5Me_5$ derivative possible. The sublimation was performed to separate the product from small amounts of a formed decomposition product of the Li/Cl phosphinidenoid complex (the self-reaction product **XXXVIII**). Separation was therefore only possible due to the high thermal stability of the 1,2-oxaphosphetane complex. The yield was below 50% (yield for **34.2**: 20 %) as expected from the reaction stoichiometry.

Complex **34.2** could be unambiguously characterised using multinuclear NMR spectroscopy, high resolution mass spectrometry and elemental analysis. The complex shows typical values for the $^{31}P$ NMR resonance signal (204.8 ppm, $^1J_{W,P}$ = 275.5 Hz); the latter being close to the values observed for the *P*-$CH(SiMe_3)_2$-substituted complex **34.1$_W$**.

To provide first evidence that the synthetic method described beforehand has a broader applicability in the synthesis of new, differently sized heterocyclic phosphorus ligands, an additional reaction was performed. Starting from Li/Cl phosphinidenoid complex **2.1** and 3-bromopropane-1-ol **38**, a phosphinite ligand **39.1** bearing a $C_3$ spacer between the oxygen and halogen atom was synthesized (scheme 6.7).




***Scheme 6.7:*** Synthesis of the 1,2-oxaphospholane complexes **19.1**$^{1\text{-}2}$ (R = $CH(SiMe_3)_2$).

In analogy to the reaction with 2-iodoethanol, a selective insertion of the $P_1$-fragment (from **2.1**) into the OH bond of the alcohol was observed. Nevertheless, some minor impurities were present that may arise from deprotonation of the alcohol by the Li/Cl phosphinidenoid complex. These side products (the chloro(organo)phosphane complex **10.1** and the primary phosphane complex **11.1**) could be separated by sublimation in *vacuo* at elevated temperatures (130 °C, $2 \cdot 10^{-2}$ mbar).

The $^{31}$P NMR spectrum of **39.1** showed typical values for phosphinite complexes with a resonance signal at 104.7 ppm ($^1J_{W,P}$ = 268.1 Hz, $^1J_{P,H}$ = 321.5 Hz) without any significant differences compared to previously reported ones. Unfortunately **39.1** was obtained as an oil that, in contrast to **33.1**, did not solidify over time.

Deprotonation of **39.1** with KHMDS at ambient temperature finally led to the formation of the isomeric 1,2-oxaphospholane complexes **19.1**$^{1\text{-}2}$ in a selective reaction.

In the $^{31}$P NMR spectrum complexes **19.1**$^{1\text{-}2}$ showed two resonance signals. The resonance signal of the major isomer (**19.1**$^1$, 99.5% by integration) was observed at 139.5 ppm, showing a strong broadening (FWHI ($h_{1/2}$) = 760 Hz), whereas the minor isomer (**19.1**$^2$, 0.5% by integration) appeared as a sharp signal at 125.2 ppm ($^1J_{W,P}$ = 267.1 Hz). Similar broadened signals were observed before, *i.e.* for 1,3,2-dioxaphospholene complexes.[133]

A variable temperature NMR study (figure 6.5) revealed some sharpening of the resonance signal for **19.1b**$^1$ at elevated temperature, but no splitting, allowing to observe the tungsten satellites with a $^1J_{W,P}$ of approximately 275.5 Hz ($\delta^{31}$P (60°C) = 138.4 ppm). It is assumed that the origin of the signal broadening is due to an interaction between the CH proton from the $CH(SiMe_3)_2$ group and the oxygen atom in the five-membered ring. The $^2J_{P,H}$ coupling constant magnitude is, with 12.8 Hz, significantly higher than it is expected for an s-*cis* conformation. An s-*trans* conformation would also be in accordance with the necessary orientation for this interaction. Surprisingly the determined molecular structure (figure 6.6) showed the s-*cis* configuration so that the interaction may be disfavoured in the solid state.

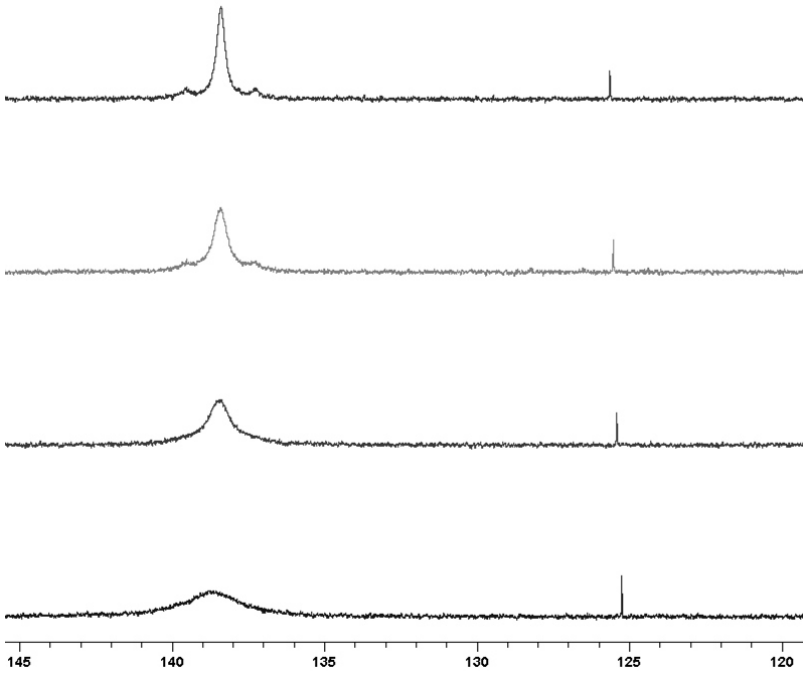



***Figure 6.5:*** Variable temperature $^{31}P\{^{1}H\}$ NMR measurement of **19.1**$^{1-2}$ at 25 °C, 40 °C, 50 °C and 60 °C (from bottom to top) in $CDCl_3$.

The heterocyclic ligand structure was confirmed by a single crystal X-ray diffraction study of **19.1** (figure 6.6). Most structural data are similar to those obtained for the 1,2-oxaphosphetane complex **34.1$_W$**, but an (expected) increase from 80.5(2)° (**34.1$_W$**) to 93.4(3)° (**19.1**) was observed for the endocyclic OPC angle.

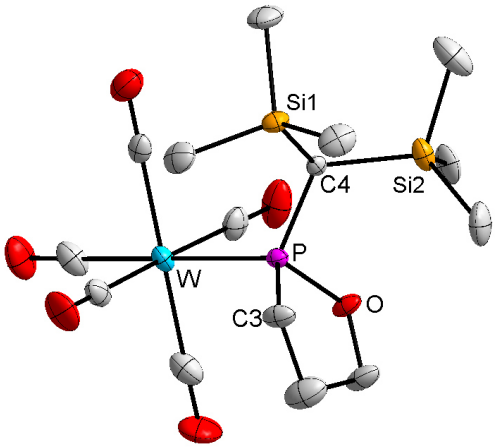
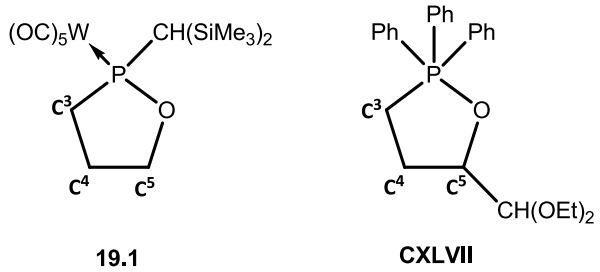



***Figure 6.6:*** DIAMOND plot of the molecular structure of the first 1,2-oxaphospholane complex **19.1** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. Selected bond lengths in Å and angles in °: W-P 2.4937(17), P-C3 1.835(7), P-O 1.640(5), P-C4 1.816(6), W-P-C3 119.8(3), W-P-C4 116.5(2), C3-P-O 93.4(3), and O-P-C4 105.7(3).

A similar 1,2-oxaphospholane complex was described by Mathey in 1982, synthesized by the oxidative desulfurization of the corresponding 1,2-oxaphospholane sulfide with $Fe(CO)_5$.[112] While no structural data were described, the $^{31}P$ NMR resonance signal ($\delta^{31}P(CDCl_3)$ = 173.7 ppm) was found low field shifted in comparison to the ones found for **19.1**. This is in accordance with the expected difference based on the different metal fragment (*e.g.* $(OC)_4Fe(PPh_3)$[134]: $\delta^{31}P$ $(CD_2Cl_2)$ = 71.7 ppm vs. $(OC)_5W(PPh_3)$[135]: $\delta^{31}P(CD_2Cl_2)$ = 20.95 ppm).

Structural proof obtained from X-ray diffraction studies was given for a $\sigma^5,\lambda^5$1,2-oxaphospholane **CXLVII**,[101] showing similar data for bond lengths and the bond angles in the ring (figure 6.7, table 6.3). Interestingly the biggest difference between the two structures is found at the bond lengths and angles around the phosphorus atom. The complex shows a significant shorter P-O bond, a slight elongation of the O-C bond as well as a significant bigger intra-ring angle at the phosphorus.




**19.1** **CXLVII**

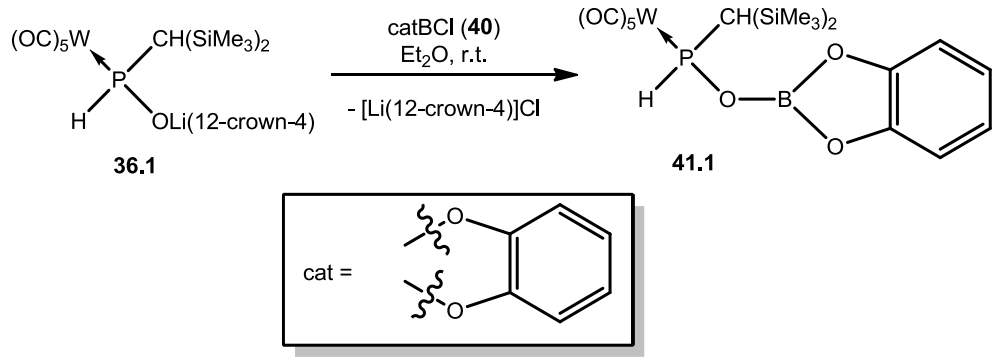
***Figure 6.7:*** Lewis-structures of **19.1** and **CXLVII**[101] and assignment of the ring carbon atoms.

***Table 6.3:*** Selected bond lengths in Å and angles in ° for 1,2-oxaphospholane complex **19.1** and $\sigma^5,\lambda^5$1,2-oxaphospholane **CXLVII**.

| | P-O | P-$C^3$ | O-C | $C^3$-$C^4$ | $C^4$-$C^5$ | O-P-C | P-O-C | O-C-C |
|---|---|---|---|---|---|---|---|---|
| **19.1** | 1.640(4) | 1.835(7) | 1.449(8) | 1.499(11) | 1.520(9) | 93.4(3) | 114.3(4) | 109.2(6) |
| **CXLVII**[101] | 1.789 | 1.855 | 1.399 | 1.508 | 1.515 | 87.1 | 111.7 | 110.9 |

As shown in chapter 3.1, phosphanes of the general formula $R_2POR'$ tend to rearrange to the corresponding phosphane oxides and phosphanes bearing a hydrogen atom together with the alkoxy substituent can in addition undergo formal $\alpha$-eliminations.[47][48] One way to stabilize the phosphanes was achieved by coordination of the electron pair to a transition metal fragment, but no general synthetic procedure of these complexes was developed so far. Therefore a complex that allows the easy synthesis of a variety of such derivatives would be of great interest for further investigations.

Phosphinito complex **36.1**, obtained from the reaction of **33.1$_W$** with $^t$BuLi, can act as oxygen-centred nucleophile and due to the large amount of possible electrophiles it can be seen as a general building block for complexes bearing a P-H function as well as a P-O-E motif in the ligand. While Duan could already show that phosphinito complex **36.1** does not react with typical carbon nucleophiles like MeI or $^t$BuCl, it did react with the oxophilic electrophile $Me_3SiCl$. Based on the observation for $Me_3SiCl$, a first reaction was performed using the oxophilic catechol(chloro)borane (**40**) which is easy to access and handle. The reaction yielded complex **41.1**, bearing a POB unit, selectively (scheme 6.8).




***Scheme 6.8:*** Reaction of phosphinito complex **36.1** with catechol(chloro)borane.

In the $^{31}$P NMR spectrum, complex **41.1** shows a highfield-shifted resonance signal in comparison to most of the previously described phosphinite complexes (**41.1**: $\delta^{31}$P = 97.7 ppm, $^1J_{W,P}$ = 277.1 Hz, $^1J_{P,H}$ = 331.6 Hz). The difference in the chemical shift is explainable due to the electron deficient Boron centre connected to the oxygen atom. This highfield shift is comparable to the one found for an acyl-substituted complex, described by Duan in 2011, ([(OC)$_5$W{PCH(SiMe$_3$)$_2$(H)OC(O)CH$_3$}], $\delta^{31}$P = 88.6 ppm, $^1J_{W,P}$ = 275.8 Hz, $^1J_{P,H}$ = 354.2 Hz).[132]

The molecular structure of **41.1** (figure 6.8) was confirmed by a single-crystal X-ray diffraction study. The boron bonding environment has the expected trigonal planar geometry ($\sum \measuredangle$ B = 360°), but as geometrical data of complex **41.1** revealed similar bond lengths and angles similar to known phosphinite complexes[10,56,132] further discussion is not necessary.

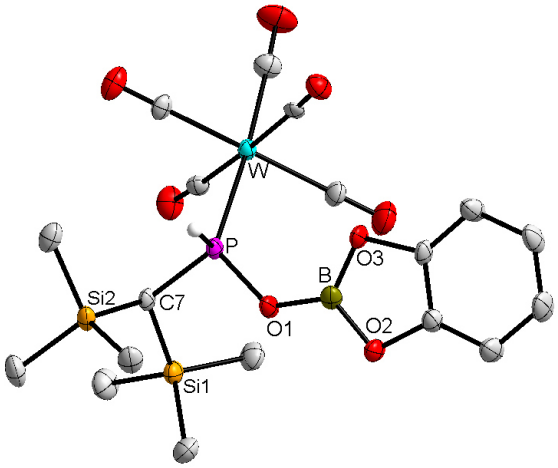



***Figure 6.8:*** DIAMOND plot of the molecular structure of complex **41.1** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at phosphorus are omitted for clarity. Selected bond lengths in Å and angles in °: W-P 2.4695(9), P-C7 1.798(4), P-O1 1.656(3), O1-B 1.353(5), P-O1-B 127.2(3), ∑∡ B = 360°.

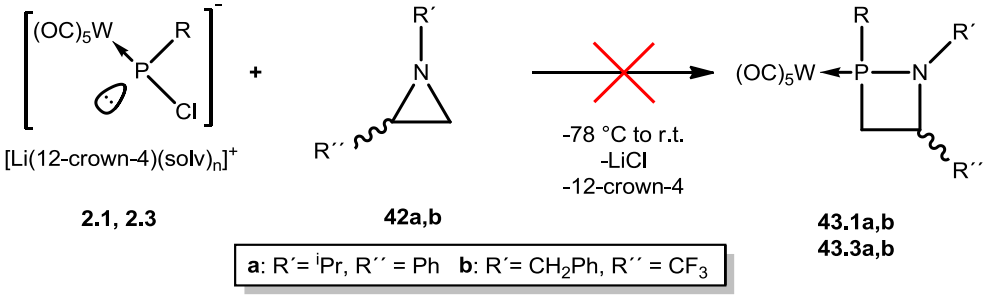
Further investigations towards the potential of **36.1** as building block for phosphorus ligands were performed by R. Kunzmann, focussing on group 14 and 15 element electrophiles. Here the case of $Cy_2BCl$ deserves special mention as the reaction product was used as precursor for the first monomolecular, anionic FLP complex.[136]

# 7 Reactions of Li/Cl phosphinidenoid complexes with aziridines and thiiranes

In the following chapter, reactions of Li/Cl phosphinidenoid complexes **2.1** and **2.3** with aziridines and a thiirane (instead of an expoxide) will be described that allow for a better comparison between the heterocycles and, additionally, to the outcome in case of electrophilic terminal phosphinidene complexes **LVI**. This is of special interest as a comparable reaction, described by Mathey, allowed for the synthesis of the first 1,2-azaphosphetidine complex[72] (cf. chapter 3.1).

Not only the complex described by Mathey,[72] but also one cationic azaphosphetidine iron complex is known.[137] Besides these complexes, several $\sigma^4,\lambda^5$-P derivatives[138] and a $\sigma^3,\lambda^3$-P derivative[139] has been described.

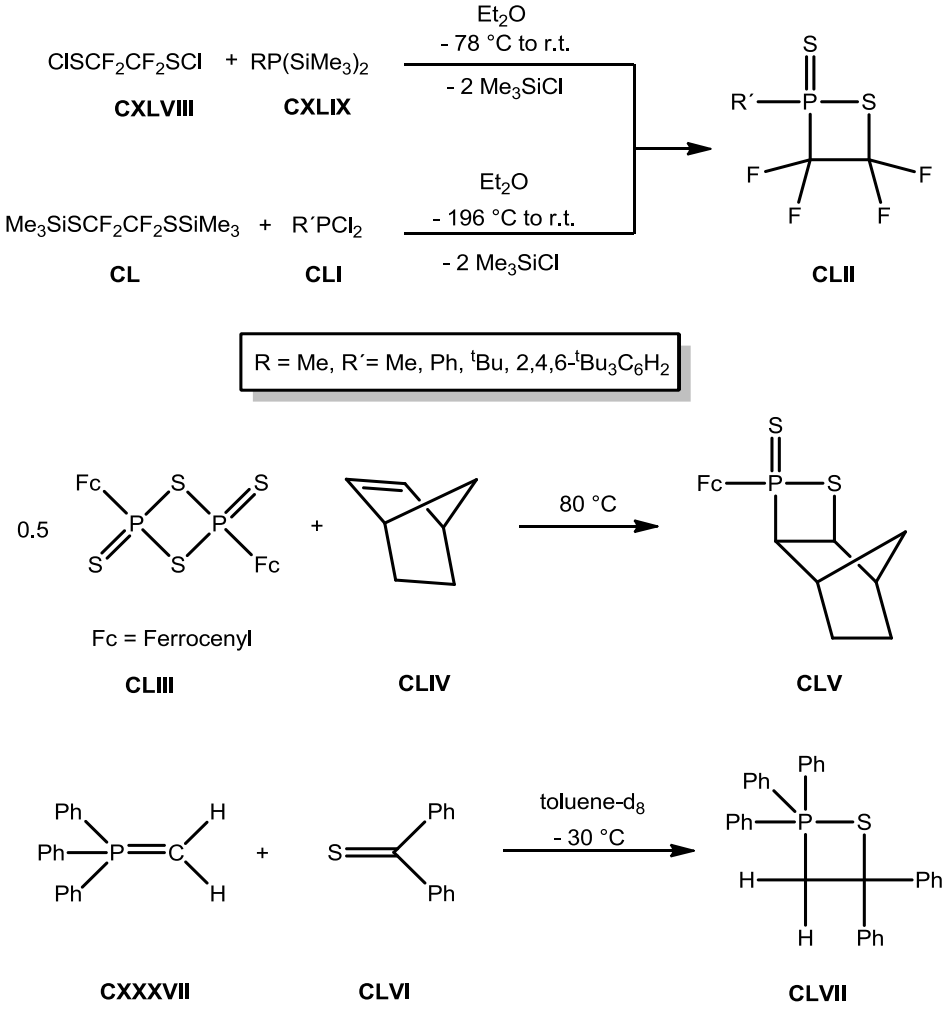
To start this study, two different aziridines (**42a,b**) were prepared for comparison: **42a** with a phenyl in 2-position and with $^i$Pr at the N centre.[140] Furthermore, **42b** was synthesized with benzyl at the N centre, to reduce the steric hindrance, and *C*-$CF_3$[141] in order to activate the ring for an initial nucleophilic attack (cf. chapter 5 for the activation effect of $CF_3$ groups). Despite aziridines with other N-substituents are easier to synthesize, it was decided to avoid an N-substitutionpattern having a proton, in order to suppress a possible insertion reaction into the N-H bond; the latter could be expected due to the similarity to the reaction of **2.3** with other secondary amines (cf. chapter 3).




***Scheme 7.1.*** Performed test-reactions of Li/Cl phosphinidenoid complexes **2.1** and **2.3** with the aziridines **42a**[140] and **42b.**[141]

As cases in point, reactions were tested using the *P*-$CH(SiMe_3)_2$ complex **2.1** and the *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complex **2.3** and both aziridines. Surprisingly, neither of the phosphinidenoid complexes showed any reaction with the substrates. For R = $CH(SiMe_3)_2$, only the formation of the diphosphene complexes **22** and **23** was observed. For R = $CPh_3$ mainly the Li/Cl phosphinidenoid complex **2.3** was observed, alongside with some substrate-independent decomposition products after prolonged reaction times which could not be identified.

A different behaviour was observed in the reaction of these Li/Cl phosphinidenoid complexes and propylene sulphide (methyl-thiirane). It is noteworthy to mention that, in contrast to the well-established 1,2$\sigma^5$,$\lambda^5$ and 1,2$\sigma^4$,$\lambda^5$-oxaphosphetane chemistry, the chemistry of the corresponding 1,2-thiaphosphetanes is rather underdeveloped. Three synthetic strategies to access 1,2-thiaphosphetanes are described, two of which led to thiaphosphetane sulfides,[142,143] starting either from fluorinated alkanes **CXLVIII** and **CL**[143] or a modified Lawesson´s reagent **CLIII**[142]. A third synthetic strategy employed the [2+2]-addition of phosphorus ylides (*e.g.* **CXXXVII**) and thiobenzophenone **CLVII**,[144] in analogy to the Wittig reaction (scheme 7.2).

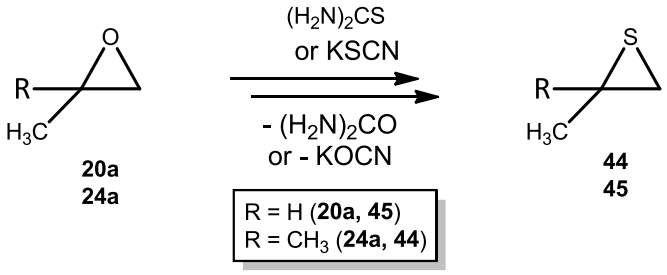



***Scheme 7.2:*** Examples for the syntheses of $P^V$ 1,2-thiaphosphetanes.[142,143][144]

The 1,2-thiaphosphetanes show strong similarities to 1,2-oxaphosphetanes, *e.g.* a solvent dependant equilibrium between the thiaphosphetane and a betain-type structure as well as a decomposition pathway leading to phosphane sulfides by elimination of the corresponding alkene.[145]

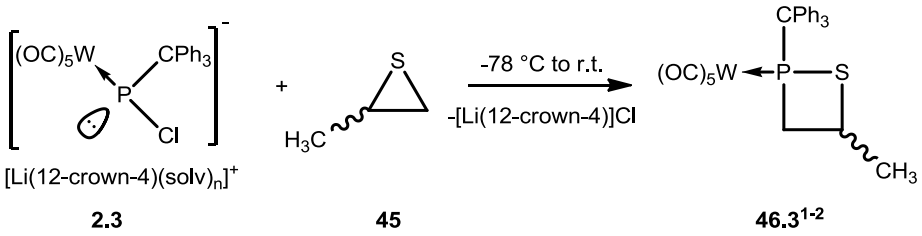
Also, similar to 1,2-oxaphosphetanes, no $P^{III}$ analogues were described so far and the only synthetic attempt to a 1,2-tiaphosphetane complex was described by Mathey using a transient terminal electrophilic phosphinidene complex.[72] In this reaction, the ring system could not be detected, due to loss of sulfur from the starting material, presumably due to the harsh reaction conditions. Formation of a phosphirane complex by reaction of the phosphinidene complex and the formed stilbene was described.

While hardly commercially available, the straightforward syntheses of thiiranes starts from the corresponding epoxides utilizing either KSCN or $S=C(NH_2)_2$, leading to a broad scope of possible reagents for ring expansion reactions (scheme 7.3).[146]




***Scheme 7.3:*** Conversion of epoxides into thiiranes, showing propylene oxide **20a** and 1,1-dimethyloxirane **24a** as examples.[146,147]

Reaction of Li/Cl phosphinidenoid complex **2.1** with propylene sulphide (**45**) led to several unidentified products in an inseparable mixture. In contrast, reaction of **2.3** with propylene sulfide (**45**) led to the selective formation of two isomers of 1,2-thiaphosphetane complex **46.3**$^{1\text{-}2}$ (scheme 7.4). The $^{31}P$ resonance signals for complexes **46.3**$^{1}$ and **46.3**$^{2}$ appeared in a ratio of 56:44 and significantly shifted to higher field with a decreased magnitude of the $^{1}J_{W,P}$ coupling constant (**46.3**: $\delta^{31}P$ = 65.3 ppm ($^{1}J_{W,P}$ = 256.7 Hz) and 50.5 ppm ($^{1}J_{W,P}$ = 254.6 Hz)) compared to the 1,2-oxaphosphetane complexes **21.3a**$^{1\text{-}2}$ ($\delta^{31}P$ = 180.2 ppm ($^{1}J_{W,P}$ = 283.1 Hz) and 161.0 ppm ($^{1}J_{W,P}$ = 278.3 Hz)) (figure 7.1).




***Scheme 7.4:*** Synthesis of the first 1,2-thiaphosphetane complexes **46.3**$^{1\text{-}2}$.

The $^{1}H$ NMR and $^{13}C\{^{1}H\}$ NMR data are quite similar to those of 1,2-oxaphosphetane complexes **21.3a**$^{1\text{-}2}$. However, a large influence is found on the CH group, the $^{1}H$ NMR signals show a slight high-field-shift of approximately 1 ppm and the corresponding $^{13}C\{^{1}H\}$

NMR signals show a high-field-shift of approximately 43 ppm, indicating the presence of the less electronegative sulphur instead of the oxygen atom.

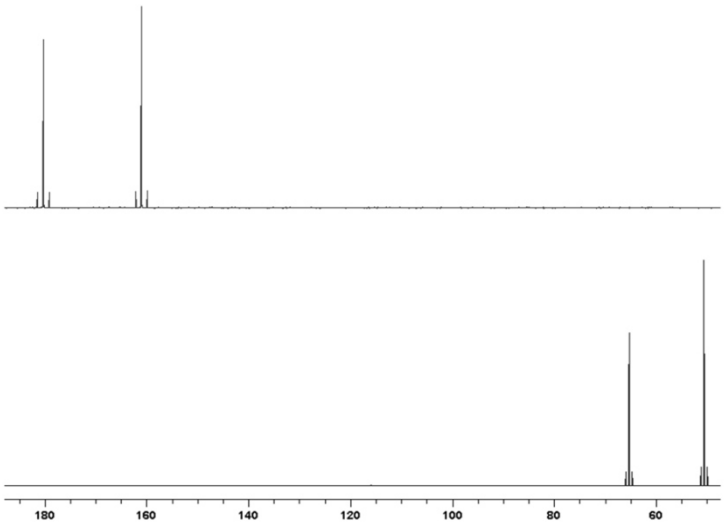



***Figure 7.1:*** Comparison of the $^{31}P\{^{1}H\}$ NMR spectra of 1,2-oxaphosphetane complexes **21.3a**[1-2] (top) and 1,2-thiaphosphetane complexes **46.3**[1-2] (bottom), both spectra measured in $CDCl_3$.

The molecular structure of the first 1,2-thiaphosphetane complex **46.3** proves the four-membered ring ligand structure (figure 7.2). Suitable single crystals for the X-ray diffraction study were obtained by slow evaporation of a saturated diethyl ether solution at 4 °C. Three independent molecules were found in the unit cell and selected data for all are given in table 7.1. No significant differences were observed comparing the data of the three independent molecules. Compared to **21.3a**, the P-S and the C-S bonds are elongated due to the larger sulfur atom. Also the P-W and the exocyclic P-C bonds are elongated (table 8.1). Surprisingly, no significant increase of the C(1)-P-S angle was observed.

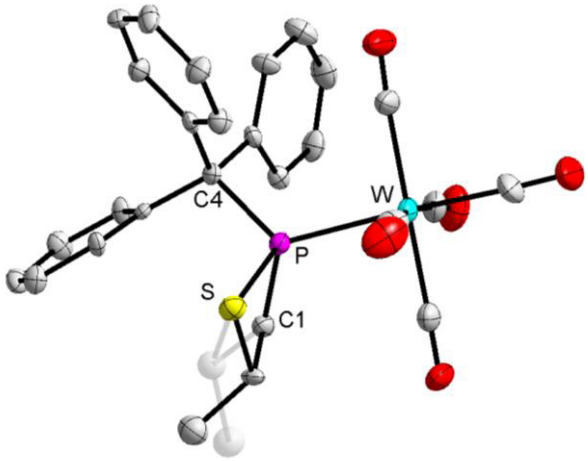



***Figure 7.2:*** DIAMOND plot of the molecular structure of complex **46.3** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. Only one of three independent molecules in the unit cell is shown for clarity. The split-site (1:1) for the C-Me unit is represented using a transparent mode for clarity.

Like in case of the 1,2-oxaphosphetane complex **21.3a** two orientations were found for the C-Me group, leading to two folding angles at the ring. Both folding angles are in the range found for the 1,2-oxaphosphetane complexes (24.3°/25.7°/26.8° (C-Me oriented towards the $CPh_3$ substituent) and 18.1°/15.2°/11.3° (C-Me orientated towards the $W(CO)_5$ fragment)).

***Table 7.1:*** Selected bond lengths in Å and angles in ° for 1,2-oxaphosphetane complex **21.3a** and the three independent molecules of 1,2-thiaphosphetane complex **46.3**.

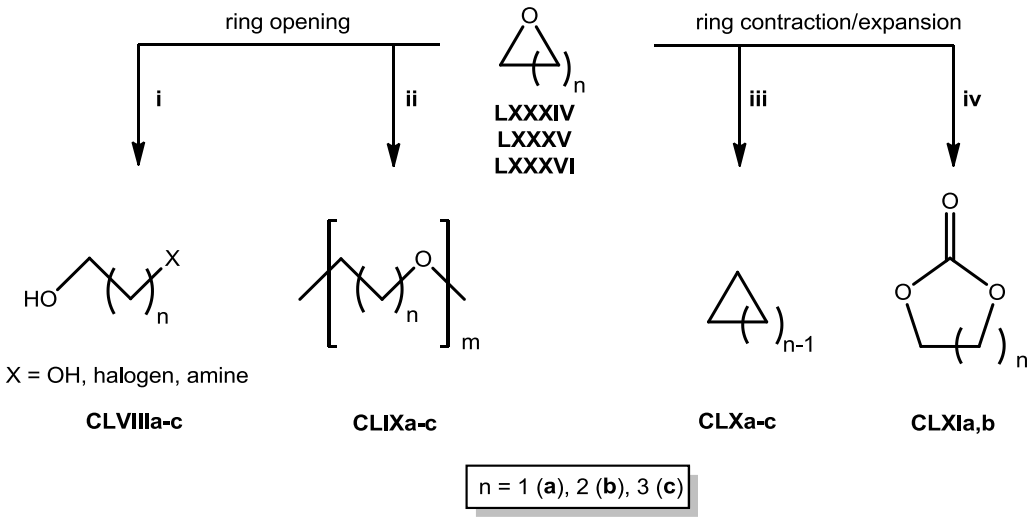
| | P-W | P-$C^{ring}$ | P-$C^{exo}$ | P-chalcogen | CH-chalcogen | chalcogen-P-$C^{ring}$ |
|---|---|---|---|---|---|---|
| **21.3a** | 2.4926(12) | 1.843(4) | 1.905(4) | 1.656(3) | 1.515(8) | 80.49(18) |
| | 2.5158(18) | 1.861(7) | 1.922(7) | 2.125(3) | 1.876(10) | 80.8(2) |
| **46.3** | 2.5060(18) | 1.856(7) | 1.920(7) | 2.132(2) | 1.901(11) | 80.6(2) |
| | 2.539(2) | 1.872(8) | 1.936(7) | 2.115(3) | 1.832(16) | 81.8(3) |

To check the influence of the chalcogen on the reactivity two exemplary reactions were tested: the ring opening reaction using $HBF_4{\cdot}OEt_2$ and an acid induced ring expansion reaction with HOTf and acetonitrile, as both of which showed selective reactions for 1,2-oxaphosphetane complexes (see later on chapter 8). Surprisingly, in both cases no reaction was observed for **46.3**, even at elevated temperatures. In addition to this low reactivity, complex **46.3** showed a high thermal stability; no decomposition was observed in toluene up to the boiling point.

# 8 Reactions of 1,2-oxaphosphetane complexes

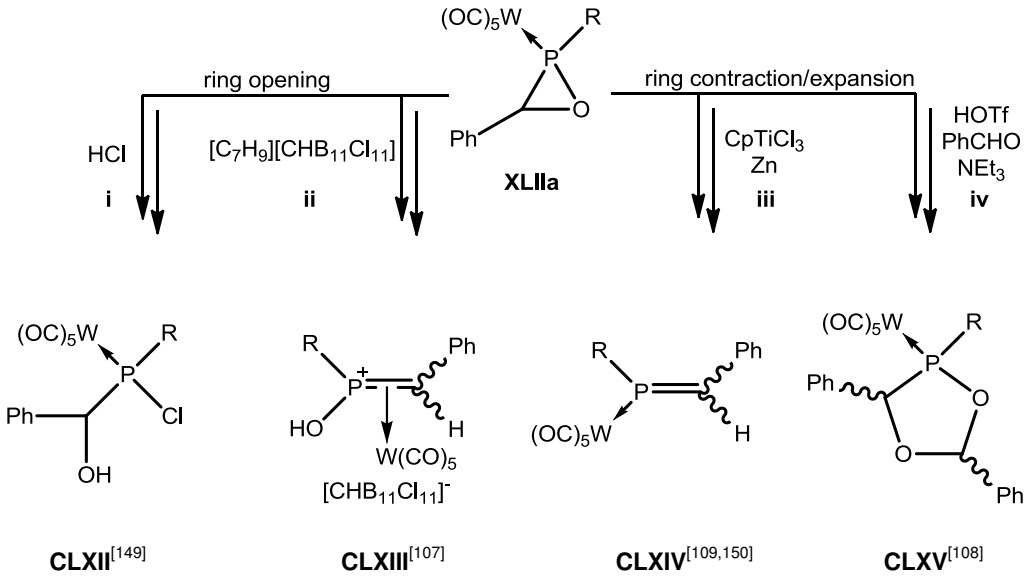
## 8.1 Introduction – general reactivity of epoxides, oxetanes and tetrahydrofuranes

Hydrolytic or acidic ring opening, ring opening polymerizations, deoxygenation reactions, ring expansion reactions, and subsequent reactions, *e.g.* of, by hydrolysis, formed $\alpha,\omega$-dioles, led to the immense importance of small heterocycles as building blocks in Organic Chemistry and material science. Oxiranes are by far the best investigated derivatives of the heterocyclic ring systems, but also larger and less reactive heterocycles such as oxetane (scheme 8.1 n = 2) and tetrahydrofurane (scheme 8.1, n = 3) can be used as raw material for numerous high-end applications.[80] The reactivity of the oxygen-containing heterocycles can mainly be separated into two formal reaction patterns, based on the products obtained: formal ring opening reactions, e.g. with electrophiles or nucleophiles (**i**)[80] or in polymerization reactions (**ii**),[124] or change of the ring size by a sequential bond breaking and bond forming process, *e.g.* the deoxygenation of epoxides (**iii**) or the reaction with $CO_2$ to cyclic carbonates (**iv**).[148]




***Scheme 8.1:*** Examples for ring opening and ring expansion or contraction reactions of small-sized oxygen containing heterocycles.

Oxaphosphirane ligands, *e.g.* in complex **CLXIV**, are the phosphorus analogues of epoxides, and due to their synthetic potential the Streubel research group has shown a longstanding interest in the development of their synthesis and the investigation of their reactivity. A set of typical reactions such as Brønsted acid-induced ring opening reactions, leading to halophosphane complexes (**i**)[149] or side-on bonded phosphaalkene complexes (**ii**),[107] deoxygenation reactions (**iii**),[109,150] being a form of "ring contraction", as well as ring expansion reactions (**iv**)[108] could be developed over the past decade (scheme 8.2).

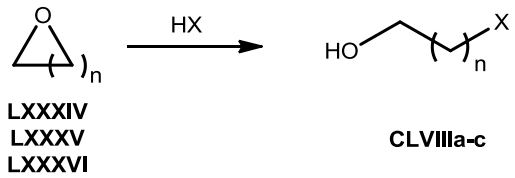



***Scheme 8.2:*** Typical reactions of oxaphosphirane complexes as the smallest O,P-heterocyclic complexes (R = $CH(SiMe_3)_2$).

After the development of synthetic routes for 1,2-oxaphosphetane complexes, the potential of this new phosphorus heterocycle should be investigated. Here, particular emphasis was on the discovery of reactivity similarities compared to oxaphosphirane ligands. The results will be presented in the following chapters.

## 8.2 Ring opening reactions with HCl or $HBF_4 \cdot OEt_2$

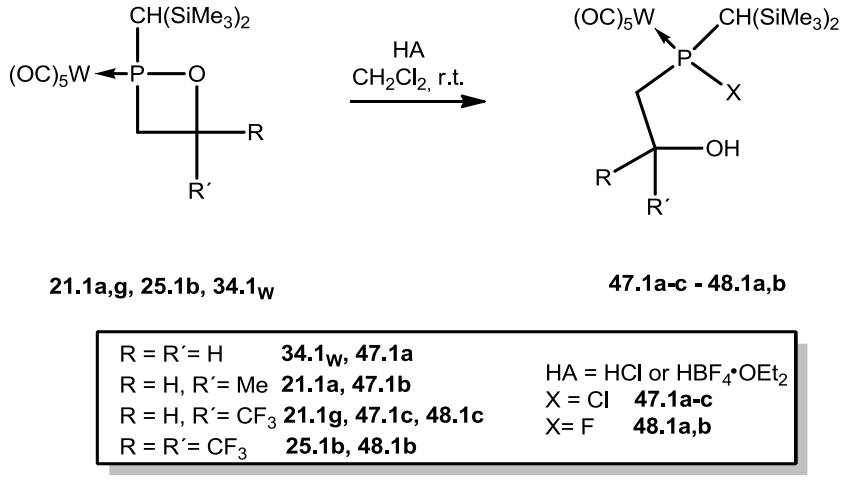
The reaction of small oxygen-containing heterocycles like oxiranes, *e.g.* propylene oxide[151], oxetanes, *e.g.* 2-methyloxetane[152], and tetrahydrofuranes[153] with most Brønsted acids in the absence of water leads to asymmetric $\alpha,\omega$-substituted alcohols, as shown in scheme 8.3.




***Scheme 8.3:*** Ring opening reactions of oxygen containing heterocycles with Brønsted acids (X = variable, *e.g.* F, Cl, Br, I; n = 1-3).

In the present case, surprisingly, no reaction of 1,2-oxaphosphetane complexes with hydrogen chloride in diethyl ether was observed, possibly due to the low basicity of the O-centres in these complexes, which prevents the initial protonation as the solvent is preferrably protonated. By changing the solvent to dichloromethane and using $HCl_{(g)}$ this

problem could be overcome, allowing a first regioselective ring opening of 1,2-oxaphosphetane complexes at the P-O bond (scheme 8.4).




***Scheme 8.4:*** Ring opening reactions of 1,2-oxaphosphetane complexes with Brønsted acids.

In case of **$34.1_W$** a complete conversion was observed using $HCl_{(g)}$ (after less than 30 minutes). The product was isolated by evaporation of the solvent and had to be, due to the oily nature at that point, recrystallized from *n*-pentane. The complex **47.1a** showed a resonance signal 79.9 ppm high-field-shifted in the $^{31}P$ NMR spectrum, compared to the starting 1,2-oxaphosphetane complex ($\delta^{31}P$ = 191.4, $^1J_{W,P}$ = 268.5 Hz) with the magnitude of the $^1J_{W,P}$ coupling increased by 4.4 Hz (table 8.1).

***Table 8.1:*** $^{31}P\{^1H\}$ NMR data in $CDCl_3$ and yields of complexes **47.1a-c** and **48.1a,b**.

| | R/R´/X | $\delta^{31}P$ in ppm ($^1J_{W,P}$ [Hz]) {$^1J_{P,F}$ [Hz]} | | isomeric ratio | yield [%] |
|---|---|---|---|---|---|
| | | Isomer 1 | Isomer 2 | | |
| **47.1a** | H / H / Cl | 111.5 (272.9) | - | - | 71 |
| **47.1b** | Me / H / Cl | 119.8 (276.0) | 115.1 (274.2) | 25:75 | 100 |
| **47.1c** | $CF_3$ / H / Cl | 113.4 (br) | 110.6 (281.3) | 12:88 | 33 |
| **48.1a** | $CF_3$ / H / / F | 194.0 (290.0) {823.0} | 185.6 (294.0) {821.8} | 26:74 | 39 |
| **48.1b** | $CF_3$ / $CF_3$ / F | 180.4 (302.1) {852.4} | - | - | 70 |

A single crystal suitable for X-ray diffraction studies could be obtained for **47.1a** from an *n*-pentane solution. The molecular structure showed four independent molecules in the unit cell and an additional water molecule for two molecules of **47.1a**. Nevertheless, the structural motif and, with this, the regioselective reaction was proven (figure 8.1).

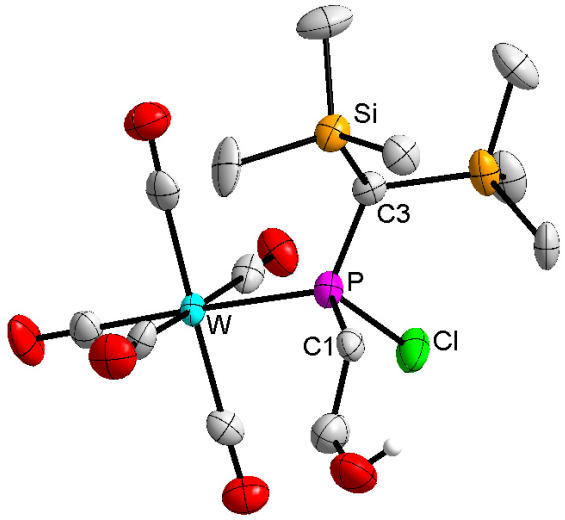



***Figure 8.1:*** DIAMOND plot of the molecular structure of complex **47.1a** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except the OH and a quarter of an equivalent of water are omitted for clarity. Only one of the four independent molecules in the unit cell is shown for clarity.

***Table 8.2:*** Selected bond lengths in Å and angles in ° for complex **47.1a**. The data of all four independent molecules in the unit cell are given.

| Independent molecule | P-W | P-C1 | P-X | W-P-C1 | Cl-P-C1 |
|---|---|---|---|---|---|
| **1** | 2.491(3) | 1.842(11) | 2.082(4) | 118.8(4) | 97.7(4) |
| **2** | 2.494(3) | 1.823(10) | 2.101(4) | 121.1(3) | 97.6(3) |
| **3** | 2.501(2) | 1.816(9) | 2.085(3) | 122.2(4) | 96.8(4) |
| **4** | 2.490(2) | 1.836(9) | 2.090(3) | 118.9(3) | 97.6(3) |

In case of **21.1a**, bearing the *C*-Me substituent, the reaction with $HCl_{(g)}$ also led to the same outcome in a highly selective reaction and less than an hour reaction time. Work-up was performed similar to the procedure described above for **47.1a**.

An interesting strong decrease of the reactivity was observed using different C-substituted 1,2-oxaphosphetane complexes and introduction of electron withdrawing $CF_3$ substituents. When complex **21.1g**, bearing one $CF_3$ substituent, was used in the reaction a significant slower reaction with $HCl_{(g)}$ was observed. To check the dependency of the reaction progression on different acids $HBF_4{\cdot}OEt_2$ was used; the $HBF_4{\cdot}OEt_2$ acted here formally as a source of HF. The reaction of **21.1g** and **25.1b** with $HBF_4{\cdot}OEt_2$ yielded almost instantaneously the products **48.1a** and **48.1b**, respectively. This is in contrast to the case of **25.1b**, bearing two $CF_3$ groups, and $HCl_{(g)}$ in which the reaction was completely suppressed.

$^{31}P\{^{1}H\}$ NMR spectroscopic data of chloro(organo)phosphane complexes **47.1a-c** and fluoro(organo)phosphane complexes **48.1a,b** are given in table 8.1. The $^{31}P\{^{1}H\}$ NMR resonances of chloro(organo)phosphane complexes **47.1a-c** are observed in a chemical shift range between 110 and 120 ppm with $^{1}J_{W,P}$ constants between 272 and 281 Hz, which is in good accordance with the ones observed for other *P*-$CH(SiMe_3)_2$-substituted chlorophosphane complexes, *e.g.* $[(OC)_5W\{P(CH_3)CH(SiMe_3)_2(Cl)\}]$ ($\delta^{31}P$ = 105.4 ppm, $^{1}J_{W,P}$ = 273.4 Hz).[31] Complexes **48.1a,b**, possessing P-F bonds, show significantly downfield-shifted values at around 180-195 ppm and a coupling to the fluoride. The changes in chemical shifts and coupling constants are in accordance with the higher electronegativity of the P-bound halogens (F vs Cl) in these cases, which is also reflected by the tungsten-phosphorus couplings.[121] The fluorophosphane complex **48.1b**, bearing two $CF_3$ substituents, displays the largest coupling constants in this series (table 1), accordingly.

In the IR spectra the absorption due to O-H valence bond stretching vibrations of **47.1b,c** and **48.1a,b** were found around 3600 $cm^{-1}$. In case of **47.1a** a broad absorption band at 3298 $cm^{-1}$ was found, which indicates the presence of hydrogen bonding.

Single crystals could be obtained of all complexes and X-ray diffraction studies proved the high regioselectivity of the reactions. All bond lengths and angles, apart from the expected difference in the P-X bond lengths for X = Cl and X = F, are very similar and shall therefore not be discussed further (table 8.3).

***Table 8.3:*** Selected bond lengths in Å and angles in ° for complexes **47.1b** to **48.1b**.

| | P-W | P-C1 | P-X | W-P-C1 | X-P-C1 |
|---|---|---|---|---|---|
| **47.1b** | 2.503(5)/ 2.504(5) | 1.84(2)/ 1.796(19) | 2.098(7)/ 2.117(6) | 122.2(6)/ 117.8(6) | 108.0(2)/ 105.9(6) |
| **47.1c** | 2.4872(4) | 1.8463(16) | 2.0969(5) | 123.67(5) | 96.28(5) |
| **48.1a** | 2.4682(9) | 1.835(4) | 1.614(2) | 123.32(13) | 108.53(9) |
| **48.1b** | 2.4767(9) | 1.844(4) | 1.600(2) | 125.75(12) | 109.63(9) |

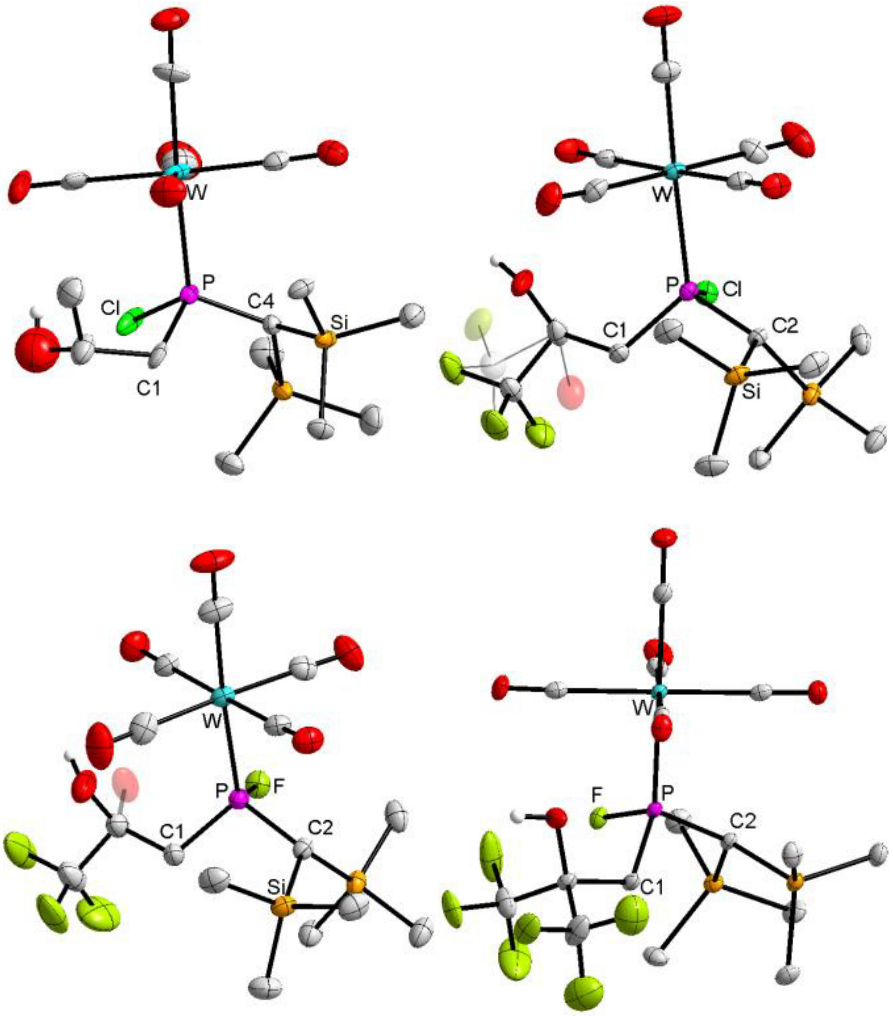
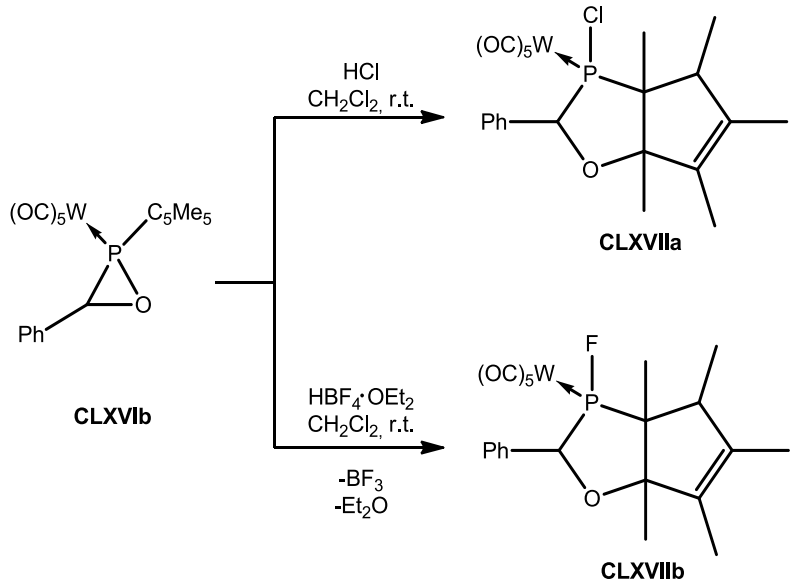


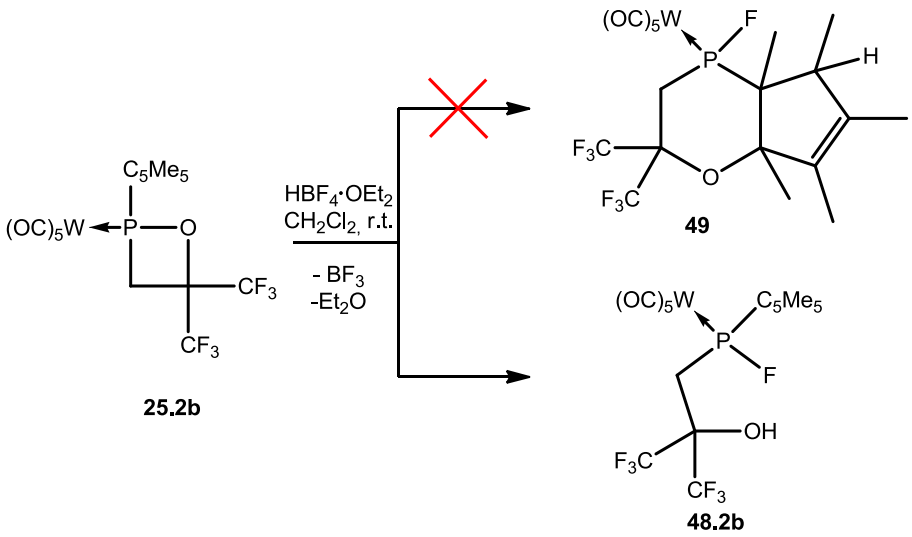

***Figure 8.2:*** DIAMOND plot of the molecular structures of complexes **47.1b**, **47.1c**, **48.1a** and **48.1b** (from top left to bottom right) in the solid state; the thermal ellipsoids are set at 50 % probability level and hydrogen atoms except the OH are omitted for clarity. In case of **47.1b** only one of two independent molecules in the unit cell is shown for clarity. The split-sites (1:1) for the R-C and C-O units are represented using a transparent mode for clarity.

The reaction of the *P*-$C_5Me_5$-substituted 1,2-oxaphosphetane complex **25.2b** was of greater interest: This reaction could formally lead to a different possible outcome, as it was observed in the case of oxaphosphirane complexes. Instead of the ring opening reaction, a ring expansion involving the *P*-$C_5Me_5$ moiety (scheme 8.5) was observed for **CLXVIb**.[39,149]




***Scheme 8.5:*** Reactions of *P*-$C_5Me_5$-substituted oxaphosphirane complex **CLXVIb** with HCl[149] or $HBF_4{\cdot}OEt_2$.[39]

The reaction of complex **25.2b** with $HBF_4{\cdot}OEt_2$ was performed and led to only one product in a clean conversion.




***Scheme 8.6:*** Proposed and found acid-induced ring opening reaction of the *P*-$C_5Me_5$-substituted 1,2-oxaphosphetane complex **25.2b**.

A broad resonance signal was observed for **48.2b** in the $^{31}P\{^1H\}$ NMR spectrum ($\delta^{31}P$ = 190.3 ppm, FWHI ($h_{1/2}$) = 440 Hz), exhibiting a $^1J_{P,F}$ coupling constant of 830 Hz. These $^{31}P$ NMR data are similar to the ones found for the *P*-$CH(SiMe_3)_2$-substituted derivative **48.1b** ($\delta^{31}P$ = 180.4 ppm ($^1J_{P,F}$ = 852.4 Hz, $^1J_{W,P}$ = 302.1 Hz)). Due to the presence of all 4 expected signals of the C=C bonds of the $C_5Me_5$ group in the $^{13}C\{^1H\}$ NMR spectrum, a ring expansion reaction similar to the one for oxaphosphirane complexes could already be ruled out. The nature of the proposed ring opening reaction product was further confirmed by a single

crystal X-ray diffraction study (figure 8.3). All structural data are similar to the ones observed for **48.1b** and shall therefore not be discussed further.

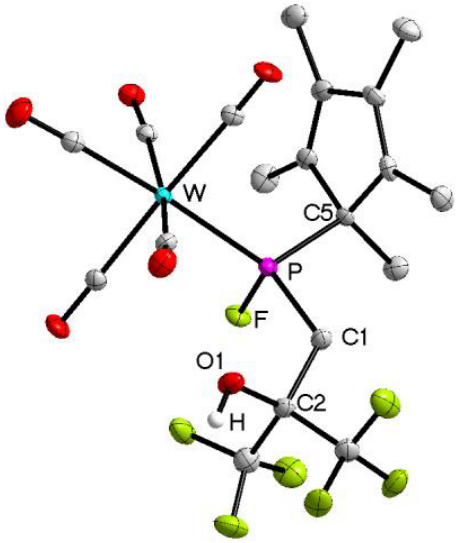



***Figure 8.3:*** DIAMOND plot of the molecular structure of complex **48.2b** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at the OH group are omitted for clarity. Only one of two independent molecules is shown, both sets of data are given (molecule1/molecule2). Selected bond lengths in Å and angles in °: W-P 2.5014(15)/2.4793(16), P-F 1.600(4)/1.598(4), P-C1 1.849(6)/1.840(7), P-C5 1.872(6)/1.862(6), F-P-C1 99.8(2)/100.5(3).

Besides the typical bond lengths and angles one aspects of the molecular structures of **47.1a-c** and **48.1a,b** deserve closer inspection: All obtained structures are dominated by hydrogen bond interactions of the C-OH groups. In case of **47.1a** the packing is dominated by hydrogen bridging between the OH groups of the molecule and the water molecules present. The molecules form a structure with one molecule of water in the centre, coordinated by one C-OH from each side. These C-OH-O-OH-C moieties are then connected to a second C-OH unit by a hydrogen bond (figure 8.4). Further elongation of this hydrogen bridging network is suppressed, presumably by steric effects.

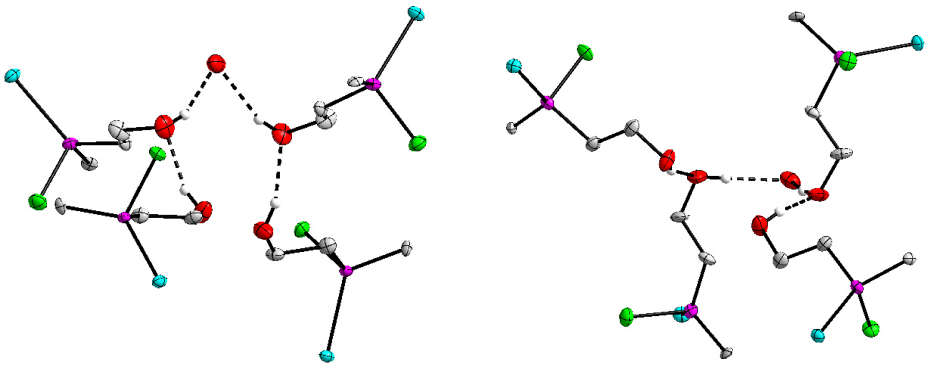


***Figure 8.4:*** DIAMOND plots, indicating the OH-OH-O-HO-HO unit (hydrogen bonds as dashed lines) in the molecular structure of complex **47.1a** in the solid state; the thermal ellipsoids are set at 50 % probability level. All hydrogen atoms except at the C-OH groups and parts of the P-substituents are omitted for clarity. The view from top (left) and from the side (right) of the unit is shown.

Two different types of interaction were observed in the structure of complex **47.1b**. Here, a hydrogen bridge between two C-OH groups was observed (figure 8.5, left side). However, this bridge was only observed for one of two independent molecules as the second one shows an intramolecular hydrogen bridge to the chlorine atom (figure 8.5, right side).

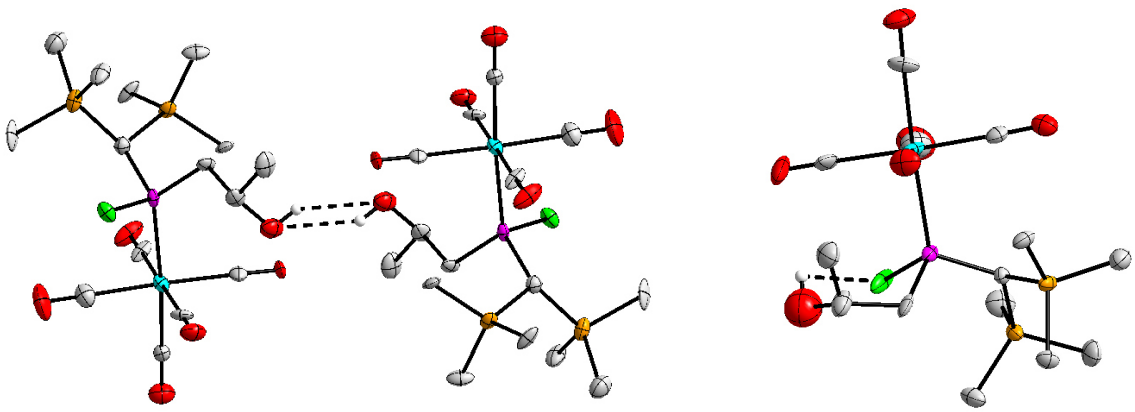


***Figure 8.5:*** DIAMOND plots, indicating the OH-HO unit (left) and the intramolecular hydrogen bridge (right) (hydrogen bonds are depicted as dashed lines) in the molecular structure of complex **47.1b** in the solid state; the thermal ellipsoids are set at 50 % probability level. All hydrogen atoms except at the C-OH groups are omitted for clarity.

In the molecular structures of complexes **47.1c**, **48.1a,b** and **48.2b** no hydrogen bridging between the OH and the P-F group was observed. Weak interactions between the OH group and one of the *cis*-CO groups of the metal fragments were present, thus leading to coordination dimers in the solid state. Figure 8.6 shows the sixteen-membered rings that are formed by this interaction for complexes **48.1d** and **48.2b**. In case of **47.1c** and **48.1a** this interaction is only observed for one of the two split sites shown in figure **8.2** (shown as solid part in both cases).

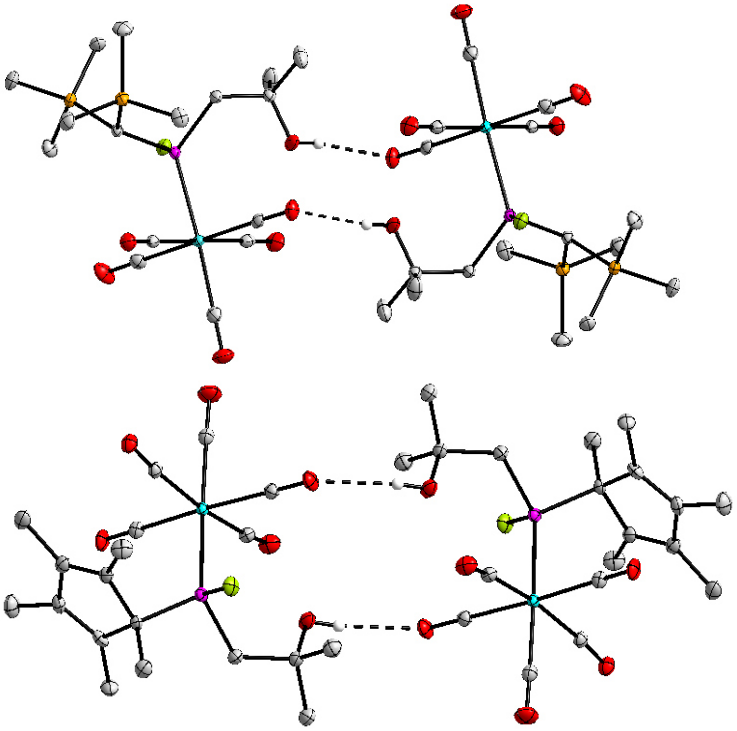
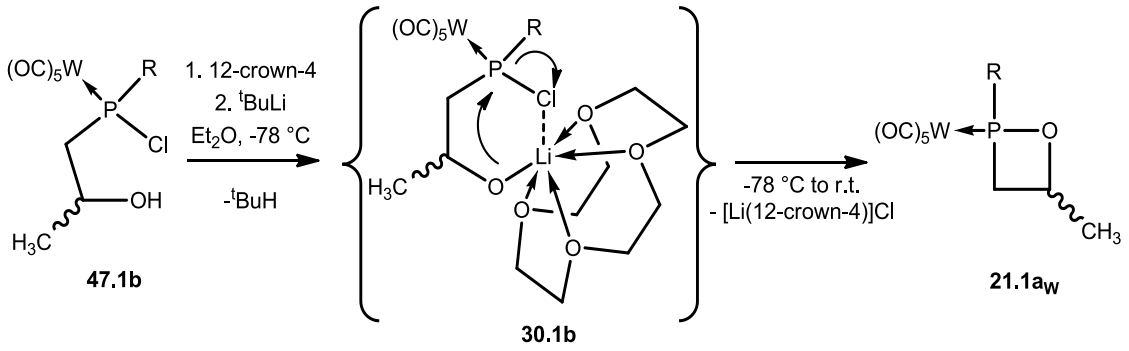


***Figure 8.6:*** DIAMOND plots, indicating the OH-OCW interaction (dashed line) in the molecular structures of complex **48.1b** and **48.2b** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms except at the OH group, as well as the fluorine atoms of the $CF_3$ groups are omitted for clarity. Only one of two independent molecules is shown for **48.2b**.

A strong influence of the substitution pattern on this effect, especially the presence of the electron-withdrawing $CF_3$ groups can be assumed based on the obtained structures. Unfortunately no assignment to the nature of this hydrogen bond can be presented at this point, and calculations would be very helpful in this regard. However, such non-bonding interactions between the CO groups of the $W(CO)_5$ unit and electron deficient groups were described just recently by Streubel.[154]

After the ring opening was successfully performed, it was examined if the ring closing reaction is possible, too, by applying typical phosphinidenoid-type conditions, *i.e.* using $^{t}$BuLi and 12-crown-4. This reaction is of great importance as it would also represents an independent route to synthesize intermediate **30.1c**, proposed in the reaction mechanism for the reaction of Li/Cl phosphinidenoid complexes with epoxides (chapter 5.5).




***Scheme 8.7:*** Synthesis of complexes **21.1a$_W$**[1-4] via deprotonation of complex **47.1b** using $^{t}$BuLi/12-crown-4.

The reaction is selective according to the $^{31}P\{^{1}H\}$ NMR spectrum (figure 8.7), but showed a significant change of the iratio of the isomeric products (original synthesis: 29:4:48:19, this route: 10:0:60:30). This is similar to a case previously observed for an oxaphosphirane complex; there, the stepwise ring opening and ring closing reaction even featured a complete conversion of the s-*cis* into the s-*trans* isomer.[114]

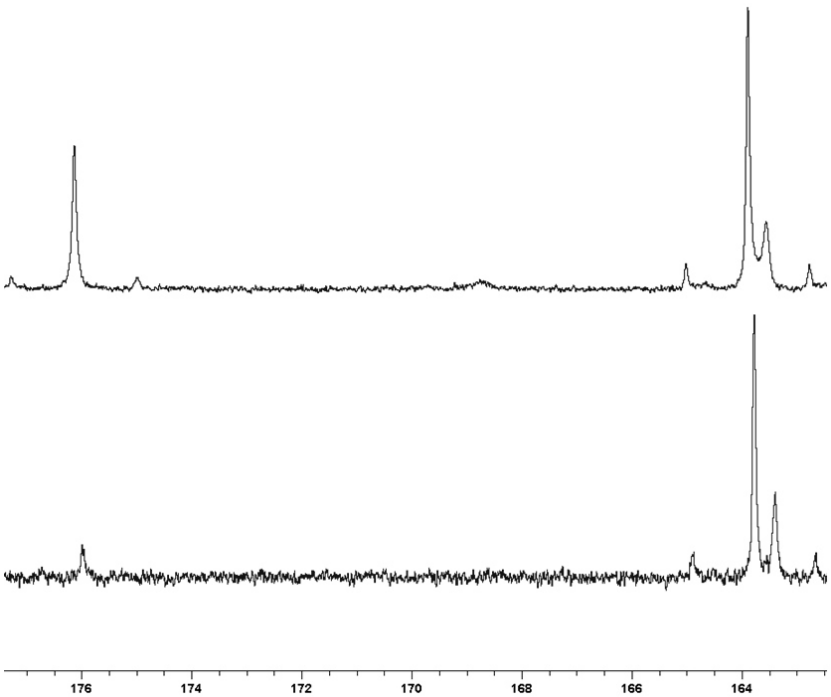
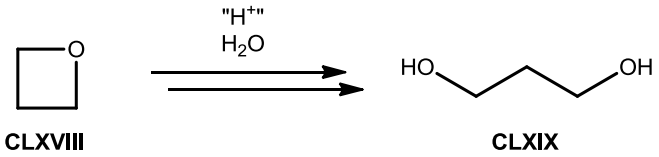



***Figure 8.7:*** $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture for the syntheses of **21.1a$_W$**[1-4] using the Li/Cl phosphinidenoid complex **2.1** and propylene oxide **20a** (top) and of the reaction using complex **47.1b** and $^{t}$BuLi/12-crown-4 (bottom), both measured as reaction mixture in $Et_2O$.

## 8.3 Hydrolysis and decomposition reaction using triflic acid and water

Although the ring opening reaction of oxiranes with water is slow, it is often observed. In contrast to this, it is normally not observed for oxetanes or tetrahydrofuranes. Nevertheless, an activation of the ring (via additional interactions of the heteratom) can lead to a fast(er) reaction which is usually achieved for example by addition of Brønsted acids. Therefore reaction of epoxides, oxetanes or tetrahydrofuranes with acids in the presence of water leads to the corresponding α,ω-dioles; this is illustrated for oxetane in scheme 8.8.[155]

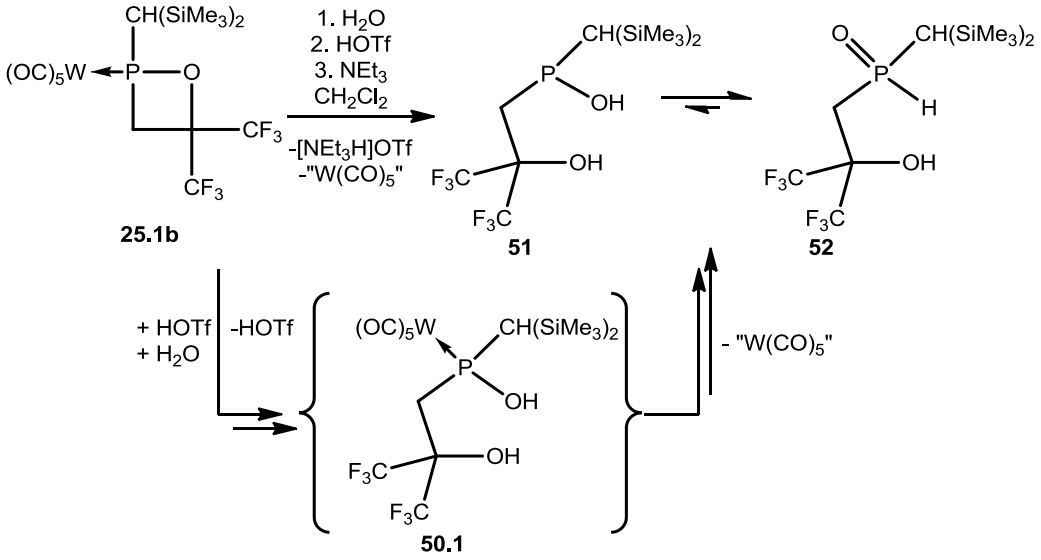



**CLXVIII** **CLXIX**

***Scheme 8.8:*** Acid-catalyzed hydrolysis of oxetane.[155]

In order to mimic this α,ω-diole formation, the reaction of 1,2-oxaphosphetane complex **25.1b** with $H_2O$ in presence of HOTf (scheme 8.9) was performed. The hydrolysis took place, but unexpectedly loss of the $W(CO)_5$ fragment was observed, additionally. This loss was surprising, as complexes bearing a POH motif were described before as stable derivatives, *e.g.* $[(OC)_5W\{PH(OH)(Ph)\}]$[47] or even $[(OC)_5M\{P(OH)_3\}]\cdot n\ H_2O$ (M = Cr (n = 1),[156] M = Mo (n = 2)[157]).

For the present case, the proposed mechanism consists of the formation of hydrolysis product **50.1**, presumably after intermediate protonation of the 1,2-oxaphosphetane complex for activation, which then loses the metal fragment under the reaction conditions. The initially formed phosphinic acid **51** is thereby in equilibrium with the phosphane oxide and rapidly rearranges to the thermodynamically more favoured product **52**.




***Scheme 8.9:*** Acid-induced hydrolysis of 1,2-oxaphosphetane complex **25.1b**.

Phosphane oxide **52** could be purified by addition of water, acidification of the solution and extraction with dichloromethane. The tungsten complex **50.1** decomposed under these conditions yielding $W(CO)_6$ and unidentified metal compounds in the aqueous phase. The $W(CO)_6$ was separated by sublimation at elevated temperature (0.014 mbar and 55 °C), and the purification of **52** was monitored by IR spectroscopic measurements, *i.e.* following the intensity decrease of the CO absorption in the IR spectrum.

The $^{31}P$ NMR spectrum of phosphane oxide **52** revealed only one resonance signal at $\delta^{31}P$ = 34.3 ppm ($^1J_{P,H}$ = 486.8 Hz) indicating the loss of the P-W bond by absence of $^{183}W$ satellites (figure 8.8). The resonance signal is strongly shielded in comparison to the starting material (**25.1b**[1,2]: $\delta^{31}P$ = 198.2/191.5 ppm) and in a typical range for phosphane oxides.

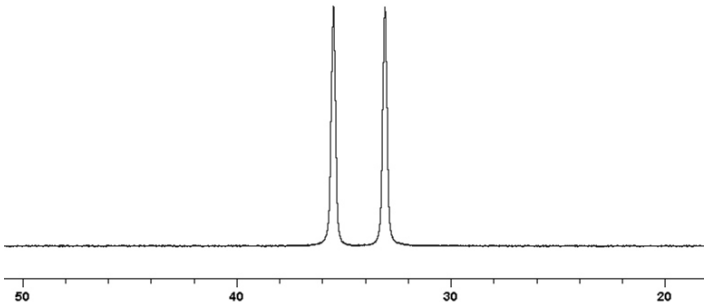



***Figure 8.8:*** Zoom in on the $^{31}P$ NMR spectrum of **52**.

Absence of carbonyl resonance signals in the $^{13}C\{^1H\}$ NMR spectrum (figure 8.9) as well as the MS measurement and an elemental analysis further verified the loss of the $W(CO)_5$ moiety.

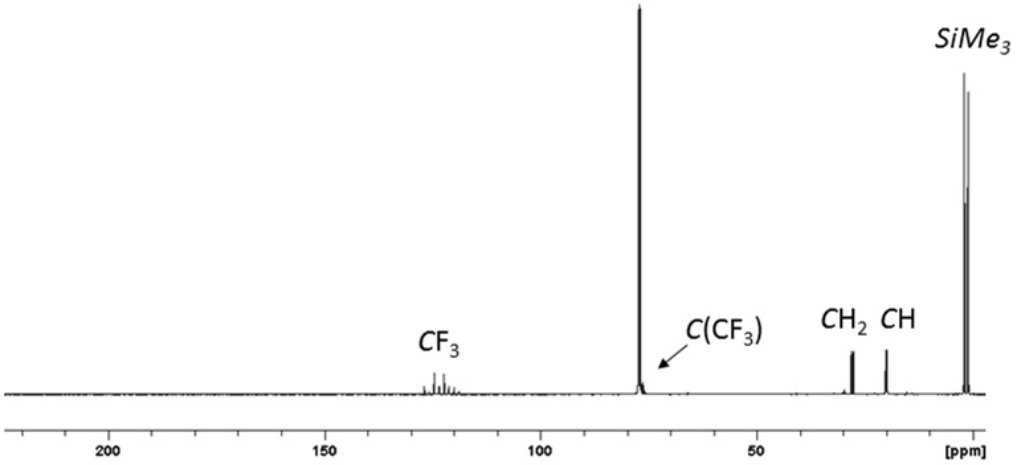
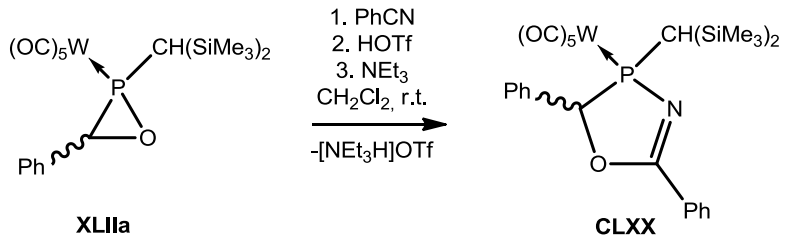



***Figure 8.9:*** $^{13}C\{^{1}H\}$ NMR spectrum of **52**.

The hydrolysis was also proven by the presence of an OH resonance signal at 7.53 ppm in the $^{1}H$ NMR spectrum as well as an absorption band for the OH group in the IR spectrum at 2961 $cm^{-1}$.

## 8.4 Ring expansion reactions using the system triflic acid/triethylamine in the presence of nitriles

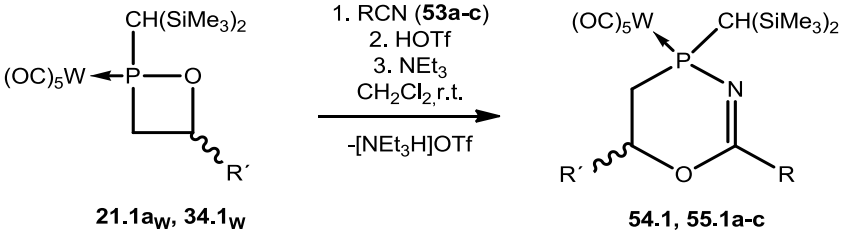
A further possible 1,2-oxaphosphetane ring activation was tested, based on a reaction procedure developed in the research group of Streubel for oxaphosphirane complexes. In the presence of triflic acid (HOTf, trifluoromethanesulfonic acid), containing the weakly coordinating anion $OTf^{-}$, the regioselective insertion of nitriles was observed into the PO bond of the oxaphosphirane complex **XLIIa** (scheme 8.10).[158]




**XLIIa** **CLXX**

***Scheme 8.10:*** Acid induced ring expansion reaction of oxaphosphirane complex **XLIIa**.[158]

A P-O bond-selective ring expansion took also place when a methylene chloride solution of complexes **21.1a$_W$**[1-4] (30:4:19:47) was treated with $CF_3SO_3H$ (HOTf) at ambient temperature in presence of benzonitrile (**53b**), followed by addition of triethylamine. The reaction of **21.1a$_W$** with benzonitrile (**53b**) (in the presence of triflic acid) yielded a mixture of isomers (ratio 93:7) of 1,3,4-oxazaphosphacyclohex-2-ene complex **54.1** (scheme 8.11).




**21.1a$_W$, 34.1$_W$** **54.1, 55.1a-c**

R´=Me , R = Ph (**21.1a$_W$, 54.1**)
R´= H (**34.1$_W$**, **55.1**), R = $CH_3$ (**53a**,**55.1a**), Ph (**53b**, **55.1b**), $CMe_3$ (**53c**, **55.1c**)

***Scheme 8.11:*** Ring expansion reactions of 1,2-oxaphosphetane complexes **21.1a$_W$** and **34.1$_W$** with different nitriles.

In case of **54.1**, the major isomer (**54.1$^1$**) was isolated in pure form by column chromatography; the minor isomer could not be obtained. Complex **54.1$^1$** displays a $^{31}P\{^1H\}$ NMR resonance at $\delta$ = 40.0 ppm ($^1J_{W,P}$ = 258.8 Hz) while the minor product was observed at $\delta$ = 31.0 ppm. Yellow single crystals of **54.1$^1$** were obtained by subsequent recrystallization from a diethyl ether solution and, hence, X-ray diffraction studies were possible to establish the regiochemistry of the ring expansion product (Figure 8.10).

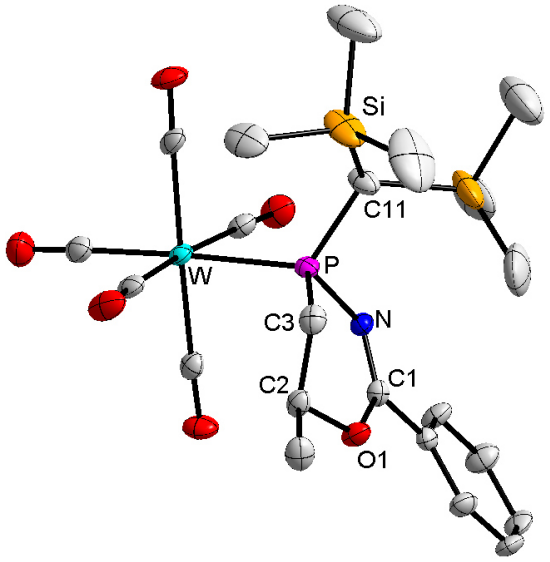



***Figure 8.10:*** DIAMOND plot of the molecular structure of complex **54.1$^1$** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. Selected bond lengths in Å and angles in °:W-P 2.4989(10), P-N 1.703(3), P-C3 1.828(4), P-C11 1.821(4), C3-P-N 99.80(16), C11-P-N 104.83(17), C11-P-C3 105.63(18), N-P-W 107.06(11), C3-P-W 118.70(13), C11-P-W 118.40(15).

Afterwards, an in-depth study including an optimization of the reaction conditions was performed using the *C*-unsubstituted 1,2-oxaphosphetane complex **34.1$_W$** to supress the formation of isomers.

***Table 8.4:*** Selected NMR data (in $CDCl_3$), IR data and yields for complexes **55.1a-c**.

| | $\delta^{31}P$ [ppm] ($^1J_{W,P}$ [Hz]) | $\delta^{13}C\{^1H\}$ (C=N) [ppm] ($^2J_{P,C}$ [Hz]) | IR ($\nu$(C=N)) [$cm^{-1}$] | yield [%] |
|---|---|---|---|---|
| **55.1a** | 34.1 (259.2) | 160.0 (13.7) | 1642 | 99 |
| **55.1b** | 36.1 (259.6) | 156.9 (12.6) | 1626 | 99 |
| **55.1c** | 34.2 (260.9) | 168.8 (14.7) | 1631 | 99/43* |

* after recrystallization

The $^{31}P\{^1H\}$ NMR spectra showed only a small influence of the C-substituent on the NMR characteristics and all data are in good accordance with the ones described for the *C*-Me-substituted derivative **54.1**[1]. In the $^{13}C\{^1H\}$ NMR measurement a resonance signal for the C=N motif was observed in all cases between 156.9 and 168.8 ppm and could be further confirmed by the typical absorptions between 1626 and 1642 $cm^{-1}$ in the IR spectra (table 8.4).

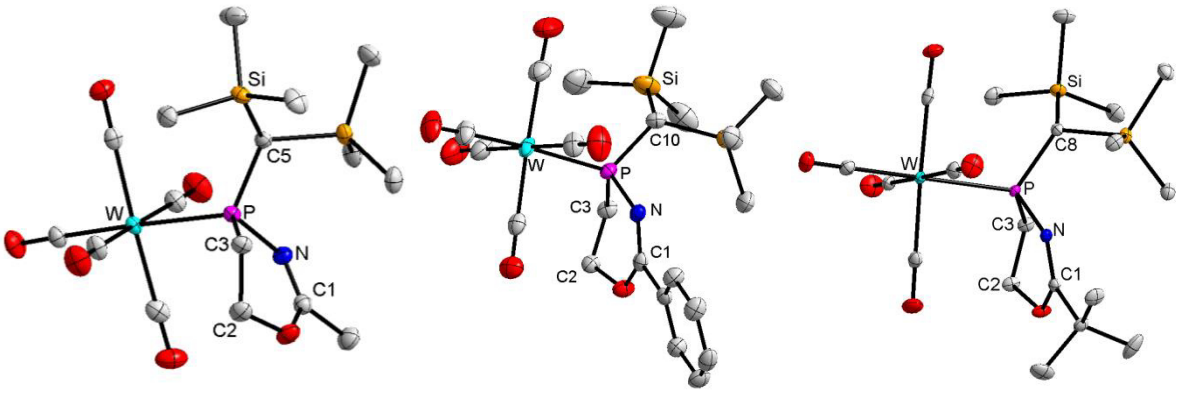



***Figure 8.11:*** DIAMOND plot of the molecular structures of complexes **55.1a**, **55.1b** and **55.1c** (from left to right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. In case of **55.1c** only one of two independent molecules is shown for clarity.

Single crystals suitable for X-ray diffraction studies (figure 8.11) could be obtained from saturated diethyl ether solutions. The C1-N bond shows typical values for a C=N double bond in all three cases and only the exocyclic C-C bond is slightly elongated in case of **55.1c** as result of the sterically more demanding $^t$Bu substituent.

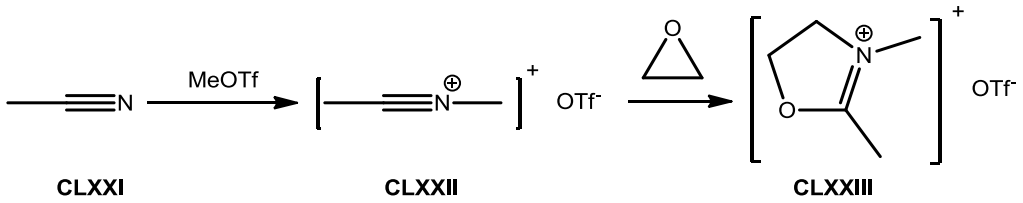
***Table 8.5:*** Selected bond lengths in Å and angles in ° for complexes **55.1a-c**.

| | P-W | P-C3 | P-N | C1-N | C1-$C^{exo}$ | C3-P-N |
|---|---|---|---|---|---|---|
| **55.1a** | 2.5089(12) | 1.835(5) | 1.700(4) | 1.268(6) | 1.497(7) | 98.8(2) |
| **55.1b** | 2.5171(8) | 1.833(3) | 1.696(3) | 1.272(4) | 1.485(4) | 100.12(15) |
| **55.1c** | 2.5084(8)/ 2.5030(8) | 1.830(3)/ 1.826(3) | 1.702(3)/ 1.705(3) | 1.270(4)/ 1.265(4) | 1.526(4)/ 1.532(4) | 99.46(14)/ 99.04(14) |

Two reaction pathways are possible for these ring expansion reactions. The first one is initiated by protonation of the 1,2-oxaphosphetane complex, followed by a nucleophilic attack of the nitrile at the now more electrophilic P-centre. This leads to a breaking of the P-O bond and the subsequent ring expansion. This first reaction pathway would be in accordance to the previously calculated mechanism for oxaphosphirane complexes.[158]

Another possibility is the initial protonation of the nitrile and a subsequent nucleophilic attack of the ring-O-atom at the electrophilic carbon centre. A similar reaction is known from carbon chemistry (scheme 8.12): the reaction of methyl triflate with acetonitrile **CLXXI** leads to nitrilium salt **CLXXII** which can be isolated; subsequently it reacts with ethylene oxide to the *N*-alkylated oxazolium salt **CLXXIII**.[159]

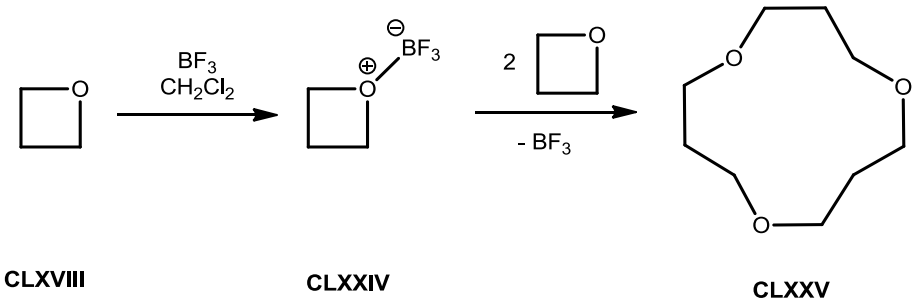
Unfortunately no clear-cut assignment to one or the other reaction pathway was possible with the data at hand.




***Scheme 8.12.*** Ring expansion reaction of ethylene oxide using nitrilium salt **CLXXII**.[159]

## 8.5 Ring opening reactions with catechol(chloro)borane

Another example of activation of the heterocycles is the ring opening polymerization (ROP) or oligomerization in the presence of haloboranes. For example, the reaction of oxetane with $BF_3$ in methylene chloride leads to 1,5,9-trioxacyclododecane as the main product (scheme 8.13). The initiation of this reaction is the coordination of $BF_3$ to an electron pair of the oxygen atom, thus forming a more electrophilic carbon centre in $\alpha$-position where a second equivalent of the epoxide can attack. Under other reaction conditions, and especially in the presence of water, the formation of linear polymers is favoured.[160]

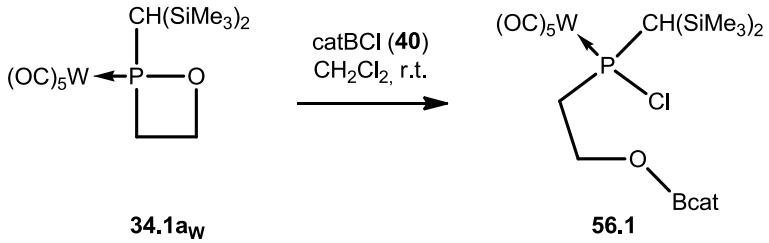



**CLXVIII** **CLXXIV** **CLXXV**

***Scheme 8.13:*** Cyclotrimerization of oxetane in the presence of $BF_3$ as catalyst.[160]

No reactions of boranes with oxaphosphirane complexes were described so far, but first calculations regarding the ring opening reactions of oxaphosphiranes by borane complexation and migration of borane substituents were presented just recently by Espinosa and Streubel.[161]

Catechol(chloro)borane **40** was used, instead of $BF_3$, to investigate first reactions between 1,2-oxaphosphetane complexes and haloboranes. The presence of two oxygen substituents and only one chloro functionality was chosen to reduce the amount of possible side reactions, e.g. the multiple substitution reaction that could occur at the boron halogen bonds in $BX_3$ (X = Cl, F).




**34.1a$_W$** **56.1**

***Scheme 8.14:*** Ring opening reaction of 1,2-oxaphosphetane complex **34.1a$_W$** with catechol(chloro)borane **40**.

A full and selective conversion of **34.1a$_W$** to **56.1** was observed in a slow reaction (7 days) (scheme 8.14). All volatiles were removed in *vacuo* and the product subsequently analysed (figure 8.12).

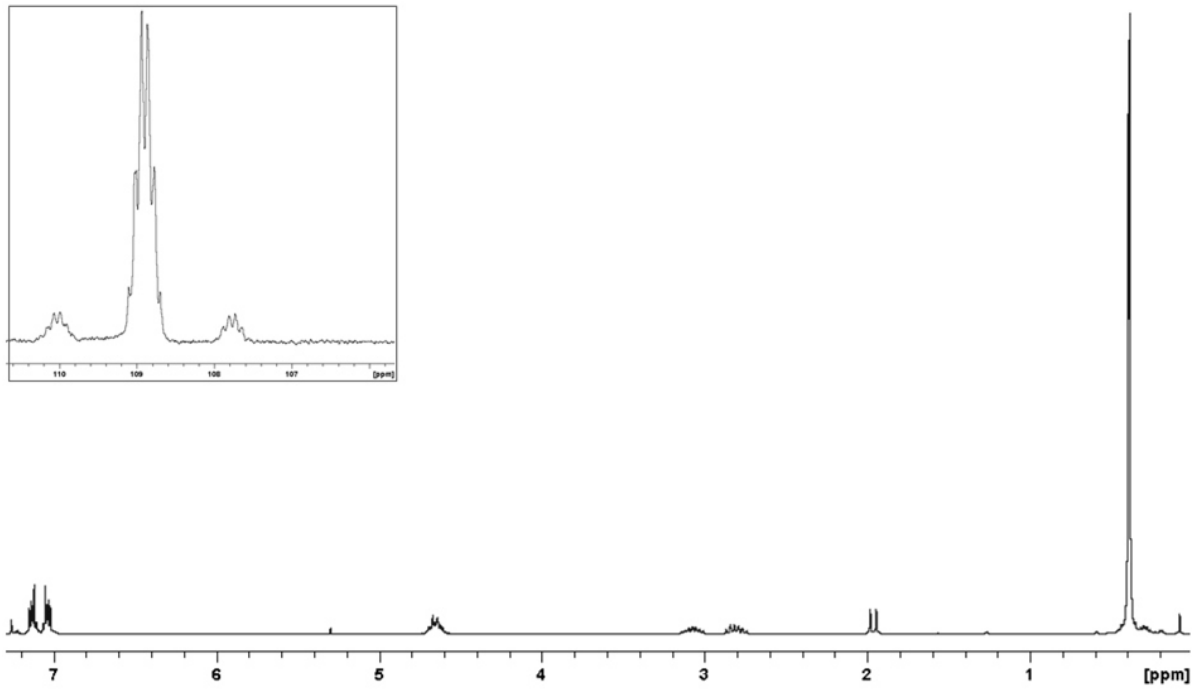



***Figure 8.12:*** $^{31}$P NMR spectrum (in the box) and $^{1}$H NMR spectrum of **56.1**.

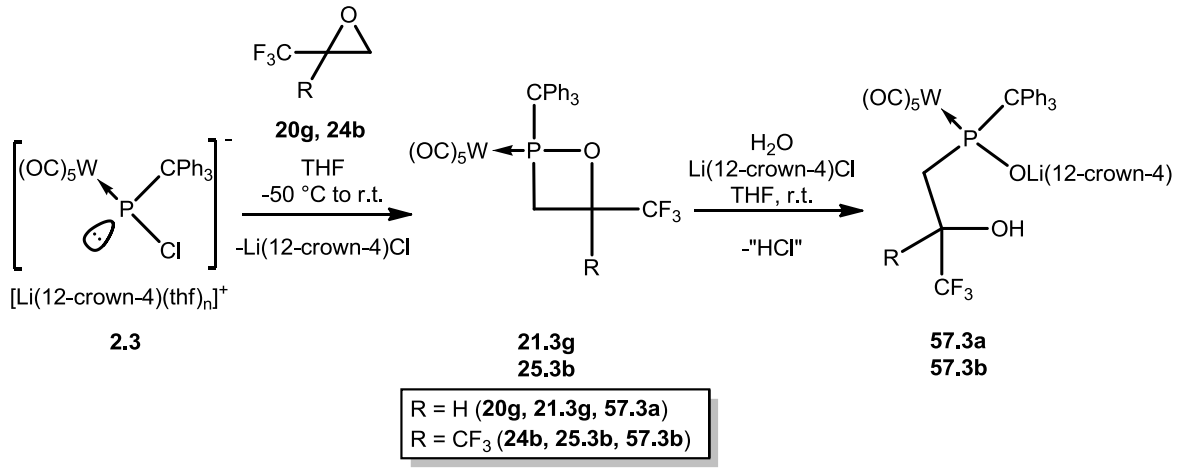
Complex **56.1** showed $^{31}$P NMR spectroscopic characteristics similar to the data of complex **47.1a** ($\delta^{31}$P = 115.5 ppm, $^{1}J_{W,P}$ = 272.9 Hz), obtained by reaction of **34.1a$_W$** with $HCl_{(g)}$. Only a slight shift to higher field and a 1.4 Hz larger coupling constant (**56.1**: $\delta^{31}$P = 108.9 ppm, $^{1}J_{W,P}$ = 274.3 Hz) were observed.

Additional support for the successful reactions was obtained from the $^{11}$B{$^{1}$H} NMR spectrum, here a resonance signal at 23.3 ppm for **56.1** was observed, which is in the expected range, compared to $R_2P(O)$-$OB(OR)_2$ compounds.[162]

## 8.6 Lewis acid induced ring opening reactions

As already pointed out in the introduction of chapter 8, Lewis acid-induced activation is an interesting option for small-ring heterocycles. Therefore, the effect of the abundant Li(12-crown-4)-cation, often present in solution was tested. Whereas for most of the syntheses described beforehand, no significant interaction between this cation and the ring P-ligands could be detected, an interesting reaction was observed in case of **21.3g** and **25.3b**. Here, P-O bond-selective ring opening was achieved, using a one-pot reaction protocol. As comparison of **25.3b** to **21.3g** revealed, steric crowding at the phosphorus centre, induced by the bulky $CPh_3$ group, and the $CF_3$ groups, combined with the electron-withdrawing influence of the latter played a crucial role. In case of the corresponding complexes bearing the *P*-$CH(SiMe_3)_2$ substituent as well as the *P*-$C_5Me_5$ substituent no reaction was observed with water, even at elevated temperature. In contrast, addition of water to the reaction mixture of **25.3b** yielded the novel 1,3-functional phosphinito complex **57.3b** (scheme 8.15); the formally generated HCl might be consumed by the solvent THF;[153] this wasn't further investigated. The exact same protocol only led to traces of product in case of **21.3g** and a conversion of only 55 % was observed even after 5 days at ambient temperature. Nevertheless, full conversion was achieved after 16 h by slight heating (40 °C), providing more evidence for the influence of the $CF_3$ substituents.

In order to proof the importance of solvated lithium cations, the following test was undertaken: addition of water to a THF solution of complex **25.3b** in the absence of the lithium salt did not lead to any observable reaction, even at elevated temperatures (up to 65 °C). The activation therefore requires the presence of a Lewis acid and not only the steric crowding. It should be noted here that ring opening of penta-coordinated 1,2-oxaphosphetanes and formation of betaine-type structures was observed in the presence of lithium salts as it was stated by Schlosser in 1967.[163] Although the involvement of compounds with betain structure in the stereoselectivity of the Wittig reaction especially in salt free reactions is still discussed today.[164]




***Scheme 8.15:*** Syntheses and Lewis acid-induced hydrolytic ring opening reactions of 1,2-oxaphosphetane complexes **21.3g** and **25.3b**.

Starting from an isomeric mixture of complexes **21.3g[1]** and **21.3g[2]** (ratio 42:58), a mixture of two isomers was observed for **57.3a**. The resonance signals were observed in the $^{31}P\{^1H\}$ NMR (in $CDCl_3$) at 116.7 ppm ($^1J_{W,P}$ = 283.7 Hz) and 109.2 ppm ($^1J_{W,P}$ = 284.9 Hz) and in a ratio of 47:53.

For complex **57.3b** a resonance signal was observed in the $^{31}P\{^1H\}$ NMR spectrum at $\delta$ = 125.6 ppm ($^1J_{W,P}$ = 300.9 Hz). The signal shows a slight deshielding compared to the mono-$CF_3$-substituted derivatives **21.3g[1,2]**. In addition, hydrogen bridging in solution was indicated by the strongly deshielded signal for the *C*-OH proton at 9.41 ppm; this is similar to the situation found for enolic OH protons in 1,3-diketones.[165]

The molecular structures of **21.3g** and **57.3b** in the single crystal (Figure 8.13, suitable crystals were obtained from diethyl ether solutions) show PO-Li interactions and the 12-crown-4 units coordinate the Li-cations from the far side. Orientation of the C-OH group towards the PO moiety indicates the proposed bridging O-H-O unit.

A comparable complex bearing the P-O-Li motif and an OMe group instead of the alcohol substituent ([Li(12-crown-4)][$(OC)_5W\{P(O)(CPh_3)(OMe)\}$]) was presented just recently.[10] A similar deshielded signal at $\delta$ = 140.1 ppm ($^1J_{W,P}$ = 314.0 Hz) was described. The P-O-Li angle of **57.3b** was found to be, with an average of 160.5°, smaller than in that complex (P-O-Li angle: 170.2(4)°). Also the data for *P*-$CH(SiMe_3)_2$-substituted phosphinito complexes [Li(12-crown-4)][$(OC)_5W\{P(CH(SiMe_3)_2)F(O)\}$][166] (P-O-Li angle = 165.3(9)°) and [Li(12-crown-4)][$(OC)_5W\{PH(CH(SiMe_3)_2)(O)\}$][132] (P-O-Li angle = 166.7(5)°) showed a more linear geometry at the oxygen atom. The stronger deviation from the linear geometry in **57.3b** is presumably due to the hydrogen bridging in the OH-O unit.

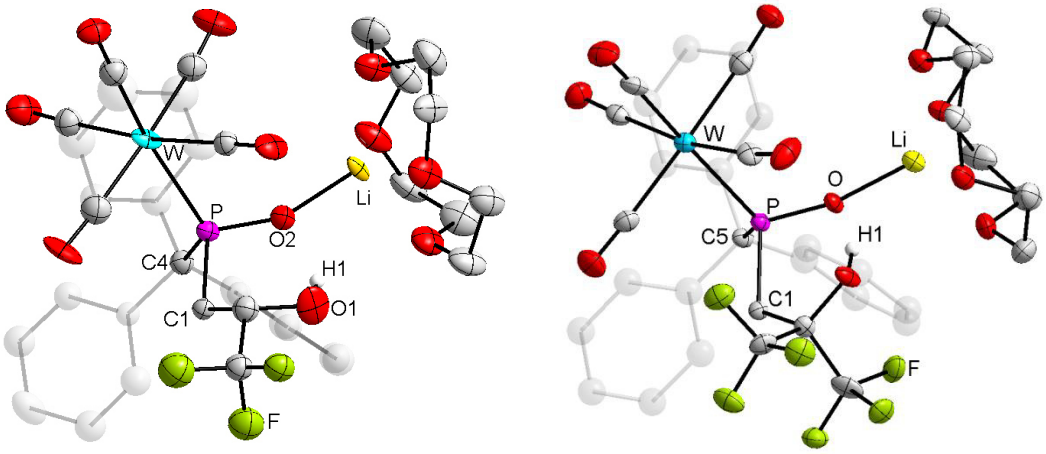



***Figure 8.13:*** DIAMOND plot of the molecular structures of complexes **57.3a** (left) and **57.3b** (right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. Only one of two independent molecules is shown for both complexes and the phenyl rings of the $CPh_3$ unit are represented using a transparent mode for clarity.

***Table 8.6:*** Selected bond lengths in Å and angles in ° for complexes **57.3a** and **57.3b**. In both cases two sets of data for two independent molecules in the unit cell are given (molecule 1/molecule 2)

| | P-W | P-C1 | P-$CPh_3$ | P-O | C1-P-O | P-O-Li |
|---|---|---|---|---|---|---|
| **57.3a** | 2.553(4)/ 2.569(4) | 1.856(16)/ 1.88(2) | 1.965(18)/ 1.943(17) | 1.547(13)/ 1.556(12) | 102.3(7)/ 103.6(8) | 156.7(12)/ 164.6(13) |
| **57.3b** | 2.5759(16)/ 2.5633(15) | 1.892(5)/ 1.903(6) | 1.952(6)/ 1.948(6) | 1.542(4)/ 1.542(4) | 103.3(2)/ 103.0(2) | 160.4(4)/ 160.6(4) |

To test the potential of complex **57.3b** as synthetic building block for novel phosphorus heterocyclic ligands a preliminary study were investigated exemplarily, *i.e.* the ring closing reactions using dichloro-tetrel derivatives $Me_2ECl_2$ (E = Si (**58a**), Ge (**58b**)). Addition of $Me_2SiCl_2$ to a THF solution of **57.3b** showed a clean reaction and a conversion of 89 % after 4.5 h with a good selectivity. Further tests revealed that addition of DBU as a nitrogen base to the reaction mixture, to achieve HCl elimination, increased the reaction rate significantly (full conversion was observed in less than three hours).

If the reaction of complex **57.3b** with $Me_2GeCl_2$ was performed under base free conditions a set of broad resonance signals was observed in the $^{31}P\{^1H\}$ NMR spectrum after 21 h ($\delta$ = 124.7 ppm, 34 %, $h_{1/2}$ = 65 Hz and $\delta$ = 123.6 ppm, 46 %, $h_{1/2}$ = 55 Hz), in addition to 20 % of the final product (figure 8.14). The intermediate was selectively converted to complex **60.3b** after addition of triethylamine to enhance the reaction progression.

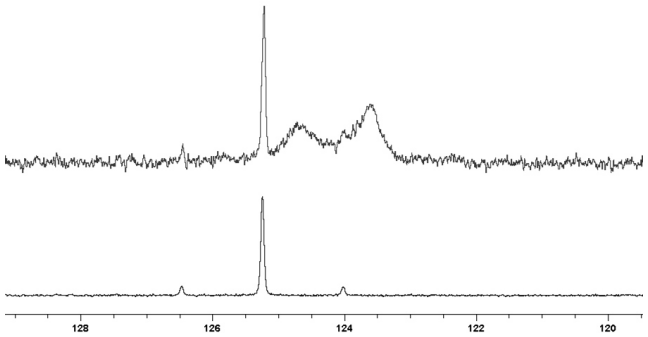
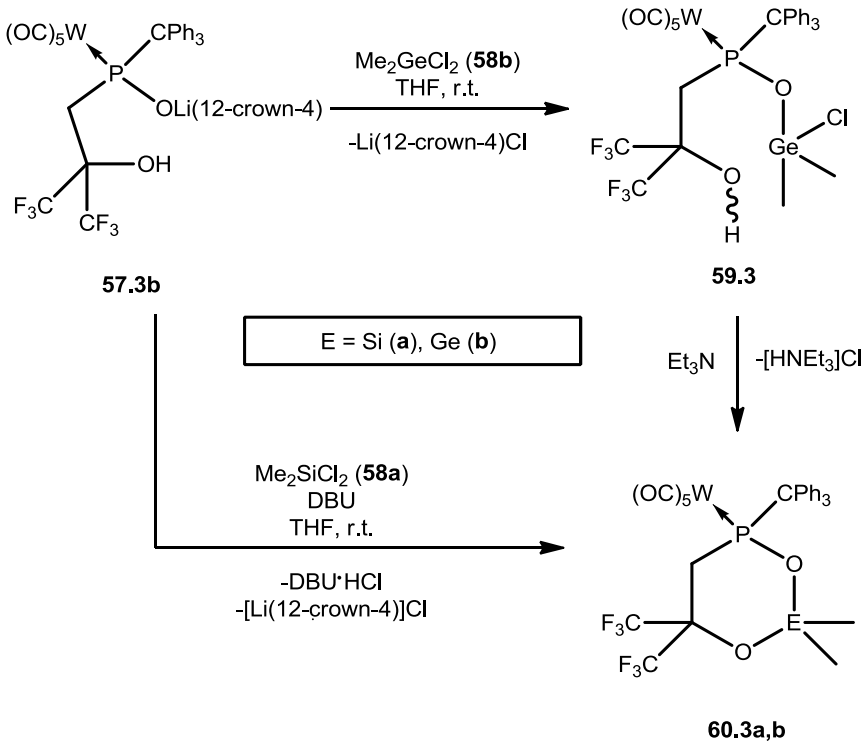



***Figure 8.14:*** $^{31}P\{^{1}H\}$ NMR spectra before (top) and after addition of $Et_3N$ (bottom) for the reaction of **57.3b** with $Me_2GeCl_2$ (**58b**).

Weak intra- and/or intermolecular interactions of the hydroxyl groups of intermediates **59.3** (scheme 8.16) are likely to be the reason for the broadening observed for the signals.




***Scheme 8.16*:** Ring closing reactions of complex **57.3b** using $Me_2ECl_2$ (E = Si, Ge).

**60.3a** could be isolated by filtration and recrystallization (yield 54%). The presence of the $Me_2Si$ unit in the ring was clearly established by the observation of a signal with a $^{2}J_{P,Si}$-coupling of 9.6 Hz in the $^{29}Si\{^{1}H\}$ NMR spectrum. Surprisingly, only a very small influence of the $Me_2Si$ linker on the $^{31}P\{^{1}H\}$ NMR parameters were observed. The ring closing results only in a slight low-field shift and a 4.8 Hz bigger $^{1}J_{W,P}$ coupling constant ($\delta$ = 123.8 ppm, $^{1}J_{W,P}$ = 295.0 Hz, in THF for **57.3b**, and 125.2 ppm, $^{1}J_{W,P}$ = 299.8 Hz in THF for **60.3a**).

Complex **60.3b** showed a similar chemical shift for the resonance signal in the $^{31}P\{^{1}H\}$ NMR spectrum ($\delta$ = 126.2 ppm, $^{1}J_{W,P}$ = 299.0 Hz) and the influence of the $Me_2Ge$ linker was again rather negligible.

Similar $^{1}H$ NMR and $^{13}C\{^{1}H\}$ NMR spectroscopic parameters to **60.3a** were observed for **60.3b** and the only notable difference was observed in case of the methyl groups bound to the group 14 elements. Strong deshielding was observed for the resonance signals of the E-$CH_3$ groups in the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra when going from the Si derivative **60.3a** to the Ge derivative **60.3b**.

Single-crystals suitable for X-ray diffraction studies could be obtained from saturated diethyl ether solutions at 4 °C for the Si- and Ge-containing complexes (Figure 8.15).

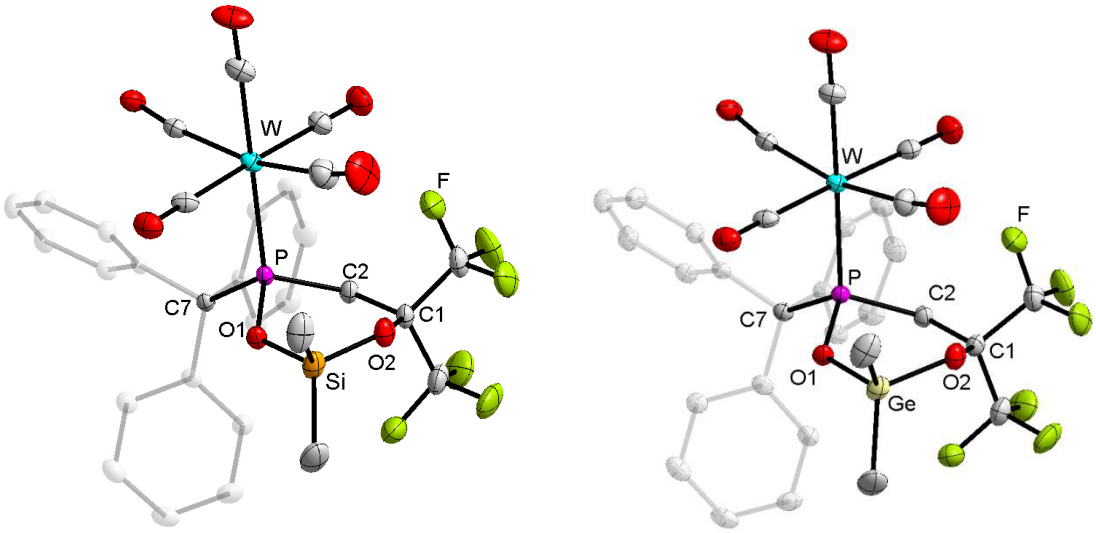



***Figure 8.15:*** DIAMOND plot of the molecular structures of complex **60.3a** (left) and complex **60.3b** (right) in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms are omitted for clarity. The phenyl rings of the $CPh_3$ units are represented using a transparent mode for clarity.

***Table 8.7:*** Selected bond lengths in Å and angles in ° for complexes **60.3a** and **60.3b**.

| | P-W | P-O1 | P-C2 | P-C7 | C2-P-O1 |
|---|---|---|---|---|---|
| **60.3a** | 2.5376(7) | 1.623(2) | 1.869(3) | 1.957(3) | 101.81(11) |
| **60.3b** | 2.5439(7) | 1.613(2) | 1.875(3) | 1.959(3) | 103.45(12) |

In the solid state complexes **60.3a** and **60.3b** show a boat conformation of the distorted six-membered rings. All differences in the bond lengths and angles show the expected changes due to the atom size difference between the Si and Ge atoms (table 7.8, figure 8.16), *e.g.* a bigger O-E-O angle and longer O-E bonds for E = Ge.

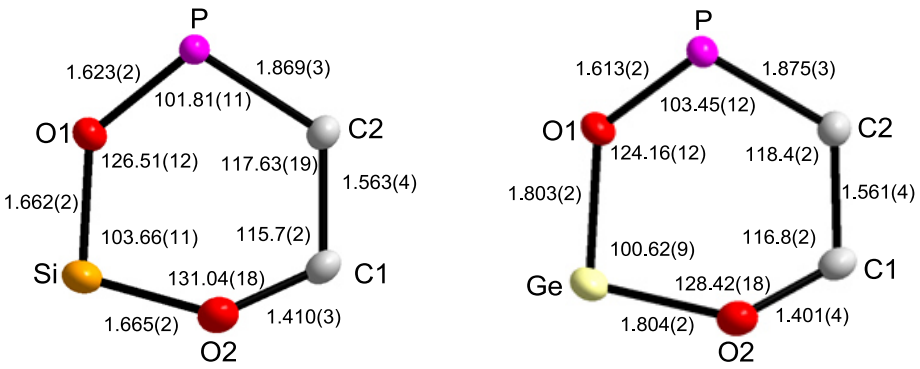
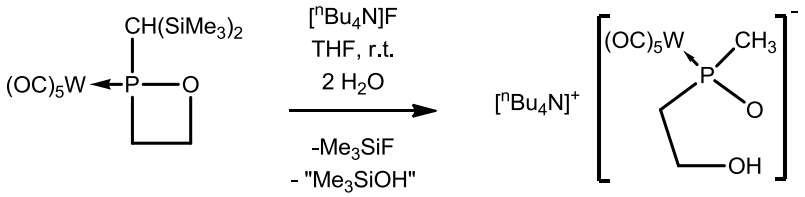



**Figure 8.16:** Bond lengths in Å (outside the rings) and angles in ° (inside the rings) of the six membered heterocyclic rings of complexes **60.3a** (left) and **60.3b** (right). The atoms are displaced as ellipsoids, set at 50% probability level and all substituents are omitted for clarity.

## 8.7 Fluoride mediated hydrolytic ring opening reaction

The reactions of epoxides or oxetanes with nucleophiles are of great importance in carbon chemistry, leading to many useful products in ring opening reactions. So for example the hydrolytic ring opening to diols utilizing metal hydroxides[167] or opening of epoxides to halohydrines, *e.g* with tetrabutylammonium fluoride in THF.[168] In contrast, only very few examples of reactions using nucleophiles are known for the phosphorus analogues, the oxaphosphirane complexes or the oxaphosphetanes. In case of the oxaphosphirane complexes, mainly decomposition of the ring systems by formal simultaneous splitting of the P-O and P-C bond were observed, *e.g.* leading to secondary phosphane complexes in the reaction with Grignard reagents, after protonation of the intermediately formed phosphanido complexes.[169] As there are only very few isolable oxaphosphetanes their reactivities have been only poorly investigated in this regard. Some ring openings by nucleophilic reagents, e.g. with NaOH,[170] were described. Also deprotonation of the ring and subsequent reaction with electrophiles without destruction of the cyclic structure were shown, proving the low reactivity of 1,2-oxaphosphetanes.[95]

First insight into the reaction of nucleophiles with 1,2-oxaphosphetane complexes was obtained when [$^n$Bu$_4$N]F was added to a THF solution of 1,2-oxaphosphetane complex **34.1$_W$**. This complex was chosen as a case in point to avoid problems with isomerism, as often caused by C-substitution.




**34.1$_W$** **61**

***Scheme 8.17:*** Fluoride mediated hydrolysis of 1,2-oxaphosphetane complex **34.1$_W$**.

Surprisingly, not the nucleophilic ring opening of the 1,2-oxaphosphetane complex was observed. Instead a hydrolytic ring opening and an additional desilylation of the *P*-CH(SiMe$_3$)$_2$ substituent, presumably caused by contamination of the used [$^n$Bu$_4$N]F solution with water, was observed (scheme 8.17).

Selective conversion of **34.1$_W$** to **61** was proven by only one observable signal in the $^{31}$P{$^1$H} NMR spectrum ($\delta$ = 67.2 ppm, $^1J_{W,P}$ = 233.9 Hz). These data are comparable to those observed for phosphinito complex **36.1** ($\delta$ = 46.0 ($^1J_{W,P}$ = 244.1 Hz)), indicating the anionic PO motif. The stronger deshielding, by 23.2 ppm, is in accordance with the expectation for

changing the P-H to a P-C motif. A desilylation was proposed based on the absence of all resonance signals in the typical range for $Me_3Si$ groups in the $^1H$ NMR measurement (below 1 ppm) after removal of all volatiles from the reaction mixture. A signal for the formed $CH_3$ group was observed at 1.68 ppm ($^2J_{P,H}$ = 6.5 Hz), correlating to a signal in the $^{13}C\{^1H\}$ NMR at 29.9 ppm ($^1J_{P,C}$ = 17.8 Hz). In addition to two resonance signals for the $CH_2$ groups, a broad signal at 6.43 ppm as well as an absorption band in the IR spectrum at 3203 $cm^{-1}$ could easily be assigned to an OH group. The IR measurement also revealed the presence of the intact $W(CO)_5$ fragment by presence of the three expected absorption bands for the CO groups. A mass spectrometric measurement (ESI+/-) revealed the presence of the [$^nBu_4N$]-cation and a mass for the anion correlating to the formula $C_8H_8O_7PW$.

Formation of **61** was proposed on basis of these observations and the structural motiv could finally be proven by a single crystal X-rax diffraction study (figure 8.17). Single crystals of **61**, suitable for the X-ray diffraction study, were obtained after evaporation of all volatiles in *vacuo* and slow crystallization of the initially formed oil.

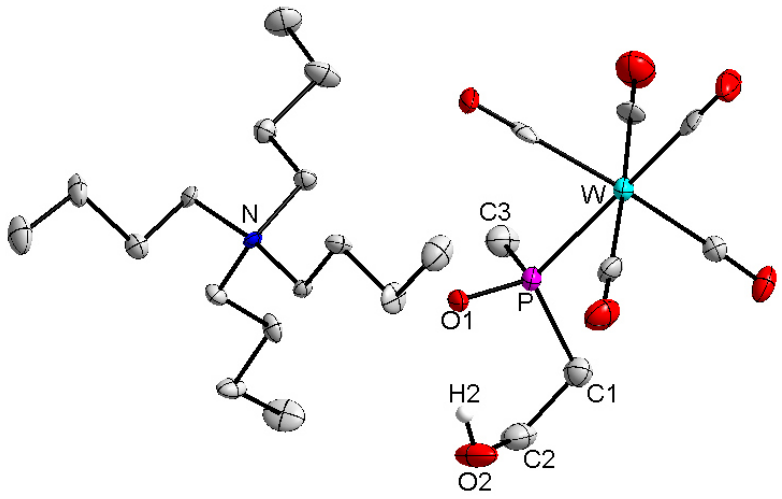



***Figure 8.17:*** DIAMOND plot of the molecular structure of **61** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogen atoms, except H2 are omitted for clarity. Selected bond lengths in Å and angles in °: P-W 2.529(3), P-C3 1.843(13), P-C1 1.858(13), P-O1 1.526(8), O1-P-C1 106.2(5), O1-P-C3 108.4(6), C1-P-C3 100.6(6).

All structural data of **61** are in accordance to the ones described for phosphinito complexes **36.1** and **57.3b** and no significant differences in the bond lengths and angles were observed.

Two side products ($Me_3SiF$ and $(Me_3Si)_2O$) were observed and unambigiously characterized by their characteristic $^1H$, $^{13}C$, $^{29}Si$ and $^{19}F$-NMR signals,[171,172] respectively, when the reaction was carried out in deuterated THF. The $Me_3SiF$ had to be removed from the reaction mixture (via evaporation) and measured in $CDCl_3$ for identification as a presumed interaction between **61** and the $Me_3SiF$ led to a broadening of the $^{19}F$ NMR signal, a vanishing of the $^1H$ and $^{13}C$ couplings to fluoride as well as vanishing of the resonance

signal in the $^{29}Si$ NMR spectrum. No such problem was observed in $CDCl_3$ after recondensing and all signals were in accordance to literature known values.[171]

A variable temperature NMR experiment was performed and revealed that, already at -70 °C, no signal in the range of 1,2-oxaphosphetane complexes (between 150 and 220 ppm) was observed. Instead several signals close to the resonance signal of the final product were detected (figure 8.18).

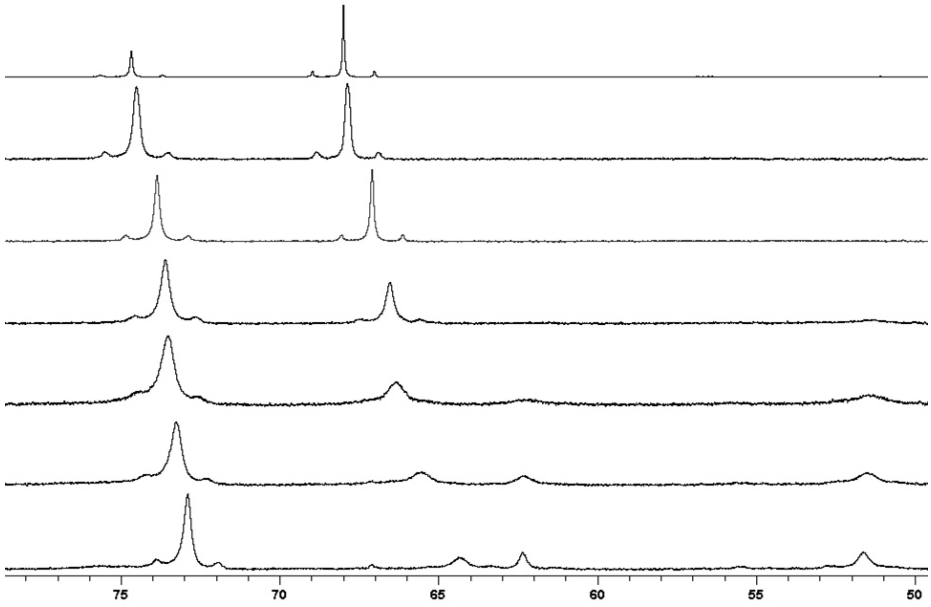
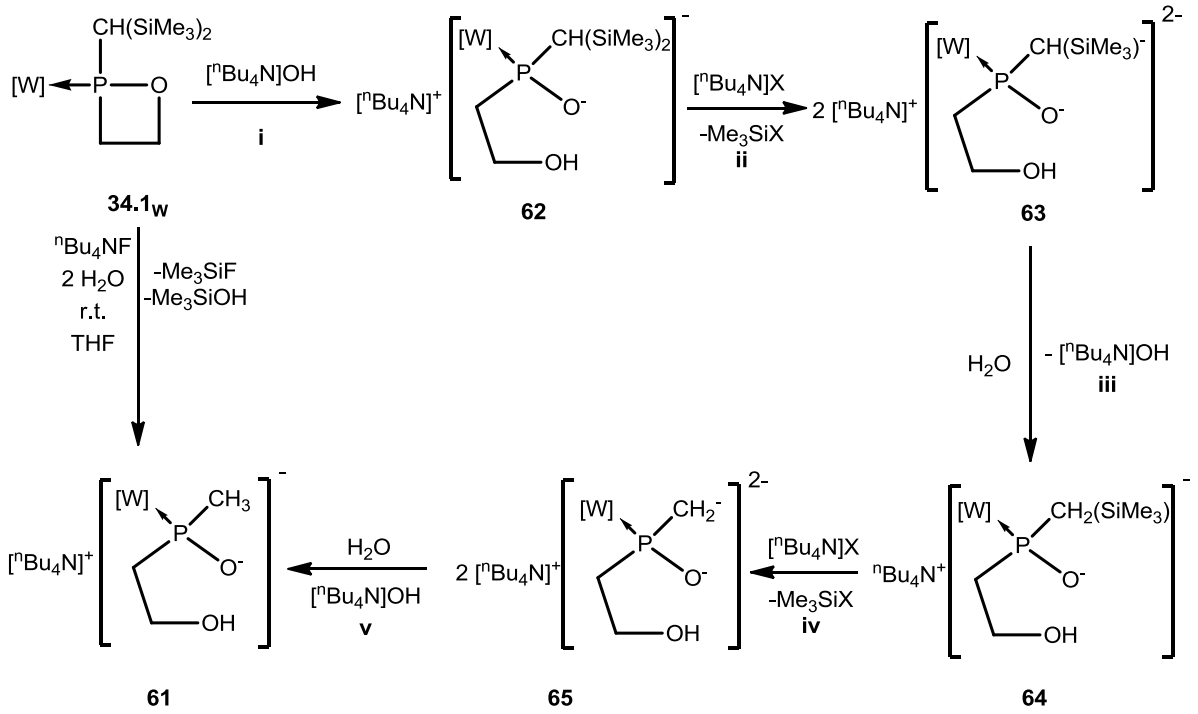



***Figure 8.18:*** Variable temperature NMR measurement of the reaction between **34.1$_W$** and [$^n$Bu$_4$N]F. Shown are the $^{31}P\{^1H\}$ NMR spectra at -70 °C, -60 °C, -50 °C, -40 °C, -20 °C, 0 °C and at room temperature (from bottom to top).

Based on this result, a stepwise mechanism was proposed for the product formation (scheme 8.18): a hydrolytic ring opening of the 1,2-oxaphosphetane complex **34.1$_W$** by [$^n$Bu$_4$N]OH takes place as the initial step (**i**). The complex then undergoes a desilylation reaction at the $CH(SiMe_3)_2$ group, forming the dianionic complex **63** (**ii**). The carbanion subsequently deprotonates water, forming the *P*-sila-neopentyl-substituted phosphinito complex **64** as well as one equivalent of [$^n$Bu$_4$N]OH (**ii**). A second desilylation step forms dianion **65** (**iii**). The carbanion can deprotonate one more equivalent of water, liberating a second equivalent of [$^n$Bu$_4$N]OH (**v**), forming the phosphinito complex **61**, as final product. Only catalytic amounts of [$^n$Bu$_4$N]OH are necessary to initiate the reaction, as it is regained in the last step of the reaction sequence.

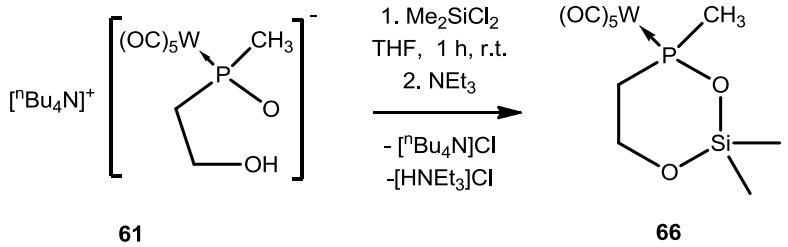
An initial desilylation reaction by the [$^n$Bu$_4$N]F was excluded as reaction mechanism. The subsequent stepwise degradation of the $CH(SiMe_3)_2$ group to the $CH_3$ group and a hydrolytic ring opening in the last step would yield resonance signals in the $^{31}P$ NMR spectrum in a region very close to the one of the starting material.

Two aspects are of greater importance. In one of the desilylation steps (**ii** or **iv**) the fluoride salt has to react, as $Me_3SiF$ was found as reaction product. Unfortunately, no differentiation can be made between the steps based on the products. Also, the reaction only requires the presence of 1.5 equivalents of water, as two molecules $Me_3SiOH$ condensate to $(Me_3Si)_2O$, liberating half an equivalent of water.




***Scheme 8.18:*** Proposed mechanism for the fluoride mediated hydrolysis of 1,2-oxaphosphetane complex **34.1$_W$** ([W] = $W(CO)_5$, X = F, OH).

As complex **61** showed structural similarities to phosphinito complex **57.3b** described in chapter 8.6, a ring closing reaction could be envisaged. Therefore, the reaction with $Me_2SiCl_2$ was performed using the previously developed protocol (scheme 8.19) and proceeded with quantitative conversion to complex **66**.




**61** **66**

***Scheme 8.19:*** Ring formation reaction of phosphinito complex **61** with dichlorodimethylsilane.

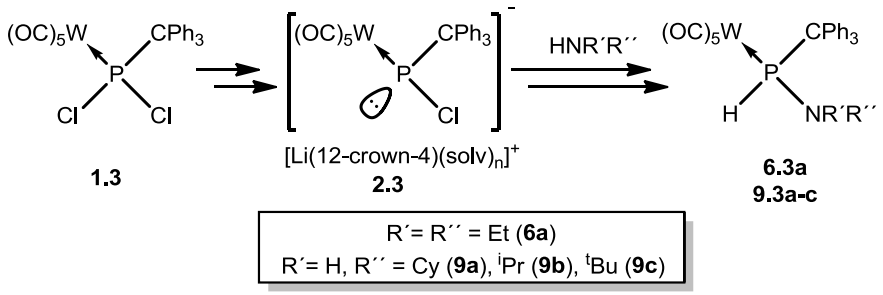
The formation of complex **66** was very selective which is somewhat surprising as no steric protection could favour the ring formation and disfavour chain growth; a possible preorientation, similar to the one described in the synthesis of the Ge-containing ring **60.3b**, cannot be ruled out and might thus be operative.

Complex **66** showed similar analytic data to complex **60.3a** (cf. chapter 8.6), *e.g.* the NMR data (**66**: $\delta^{31}P\{^1H\}$ = 105.2 ppm, $^1J_{W,P}$ = 279.6 Hz; $CDCl_3$, **60.3a**: $\delta^{31}P\{^1H\}$ = 125.6 ppm, $^1J_{W,P}$ = 300.9 Hz, $CDCl_3$).

# 9 Summary

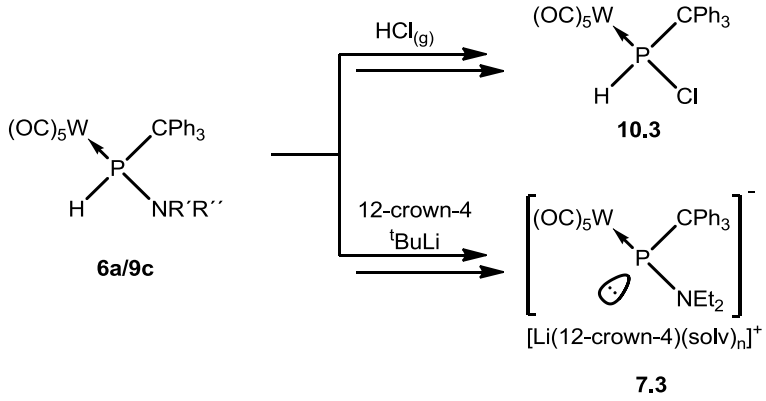
The research in this thesis focused on the formal insertion reaction of Li/Cl phosphinidenoid complexes into polar E-E´ bonds of alcohols, amines and strained heterocycles, in particular epoxides. The obtained new and novel complexes were characterized by multinuclear NMR and infrared spectroscopy, mass spectrometry and elemental analysis, as well as single crystal X-ray diffraction studies in most cases. Furthermore, focused investigations towards the potential of some products as novel building blocks in P-ligand complex chemistry were performed.

In the first part of the thesis, research on the reactions of Li/Cl phosphinidenoid complexes with primary and secondary amines was performed. First examples of highly efficient insertion reactions of the $P_1$-fragment into N-H bonds yielded 1,1'-bifunctional amino-phosphane complexes in very good isolated yields (**6a:** 81%, **9a**: 77 %, **9b**: 71 %, **9c**: 84%) (scheme 9.1).



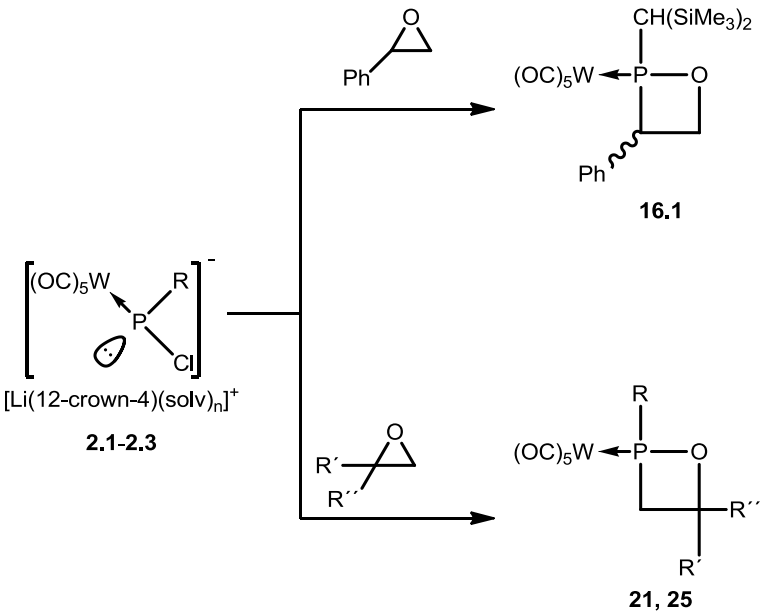

***Scheme 9.1:*** Formal insertion reaction of Li/Cl phosphinidenoid complexes into N-H bonds.

The substitution reaction of the amino group by Cl using $HCl_{(g)}$ in dichloromethane yielded the corresponding chlorophosphane complex **10.3**. Furthermore, a P-H deprotonation reaction using $^{t}$BuLi in presence of 12-crown-4 proved that synthesis of Li/$NEt_2$ phosphinidenoid complex **7.3** is also possible; the latter represents the first stable derivative.




***Scheme 9.2:*** First reactions of aminophosphane complexes by amino/chloro exchange and deprotonation.

In the second part of this thesis, synthetic routes to 1,2-oxaphosphetane complexes and reactions thereof were investigated. The first route used the formal insertion reaction of Li/Cl phosphinidenoid complexes into the C-O bond of different epoxides (scheme 9.3).




| R´/R´´ / R | H/$CH_3$ | H/Et | H/$^i$Pr | H/$CH_2Cl$ | H/$C_2H_3O$ | H/$CF_3$ | $CH_3/CH_3$ | $CF_3/CF_3$ |
|---|---|---|---|---|---|---|---|---|
| Bis | **21.1a** | **21.1b** | **21.1c** | **21.1e** | **21.1f** | **21.1g** | **25.1a** | **25.1b** |
| Cp* | **21.2a** | | | **21.2e** | | **21.2g** | | **25.2b** |
| Trt | **21.3a** | | | | | **21.3g** | | **25.3b** |

***Scheme 9.3:*** Syntheses of 1,2-oxaphosphetane complexes using the formal insertion reaction of Li/Cl phosphinidenoid complexes into the CO bond of epoxides.

While the reaction with styrene oxide led selectively to 3-substituted 1,2-oxaphosphetane complex **16.1** (figure 9.1), *C*-alkyl-substituted epoxides led exclusively to 4-substituted 1,2-oxaphosphetane complexes in selective reactions. In the latter cases the nucleophilic attack at the least hindered side of the epoxide was identified as the initial reaction step.

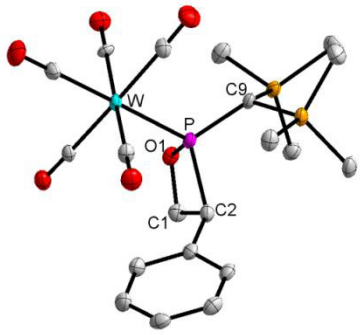



***Figure 9.1:*** Molecular structure of the first isolated 1,2-oxaphosphetane complex in the solid state (all hydrogen atoms are omitted for clarity).

Most complexes were obtained in good yields (up to 61 %) either via extraction/seperation from the formed salt and subsequent precipitation from *n*-pentane or diethyl ether at low temperature or by low temperature column chromatography. In case of $CH(SiMe_3)_2$ as the phosphorus substituent, a particular problem was observed: the formation of atropisomers arising from the relative orientation of the $CH(SiMe_3)_2$ proton with respect to the P-metal bond. This results in two isomers (s-*cis* and s-*trans*) due to a hindered rotation around this (exocyclic) P-C bond, which was studied in detail.

Apart from the regiochemistry aspect, stereoelectronic effects were investigated, using complex **2.1** as a case in point with a special focus on alkyl-derived C-substituted epoxides. While linear aliphatic derivatives furnished the corresponding products selectively, the *C*-$^{i}$Pr-substituted epoxide led to a mixture of 1,2-oxaphosphetane complexes **21.1c** and diphosphene complexes (**22**, **23**). In addition almost no reaction occurred with the *C*-$^{t}$Bu epoxide. Contrary, reactions proceeded with epoxides bearing sterically demanding and electron-withdrawing groups, *i.e.* with one or two $CF_3$ groups, thus illustrating substrate activation towards a nucleophilic attack.

Additional studies on the functional group tolerance showed that C-substitution of epoxides with a $CH_2Cl$, $CF_3$ and even an epoxy substituent did neither influence the selectivity of the ring formation in a negative way nor was the ratio of the formed isomers affected. Formation of two isomers was found for all C-monosubstituted derivatives, based on the relative orientation of the *C*-substituent of the ring either towards or away from the metal fragment. Indications of these isomers were often found as a split site in the molecular structure as they co-crystallised. In addition, a high flexibility was found for the ring itself, adapting folding angles in the range of approximately 2 to 35°.

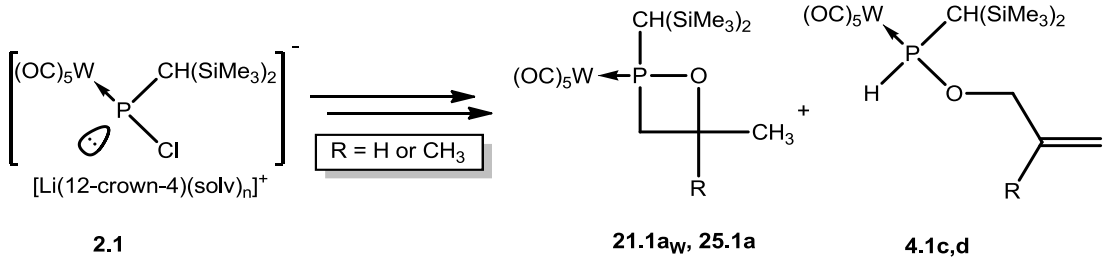
In addition, derivatives of **21.1a**, bearing not only the $W(CO)_5$ but also the $Mo(CO)_5$ and $Cr(CO)_5$, were synthesized. The change of the metal did neither influence the reaction outcome nor most of the analytical data. Significant but typical changes were only observed in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR for the atoms directly bonded to the metal and for the metal phosphorus bond in the molecular structure.

A striking difference between the 1,2-oxaphosphetane complexes and 1,2$\sigma^5$,$\lambda^5$- or 1,2$\sigma^4$,$\lambda^5$-oxaphosphetanes is the high thermal stability which was found for all derivatives. Only slow and unselective decomposition was observed in toluene solutions at temperatures above 100 °C for most derivatives.

A significant influence of the C-substituent on the $^{31}P$ NMR spectroscopic data was observed. $^{31}P$ NMR resonances were observed in the range of 150 to 200 ppm with $^{1}J_{W,P}$ of 260 - 300 Hz, whereby a stronger deshielding as well as higher magnitudes for the coupling

constants were observed with the introduction of electron-withdrawing groups. This is of special interest as no such influence is known for the smaller heterocycles, the oxaphosphirane complexes. The other NMR and IR data as well as crystallographic parameters for all 1,2-oxaphosphetane complexes presented in this work are close to invariant.

1,2-Oxaphosphetane complexes bearing different *P*-substituents as well as 4,4-disubstituted complexes were prepared in a detailed study to evaluate the influence of the substitution pattern on the number of isomers formed and the general synthetic applicability. Change of the epoxides to either isobutylene oxide or hexafluoroisobutylene oxide showed a reduction to two isomers in case of the *P*-$CH(SiMe_3)_2$-substituted 1,2-oxaphosphetane complexes.




**2.1** **21.1a$_W$, 25.1a** **4.1c,d**

***Scheme 9.4:*** Reaction of Li/Cl phosphinidenoid complex **2.1** with *C*-Me-substituted epoxides **20a** and **24a**.

During the studies phosphinite complexes **4.1a** and **4.1d** could be identified as side products in the reaction of Li/Cl phosphinidenoid complex **2.1** with *C*-Me-substituted epoxides. **4.1d** was isolated and characterized in case of the reaction with isobutylene oxide. Of particular interest was not only the formation of this side product but also the molecular structure of the corresponding 1,2-oxaphosphetane complex **25.1a**, as it showed the s-*trans* conformation of the *P*-$CH(SiMe_3)_2$ substituent for the first time.

In case of complex **25.1b** the presence of atropisomers by a hindered rotation could be proven by thermal change of the ratio between both complexes.

A reduced number of isomers was also observed using derivatives having the *P*-$C_5Me_5$ or the *P*-$CPh_3$ substituent, *i.e.* two isomers were observed for the 4-monosubstituted complexes (R = $C_5Me_5$: **21.2a,e,g**; R = $CPh_3$: **21.3a,g**). Consequently, only one isomer was observed in cases of the 4,4-disubstituted complexes **25.2b** and **25.3b**.

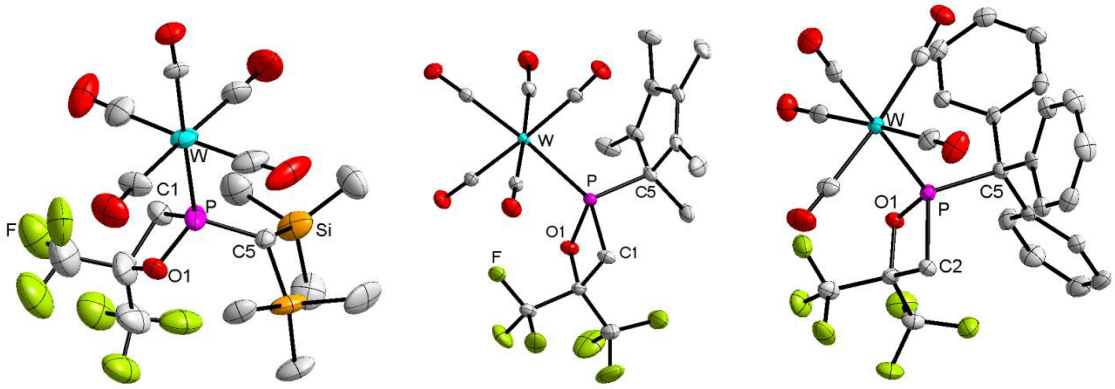



***Figure 9.2:*** Molecular structures of bis-$CF_3$-substituted 1,2-oxaphosphetane complexes **25.1b**-**25.3b** in the solid state (all hydrogen atoms are omitted for clarity).

An investigation on the synthetic accessibility of bis-oxaphosphetane complexes revealed a strong influence of the chain lengths of the used bis-epoxide on the reaction outcome. A selective reaction of **2.1** was only observed in the reaction with 1,7-octadiene diepoxide. Isolation of the first bis-oxaphosphetane complex was achieved and the product unambigiously characterized (figure 9.3).

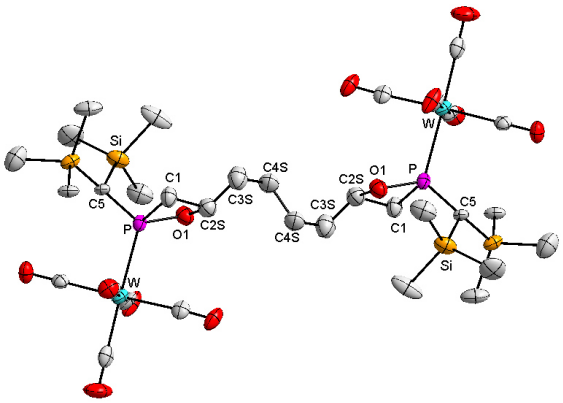
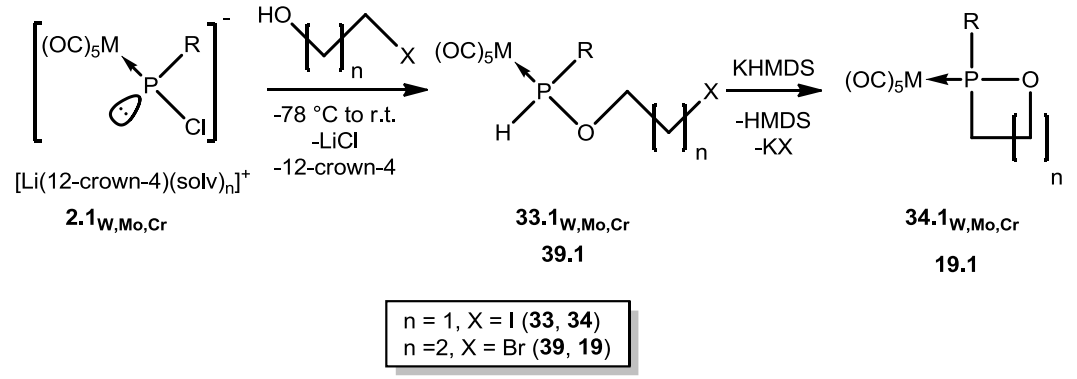



***Figure 9.3:*** DIAMOND plot of the molecular structure of complex **29.1c** in the solid state; the thermal ellipsoids are set at 50 % probability level and all hydrogens are omitted for clarity. Only the main orientation of the bridging $C_4$-unit and the ring folding is shown for clarity.

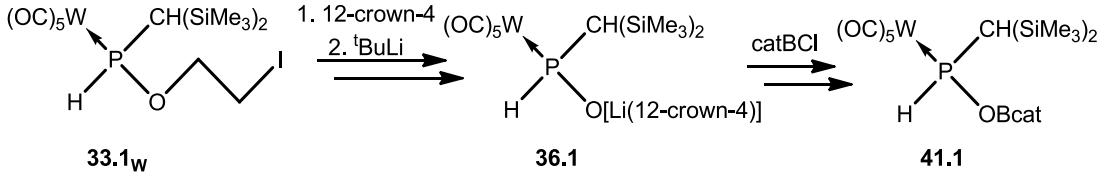
The second synthetic route to 1,2-oxaphosphetane complexes and a novel route to a 1,2-oxaphospholane complex was developed starting from the selective insertion reaction of Li/Cl phosphinidenoid complexes into the O-H bond of $\alpha,\omega$-bifunctional alcohols, *i.e.* 2-iodoethanol or 3-bromopropan-1-ol. Using the *P*-$CH(SiMe_3)_2$-substituted Li/Cl phosphinidenoid complex **2.1** and the subsequent deprotonation with KHMDS and HI or HBr elimination in **33.1** or **39.1**, opened access to the novel C-unsubstituted O,P heterocyclic ligands in **19.1** and **34.1**$_{W,Mo,Cr}$. In addition, formation of only one isomer of the C-unsubstituted 1,2-oxaphosphetane complexes **34.1**$_{W,Mo,Cr}$ allowed to broaden further reactivity studies due the simplification of otherwise unnecessarily complicated spectra.




***Scheme 9.5:*** Syntheses of C-unsubstituted 1,2-oxaphosphetane complexes (n = 1, M = Cr, Mo, W, X = I) and a 1,2-oxaphospholane complex (n = 2, M = W, X = Br).

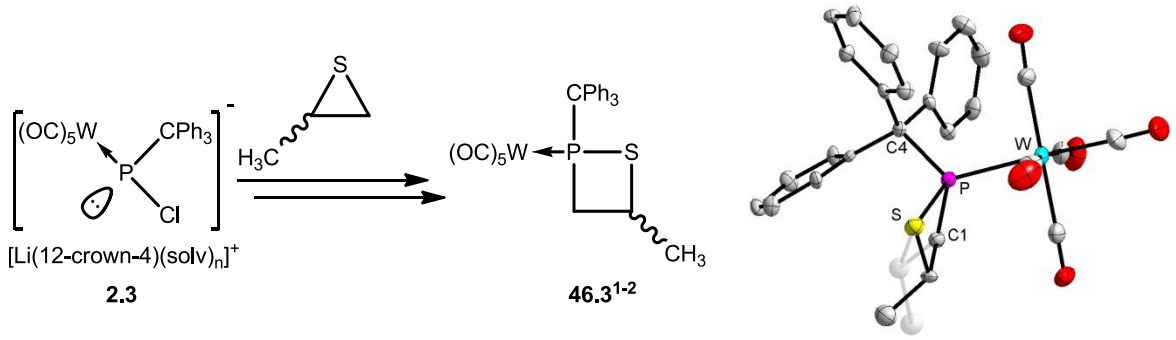
In the reactions of the *P*-$C_5Me_5$ and *P*-$CPh_3$-substituted Li/Cl phosphinidenoid complexes **2.2** and **2.3** with 2-iodoethanol the formation of 1,2-oxaphosphetane complexes as well as chloro(organo)phosphane complexes **10.2** and **10.3**, respectively were observed in a 1:1 ratio. Nevertheless, the *P*-$C_5Me_5$-substituted complex **34.2** could be isolated and unambigiously characterized.

A different result was obtained when *tert*-butyl lithium in the presence of 12-crown-4 instead of KHMDS was used in the reaction with 2-iodoethylphosphinite complex **33.1**$_W$. Not the P-H deprotonation, but a lithium/iodine exchange with subsequent elimination of ethylene to yield phosphinito complex **36.1** was observed. The complex was described by the group of Streubel before, but the previous route was too laborious and expensive to be fully exploited. With a far better yield (75 %) it was now possible to inverstigate further reactivity: In a first test, complex **36.1** could be used as synthetic building block for the preparation of complex **41.1**, being the first example of a complex bearing a P-ligand with the structural POB motif.



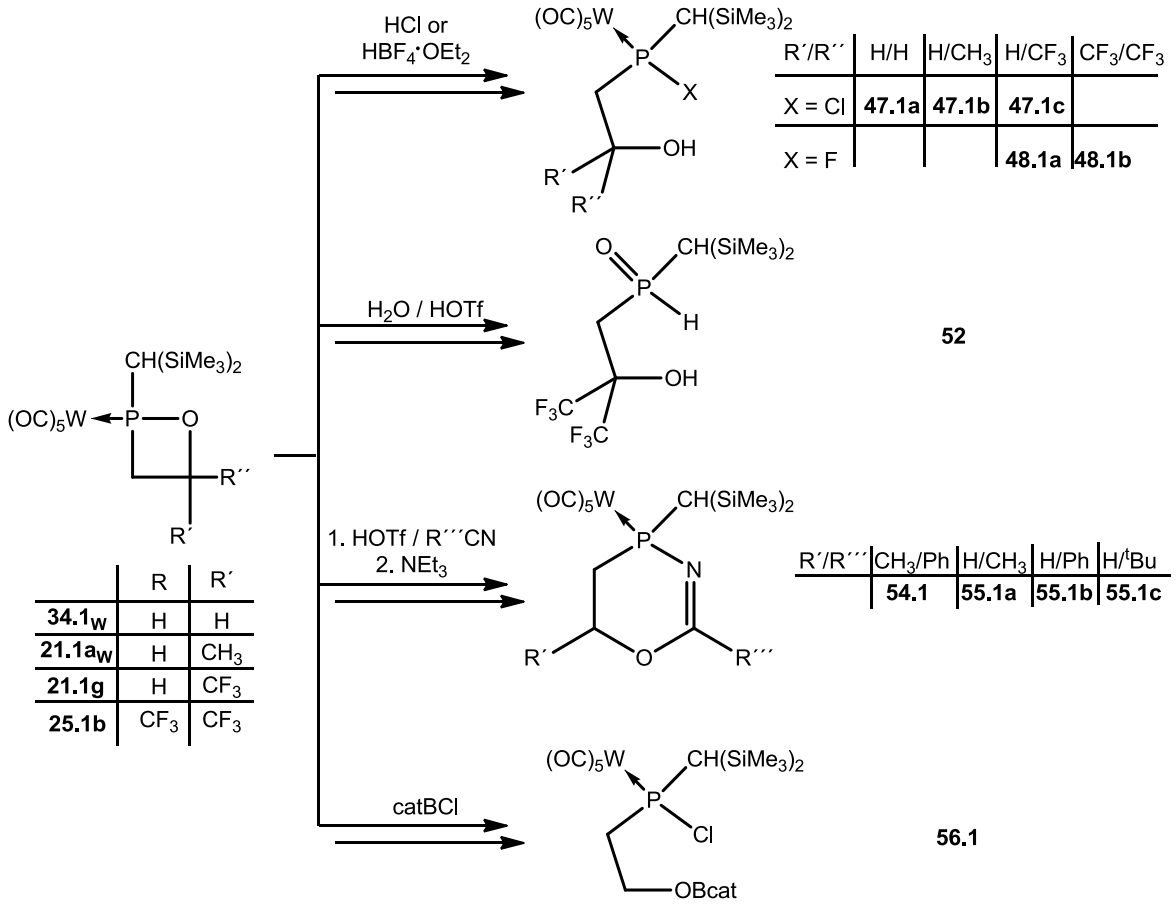

***Scheme 9.6:*** Syntheses of phosphinito complex **36.1** and phosphinite complex **41.1**.

Before this work was started, the heavier homologues of the 1,2-oxaphosphetane complexes were unknown. A first investigations towards the reaction of Li/Cl phosphinidenoid complex **2.3** with propylene sulfide showed that also 1,2-thiaphosphetane complexes are accessible using the strategy developed for the synthesis of 1,2-oxaphosphetane complexes. Complexes **46.3**$^{1\text{-}2}$ were formed selectively in form of two isomers and showed high-field shifted resonance signals in the $^{31}P\{^1H\}$ NMR spectra with smaller $^1J_{W,P}$ coupling constants compared to the otherwise similar complexes **21.3a**.




***Scheme 9.7:*** Synthesis and molecular structure of 1,2-thiaphosphetane complex **46.3**.

In chapter 8 the chemical behaviour of 1,2-oxaphosphetane complexes was presented with the special focus on an acid-induced reactivity.




| R´/R´´ | H/H | H/CH3 | H/CF3 | CF3/CF3 |
|---|---|---|---|---|
| X = Cl | **47.1a** | **47.1b** | **47.1c** | |
| X = F | | | **48.1a** | **48.1b** |

| R´/R´´´ | CH3/Ph | H/CH3 | H/Ph | H/tBu |
|---|---|---|---|---|
| | **54.1** | **55.1a** | **55.1b** | **55.1c** |

| | R | R´ |
|---|---|---|
| **34.1W** | H | H |
| **21.1aW** | H | CH3 |
| **21.1g** | H | CF3 |
| **25.1b** | CF3 | CF3 |

***Scheme 9.8:*** Acid-induced reactions of 1,2-oxaphosphetane complexes (R = $CH(SiMe_3)_2$).

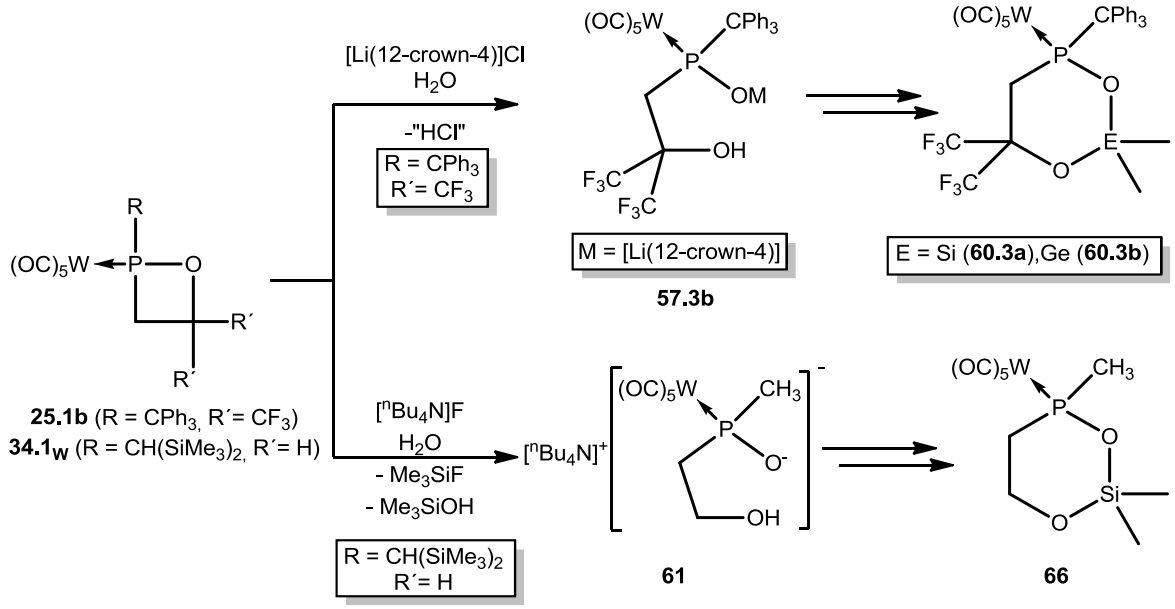
Brønsted acid-induced ring opening reactions were achieved using either $HCl_{(g)}$ or tetrafluoroboric acid diethyl ether complex ($HBF_4{\cdot}OEt_2$) in dichloromethane, yielding the corresponding chloro(organo)phosphane complexes **47.1a-c** or fluoro(organo)phosphane complexes **48.1a,b**, respectively. The reaction with $HCl_{(g)}$ was found to be dependent on the *C*-substituent as introduction of one $CF_3$ group reduced the reaction speed noticeably and introduction of a second $CF_3$ group completely suppressed the reaction. In contrast to reactions of oxaphosphirane complexes, where the $C_5Me_5$ group is involved in the reaction

with Brønsted acids, the analogous reaction of a *P*-$C_5Me_5$-substituted 1,2-oxaphosphetane complex **25.2b** yielded the fluoro(organo)phosphane complex **48.2b** by simple ring opening.

Of particular interest was the activation of 1,2-oxaphosphetane complexes using triflic acid. In the presence of water, hydrolysis of the ring and loss of the $W(CO)_5$ moiety was observed to form phosphane oxide **52** as the single P-containing product. In the presence of nitriles, a ring expansion reaction yielding 1-oxa-3-aza-5,6-dihydrophosphinines **54.1** and **55.1a-c** was achieved using a subsequent treatmend with triflic acid and triethylamine. Optimization of the reaction conditions led to the isolation of complexes **55.1a-c** in almost quantitative yields.

In a preliminary study, reaction of the 1,2-oxaphosphetane complex **34.1$_W$** with catechol(chloro)borane as Lewis acid afforded the chloro(diorgano)phosphane complex **56.1** in a ring opening reaction, being similar to the one observed with $HCl_{(g)}$.

A hydrolytic ring opening reaction was observed in case of the sterically crowded 1,2-oxaphosphetane complex **25.1b** in presence of Li(12-crown-4)Cl. The reaction led selectively to phosphinito complex **57.3b**. Interestingly, no reaction was observed in the absence of the lithium salt, *i.e.* an additional activation by this Lewis acid was necessary.




***Scheme 9.9:*** Hydrolytic ring opening reactions of 1,2-oxaphosphetane complexes and their use in medium sized P-ligand formation.

A somewhat similar product was observed by an [$^n$Bu$_4$N]F-mediated hydrolysis in case of the *P*-$CH(SiMe_3)_2$-substituted 1,2-oxaphosphetane complex **34.1$_W$.** Surprisingly, a desilylation was observed in case of **34.1$_W$**, leading to complex **61**. Analysis of the molecular structures in the solid state showed a preformed ring by a hydrogen bond between the OH and the PO moiety in the ligand framework.

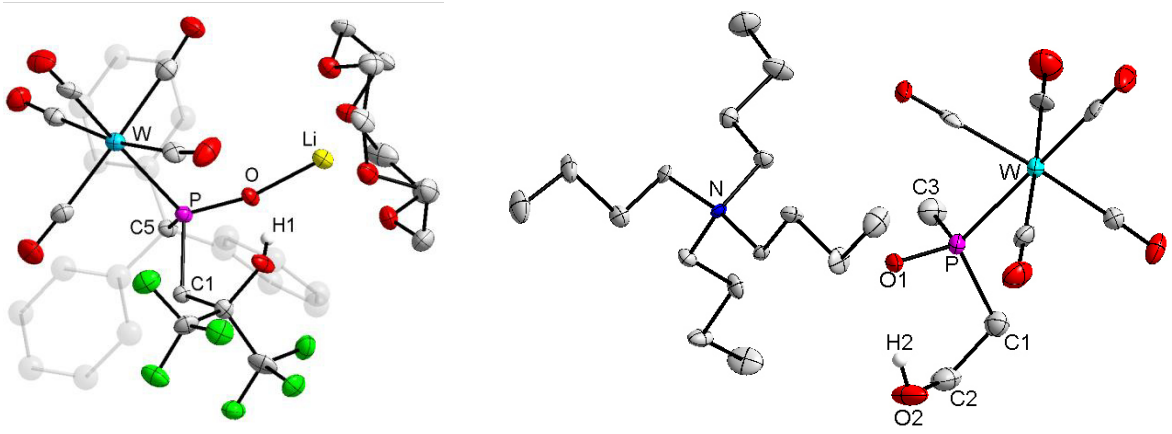



***Figure 9.4:*** Molecular structures of phosphinito complexes **57.3b** and **61**.

The synthetic potential of phosphinito complexes **57.3b** was illustrated by reactions with $Me_2SiCl_2$ and $Me_2GeCl_2$ and in case of **61** with $Me_2SiCl_2$ in ring closing reactions, thus leading to novel 6-membered heterocyclic ligands in **60a,b** and **66**.

# 10 Experimental section

## 10.1 General part

All reactions were performed under strict exclusion of moisture and oxygen using standard Schlenk or glove box techniques under an atmosphere of deoxygenated and dried argon. The used argon gas was commercially received with a purity of > 99.999 % and purified by passing through a system of three columns, one for deoxygenating using the BTS copper catalyst (BASF AG, 100 – 130 °C), one for drying, filled with phosphorus pentoxide and one with silica gel. The glove box (build by MBRAUN) was maintained under an argon atmosphere ($O_2$ content below 0.1 ppm and $H_2O$ content below 0.1 ppm) with an excess pressure of 1.5 mbar.

All solvents were dried by standard procedures:[173] THF and $Et_2O$ over benzophenone and sodium-wire, *n*-pentane, petroleum ether and toluene over sodium wire and dichloromethane over $CaH_2$. The solvents were refluxed for several days and either distilled prior to use or distilled and kept in brown glass bottles with Argon inlet over sodium wire or 4 Å molecular sieves. Solvents used for the preparation of extremely air and moisture sensitive compounds were degassed and recondensed from either potassium or $CaH_2$ prior to use.

The transfer of solvents or solutions was performed using stainless steel cannulas that were dried prior to use in an oven at 75 °C for at least one hour and facilitated by positive argon pressure at one side and a pressure relieve valve at the side of the receiving flask. For filtration either a Schlenk-frit or a stainless steel filtration cannula with an attached filtration head was used. For the filtration with the stainless steel cannula either standard filter paper or Whatmann glass filter paper was used, depending on the sensitivity of the material, which was fixed at the filtration head with Teflon tape. In both cases the filter paper and cannula were dried at 75 °C in the oven for at least an hour prior to use. The cannulas were cleaned after use with acetone, water, diluted hydrochloric acid, water and again acetone.

All glassware was cleaned by storage in a KOH/water bath, containing some NaClO for oxidation of all metal contaminations. The glassware was stored in the bath for at least two days and subsequently washed with tap water/soap, diluted $HCl_{(aq)}$ and finally with acetone and petroleum ether to remove all traces of grease. All clean glassware was dried overnight in an oven at 75 °C.

Prior to use all joints were greased with OKS grease type 1112. The glassware was heated under active vacuum (0.02 mbar) to 400-500 °C, filled with argon while it was still hot, evacuated, again heated, allowed to cool down to ambient temperature under active vacuum to remove adsorbed water from the surface and refilled with argon.

Low temperatures (< 0 °C to -100 °C) were achieved using either a petroleum ether or ethanol bath and liquid nitrogen.

Several compounds were purified using low temperature column chromatography. The chromatographic columns were equipped with an integrated cooling mantle, cooled with a connected cryostat and ethanol (technical grade) as cooling medium for constant cooling of the column material as well as a vacuum mantle to avoid ice formation on the surface. Neutral Silica (Merck 60-200) or aluminum oxide (Merck 90 neutral) was used as stationary phase. The column´s dimensions (diameter x length), the used stationary phase and eluents are given in the experimental details for each case.

## 10.2 Analytical Methods

### 10.2.1 Melting point determination

Melting points were determined on a Büchi 535 Type S melting point apparatus in both sided clothed glass tubes; the values are not corrected.

### 10.2.2 NMR spectroscopy

All NMR spectra were recorded on a Bruker Avance DMX-300, DPX-300, DPX-400 or DMX-500 spectrometer. The $^{1}H$ NMR resonance signals and the $^{13}C\{^{1}H\}$ NMR resonance signals were referenced to the solvent residual signals. Deuterated solvents ($CDCl_3$, THF-$d_8$ or $C_6D_6$) were dried using literature procedures and used for the multi nuclear NMR characterizations and the chemical resonances are given relative to Tetramethylsilane ($^{1}H$, $^{13}C$, $^{29}Si$ NMR), 1 M LiCl in $D_2O$ ($^{7}Li$ NMR), 15 % $BF_3{\cdot}OEt_2$ in $CDCl_3$ ($^{11}B$ NMR), $CFCl_3$ ($^{19}F$ NMR) or 85% $H_3PO_4$ ($^{31}P$ NMR), respectively. The chemical shift is given in parts per million, ppm. Magnitudes of coupling constants are abbreviated as $^{n}J_{X,Y}$, where X and Y denote the coupling nuclei (ordered by decreasing atomic number, the nuclear numbers are omitted), and n denotes the number of bonds that separate X and Y; only absolute values were determined.

***Table 10.1:*** Chemical shifts of the deuterated solvents and multiplicity of the residual signals used for the calibration.[174]

| Solvent | $^{1}H$ NMR ($\delta$ in ppm) | $^{13}C\{^{1}H\}$ NMR ($\delta$ in ppm) |
|---|---|---|
| **$CDCl_3$** | 7.62 (s) | 77.16 (3) |
| **$C_6D_6$** | 7.16 (br) | 128.06 (3) |
| **THF-$d_8$** | 1.72 (br)<br>3.58 (br) | 25.31 (5)<br>67.21 |
| **toluene-$d_8$** | 2.08 (5) | 20.43 (7) |

Signals are characterized by the following abbreviations: for their form and multiplicities s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet and br

= broad signal. The $^{1}H$ NMR and $^{13}C\{^{1}H\}$ NMR signals of all compounds were assigned by a combination of HMQC, HMBC and DEPT experiments.

All measurements were performed, as long as not specified otherwise, at 298 K.

### 10.2.3 Mass spectrometry

Mass spectrometric data were recorded on a Bruker Daltonik micrOTOF-Q using ESI (+/-), a Thermo Finnigan MAT 90 sector instrument equipped with a LIFDI ion source (Linden CMS) or MAT 95 XL Finnigan using EI (70 eV). Only selected data are given for the detected ions (mass to charge ratio, relative intensity in percent). Assignments of the ionic molecule fragments is based on plausibility and on the observed isotopic distributions; for compounds containing several isotopes the given m/z values refer in each case to the most intense peak according to the combination of elements each with the highest abundance.

### 10.2.4 IR spectroscopy

Infrared spectra were recorded of the pure solids on a Thermo IR spectrometer with an attenuated total reflection (ATR) attachment or on a Bruker Alpha Diamond ATR FTIR spectrometer at room temperature. A selection of the registered bands is given for each compound where the intensity is marked with the following abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

### 10.2.5 Elemental analysis

Elemental analysis was performed with an Elementar Vario Micro elemental analyser by the micro analysis laboratory of the Chemical Institute of the University of Bonn. The mean value of at least three measurements is given.

### 10.2.6 Single crystal X-ray diffraction studies

Suitable single crystals were separated from the supernatant solution at the temperature of the crystallization and covered with Formblin® Y lubricant to protect them from air and moisture. A crystal suitable for measurement was selected on a microscope and transferred to the diffractometer. The data were collected on a Bruker D8-Venture, Bruker X8-KappaApexII, Bruker APEX-II CCD, Nonius KappaCCD or STOE IPDS 2T diffractometer equipped with a low-temperature device (Cryostream, Oxford Cryosystems) using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) or Cu-$K_\alpha$ radiation ($\lambda$ = 1.54178). The absorption correction, structure solution was performed by Patterson methods or direct methods (SHELXS-97[175]) and structure refinemend by full-matrix least squares on $F^2$ (SHELXL-97[176], SHELXL-2015[177] or OLEX2[178]) programs. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included isotropically using the riding model on the bound carbon atoms.

Data analysis and preparation of the pictures of the molecular structures were prepared using the program DIAMOND 3.0. Details on the structure solutions presented in this thesis are included in the appendix.

### 10.2.7 Used chemicals

The following chemicals were purchased and purified or distilled prior to use according to literature procedures:[173]

- acetonitrile **VWR**
- aluminium oxide Merck 90 neutral (70-230 mesh ASTM) **Merck**
- benzene-$d_6$ **deutero**
- benzonitrile **Merck**
- boron trichloride **Acros**
- 3-bromopropan-1-ol **abcr**
- 1,3-butadiene diepoxide **Alfa Aeser**
- 1,2-butylene oxide **TCI**
- calcium chloride (anhydrous) **VWR**
- chloroform-$d_1$ **deutero**
- chlorotrimethylsilane **Aldrich**
- chromium hexacarbonyl **Aldrich**
- 12-crown-4 **Acros**
- cyclohexylamine **Chimica**
- dichloromethane **Fisher**
- diethylamine **Acros**
- diethyl ether **VWR**
- dichlorodimethylgermane **Fluorochem**
- dichlorodimethylsilane **Alfa Aeser**
- 2,3-diphenylcyclopropenone **Alfa Aeser**
- epichlorohydrin **Acros**
- 1,2-epoxy-3-methylbutane **Alfa Aeser**
- hexafluoro isobutylene oxide **abcr**
- 1,5-hexadiene diepoxide **abcr**
- hydrochloric acid (35%) **Acros**
- isobutylene oxide **Acros**
- isopropylamine **Acros**
- 2-iodoethanol **Acros or Alfa Aeser**
- KHMDS (potassium hexamethyldisilazide) **Aldrich**

- molybdenum hexacarbonyl **Aldrich**
- *n*-pentane **VWR**
- 1,7-octadiene diepoxide **Alfa Aeser**
- petroleum ether 40/60 **Hoesch**
- phosphorus pentoxide (SICAPENT®) **Merck**
- phosphorus trichloride **Acros**
- propylene oxide **Aldrich**
- R(+)-propylene oxide **Alfa Aeser**
- propylene sulfide **Aldrich**
- Silica gel Merck 60 (0.063 – 0.2 mm, pH = 6.5 – 7.5) **Merck**
- styrene oxide **Merck**
- *tert*-butyllithium (1.7 M in *n*-pentane) **Aldrich**
- *tert*-butylamine **Acros**
- tetrabutylammonium fluoride (1 M in THF) **Alfa Aeser**
- tetrafluoroboric acid diethyl ether complex **Aldrich**
- tetrahydrofurane **Fisher**
- tetrahydrofurane-$d_8$ **deutero**
- toluene **VWR**
- toluene-$d_8$ **Euriso-top**
- triethylamine **Acros**
- 1,1,1-trifluoro-2,3-propylene oxide **abcr**
- trifluoromethanesulfonic acid **Aldrich or Acros**
- trimethylacetonitrile **Acros**
- trimethylamine-N-oxide dihydrate **Alfa-Aeser**
- tungsten hexacarbonyl **Aldrich or abcr**

<u>The following starting materials were synthesized according to described procedures</u>

- acetonitrile(pentacarbonyl)tungsten(0)[179]
- acetonitrile(pentacarbonyl)molybdenum(0)[179]
- acetonitrile(pentacarbonyl)chromium(0)[179]
- dichloro[bis(trimethylsilyl)methyl]phosphane[180]
- dichloro(triphenylmethyl)phosphane[181]
- dichloro(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)phosphane[182]
- pentacarbonyl[dichloro(triphenylmethyl)phosphane-κP]tungsten(0)[33]
- pentacarbonyl{dichloro[bis(trimethylsilyl)methyl]phosphane-κP}tungsten(0)[114]
- pentacarbonyl{dichloro[bis(trimethylsilyl)methyl]phosphane-κP]molybdenum(0)[114]

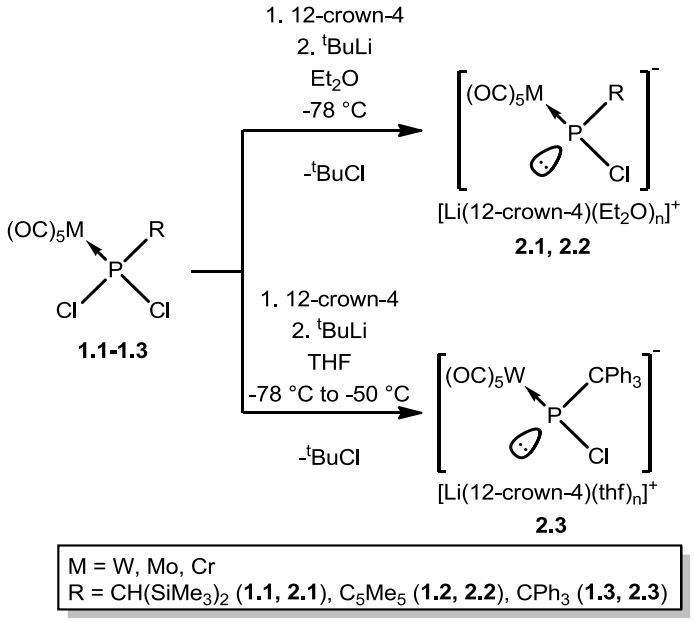
- pentacarbonyl{dichloro[bis(trimethylsilyl)methyl]phosphane-κP}chromium(0)[114]
- pentacarbonyl[dichloro(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)phosphane-κP]tungsten(0)[125]
- pentacarbonyl{(2-iodoethoxy)[bis(trimethylsilyl)methyl]phosphane-κ*P*}molybdenum(0)[183]
- pentacarbonyl{(2-iodoethoxy)[bis(trimethylsilyl)methyl]phosphane-κ*P*}chromium(0)[183]
- 1-(1-methylethyl)-2-phenyl-aziridine[140]
- 1-(phenylmethyl)-2-(trifluoromethyl)-aziridine[141]

### 10.2.8 Waste disposal

The waste disposal was performed according to the institutes waste disposal policy. Single use syringes and cannulae, solvents, column material and other contaminated materials were collected in special containers. Alkaline metals were first treated with isopropanol, using appropriate safety measurements, to obtain the corresponding salts and subsequently disposed. All contaminated waste was submitted to the department 4.2 “Arbeits und Umweltschutz” of the University of Bonn for further handling and disposal.

# 11 Syntheses and analytical data

## 11.2.1 Preparation of Li/Cl phosphinidenoid complexes 2.1-2.3 at low temperature



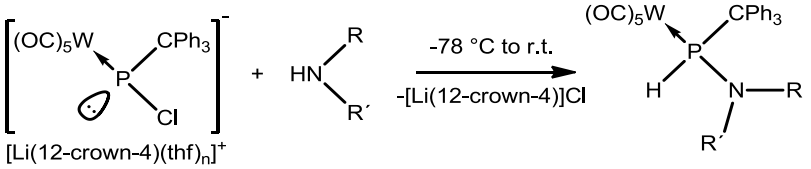

### 11.2.1.1 Preparation of 2.1[31] and 2.2[32]

One equivalent of dichlorophosphane complex $[(OC)_5M\{PCl_2(R)\}]$ **1.1** (R = $CH(SiMe_3)_2$, M = Cr, Mo, W) or **1.2** (R = $C_5Me_5$) and one equivalent of 12-crown-4 are dissolved in diethyl ether (20 mL per mmol of reagent) in an appropriate Schlenk tube (approximately twice the volume of the solvent). The solution is cooled to -78 °C and subsequently 1.05 equivalents of *tert*-butyllithium (1.7 M solution in *n*-pentane) are added dropwise. The solution is stirred for 10 minutes at -78 °C to ensure complete conversion to the Li/Cl phosphinidenoid complexes **2.1** or **2.2**, respectively.

### 11.2.1.2 Preparation of 2.3[33]

One equivalent of the dichlorophosphane complex $[(OC)_5W\{PCl_2(CPh_3)\}]$ (**1.3**) and one equivalent of 12-crown-4 are dissolved in THF (12 mL per mmol) in an appropriate Schlenk tube (approximately twice the volume of the used solvent). The solution is cooled to -78 °C and subsequently 1.05 equivalents of *tert*-butyllithium (1.7 M solution in *n*-pentane) are added dropwise. The solution is allowed slowly warming up to -50 °C (ca. 1 h) to ensure complete conversion to the Li/Cl phosphinidenoid complex **2.3**.

## 11.2.2 Syntheses of aminophosphane complexes

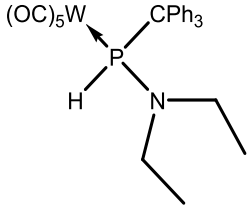



A solution of Li/Cl phosphinidenoid complex **2.3** was prepared as described in chapter 11.2.1, starting from $[(OC)_5W\{PCl_2(CPh_3)\}]$ (**1.3**). The solution was cooled subsequently to -78 °C and the corresponding amine was added. The solution was allowed slowly warming up to 0 °C before removing the cooling bath. Formation of a white precipitate was observed during the warm up period and the solution was stirred for at least 30 more minutes at ambient temperature. (In case of **9.3c** the solution was kept on stirring overnight.)

***Table 11.1:*** Amounts of used dichloro(organo)phosphane complex **1.3** and amines.

| . | R | R´ | m (**1.3**) [mg] | n (**1.3**) [mmol] | amine | V (amine) [mL] | n (amine) [mmol] |
|---|---|---|---|---|---|---|---|
| **6.3a** | Et | Et | 333.5 | 0.50 | **5a** | 0.06 | 0.57 |
| **9.3a** | H | Cy | 167.0 | 0.25 | **8a** | 0.03 | 0.26 |
| **9.3b** | H | $^{i}$Pr | 167.0 | 0.25 | **8b** | 0.03 | 0.35 |
| **9.3c** | H | $^{t}$Bu | 669.0 | 1.00 | **8c** | 0.06 | 1.10 |

### 11.2.2.1 Pentacarbonyl[diethylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [6.3a]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was extracted from the formed salt with two times 15 mL of diethyl ether and one time 10 mL of diethyl ether. The product was obtained as yellow solid after evaporation of all volatiles in *vacuo* (ca. 0.02 mbar).

**Molecular formula:** $C_{28}H_{26}NO_5PW$

**Molecular weight:** 671.324 g/mol

**Melting point:** 151-152 °C

**Yield:** 271.1 mg (0.404 mmol, 81 %).

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.88 (t, 6H, $^{3}J_{H,H}$ = 7.08 Hz, C$H_3$), 2.71 – 2.90 (m, 2H, N-C$H_2$), 2.82 – 3.10 (m, 2H, N-C$H_2$), 7.28 – 7.44 (m, 15H, $CPh_3$), 7.25 (d, 1H, $^{1}J_{P,H}$ = 352.2 Hz, P-*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** δ = 12.9 (d, $^{3}J_{P,C}$ = 1.9 Hz, *C*H$_3$), 47.0 (d, $^{2}J_{P,C}$ = 4.2 Hz, N-*C*H$_2$), 64.0 (d, $^{1}J_{P,C}$ = 1.9 Hz, P-*C*), 127.2 (d, $^{5}J_{P,C}$ = 1.9 Hz, *para*-*C*H$_{Ar}$), 127.1 (s, *C*H$_{Ar}$), 130.8 (d, $^{3}J_{P,C}$ = 6.8 Hz,

$CH_{Ar}$), 142.2 (d, $^2J_{P,C}$ = 1.9 Hz, *ipso*-C), 197.1 (d, $^2J_{P,C}$ = 6.6 Hz, $^1J_{W,C}$ = 126.7 Hz, *cis*-*C*O), 198.9 (d, $^2J_{P,C}$ = 28.1 Hz, *trans*-*C*O).

**$^{31}$P NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 74.4 (dquin$_{sat}$, $^1J_{P,W}$ = 252.1 Hz, $^1J_{P,H}$ = 352.2 Hz, $^3J_{P,H}$ = 9.5 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 671.0 (0.01) $[M]^{\bullet+}$, 614.0 (0.02) $[M - C_4H_9]^+$, 428.0 (0.04) $[M - CPh_3]^+$, 400.0 (0.02) $[M - CPh_3 - CO]^+$, 243.3 (100) $[CPh_3]^+$, 165.1 (60) $[CPh_3 - C_6H_6]^+$.

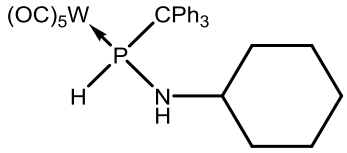
**IR (ATR Diamond, $\tilde{\nu}$ [cm$^{-1}$], selected data):** 2069 (s, $\nu$(CO)), 1979 (m, $\nu$(CO)), 1907 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 50.10 | H | 3.90 | N | 2.09 |
| found: | C | 49.78 | H | 3.92 | N | 2.00 |

**Single crystal measurement:** GSTR317, twin5-merg

## 11.2.2.2 Pentacarbonyl[cyclohexylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [9.3a]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the crude product was extracted from the formed salt with 3 times 15 mL of diethyl ether, followed by evaporation of the diethyl ether in *vacuo* (ca. 0.02 mbar) and low temperature column chromatography ($Al_2O_3$, -20 °C, eluent: petroleum ether, petroleum ether/dichloromethane 10:1). The product was obtained as an oil from the second fraction after evaporation of all volatiles in *vacuo* (ca. 0.02 mbar). The product was subsequently recrystallized by slow evaporation of a saturated diethyl ether solution at 4 °C to yield a yellow crystalline material.

Alternatively a separation by filtration with diethyl ether over aluminium oxide (ø = 2 cm, h = 3 cm) and subsequent washing with *n*-pentane was performed, giving similar yield.

**Molecular formula:** $C_{30}H_{28}NO_5PW$

**Molecular weight:** 697.361 g/mol

**Melting point:** 142 °C

**Yield:** 134.5 mg (0.190 mmol, 77 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 1.20 - 1.40 (m, 1H, N-*H*), 0.80 - 1.89 (m, 10H, Cy-*H*), 2.51 – 2.70 (m, 1H, C*H*), 7.2 – 7.5 (m, 15H, Ph), 7.43 (dd, 1H, $^1J_{P,H}$ = 333.0 Hz, $^3J_{H,H}$ = 4.0 Hz, P-*H*).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 25.1 ($s_{br}$, 2 *C*$H_2$), 25.3 (s, *C*$H_2$), 35.3 (d, $J_{P,C}$ = 4.5 Hz, *C*$H_2$), 35.6 (d, $J_{P,C}$ = 3.6 Hz, *C*$H_2$), 56.0 (d, $^2J_{P,C}$ = 4.9 Hz, *C*H), 62.1 (d, $^1J_{P,C}$ = 20.0 Hz, P-*C*), 127.2 (d, $J_{P,C}$ = 1.9 Hz, *C*$H_{Ar}$), 128.3 (s, *C*$H_{Ar}$), 130.5 (d, $J_{P,C}$ = 6.8 Hz, *C*$H_{Ar}$), 142.8 (s, *ipso-C*), 196.6 ($d_{sat}$, $^2J_{P,C}$ = 7.1 Hz, $^1Jc_{,W}$ = 126.7 Hz, *cis-C*O), 198.7 (d, $^2J_{P,C}$ = 26.8 Hz, *trans-C*O).

**$^{31}P$ NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 48.6 ($dddm_{sat,}$ $^1J_{P,H}$ = 333.0 Hz, $^2J_{P,H}$ = 7.2 Hz,$^3J_{P,H}$ = 7.1 Hz, $^1J_{W,P}$ = 260.4 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 697.2 (1) $[M]^{+\bullet}$, 613.2 (1) $[M - 3\ CO]^+$, 557.2 (20) $[M - 5\ CO]^+$, 555.1 (2) $[M - 5\ CO - H_2]^+$, 454.0 (50) $[M - CPh_3]^+$, 426.0 (20) $[M - CPh_3 - CO]^+$, 243.0 (100) $[CPh_3]^+$, 165.0 (50) $[CPh_3 - C_6H_6]^+$.

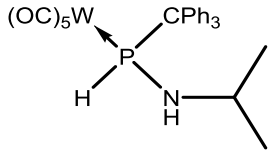
**IR (ATR Diamond, $\tilde{\nu}$ [$cm^{-1}$], selected data):** 3395 (w, $\nu$(NH)), 2311 (w, $\nu$(PH)), 2072 (s, $\nu$(CO)), 1983 (s, $\nu$(CO)), 1886 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 51.67 | H | 4.05 | N | 2.01 |
| found: | C | 51.50 | H | 4.35 | N | 2.06 |

**Single crystal measurement:** GSTR450, AKY-Cy // GXraymo_4395f

### 11.2.2.3 Pentacarbonyl[1-methylethylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [9.3b]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the crude product was separated by extraction from the formed salt with 3 times 15 mL diethyl ether, followed by evaporation of the diethyl ether in *vacuo* (ca. 0.02 mbar) and low temperature column chromatography ($Al_2O_3$, -20 °C, eluent: petroleum ether, petroleum ether/dichloromethane 10:1). The product was obtained as an oil from the second fraction after evaporation of all volatiles in *vacuo* (ca. 0.02 mbar). It was subsequently recrystallized by slow evaporation of a saturated diethyl ether solution at 4 °C to yield a yellow crystalline material.

**Molecular formula:** $C_{27}H_{24}NO_5PW$

**Molecular weight:** 657.297 g/mol

**Melting point:** 111 °C

**Yield:** 116.8 mg (0.180 mmol, 71 %)

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.89 (d, 3H, $^{3}J_{H,H}$ = 6.3 Hz, C*H*$_3$), 0.99 (d, 3H, $^{3}J_{H,H}$ = 6.3 Hz, C*H*$_3$), 1.40 (m, 1H, N-*H*), 3.04 (dsept, 1H, $^{3}J_{P,H}$ = 9.9 Hz, $^{3}J_{H,H}$ = 6.3 Hz, C*H*), 7.37 (m, 15H, $CPh_3$), 7.41 (dd, 1H, $^{1}J_{P,H}$ = 332.6 Hz, $^{3}J_{H,H}$ = 4.3 Hz, P-*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 24.8 (d, $^{3}J_{P,C}$ = 4.9 Hz, *C*H$_3$), 24.9 (d, $^{3}J_{P,C}$ = 4.0 Hz, *C*H$_3$), 49.2 (d, $^{2}J_{P,C}$ = 5.0 Hz, *C*H), 62.2 (d, $^{1}J_{P,C}$ = 19.7 Hz, P-*C*), 127.2 (d, $J_{P,C}$ = 2.0 Hz, *C*H$_{Ar}$), 128.3 (d, $J_{P,C}$ = 0.6 Hz, *C*H$_{Ar}$), 130.5 (d, $J_{P,C}$ = 6.8 Hz, *C*H$_{Ar}$), 142.0 (s, *ipso-C*), 196.5 (d$_{sat}$, $^{2}J_{P,C}$ = 6.9 Hz, $^{1}Jc_{,W}$ = 126.7, *cis-C*O), 198.6 (d, $^{2}J_{P,C}$ = 26.8 Hz, *trans-C*O).

**$^{31}$P NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 49.4 (d$_{sat}$, $^{1}J_{P,H}$ = 332.6 Hz, $^{1}J_{W,P}$ = 260.5 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 657.1 (1) $[M]^{+\bullet}$, 573.1 (1) $[M - 3\ CO]^{+}$, 413.1 (40) $[M - CPh_3]^{+}$, 243.0 (100) $[CPh_3]^{+}$, 165.0 (40) $[CPh_3 - C_6H_6]^{+}$.

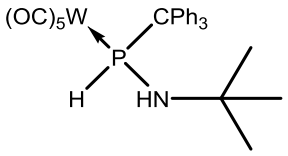
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3391 (w, $\nu$(NH)), 2327 (w, $\nu$(PH)), 2068 (s, $\nu$(CO)), 1980 (s, $\nu$(CO)), 1907 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 49.34 | H | 3.68 | N | 2.13 |
| found: | C | 50.85 | H | 4.71 | N | 1.92 |

**Single crystal measurement:** GSTR449, AKY-iPr // GXraymo_4396f

## 11.2.2.4 Pentacarbonyl[1,1-dimethylethylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [9.3c]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.008 mbar). The crude mixture was dissolved in diethyl ether, filtered over $Al_2O_3$ (ø = 2 cm, h = 3 cm) and the solvent was removed in *vacuo* (ca. 0.008 mbar). The product was obtained by recrystallization from *n*-pentane at -20 °C (overnight).

**Molecular formula:** $C_{28}H_{25}NO_5PW$

**Molecular weight:** 670.316 g/mol

**Melting point:** 135 °C

**Yield:** 562 mg (0.84 mmol, 84 %)

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.90 (d, 9H, $^{4}J_{H,H}$ = 0.68 Hz, N-$C_4H_9$), 1.10 (dd, 1H, $^{2}J_{P,H}$ = 15.9 Hz, $^{3}J_{H,H}$ = 10.2 Hz, N-*H*), 7.11 – 7.46 (m, 15H, $CPh_3$), 7.54 (dd, 1H, $^{1}J_{P,H}$ = 342.3 Hz, $^{3}J_{H,H}$ = 10.2 Hz, P-*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 31.2 (d, $^{3}J_{P,C}$ = 3.1 Hz, $^{t}$Bu-*C*$H_3$), 54.0 (d, $^{2}J_{P,C}$ = 11.5 Hz, $^{t}$Bu-*C*), 63.5 (d, $^{1}J_{P,C}$ = 7.1 Hz, P-*C*), 127.0 (d, $J_{P,C}$ = 2.0 Hz, *C*$H_{Ar}$), 128.2 (s, *C*$H_{Ar}$), 130.9 (d, $J_{P,C}$ = 7.0 Hz, *C*$H_{Ar}$), 142.6 (d, $^{2}J_{P,C}$ = 1.6 Hz, *ipso-C*), 197.0 ($d_{sat}$, $^{2}J_{P,C}$ = 7.1 Hz, $^{1}J_{C,W}$ = 126.7 Hz, *cis-C*O), 199.1 (d, $^{2}J_{P,C}$ = 27.8 Hz, *trans-C*O).

**$^{31}$P NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 37.3 ($dd_{sat}$, $^{1}J_{P,W}$ = 263.7 Hz, $^{1}J_{P,H}$ = 342.3 Hz, $^{2}J_{P,H}$ = 15.9 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 671.0 (0.02) $[M]^{\bullet+}$, 614.0 (0.01) $[M - C_4H_9]^+$, 427.9 (0.03) $[M - CPh_3]^+$, 400.0 (0.02) $[M - CPh_3 - CO]^+$, 243.3 (100) $[CPh_3]^+$, 165.1 (40) $[CPh_3 - C_6H_6]^+$.

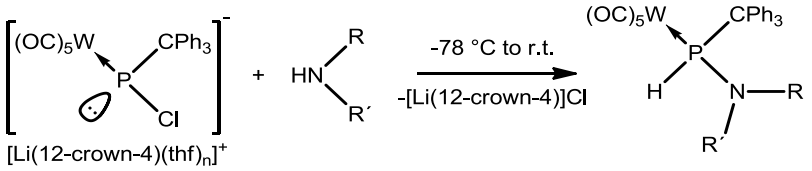
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3396 (m, $\nu$(NH)), 2369 (w, $\nu$(PH)), 2069 (s, $\nu$(CO)), 1939 (m, $\nu$(CO)), 1898 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 50.17 | H | 3.76 | N | 2.09 |
| found: | C | 50.75 | H | 4.28 | N | 1.97 |

**Single crystal measurement:** GSTR332, 3182f

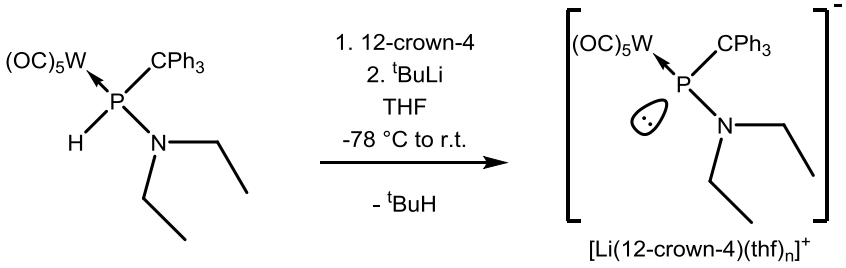
## 11.2.3 Attempted reactions of Li/Cl phosphinidenoid complex 2.3 with diisopropylamine and dicyclohexylamine




**Synthesis and analysis:** A solution of Li/Cl phosphinidenoid complex **2.3** was prepared as described in chapter 11.2.1, starting from 33.5 mg (0.05 mmol) of $[(OC)_5W\{PCl_2(CPh_3)\}]$ (**1.3**). The solution was subsequently cooled back to -78 °C and either 0.015 mL (0.1 mmol, 2 eq.) of diisopropylamine (**5b**) or 0.01 mL (0.05 mmol, 1 eq.) of dicyclohexylamine (**5c**) was added. The solution was allowed slowly warming up to 0 °C before removing the cooling bath.

$^{31}$P NMR measurements of the reaction mixtures were performed. The spectra showed the presence of the Li/Cl phosphinidenoid complex **2.3** as main component of the mixtures and some unspecific decomposition products.

## 11.2.4 Synthesis of lithium(1,4,7,10-tetraoxacyclododecane) pentacarbonyl[diethylamino(triphenylmethyl)phosphanido-κ*P*]tungsten(0) [7.3]

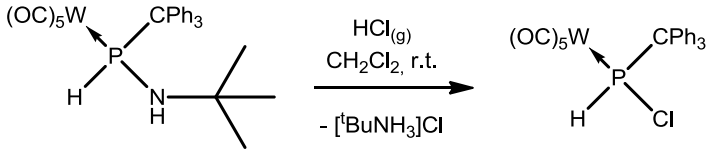



**Synthesis and analysis:** In a 10 mL Schlenk tube, 38.3 mg (0.057 mmol) of aminophosphane complex **6.3a** and 18 μL (0,11 mmol, 1.9 eq.) of 12-crown-4 were dissolved in 1.2 mL of THF. The solution was cooled to -78 °C and subsequently 0.035 mL (0.059 mmol, 1.04 eq.) of *tert*-butyllithium (1.7 M solution in *n*-pentane) was added dropwise. The solution was allowed slow warming up to ambient temperature and subsequently analysed by $^{31}$P NMR.

**$^{31}$P NMR (121.5 MHz, THF):** $\delta$ = 160.3 ($s_{sat}$, $^{1}J_{W,P}$ = 102.6 Hz).

A $^{31}$P NMR measurement of the solution after one day revealed reprotonation of the complex as well as small amounts of decomposition to unidentified products.

## 11.2.5 Synthesis of pentacarbonyl[chloro(triphenylmethyl)phosphane-κ*P*]tungsten(0) [10.3]




**Synthesis:** In a 20 mL Schlenk tube, 200 mg (0.3 mmol) of aminophosphane complex **9.3c** were dissolved in 10 mL of $CH_2Cl_2$. $HCl_{(g)}$ (prepared by dropping concentrated hydrochloric acid on anhydrous $CaCl_2$) was bubbled through the stirred solution for 30 minutes at ambient temperature. Stirring was continued for 2 h and precipitation of a white solid was observed over time.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was extracted from the formed ammonium salt with 25 mL of diethyl ether. The crude product, obtained after evaporation of all volatiles in *vacuo* (ca. 0.02 mbar), was washed two times with diethyl ether at -90 °C (one time with 3 mL and one time with 2 mL) to yield the product as white solid, after drying in *vacuo* (ca. 0.02 mbar).

**Molecular formula:** $C_{24}H_{16}ClO_5PW$

**Molecular weight:** 634.648 g/mol

**Melting point:** 163 °C (dec.)

**Yield:** 100 mg (0.158 mmol, 53 %)

**$^1$H NMR (500.1 MHz, $CDCl_3$):** $\delta$ = 7.28 – 7.46 (m, 15H, $CPh_3$), 7.94 (d, 1H, $^1J_{P,H}$ = 343.6 Hz, P*H*).

**$^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 64.3 (d, $^1J_{P,C}$ = 6.9 Hz, P-*C*), 128.2 (s, *para*-$CH_{Ar}$), 128.8 (s, $CH_{Ar}$), 130.4 (d, $^3J_{P,C}$ = 6.1 Hz, $CH_{Ar}$), 141.5 ($s_{br}$, *ipso*-*C*), 195.6 ($d_{sat}$, $^2J_{P,C}$ = 6.5 Hz, $^1J_{P,W}$ = 127.1 Hz, *cis*-*C*O), 198.3 ($d_{sat}$, $^2J_{P,C}$ = 35.7 Hz, $^1J_{P,W}$ = 144.5 Hz, *trans*-*C*O).

**$^{31}$P NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 71.2 ($d_{sat}$, $^1J_{P,W}$ = 263.7 Hz, $^1J_{P,H}$ = 342.3 Hz).

**LIFDI-MS ($^{184}$W, selected data):** m/z (%) = 634.1 (100) $[M]^{\bullet+}$, 243.2 (80) $[CPh_3]^+$.

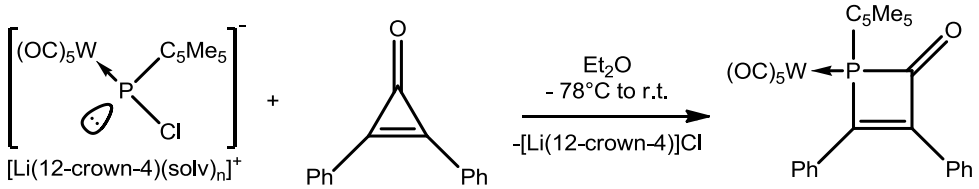
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2351 (w, $\nu$(PH)), 2078 (s, $\nu$(CO)), 1998 (m, $\nu$(CO)), 1925 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 45.42 | H | 2.54 |
| found: | C | 45.32 | H | 2.57 |

**Single crystal measurement:** GSTR534, AKY-602 // GXray4926

## 11.2.6 Synthesis of pentacarbonyl[1-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-3,4-diphenyl-1*H*-phosphet-2-on-κ*P*]tungsten(0) [14.2]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.2** was prepared like described in chapter 11.2.1, starting from 168.3 mg (0.3 mmol) of $[(OC)_5W\{PCl_2(C_5Me_5)\}]$ (**1.2**), but using only 0.8 equivalents of 12-crown-4 (40µL, 0.25 mmol), and 61.8 mg (0.3 mmol, 1.0 eq.) of diphenylcyclopropenone (**12**) were added subsequently as solid. After the addition a rapid formation of a white precipitate and a change of the colour to yellow-orange was observed. The solution was allowed warming up to 0 °C, the cooling bath was removed at this point and stirring was continued for 1 h.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was purified by extraction from the formed salt with *n*-pentane (5 times 10 mL) and subsequent recrystallization by slow evaporation of a saturated *n*-pentane solution at ambient temperature. The product was obtained as orange, crystalline solid after drying in *vacuo* (ca. 0.02 mbar).

**Molecular formula:** $C_{30}H_{25}O_6PW$

**Molecular weight:** 696.330 g/mol

**Melting point:** 126 °C

**Yield:** 103 mg (0.148 mmol, 49 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 1.34 (s, 3H, $C_5Me_5$), 1.44 (d, 3H, $J_{P,H}$ = 13.6 Hz, $C_5Me_5$), 1.75 (s, 3H, $C_5Me_5$), 1.76 (s, 3H, $C_5Me_5$), 2.02 (s, 3H, $C_5Me_5$), 7.30 – 7.70 (m, 10H, Ph).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 11.5 (d, $J_{P,C}$ = 1.5 Hz, $C_5Me_3$), 11.5 (d, $J_{P,C}$ = 1.5 Hz, $C_5Me_3$), 11.8 (s, $C_5Me_3$), 12.1 (d, $J_{P,C}$ = 1.6 Hz, $C_5Me_3$), 17.5 (d, $J_{P,C}$ = 2.9 Hz, $C_5Me_3$), 62.4 (d, $^1J_{P,C}$ = 9.9 Hz, $C_5Me_5$), 128.4 (s, $CH_{Ar}$), 128.5 (s, $CH_{Ar}$), 128.9 (d, $J_{P,C}$ = 14.9, *C*=C), 128.9 (s, 4 times $CH_{Ar}$), 129.2 (s, 2 times $CH_{Ar}$), 130.2 (s, $CH_{Ar}$), 131.0 (d, $J_{P,C}$ = 0.8 Hz, $CH_{Ar}$), 133.9 (d, $J_{P,C}$ = 9.8 Hz, *C*=C), 136.0 (d, $J_{P,C}$ = 3.6 Hz, *ipso-C*), 136.4 (d, $J_{P,C}$ = 0.6 Hz, *ipso-C*), 141.4 (d, $J_{P,C}$ = 5.8 Hz, *C*=C), 142.7 (d, $J_{P,C}$ = 7.1 Hz, *C*=C), 151.6 (d, $^1J_{P,C}$ = 46.2 Hz, P-*C*=C), 172.0 (d, $^2J_{P,C}$ = 23.6 Hz, P-C=*C*), 193.1 (d, $^1J_{P,C}$ = 26.5 Hz, *C*=O), 195.6 (dq$_{sat}$, $^1J_{W,C}$ = 125.1 Hz, $^2J_{P,C}$ = 6.1 Hz, *cis-C*O), 198.2 (d$_{sat}$,$^1J_{W,P}$ = 144.7 Hz, $^2J_{P,C}$ = 26.0 Hz, *trans-CO*).

**$^{31}$P{1H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 111.0 (s$_{sat}$, $^1J_{W,P}$ = 233.5 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 696.1 (1) $[M]^{\bullet+}$, 668.1 (50) $[M - CO]^+$, 640.1 (5) [M - 2 CO]$^+$, 612.1 (10) [M - 3 CO]$^+$, 584.1 (10) [M - 4 CO]$^+$, 556.1 (1) [M - 5 CO]$^+$, 561.0 (30) [M - $C_5Me_5$]$^+$, 533.0 (10) [M - $C_5Me_5$ - CO]$^+$, 505.0 (45) [M - $C_5Me_5$ - 2 CO]$^+$, 477.0 (50) [M - $C_5Me_5$ - 3 CO]$^+$, 449.0 (100) [M - $C_5Me_5$ - 4 CO]$^+$, 421.0 (15) [M - $C_5Me_5$ - 5 CO]$^+$, 393.0 (50) [M - $C_5Me_5$ - 6 CO]$^+$, 209.0 (25) [M - $C_5Me_5$ - CO - $W(CO)_5$]$^+$, 178.0 (60) [PhCCPh]$^+$, 135.1 (60) [$C_5Me_5$]$^+$, 119.1 (40) [$C_5Me_5$ - $CH_4$]$^+$, 105.0 (15) [$C_5Me_5$ - $C_2H_6$]$^+$.

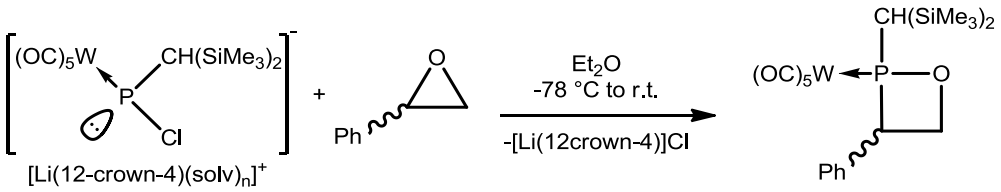
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2071 (m, $\nu$(CO)), 1991 (w, $\nu$(CO)), 1913 (vs, $\nu$(CO)) , 1729 (m, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 51.75 | H | 3.62 |
| found: | C | 52.00 | H | 3.67 |

**Single crystal measurement:** GSTR466, AKY-536 // GXraycu_4526f

## 11.2.7 Synthesis of pentacarbonyl{2-[bis(trimethylsilyl)methyl]-3-phenyl-1,2-oxaphosphetane-κ*P*}tungsten(0) [16.1]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.1** was prepared like described from 292.5 mg (0.5 mmol) of $[(OC)_5W\{P(CH(SiMe_3)_2)Cl_2\}]$ (**1.1**) and 0.06 mL (0.52 mmol, 1.04 eq.) of styrene oxide (**15**) was added subsequently. The solution was allowed warming up to ambient temperature and during the warming up period formation of a white precipitate was observed.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was separated from the formed salt by extraction with 3 times 15 mL of *n*-pentane, followed by low temperature column chromatography ($SiO_2$, -20 °C, eluents: petroleum ether, petroleum ether/diethyl ether 10:0,1) and obtained as white solid from the second fraction after removing of all volatiles in *vacuo* (ca. 0.02 mbar). The product was recrystallized by slow evaporation of a saturated *n*-pentane solution at 4 °C to yield colorless crystals. It was obtained as mixture of different isomers and all data are given for the mixture.

**Molecular formula:** $C_{20}H_{27}O_6PSi_2W$

**Molecular weight:** 634.410 g/mol

**Melting point:** 181 °C (dec.)

**Yield:** 128.0 mg (0.20 mmol, 40 %)

**Isomeric ratio:** 40 : 4 : 53 : 3

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.29 (s, 9H, Si(C*H*$_3$)$_3$), 0.40 (s, 9H, Si(C*H*$_3$)$_3$), 2.25 (d, 1H, $^2J_{P,H}$ = 6.4 Hz, P-C*H*), 4.93 – 5.10 (m, 1H, C*H*), 5.02 – 5.15 (m, 2H, C*H*$_2$), 7.30 – 7.56 (m, 5H, Ph).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.3 (s, Si(*C*H$_3$)$_3$), 2.4 (s, Si(*C*H$_3$)$_3$), 41.0 (d, $^1J_{P,C}$ = 16.6 Hz, *C*H), 52.1 (d, $^1J_{P,C}$ = 21.3 Hz, *C*H), 74.9 (d, $^2J_{P,C}$ = 15.9 Hz, O-*C*H$_2$), 128.1 (d, $^5J_{P,C}$ = 3.7 Hz, *para*-*C*H$_{Ar}$), 128.9 (d, $J_{P,C}$ = 3.0 Hz, *C*H$_{Ar}$), 129.1 (d, $J_{P,C}$ = 5.4 Hz, *C*H$_{Ar}$), 136.0 (s$_{br}$, *ipso*-*C*), 196.6 (d$_{sat}$, $^1J_{W,C}$ = 126.1 Hz, $^2J_{P,C}$ = 7.7 Hz, *cis*-*C*O), 200.1 (d, $^2J_{P,C}$ = 25.0, *trans*-*C*O).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 220.2 (s$_{sat}$, $^1J_{W,P}$ = 275.4 Hz).

***Isomer 2:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = -0.20 (s, 9H, Si(C*H*$_3$)$_3$), 1.70 (d, 1H, $^2J_{P,H}$ = 4.0 Hz, P-C*H*), 3.89 (ddd, $^3J_{H,H}$ = 9.9 Hz, $^2J_{H,H}$ = 8.7 Hz, $^3J_{P,H}$ = 0.7 Hz, C*H*$_2$), 4.54 (ddd, 1H, $^3J_{P,H}$ = 19.0 Hz, $^2J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 5.9 Hz, C*H*$_2$), 5.39 (dd, 1H, $^3J_{H,H}$ = 9.9 Hz, $^3J_{H,H}$ = 5.9, C*H*), 7.30 – 7.55 (m, 5H, Ph).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** δ = 2.1 (d, $^3J_{P,C}$ = 4.2 Hz Si(*C*H$_3$)$_3$), 40.5 (s$_{br}$, *C*H), 58.7 (d, $^1J_{P,C}$ = 19.8 Hz, *C*H), 70.4 (s$_{br}$, O-*C*H$_2$), 124.7 (s$_{br}$, *para-C*H$_{Ar}$), 126.1 (s, *C*H$_{Ar}$), 128.8 (s, *C*H$_{Ar}$), 135.4 (s$_{br}$, *ipso-C*), 196.6 (d, $^2J_{P,C}$ = 9.1 Hz, *cis-C*O), 201.1 (d, $^2J_{P,C}$ = 26.8, *trans-C*O).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 210.7 (s$_{br}$).

***Isomer 3:***

**$^1H$ NMR (300.1 MHz, $CDCl_3$):** δ = 0.29 (s, 9H, Si(C*H*$_3$)$_3$), 0.35 (s, 9H, Si(C*H*$_3$)$_3$), 2.59 (d, 1H, $^2J_{P,H}$ = 19.4 Hz, P-C*H*), 4.86 (ddd, 1H, $^3J_{H,H}$ = 8.0 Hz, $^2J_{H,H}$ = 7.0, $^3J_{P,H}$ = 5.9, C*H*$_2$), 5.05 (dd, 1H, $^3J_{H,H}$ = 8.4 Hz, $^2J_{H,H}$ = 7.0 Hz, C*H*$_2$), 5.26 (ddd, 1H, $^2J_{P,H}$ = 12.7 Hz, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 8.0 Hz, C*H*), 7.30 – 7.55 (m, 5H, Ph).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** δ = 2.5 (d, $^3J_{P,C}$ = 2.5 Hz, Si(*C*H$_3$)$_3$), 2.8 (d, $^3J_{P,C}$ = 2.6 Hz, Si(*C*H$_3$)$_3$), 28.5 (d, $^1J_{P,C}$ = 34.0 Hz, *C*H), 58.6 (d, $^1J_{P,C}$ = 22.5 Hz, *C*H), 74.0 (d, $^2J_{P,C}$ = 16.0 Hz, O-*C*H$_2$), 127.8 (d, $^5J_{P,C}$ = 3.0 Hz, *para-C*H$_{Ar}$), 128.9 (d, $J_{P,C}$ = 4.1 Hz, *C*H$_{Ar}$), 129.0 (d, $J_{P,C}$ = 3.0 Hz, *C*H$_{Ar}$), 135.9 (d, $^2J_{P,C}$ = 10.2 Hz, *ipso-C*), 197.2 (d$_{sat}$, $^1J_{W,C}$ = 126.0 Hz, $^2J_{P,C}$ = 7.8 Hz, *cis-C*O), 199.1 (d, $^2J_{P,C}$ = 26.8, *trans-C*O).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 195.1 (s$_{sat}$, $^1J_{W,P}$ = 273.1 Hz).

***Isomer 4:***

**$^1H$ NMR (300.1 MHz, $CDCl_3$):** δ = 0.09 (s, 9H, Si(C*H*$_3$)$_3$), 0.40 (s, 9H, Si(C*H*$_3$)$_3$), 2.29 (d, 1H, $^2J_{P,H}$ = 19.5 Hz, P-C*H*), 3.42 – 3.53 (m, 1H, C*H*$_2$), 3.70 – 4.00 (m, 1H, C*H*$_2$), 6.00 – 6.20 (m, 1H, C*H*), 7.30 – 7.55 (m, 5H, Ph).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** Due to the isomers low percentage of the mixture only very few resonance signals could be observed in the $^{13}C\{^1H\}$ NMR: δ = 2.4 (d, $^3J_{P,C}$ = 4.3 Hz, Si(*C*H$_3$)$_3$), 128.1 (s, *para-C*H$_{Ar}$), 128.5 (s, *C*H$_{Ar}$), 128.8 (s, *C*H$_{Ar}$), 196.9 (d, $^2J_{P,C}$ = 7.7 Hz, *cis-C*O).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 179.7 (s$_{sat}$, $^1J_{W,P}$ = 281.1 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 650.1 (5) $[M + O]^+$, 634.1 (1) $[M]^{\bullet+}$, 619.1 (5) $[M - O]^+$, 530.0 (90) [M - styrene]$^+$, 501.9 (30) [M - styrene - CO]$^+$, 474.0 (30) [M - styrene - 2 CO]$^+$, 446.0 (50) [M - styrene - 3 CO]$^+$, 418.0 (60) [M - styrene - 4 CO]$^+$, 389.9 (80) [M - styrene - 5 CO]$^+$, 104.0 (30) [styrene]$^+$, 73.1 (100) $[SiMe_3]^+$.

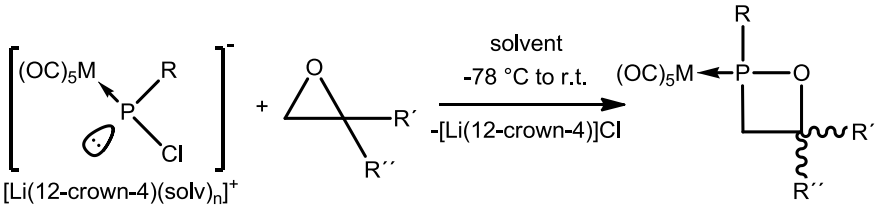
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2071 (s, ν(CO)), 1986 (m, ν(CO)), 1895 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 37.86 | H | 4.29 |
| found: | C | 38.10 | H | 4.41 |

**Single crystal measurement:** AKY-295 GSTR314, 2987f

## 11.2.8 Syntheses of 4-substituted 1,2-oxaphosphetane complexes:

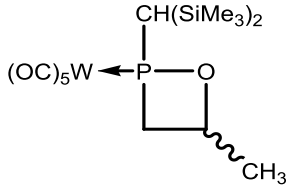



Solutions of the Li/Cl phosphinidenoid complexes **2.1**-**2.3** were prepared starting from complexes **1.1**-**1.3** as described in chapter 11.2.1. The corresponding epoxide was added via syringe and the solution was allowed slowly warming up. During the warming up period formation of a white precipitate was observed. The cooling bath was removed after reaching 0 °C and the solution was stirred for further 30 min.

***Table 11.2:*** Used amounts of dichloro(organo)phosphane complexes and epoxides for the syntheses of 1,2-oxaphosphetane complexes.

| | M | R | R´ | R´´ | m (**1**) [mg] | n (**1**) [mmol] | epoxide | V (epoxide) [mL] | n (epoxide) [mmol] |
|---|---|---|---|---|---|---|---|---|---|
| **21.1a$_W$** | W | $CH(SiMe_3)_2$ | H | $CH_3$ | 292.5 | 0.5 | **20a** | 0.04 | 0.57 |
| **21.1a$_{Mo}$** | Mo | $CH(SiMe_3)_2$ | H | $CH_3$ | 497.3 | 1.0 | **20a** | 0.15 | 2.14 |
| **21.1a$_{Cr}$** | Cr | $CH(SiMe_3)_2$ | H | $CH_3$ | 453.3 | 1.0 | **20a** | 0.15 | 2.14 |
| **21.1b** | W | $CH(SiMe_3)_2$ | H | Et | 292.5 | 0.5 | **20b** | 0.1 | 1.15 |
| **21.1c** | W | $CH(SiMe_3)_2$ | H | $^{i}Pr$ | 292.5 | 0.5 | **20c** | 0.1 | 0.95 |
| **21.1d** | W | $CH(SiMe_3)_2$ | H | $^{t}Bu$ | 58.5 | 0.1 | **20d** | 0.012 | 0.1 |
| **21.1e** | W | $CH(SiMe_3)_2$ | H | $CH_2Cl$ | 292.5 | 0.5 | **20e** | 0.04 | 0.51 |
| **21.1f** | W | $CH(SiMe_3)_2$ | H | $C_2H_3O$ | 292.5 | 0.5 | **20f** | 0.045 | 0.5 |
| **21.1g** | W | $CH(SiMe_3)_2$ | H | $CF_3$ | 585.0 | 1.0 | **20g** | 0.095 | 1.1 |
| **25.1a** | W | $CH(SiMe_3)_2$ | $CH_3$ | $CH_3$ | 585.0 | 1.0 | **24a** | 0.15 | 1.68 |
| **25.1b** | W | $CH(SiMe_3)_2$ | $CF_3$ | $CF_3$ | 585.0 | 1.0 | **24b** | 0.13 | 1.1 |
| **21.2a** | W | $C_5Me_5$ | H | $CH_3$ | 56.1 | 0.1 | **20a** | 0.01 | 0.14 |
| **21.2e** | W | $C_5Me_5$ | H | $CH_2Cl$ | 56.1 | 0.1 | **20e** | 0.01 | 0.13 |
| **21.1g** | W | $C_5Me_5$ | H | $CF_3$ | 561.0 | 1.0 | **20g** | 0.095 | 1.1 |
| **25.2b** | W | $C_5Me_5$ | $CF_3$ | $CF_3$ | 561.0 | 1.0 | **24b** | 0.13 | 1.1 |
| **21.3a** | W | $CPh_3$ | H | $CH_3$ | 334.5 | 0.5 | **20a** | 0.1 | 1.4 |
| **21.3d** | W | $CPh_3$ | H | $^{t}Bu$ | 66.9 | 0.1 | **20d** | 0.013 | 0.11 |
| **21.3g** | W | $CPh_3$ | H | $CF_3$ | 669.0 | 1.0 | **20g** | 0.13 | 1.1 |
| **25.3b** | W | $CPh_3$ | $CF_3$ | $CF_3$ | 501.8 | 0.75 | **24b** | 0.081 | 0.75 |

### 11.2.8.1 Pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1a$_W$]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was separated from the formed salt by extraction with 3 times 15 mL *n*-pentane followed by low temperature column chromatography ($SiO_2$, -20 °C, eluent: petroleum ether, petroleum ether/diethyl ether 10:0,1). The crude product was obtained as a solid from the second fraction after removal of all volatiles in *vacuo* (ca 0.02 mbar). It was recrystallized by slow evaporation of a saturated *n*-pentane solution at 4 °C to yield colourless crystals and the product was obtained as mixture of different isomers. All data are given for the mixture.

**Molecular formula:** $C_{15}H_{25}O_6PSi_2W$

**Molecular weight:** 572.340 g/mol

**Melting point:** 97 - 99 °C

**Yield:** 165 mg (0.29 mmol, 58 %)

**Isomeric ratio:** 30 : 4 : 19 : 47

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.27 (s, 9H, Si(C*H*$_3$)$_3$), 0.31 (s, 9H, Si(C*H*$_3$)$_3$), 1.64 (d, 3H, $^4J_{P,H}$ = 6.2 Hz, C*H*$_3$), 1.99 (d, 1H, $^2J_{P,H}$ = 6.2 Hz, P-C*H*), 3.04 (dd, 1H, $^2J_{P,H}$ = 13.9 Hz, $J_{H,H}$ = 6.20 Hz, C*H*$_2$), 3.49 – 3.67 (m, 1H, C*H*$_2$), 5.19 – 5.40 (m, 1H, C*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.0 (d, $^2J_{P,C}$ = 3.6 Hz, Si(*C*H$_3$)$_3$), 25.3 (d, $^3J_{P,C}$ = 5.0 Hz, *C*H$_3$), 38.1 (d, $^1J_{P,C}$ = 12.9 Hz, P-*C*H), 40.5 (d, $^1J_{P,C}$ = 29.3 Hz, P-*C*H$_2$), 78.9 (d, $^2J_{P,C}$ = 13.1 Hz, O-*C*H), 197.3 (d, $^2J_{P,C}$ = 7.7 Hz, *cis*-*C*O), 199.1 (d, $^2J_{P,C}$ = 23.1 Hz, *trans*-*C*O).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 176.4 ($s_{sat}$, $^1J_{W,P}$ = 273.4 Hz).

***Isomer 2:***

No resonance signals except in the $^{31}$P NMR and the $^1$H NMR signal of the C*H*(SiMe$_3$)$_2$ group could be observed due to the isomers low percentage of the mixture.

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 2.46 ppm ($^2J_{P,H}$ ~ 19 Hz).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 169.2 ($s_{br}$).

***Isomer 3:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.27 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 1.51 (s, 3H, C$H_3$), 2.24 (d, 1H, $^{2}J_{P,H}$ = 19.5 Hz, P-C*H*), 2.77-2.94 (m, 1H, C$H_2$), 3.45 – 3.59 (m, 1H, C$H_2$), 5.05 – 5.21 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 1.9 (d, $^{2}J_{P,C}$ = 3.8 Hz, Si(*C*H$_3$)$_3$), 27.5 (s$_{br,}$ *C*H$_3$), 37.6 (d, $^{1}J$ = 10.6 Hz, P-*C*H), 48.7 (d, $^{1}J_{P,C}$ = 28.3 Hz, P-*C*H$_2$), 76.8 (d, $^{2}J_{P,C}$ = 13.3 Hz, O-*C*H), 198.0 (d, $^{2}J_{P,C}$ = 8.1 Hz, *cis*-*C*O), the resonance signal for the *trans*-CO could not be observed due to its low intensity.

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 164.5 (s$_{sat}$, $^{1}J_{W,P}$ = 267.8 Hz).

***Isomer 4:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.27 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 1.50 (d, 3H, $^{4}J_{P,H}$ = 6.3 Hz, C$H_3$), 1.93 (d, 1H, $^{2}J_{P,H}$ = 6.0 Hz, P-C*H*), 3.20 (dd, 1H, $^{2}J_{P,H}$ = 12.6 Hz, $J_{H,H}$ = 6.1 Hz, C$H_2$), 3.25 – 3.42 (m, 1H, C$H_2$), 5.05 – 5.21 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 2.4 (d, $^{2}J_{P,C}$ = 1.6 Hz, Si(*C*H$_3$)$_3$), 2.7 (d, $^{2}J_{P,C}$ = 2.0 Hz, Si(*C*H$_3$)$_3$), 25.3 (d, $^{3}J_{P,C}$ = 5.8 Hz, *C*H$_3$), 38.4 (d, $^{1}J_{P,C}$ = 12.4 Hz, P-*C*H), 44.9 (d, $^{1}J_{P,C}$ = 25.1 Hz, P-*C*H$_2$), 75.8 (d, $^{2}J_{P,C}$ = 14.0 Hz, O-*C*H), 197.1 (d$_{sat}$, $^{1}J_{W,C}$ = 124.2 Hz, $^{2}J_{P,C}$ = 7.7 Hz, *cis*-*C*O), 200.1 (d, $^{2}J_{P,C}$ = 25.0, *trans*-*C*O).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 164.4 (s$_{sat}$, $^{1}J_{W,P}$ = 268.7 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 572.0 (40) $[M]^{\bullet+}$, 544.0 (1) $[M\text{-}CO]^{+}$, 530.0 (5) $[M - C_3H_6]^{+}$, 516.0 (2) $[M - 2\ CO]^{+}$, 502.0 (5) $[M - C_3H_6 - CO]^{+}$, 488.1 (10) $[M - 3\ CO]^{+}$, 474.0 (20) $[M - C_3H_6 - 2\ CO]^{+}$, 460.1 (2) $[M - 4\ CO]^{+}$, 446.0 (30) $[M - C_3H_6 - 3\ CO]^{+}$, 432.1 (10) $[M - 5\ CO]^{+}$, 418.0 (50) $[M - C_3H_6 - 4\ CO]^{+}$, 390.0 (5) $[M - C_3H_6 - 5\ CO]^{+}$, 73.1 (50) $[SiMe_3]^{+}$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2069 (s, $\nu$(CO)), 1987 (w, $\nu$(CO)), 1899 (vs, $\nu$(CO)).

**Elemental analysis:**

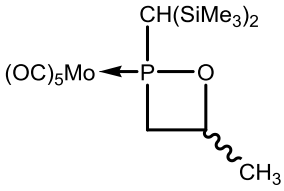
| | | | | |
|---|---|---|---|---|
| calc.: | C | 31.48 | H | 4.40 |
| found: | C | 31.46 | H | 4.56 |

**Single crystal measurement:** AKY-301 GSTR321, 3087

### 11.2.8.2 Synthesis of pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1a$_W$] using R(+)-propylene oxide

The synthesis was performed analogue to the one using the racemic mixture of the epoxide starting from 58.5 mg (0.1 mmol) of complex **1.1**. The reaction mixture was analysed by $^{31}P\{^1H\}$ NMR after reaching ambient temperature. The $^{31}P$ NMR spectrum shows no significant difference to the one obtained for a reaction mixture using the racemic mixture of propylene oxide.

### 11.2.8.3 Pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}molybdenum(0) [21.1a$_{Mo}$]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was separated from the formed salt by extraction with 3 times 8 mL diethyl ether. The crude product was obtained as an oil after removal of all volatiles in *vacuo* (ca. 0.02 mbar). The product was then precipitated from *n*-pentane at -100 °C and subsequently recrystallized by slow evaporation of a saturated *n*-pentane solution at 4 °C to yield colourless crystals. The product was obtained as mixture of different isomers and all data are given for the mixture.

**Molecular formula:** $C_{15}H_{25}O_6PSi_2Mo$

**Molecular weight:** 484.86 g/mol

**Melting point:** 80-81 °C

**Yield:** 132 mg (0.27 mmol, 27 %)

**Isomeric ratio:** 30 : 6 : 46 : 18

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.26 (s, 9H, Si(C*H*$_3$)$_3$), 0.30 (s, 9H, Si(C*H*$_3$)$_3$), 1.63 (d, 3H, $^4J_{P,H}$ = 5.9 Hz, C*H*$_3$), 1.78 (d, 1H, $^2J_{P,H}$ = 3.80 Hz, P-C*H*), 2.79 – 2.95 (m, 1H, C*H*$_2$) , 3.25 – 3.49 (m, 1H, C*H*$_2$), 5.02 – 5.26 (m, 1H, C*H*).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** δ = 2.0 – 3.0 (m, Si(*C*H$_3$)$_3$), 25.7 (d, $^3J_{P,C}$ = 4.2 Hz, *C*H$_3$), 38.2 (d, $^1J_{P,C}$ = 18.0 Hz, P-*C*H), 40.5 (d, $^1J_{P,C}$ = 26.6 Hz, P-*C*H$_2$), 79.6 (d, $^2J_{P,C}$ = 13.3 Hz, O-*C*H), 205.7 (d, $^2J_{P,C}$ = 10.0 Hz, *cis*-*C*O), 210.6 ($d_{br}$, $^2J_{P,C}$ = ca. 27 Hz, *trans*-*C*O).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 209.8 (s).

***Isomer 2:***

No resonance signals except in the $^{31}P$ NMR could be observed due to the isomers low percentage of the mixture.

**$^{31}P\{^1H\}$ NMR** (121.5 MHz, 25 °C, $CDCl_3$, in ppm): $\delta$ = 201.0 (s).

***Isomer 3:***

**$^1H$ NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.26 (s, 9H, Si(C$H_3$)$_3$), 0.30 (s, 9H, Si(C$H_3$)$_3$), 1.48 (d, 3H, $^4J_{P,H}$ = 5.8 Hz, C$H_3$), 1.72 (d, 1H, $^2J_{P,H}$ = 3.3 Hz, P-C*H*), 2.96 – 3.22 (m, 2H, C$H_2$), 5.02 – 5.26 (m, 1H, C*H*).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 2.0 – 3.0 (m, Si(*C*H$_3$)$_3$), 25.5 (d, $^3J_{P,C}$ = 4.5 Hz, *C*H$_3$), 38.6 (d, $^1J_{P,C}$ = 18.4 Hz, P-*C*H), 44.5 (d, $^1J_{P,C}$ = 21.0 Hz, P-*C*H$_2$), 76.0 (d, $^2J_{P,C}$ = 12.6 Hz, O-*C*H), 205.7 (d, $^2J_{P,C}$ = 10.0 Hz, *cis*-*C*O), 210.6 (d$_{br}$, $^2J_{P,C}$ = ca. 27 Hz, *trans*-*C*O).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 196.2 (s).

***Isomer 4:***

**$^1H$ NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.26 (s, 9H, Si(C$H_3$)$_3$), 0.30 (s, 9H, Si(C$H_3$)$_3$), 1.53 (d, 3H, $^4J_{P,H}$ = 6.7 Hz, C$H_3$), 1.96 (d, 1H, $^2J_{P,H}$ = 18.1 Hz, P-C*H*), 2.52 – 2.70 (m, 1H, C$H_2$), 3.25 – 3.49 (m, 1H, C$H_2$), 5.02 – 5.26 (m, 1H, C*H*).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 2.0 – 3.0 (m, Si(*C*H$_3$)$_3$), 27.6 (s$_{br}$, *C*H$_3$), 40.5 (overlapping with the signal of a $CH_2$), 48.3 (d, $^1J_{P,C}$ = 22.6 Hz, P-*C*H$_2$), 77.3 (d, $^2J_{P,C}$ = 13.0 Hz, *C*H), 205.7 (d, $^2J_{P,C}$ = 10.0 Hz, *cis*-*C*O), 210.6 (d$_{br}$, $^2J_{P,C}$ = ca 27 Hz, *trans*-*C*O).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 195.7 (s).

**MS (EI, 70 eV, $^{98}$Mo, selected data):** m/z (%) = 486.0 (40) $[M]^{\bullet+}$, 458.0 (5) $[M\text{-}CO]^+$, 430.0 (5) [M - 2 CO]$^+$, 416.0 (40) [M - CO - $C_3H_6$]$^+$, 402.0 (30) [M - 3 CO]$^+$, 388.0 (60) [M - 2 CO - $C_3H_6$]$^+$, 374.0 (10) [M - 4 CO]$^+$, 360.0 (30) [M - 3 CO - $C_3H_6$]$^+$, 344.0 (40) [M - 5 CO]$^+$, 332.0 (50) [M - 4 CO - $C_3H_6$]$^+$, 304.0 (90) [M - $C_3H_6$ - 5 CO]$^+$, 73.1 (50) $[SiMe_3]^+$.

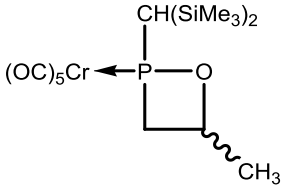
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2070 (s, $\nu$(CO)), 1993 (w, $\nu$(CO)), 1993 (m, $\nu$(CO)), 1911 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 37.19 | H | 5.20 |
| found: | C | 37.08 | H | 5.32 |

**Single crystal measurement:** GSTR370, 3621.

### 11.2.8.4 Pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}chromium(0) [21.1a$_{Cr}$]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was separated from the formed salt by extraction with three times 8 mL of diethyl ether. The crude product was obtained as green oil after removal of all volatiles in *vacuo* (ca. 0.02 mbar). The product was precipitated from *n*-pentane at -100 °C, the supernatant was filtered off and the product subsequently recrystallized by slow evaporation of a saturated *n*-pentane solution at 4 °C, yielding slightly green coloured crystals. The product was obtained as mixture of different isomers and all data are given for the mixture.

**Molecular formula:** $C_{15}H_{25}O_6PSi_2Cr$

**Molecular weight:** 440.496 g/mol

**Melting point:** 76 - 77 °C

**Yield:** 50 mg (0.11 mmol, 11 %)

**Isomeric ratio:** 23 : 3 : 14 : 60

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.26 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 1.63 (d, 3H, $^4J_{P,H}$ = 6.0 Hz, C$H_3$), 1.88 (d, 1H, $^2J_{P,H}$ = 6.80 Hz, P-C*H*), 2.92 – 3.04 (m, 1H, C$H_2$) , 3.36 – 3.50 (m, 1H, C$H_2$), 5.10 – 5.30 (m, 1H, C*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.1 (d, $^2J_{P,C}$ = 3.9 Hz, Si(*C*H$_3$)$_3$), 2.6 (d, $^2J_{P,C}$ = 1.9 Hz, Si(*C*H$_3$)$_3$), 25.1 (d, $^3J_{P,C}$ = 4.8 Hz, *C*H$_3$), 38.2 (d, $^1J_{P,C}$ = 17.5 Hz, P-*C*H), 40.4 (d, $^1J_{P,C}$ = 25.5 Hz, *C*H$_2$), 79.4 (d, $^2J_{P,C}$ = 12.6 Hz, O-*C*H), 216.4 (d, $J_{P,C}$ = 15.2 Hz, *cis*-*C*O), 221.4 (d, $J_{P,C}$ = 6.8 Hz, *trans*-*C*O).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 233.1 (s).

***Isomer 2:***

No resonance signals except in the $^{31}$P NMR and the $^1$H NMR signal of the C*H*(SiMe$_3$)$_2$ group could be observed due to the isomers low percentage of the mixture.

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 2.30 ($^2J_{P,H}$ = 20.3 Hz).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 226.7 (s).

***Isomer 3:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.26 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 1.52 (d, 3H, $^{4}J_{P,H}$ = 6.4 Hz, C$H_3$), 2.09 (d, 1H, $^{2}J_{P,H}$ = 20.0 Hz, P-C*H*), 2.59 – 2.73 (m, 1H, C$H_2$), 3.36 – 3.50 (m, 1H, C$H_2$), 5.10 – 5.30 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** δ = 22.3 (d, $^{2}J_{P,C}$ = 3.9 Hz, Si(*C*H$_3$)$_3$), 2.6 (d, $^{2}J_{P,C}$ = 3.2 Hz, Si(*C*H$_3$)$_3$), 27.5 ($s_{br,}$ *C*H$_3$), 42.2 (d, $^{1}J_{P,C}$ = 34.3 Hz, P-*C*H), 47.9 (d, $^{2}J_{P,C}$ = 23.9 Hz, P-*C*H$_2$), 77.3 (d, $^{2}J_{P,C}$ = 13.0 Hz, O-*C*H), 216.4 (d, $^{2}J_{P,C}$ = 14.5 Hz, *cis*-CO), the resonance signal for the *trans*-CO could not be observed due to its low intensity.

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 222.6 (s).

***Isomer 4:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.26 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 1.49 (d, 3H, $J_{P,H}$ = 6.4 Hz, C$H_3$), 1.84 (d, 1H, $^{2}J_{P,H}$ = 6.1 Hz, P-C*H*), 3.10 – 3.29 (m, 2H, C$H_2$), 5.05 – 5.21 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.2 (d, $^{2}J_{P,C}$ = 3.6 Hz, Si(*C*H$_3$)$_3$), 2.9 (d, $^{2}J_{P,C}$ = 2.3 Hz, Si(*C*H$_3$)$_3$), 25.4 (d, $^{3}J_{P,C}$ = 5.5 Hz, *C*H$_3$), 38.8 (d, $^{1}J_{P,C}$ = 17.1 Hz, P-*C*H), 44.3 (d, $^{1}J_{P,C}$ = 21.3 Hz, P-*C*H$_2$), 76.2 (d, $^{2}J_{P,C}$ = 12.9 Hz, O-*C*H), 216.5 (d, $^{2}J_{P,C}$ = 14.9 Hz, *cis*-*C*O), 221.2 (d, $^{2}J_{P,C}$ = 7.1, *trans*-*C*O).

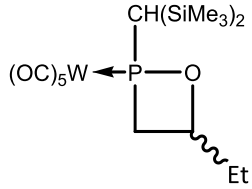
**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 221.0 (s)

**MS (EI, 70 eV, $^{52}$Cr, selected data):** m/z (%) = 440.1 (15) $[M]^{\bullet+}$, 370.0 (5) $[M - CO - C_3H_6]^+$, 328.1 (20) $[M - 4\ CO]^+$, 314.0 (5) $[M - 3\ CO - C_3H_6]^+$, 300.1 (100) $[M - 5\ CO]^+$, 286.0 (15) $[M - 4\ CO - C_3H_6]^+$, 258.1 (20) $[M - 5\ CO - C_3H_6]^+$, 73.1 (10) $[SiMe_3]^+$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2061 (s, ν(CO)), 1986 (w, ν(CO)), 1973 (w, ν(CO)), 1944 (m, ν(CO)), 1910 (vs, ν(CO)).

**Single crystal measurement:** GSTR369, 3648.

## 11.2.8.5 Pentacarbonyl{4-ethyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1b]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was separated from the formed salt by extraction with 4 times 20 mL of *n*-pentane. The *n*-pentane was removed in *vacuo* (ca. 0.02 mbar) followed by dissolving in 2 mL *n*-Pentane, precipitation at - 80 °C and filtering off the supernatant solvent. This procedure was repeated two times and the product was obtained as white powder as a mixture of different isomers. All data are given for the mixture.

**Molecular formula:** $C_{16}H_{27}O_6PSi_2W$

**Molecular weight:** 586.367 g/mol

**Melting point:** 85 °C

**Yield:** 92 mg (0.157 mmol, 31 %)

**Isomeric ratio:** 29 : 4 : 23 : 44

***Isomer 1:***

**$^1$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.27 (s, 9H, Si(C*H*$_3$)$_3$), 0.31 (s, 9H, Si(C*H*$_3$)$_3$), 0.86 – 0.96 (m, 3H, C*H*$_3$), 1.62 – 1.77 (m, 2H, C*H*$_2$), 1.99 (d, 1H, $^2J_{P,H}$ = 6.9 Hz, P-C*H*), 2.96 – 3.05 (m, 1H, P-C*H*$_2$), 3.45 – 3.56 (m, 1H, P-C*H*$_2$), 4.86 – 4.97 (m, 1H, C*H*).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.1 (d, $^2J_{P,C}$ = 3.1 Hz, Si(*C*H$_3$)$_3$), 2.5 (s, Si(*C*H$_3$)$_3$), 9.0 (s, *C*H$_3$), 32.0 (d, $^3J_{P,C}$ = 3.7 Hz, *C*H$_2$), 38.3 (d, $^1J_{P,C}$ = 13.0 Hz, P-*C*H), 39.0 (d, $^1J_{P,C}$ = 28.9 Hz, P-*C*H$_2$), 83.7 (d, $^2J_{P,C}$ = 13.0 Hz, O-*C*H), 197.4 (d$_{sat}$, $^2J_{P,C}$ = 7.7 Hz, $^1J_{W,C}$ = 125.6 Hz, *cis*-*C*O), 200.7 (d, $^2J_{P,C}$ = 25.8 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** δ = -1.85 (d, $^2J_{P,Si}$ = 3.1 Hz, *Si*(CH$_3$)$_3$), 0.44 (d, $^2J_{P,Si}$ =6.9 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 177.1 (s$_{sat}$, $^1J_{W,P}$ = 274.8 Hz).

***Isomer 2:***

No resonance signals except in the $^{31}$P NMR could be observed due to the isomers low percentage of the mixture.

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 169.8 (s$_{br}$, $^1J_{W,P}$ = ca. 271 Hz).

***Isomer 3:***

**$^{1}$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.27 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 0.86 – 0.96 (m, 3H, C$H_3$), 2.00 – 2.11 (m, 2H, C$H_2$), 2.21 (d, 1H, $^{2}J_{P,H}$ = 19.5 Hz, P-C*H*), 2.78 – 2.89 (m, 1H, P-C$H_2$), 3.37 – 3.45 (m, 1H, P-C$H_2$), 4.86 – 4.97 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.2 (s, Si(*C*H$_3$)$_3$), 2.5 (s, Si(*C*H$_3$)$_3$), 8.5 (s, *C*H$_3$), 34.1 (s, *C*H$_2$), 40.1 (d, $^{1}J_{P,C}$ = 28.3 Hz, P-*C*H), 46.8 (d, $^{1}J_{P,C}$ = 26.9 Hz, P-*C*H$_2$), 81.3 (d, $^{2}J_{P,C}$ = 13.2 Hz, O-*C*H), 197.2 (d$_{sat}$, $^{2}J_{P,C}$ = 7.6 Hz, $^{1}J_{W,C}$ = 125.1 Hz, *cis*-*C*O), 199.4 (d, $^{2}J_{P,C}$ = 24.8 Hz, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (99.4 MHz, $CDCl_3$):** δ = - 2.76 (d, $^{2}J_{P,Si}$ = 7.4 Hz, *Si*(CH$_3$)$_3$), 0.62 (s, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (202.5 MHz, $CDCl_3$):** δ = 165.1 (s$_{sat}$, $^{1}J_{W,P}$ = 268.4 Hz).

***Isomer 4:***

**$^{1}$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.26 (s, 9H, Si(C$H_3$)$_3$), 0.30 (s, 9H, Si(C$H_3$)$_3$), 0.86 – 0.96 (m, 3H, C$H_3$), 1.80 – 1.96 (m, 2H, C$H_2$), 1.93 (d, 1H, $^{2}J_{P,H}$ = 6.0 Hz, P-C*H*), 3.12 – 3.20 (m, 1H, P-C$H_2$), 3.21 – 3.33 (m, 1H, P-C$H_2$), 4.76 – 4.86 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.2 (s, Si(*C*H$_3$)$_3$), 2.8 (d, $^{2}J_{P,C}$ = 1.7 Hz, Si(*C*H$_3$)$_3$), 8.7 (s, *C*H$_3$), 32.5 (d, $^{3}J_{P,C}$ = 5.6 Hz, *C*H$_2$), 38.7 (d, $^{1}J_{P,C}$ = 12.6 Hz, P-*C*H), 43.5 (d, $^{1}J_{P,C}$ = 24.7 Hz, P-*C*H$_2$), 80.6 (d, $^{2}J_{P,C}$ = 12.8 Hz, O-*C*H), 197.3 (d$_{sat}$, $^{2}J_{P,C}$ = 7.7 Hz, $^{1}J_{W,C}$ = 126.3 Hz, *cis*-*C*O), 200.4 (d, $^{2}J_{P,C}$ = 25.1 Hz, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (99.4 MHz, $CDCl_3$):** δ = -1.37 (d, $^{2}J_{P,Si}$ = 4.3 Hz, *Si*(CH$_3$)$_3$), 0.25 (d, $^{2}J_{P,Si}$ = 6.9 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (202.5 MHz, $CDCl_3$):** δ = 165.0 (s$_{sat}$, $^{1}J_{W,P}$ = 268.8 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 586.0 (35) $[M]^{\bullet+}$, 529.9 (5) $[M - C_4H_8]^+$, 502.0 (35) $[M - C_4H_8 - CO]^+$, 474.0 (25) $[M - C_4H_8 - 2\ CO]^+$, 446.0 (45) $[M - C_4H_8 - 3\ CO]^+$, 418.0 (55) $[M - C_4H_8 - 4\ CO]^+$, 390.0 (100) $[M - C_4H_8 - 5\ CO]^+$, 73.0 (70) $[SiMe_3]^+$.

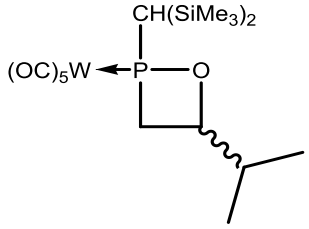
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2072 (s, ν(CO)), 1986 (w, ν(CO)), 1902 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 32.77 | H | 4.64 |
| found: | C | 32.44 | H | 4.72 |

**Single crystal measurement:** GSTR519, AKY-574 // GXray4852f

## 11.2.8.6 Pentacarbonyl{4-(1-methylethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1c]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was purified by low temperature column chromatography (ø = 2 cm, h = 5 cm, $SiO_2$, -20 °C, eluent: petroleum ether, petroleum ether/diethyl ether 10:1). The first fraction using only petroleum ether 40/60 was collected until the first yellow colour faded and contained most of the side products; the product was obtained in the second fraction using a mixture of petroleum ether 40/60 and diethyl ether in the ratio 10:1. After removing of all volatiles in *vacuo* (ca. 0.02 mbar) the crude product was recrystallized by slow evaporation of a saturated *n*-pentane solution at 4 °C to yield colorless crystals. The product was obtained as mixture of different isomers and all data are given for the mixture.

**Molecular formula:** $C_{17}H_{29}O_6PSi_2W$

**Molecular weight:** 600.393 g/mol

**Melting point:** 82 - 83 °C

**Yield:** 60 mg (0.20 mmol, 20 %)

**Isomeric ratio:** 29 : 5 : 24 : 42

***Isomer 1:***

**$^1$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.27 (s, 9H, Si(C*H*$_3$)$_3$), 0.30 (s, 9H, Si(C*H*$_3$)$_3$), 0.80 (d, 3H, $^5J_{P,H}$ = 6.7 Hz, C*H*$_3$), 0.94 – 0.99 (m, 3H, C*H*$_3$), 1.97 (d, 1H, $^2J_{P,H}$ = 6.1 Hz, P-C*H*), 2.11 – 2.20 (m, 1H, C*H*(CH$_3$)$_2$), 3.01 – 3.09 (m, 1H, P-C*H*$_2$), 3.39 – 3.50 (m, 1H, P-C*H*$_2$), 4.47 – 4.55 (m, 1H, C*H*).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.2 (d, $^2J_{P,C}$ = 3.5 Hz, Si(*C*H$_3$)$_3$), 2.6 (s, Si(*C*H$_3$)$_3$), 16.6 (s, *C*H$_3$), 17.9 (s, *C*H$_3$), 36.5 (d, $^3J_{P,C}$ = 3.5 Hz, *C*H(CH$_3$)$_2$), 37.9 (d, $^1J_{P,C}$ = 32.4 Hz, P-*C*H$_2$), 38.2 (d, $^1J_{P,C}$ = 18.1 Hz, P-*C*H), 87.5 (d, $^2J_{P,C}$ = 12.8 Hz, O-*C*H), 197.4 (d$_{sat}$, $^2J_{P,C}$ = 7.6 Hz, $^1J_{W,C}$ = 125.7 Hz, *cis*-*C*O), 200.7 (d, $^2J_{P,C}$ = 26.0 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** δ = -1.80 (d, $^2J_{P,Si}$ = 3.5 Hz, *Si*(CH$_3$)$_3$), 0.44 (d, $^2J_{P,Si}$ = 7.1 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 174.7 (s$_{sat}$, $^1J_{W,P}$ = 274.8 Hz).

***Isomer 2:***

No resonance signals except in the $^{31}P$ NMR could be observed due to the isomers low percentage of the mixture.

**$^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 167.1 ($s_{br}$ , $^1J_{W,P}$ = ca. 274 Hz).

***Isomer 3:***

**$^1H$ NMR (500.2 MHz, $CDCl_3$):** $\delta$ = 0.25 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 0.86 (d, 3H, $^5J_{P,H}$ = 6.8 Hz, C$H_3$), 0.94 – 0.99 (m, 3H, C$H_3$), 2.20 (d, 1H, $^2J_{P,H}$ = 19.3 Hz, P-C*H*), 1.94 – 2.02 (m, 1H, C*H*(CH$_3$)$_2$), 2.81 – 2.91 (m, 1H, P-C$H_2$), 3.28 – 3.37 (m, 1H, P-C$H_2$), 4.55 – 4.62 (m, 1H, C*H*).

**$^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 2.3 (d, $^2J_{P,C}$ = 3.5 Hz, Si(*C*H$_3$)$_3$), 2.5 (d, $^2J_{P,C}$ = 2.2 Hz, Si(*C*H$_3$)$_3$), 16.2 (s, *C*H$_3$), 17.5 (s, *C*H$_3$), 38.0 (s, *C*H(CH$_3$)$_2$), 39.6 (d, $^1J_{P,C}$ = 27.9 Hz, P-*C*H), 45.5 (d, $^1J_{P,C}$ = 26.7 Hz, P-*C*H$_2$), 84.6 (d, $^2J_{P,C}$ = 13.0 Hz, O-*C*H), 197.2 ($d_{sat}$, $^2J_{P,C}$ = 7.2 Hz, $^1J_{W,C}$ = 126.5 Hz, *cis-C*O), 199.3 (d, $^2J_{P,C}$ = 24.5 Hz, *trans-C*O).

**$^{29}Si\{^1H\}$ NMR (99.4 MHz, $CDCl_3$):** $\delta$ = -2.77 (d, $^2J_{P,Si}$ = 7.6 Hz, *Si*(CH$_3$)$_3$), 0.64 (s, *Si*(CH$_3$)$_3$).

**$^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 162.6 ($s_{sat}$, $^1J_{W,P}$ = 268.6 Hz).

***Isomer 4:***

**$^1H$ NMR (500.2 MHz, $CDCl_3$):** $\delta$ = 0.25 (s, 9H, Si(C$H_3$)$_3$), 0.30 (s, 9H, Si(C$H_3$)$_3$), 0.84 (d, 3H, $^5J_{P,H}$ = 6.6 Hz, C$H_3$), 0.94 – 0.99 (m, 3H, C$H_3$), 1.92 (d, 1H, $^2J_{P,H}$ = 6.1 Hz, P-C*H*), 1.87 – 1.95 (m, 1H, C*H*(CH$_3$)$_2$), 3.09 – 3.18 (m, 1H, P-C$H_2$), 3.19 – 3.28 (m, 1H, P-C$H_2$), 4.31 – 4.43 (m, 1H, C*H*).

**$^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 2.2 (d, $^2J_{P,C}$ = 3.7 Hz, Si(*C*H$_3$)$_3$), 2.8 (d, $^2J_{P,C}$ = 1.8 Hz, Si(*C*H$_3$)$_3$), 16.1 (s, *C*H$_3$), 17.9 (s, *C*H$_3$), 37.2 (d, $^3J_{P,C}$ = 5.4 Hz, *C*H(CH$_3$)$_2$), 38.6 (d, $^1J_{P,C}$ = 12.6 Hz, P-*C*H), 42.8 (d, $^1J_{P,C}$ = 24.5 Hz, P-*C*H$_2$), 84.3 (d, $^2J_{P,C}$ = 12.5 Hz, O-*C*H), 197.4 ($d_{sat}$, $^2J_{P,C}$ = 7.4 Hz, $^1J_{W,C}$ = 125.9 Hz, *cis-C*O), 200.4 (d, $^2J_{P,C}$ = 25.1 Hz, *trans-C*O).

**$^{29}Si\{^1H\}$ NMR (99.4 MHz, $CDCl_3$):** $\delta$ = -1.40 (d, $^2J_{P,Si}$ = 4.2 Hz, *Si*(CH$_3$)$_3$), 0.32 (d, $^2J_{P,Si}$ = 6.9 Hz, *Si*(CH$_3$)$_3$).

**$^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 161.7 ($s_{sat}$, $^1J_{W,P}$ = 268.7 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 600.1 (40) $[M]^{\bullet+}$, 530.0 (5) $[M - C_5H_{10}]^+$, 502.0 (20) $[M - C_5H_{10} - CO]^+$, 474.0 (20) $[M - C_5H_{10} - 2\ CO]^+$, 460.1 (25) $[M - 5\ CO]^+$, 446.0 (35) $[M - C_5H_{10} - 3\ CO]^+$, 418.0 (55) $[M - C_5H_{10} - 4\ CO]^+$, 390.0 (100) $[M - C_5H_{10} - 5\ CO]^+$, 73.0 (50) $[SiMe_3]^+$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2068 (s, $\nu$(CO)), 1979 (w, $\nu$(CO)), 1895 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 34.01 | H | 4.87 |
| found: | C | 33.84 | H | 5.06 |

**Single crystal measurement:** GSTR518, AKY-575 // GXray4851f

## 11.2.8.7 Attempted synthesis of pentacarbonyl{4-(1,1-dimethylethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1d]

The reaction was performed as described in chapter 11.2.8. The reaction mixture was submitted for $^{31}P\{^{1}H\}$ NMR measurement after reaching ambient temperature. The NMR spectrum showed the formation of diphosphen-complexes as main products (80.5 %) as well as small amounts of isomeric 1,2-oxaphosphetane complexes (9.5 %) and around 10% of unidentified compounds.

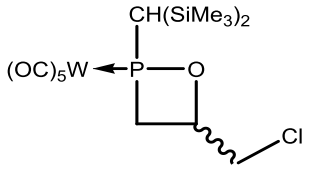
**Isomeric ratio:** 35 : 21 : 43

***Isomer 1:*** **$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 172.2 (s)

***Isomer 2:*** **$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 166.5 (s)

***Isomer 3:*** **$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 159.8 (s)

## 11.2.8.8 Pentacarbonyl{4-(chloromethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1e]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was separated from the formed salt by extraction with three times 15 mL of *n*-pentane followed by low temperature column chromatography ($SiO_2$, -20 °C, eluent: petroleum ether, petroleum ether/diethyl ether 10:0.1). It was obtained as solid from the second fraction after removing of all volatiles in *vacuo* (ca. 0.02 mbar). The crude product was crystallized by slow evaporation of a saturated *n*-pentane solution at 4 °C to yield colourless crystals. The product was obtained as mixtures of different isomers and all data are given for the mixture.

| | |
|---|---|
| **Molecular formula:** | $C_{15}H_{24}ClO_6PSi_2W$ |
| **Molecular weight:** | 606.785 g/mol |
| **Melting point:** | 128 °C (dec.) |
| **Yield:** | 186 mg (0.31 mmol, 61 %) |

**Isomeric ratio:** 44 : 7 : 19 : 30

***Isomer 1:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.29 (s, 9H, Si(C$H_3$)$_3$), 0.32 (s, 9H, Si(C$H_3$)$_3$), 2.04 (d, 1H, $^{2}J_{P,H}$ = 6.3 Hz, P-C*H*), 3.06 – 3.18 (m, 1H, C$H_2$), 3.40 – 3.59 (m, 1H, C$H_2$), 3.68 – 3.82 (m, 2H, C$H_2$), 5.03 – 5.16 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.0 (d, $^{2}J_{P,C}$ = 4.3 Hz, Si(*C*H$_3$)$_3$), 2.4 (d, $^{2}J_{P,C}$ = 1.5 Hz, Si(*C*H$_3$)$_3$), 37.4 (d, $^{1}J_{P,C}$ = 28.6 Hz, P-*C*H$_2$), 38.6 (d, $^{1}J_{P,C}$ = 12.9 Hz, P-*C*H), 47.0 (d, $^{3}J_{P,C}$ = 4.9 Hz, *C*H$_2$), 79.5 (d, $^{2}J_{P,C}$ = 12.8 Hz, O-*C*H), 196.8 (d$_{sat}$, $^{1}J_{W,C}$ = 124.1 Hz, $^{2}J_{P,C}$ = 7.5 Hz, *cis*-*C*O), 198.8 (d, $^{2}J_{P,C}$ = 25.5, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (59.6 MHz, $CDCl_3$):** δ = -3.33 (d, $^{2}J_{P,Si}$ = 7.7 Hz, *Si*(CH$_3$)$_3$), 0.00 (s, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 182.4 (s$_{sat}$, $^{1}J_{W,P}$ = 278.6 Hz).

***Isomer 2:***

No resonance signals except in the $^{31}$P NMR could be observed due to the isomers low percentage of the mixture.

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 174.8 (s$_{sat}$, $^{1}J_{W,P}$ = 281.0 Hz).

***Isomer 3:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.28 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 1.98 (d, 1H, $^{2}J_{P,H}$ = 5.9 Hz, P-C*H*), 3.25 – 3.48 (m, 2H, C$H_2$), 3.62 – 3.72 (m, 2H, C$H_2$), 4.94 – 5.05 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.0 (d, $^{2}J_{P,C}$ = 3.6 Hz, Si(*C*H$_3$)$_3$), 2.8 (d, $^{2}J_{P,C}$ = 2.3 Hz, Si(*C*H$_3$)$_3$), 38.9 (d, $^{1}J_{P,C}$ = 13.3 Hz, P-*C*H), 41.8 (d, $^{1}J_{P,C}$ = 25.3 Hz, P-*C*H$_2$), 46.8 (d, $^{3}J_{P,C}$ = 6.0 Hz, *C*H$_2$), 76.4 (d, $^{2}J_{P,C}$ = 12.6 Hz, O-*C*H), 196.9 (d, $^{2}J_{P,C}$ = 7.8 Hz, *cis*-*C*O), 199.6 (d, $^{2}J_{P,C}$ = 26.0, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (59.6 MHz, $CDCl_3$):** δ = -2.50 (d, $^{2}J_{P,Si}$ = 3.4 Hz, *Si*(CH$_3$)$_3$), -0.15 (s, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 171.0 (s$_{sat}$, $^{1}J_{W,P}$ = 274.4 Hz).

***Isomer 4:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.27 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 2.71 (d, 1H, $^{2}J_{P,H}$ = 19.9 Hz, P-C*H*), 3.20 – 3.50 (m, 4H, C$H_2$), 5.20 – 5.31 (m, 1H, C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.1 (d, $^{2}J_{P,C}$ = 3.0 Hz, Si(*C*H$_3$)$_3$), 2.2 (d, $^{2}J_{P,C}$ = 3.3 Hz, Si(*C*H$_3$)$_3$), 37.9 (d, $^{1}J_{P,C}$ = 29.2 Hz, P-*C*H), 43.8 (d, $^{1}J_{P,C}$ = 27.3 Hz, P-*C*H$_2$), 48.8 (d, $^{3}J_{P,C}$ = 2.2 Hz, *C*H$_2$), 76.5 (d, $^{2}J_{P,C}$ = 13.2 Hz, O-*C*H), 196.9 (d, $^{2}J_{P,C}$ = 7.9 Hz, *cis*-*C*O), 199.8 (d, $^{2}J_{P,C}$ = 28.1, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (59.6 MHz, $CDCl_3$):** δ = -1.92 (d, $^{2}J_{P,Si}$ = 4.6 Hz, *Si*(CH$_3$)$_3$), -0.27 (s, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 170.1 (s$_{sat}$, $^{1}J_{W,P}$ = 271.3 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 605.9 (40) $[M]^{\bullet+}$, 578.0 (5) $[M - CO]^+$, 550.0 (1) $[M - 2\ CO]^+$, 522.0 (5) $[M - 3\ CO]^+$, 502.0 (15) $[M - C_2H_3Cl - CO]^+$, 494.0 (5) $[M - 4\ CO]^+$, 474.0 (20) $[M - C_2H_3Cl - 2\ CO]^+$, 466.0 (50) $[M - 5\ CO]^+$, 446.0 (30) $[M - C_2H_3Cl - 3\ CO]^+$, 418.0 (35) $[M - C_2H_3Cl - 4\ CO]^+$, 390.0 (50) $[M - C_2H_3Cl - 5\ CO]^+$, 73.1 (100) $[SiMe_3]^+$.

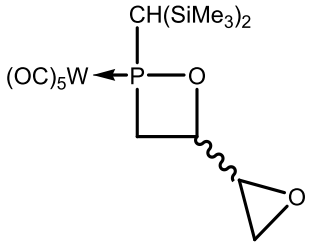
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2075 (m, $\nu$(CO)), 1988 (w, $\nu$(CO)), 1904 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 29.69 | H | 3.99 |
| found: | C | 30.53 | H | 4.74 |

**Single crystal measurement:** AKY-306 GSTR324, 3114

## 11.2.8.9 Pentacarbonyl{4-epoxy-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1f]




**Purification:** All volatiles were removed *in vacuo* (ca. 0.02 mbar). The product was separated from the formed salt by extraction with 5 times 5 mL of *n*-pentane and obtained, after removal of all volatiles in *vacuo* (ca. 0.02 mbar), as a yellow oil. The oil was solidified by precipitation from *n*-pentane (1 mL) at -100 °C and filtering off the supernatant solution. This step was repeated three times. The product was obtained as a mixture of different isomers and all data are given for the mixture.

**Molecular formula:** $C_{16}H_{25}O_7PSi_2W$

**Molecular weight:** 600.353 g/mol

**Melting point:** 84 °C

**Yield:** 147 mg (0.245 mmol, 49 %)

**Isomeric ratio:** 39 : 7 : 44 : 10

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.28 (s, 9H, Si(C*H*$_3$)$_3$), 0.30 (s, 9H, Si(C*H*$_3$)$_3$), 2.01 (d, 1H, $^2J_{P,H}$ = 5.8 Hz, P-C*H*), 2.76 - 2.93 (m, 2H, C*H*$_2$), 3.23 – 3.41 (m, 2H, C*H*$_2$), 3.42 – 3.62 (m, 1H, C*H*), 4.84 – 4.94 (m, 1H, P-O-C*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 2.2 (d, $^2J_{P,C}$ = 4.0 Hz, Si(*C*H$_3$)$_3$), 2.54 (d, $^2J_{P,C}$ = 2.0 Hz, Si(*C*H$_3$)$_3$), 35.8 (d, $^1J_{P,C}$ = 28.9 Hz, P-*C*H$_2$), 39.1 (d, $^1J_{P,C}$ = 12.9 Hz, P-*C*H), 44.8 (s, *C*H$_2$), 54.3 (s, *C*H), 80.3 (d,

$^{2}J_{P,C}$ = 12.8 Hz, O-*C*H), 197.0 ($d_{sat}$, $^{1}J_{W,C}$ = 126.1 Hz, $^{2}J_{P,C}$ = 7.9 Hz, *cis*-*C*O), 200.3 (d, $^{2}J_{P,C}$ = 27.5 Hz, *trans*-*C*O).

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 184.9 ($s_{sat}$, $^{1}J_{W,P}$ = 280.7 Hz).

***Isomer 2:***

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 177.7 ($s_{br}$).

No resonance signals except in the $^{31}P$ NMR could be observed due to the isomers low percentage of the mixture.

***Isomer 3:***

**$^{1}H$ NMR (300.1 MHz, $CDCl_3$):** δ = 0.25 (s, 9H, Si(C$H_3$)$_3$), 0.28 (s, 9H, Si(C$H_3$)$_3$), 2.84 (d, 1H, $^{2}J_{P,H}$ = 19.0 Hz, P-C*H*), 2.69 - 2.98 (m, 2H, C$H_2$), 3.14 - 3.35 (m, 2H, C$H_2$), 3.39 - 3.51 (m, 1H, C*H*), 5.12 - 5.21 (m, 1H, P-O-C*H*).

**$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$):** δ = 2.2 (d, $^{2}J_{P,C}$ = 4.0 Hz, Si(*C*$H_3$)$_3$), 2.34 (d, $^{2}J_{P,C}$ = 3.3 Hz, Si(*C*$H_3$)$_3$), 36.5 (d, $^{1}J_{P,C}$ = 27.5 Hz, P-*C*H), 43.6 (d, $^{1}J_{P,C}$ = 28.1 Hz, P-*C*$H_2$), 44.8 (s, $CH_2$), 54.3 (d, $^{3}J_{P,C}$ = 3.8 Hz, *C*H), 75.1 (d, $^{2}J_{P,C}$ = 13.1 Hz, O-*C*H), 197.0 ($d_{sat}$, $^{1}J_{W,C}$ = 125.6 Hz, $^{2}J_{P,C}$ = 7.7 Hz, *cis*-CO), 199.2 (d, $^{2}J_{P,C}$ = 25.0 Hz, *trans*-CO).

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 174.7 ($s_{sat}$, $^{1}J_{W,P}$ = 269.6 Hz).

***Isomer 4:***

**$^{1}H$ NMR (300.1 MHz, $CDCl_3$):** δ = 0.29 (s, 9H, Si(C$H_3$)$_3$), 0.32 (s, 9H, Si(C$H_3$)$_3$), 1.93 (d, 1H, $^{2}J_{P,H}$ = 5.2 Hz, P-C*H*), 2.61 – 3.76 (m, 5H, $CH_2$ + $CH_2$ + CH), 4.68 – 4.77 (m, 1H, P-O-C*H*).

**$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$):** Due to the isomers low percentage of the mixture only very few resonance signals could be observed in the $^{13}C\{^{1}H\}$ NMR: δ = 2.8 (d, $^{2}J_{P,C}$ = 2.4 Hz, Si(*C*$H_3$)$_3$), 39.2 (d, $^{1}J_{P,C}$ = 12.8 Hz, P-*C*H), 40.1 (d, $^{1}J_{P,C}$ = 25.5 Hz, P-*C*$H_2$), 44.4 (s, $CH_2$), 54.1 (d, $^{3}J_{P,C}$ = 8.0 Hz, CH).

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 173.3 ($s_{sat}$, $^{1}J_{W,P}$ = 272.5 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 600.0 (30) $[M]^{\bullet+}$, 584.0 (5) $[M - O]^{+}$, 572.0 (10) $[M - CO]^{+}$, 516.0 (5) $[M - 3\ CO]^{+}$, 488.0 (10) $[M - 4\ CO]^{+}$, 460.0 (25) $[M - 5\ CO]^{+}$, 388.0 (85) $[M - C_3H_4O_2]^{+}$, 73.1 (50) $[SiMe_3]^{+}$.

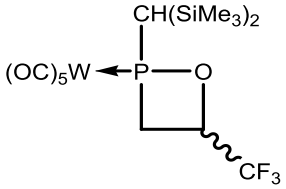
**IR (ATR Diamond; $\tilde{\nu}$[$cm^{-1}$], selected data):** 2072 (s, ν(CO)), 1984 (w, ν(CO)), 1906 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 32.01 | H | 4.20 |
| found: | C | 31.82 | H | 4.40 |

**Single crystal measurement:** GSTR382, AKY-425 // GXraycollect

## 11.2.8.10 Pentacarbonyl{4-(trifluoromethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1g]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was extracted from the formed salt with diethyl ether (two times 5 mL) and the solvent was removed in *vacuo* (ca. 0.02 mbar). The product was obtained via precipitation from *n*-pentane and filtering off the solvent at -100 °C, which was repeated three times. It was obtained as mixture of different isomers and all data are given for the mixture.

**Molecular formula:** $C_{15}H_{22}F_3O_6PSi_2W$

**Molecular weight:** 626.312 g/mol

**Melting point:** 86 - 87 °C

**Yield:** 218 mg (0.35 mmol, 35 %)

**Isomeric ratio:** 49 : 14 :31 :6 (before purification)

85 : 12 :3 :<1 (after purification)

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.31 (s, 9H, Si(C*H*$_3$)$_3$), 0.34 (s, 9H, Si(C*H*$_3$)$_3$), 2.11 (d, 1H, $^2J_{P,H}$ = 5.6 Hz, P-C*H*), 3.40 – 3.60 (m, 2H, C*H*$_2$), 5.00 – 5.20 (m, 1H, C*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.0 (d, $^2J_{P,C}$ = 3.9 Hz, Si(*C*H$_3$)$_3$), 2.4 (d, $^2J_{P,C}$ = 2.6 Hz, Si(*C*H$_3$)$_3$), 32.5 (d, $^1J_{P,C}$ = 29.7 Hz, *C*H$_2$), 39.7 (d, $^1J_{P,C}$ = 12.3 Hz, *C*H), 75.9 (qd, $^2J_{F,C}$ = 37.2 Hz, $^2J_{P,C}$ = 13.1 Hz, O-*C*H), 123.6 (qd, $^1J_{F,C}$ = 280.0 Hz, $^3J_{P,C}$ = 5.8 Hz, *C*F$_3$), 196.1 (d$_{sat}$, $^1J_{W,C}$ = 125.8, $^2J_{P,C}$ = 7.8 Hz, *cis*-*C*O), 199.5 (d, $^2J_{P,C}$ = 29.1 Hz, *trans*-*C*O).

**$^{19}$F{$^1$H} NMR (59.6 MHz, $CDCl_3$):** δ = -80.6 ($^4J_{P,F}$ = 0.84 Hz, C*F*$_3$).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $CDCl_3$):** δ = -1.97 ($^2J_{P,Si}$ = 3.9 Hz, *Si*(CH$_3$)$_3$), 0.61 ($^2J_{P,Si}$ = 6.9 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 194.9 (s$_{sat}$, $^1J_{W,P}$ = 288.1 Hz).

No resonance signals except in the $^{31}$P NMR could be observed for the other isomers.

***Isomer 2:***

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 186.9 (s$_{sat}$, $^1J_{W,P}$ = 286.3 Hz).

***Isomer 3:***

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 183.3 ($s_{sat}$, $^{1}J_{W,P}$ = 277.3 Hz).

***Isomer 4:***

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 182.8 ($s_{sat}$, $^{1}J_{W,P}$ = 284.5 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 625.9 (60) $[M]^{\bullet+}$, 570.0 (5) $[M - 2\ CO]^+$, 542.0 (60) $[M - 3\ CO]^+$, 502.0 (5) $[M - CO - C_3H_3F_3]^+$, 486.0 (10) $[M - 5\ CO]^+$, 473.9 (10) $[M - 2\ CO - C_3H_3F_3]^+$, 445.9 (15) $[M - 3\ CO - C_3H_3F_3]^+$, 418.0 (25) $[M - 4\ CO - C_3H_3F_3]^+$, 390.0 (85) $[M - 5\ CO - C_3H_3F_3]^+$, 73.1 (100) $[SiMe_3]^+$.

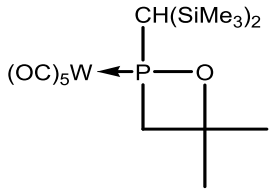
**IR (ATR Diamond; $\tilde{\nu}$[$cm^{-1}$], selected data):** 2074 (s, $\nu$(CO)), 1992 (w, $\nu$(CO)), 1909 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 28.77 | H | 3.54 |
| found: | C | 29.07 | H | 3.89 |

**Single crystal measurement:** GSTR344, 3313

## 11.2.8.11 Pentacarbonyl{4,4-dimethyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [25.1a]




**Purification:** The crude product was purified by column chromatography (ø = 2 cm, h = 6 cm, petroleum ether, - 20 °C, $SiO_2$) after removing of all volatiles in *vacuo* (ca. 0.02 mbar).

The product was obtained from the second fraction using petroleum ether to remove all acyclic side products with the first fraction and then a mixture of petroleum ether and diethyl ether (50 : 1). All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product washed six times with 2 mL of *n*-pentane at -100 °C. The product was obtained as white powder, containing a mixture of two isomers, after drying in *vacuo* (ca. 0.02 mbar). All data are given for the mixture.

**Molecular formula:** $C_{16}H_{27}O_6PSi_2W$

**Molecular weight:** 568.366 g/mol

**Melting point:** 84 °C

**Yield:** 200 mg (0.35 mmol, 35 %).

**Isomeric ratio:** 36 : 64

***Isomer 1:***

**$^{1}$H NMR (300.1 MHz, $C_6D_6$):** δ = 0.09 (s, 9H, Si(C*H*$_3$)$_3$), 0.28 (s, 9H, Si(C*H*$_3$)$_3$), 1.08 (s, 3H, C*H*$_3$), 1.47 (s, 3H, C*H*$_3$), 1.87 (d, 1H, $^{2}J_{P,H}$ = 4.6 Hz, P-C*H*), 2.80 (d, 1H, $^{2}J_{H,H}$ = 13.7 Hz, C*H*$_2$), 3.12 (dd, 1H, $^{2}J_{H,H}$ = 13.7 Hz, $^{2}J_{P,H}$ = 12.6 Hz, C*H*$_2$).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $C_6D_6$):** δ = 2.5 (d, $^{3}J_{P,C}$ = 3.1 Hz, Si(*C*H$_3$)$_3$), 2.9 (d, $^{3}J_{P,C}$ = 2.7 Hz, Si(*C*H$_3$)$_3$)), 31.0 (d, $^{3}J_{P,C}$ = 1.6 Hz, *C*H$_3$), 33.1 (d, $^{3}J_{P,C}$ = 1.7 Hz, *C*H$_3$), 39.7 (d, $^{1}J_{P,C}$ = 12.0 Hz, P-*C*H), 46.8 (d, $^{1}J_{P,C}$ = 24.7 Hz, *C*H$_2$), 85.6 (d, $^{2}J_{P,C}$ =12.5 Hz, O-*C*(CH$_3$)$_2$), 198.1 (d$_{sat}$, $^{1}J_{W,C}$ = 125.8 Hz, $^{2}J_{P,C}$ = 7.7 Hz, *cis*-*C*O), 200.4 (d, $^{2}J_{P,C}$ = 25.2 Hz, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (59.6 MHz, $C_6D_6$):** δ = -1.56 (d, $^{2}J_{P,Si}$ = 7.2 Hz, *Si*(CH$_3$)$_3$), -0.59 (d, $^{2}J_{P,Si}$ = 6.2 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P NMR (121.5 MHz, $C_6D_6$):** δ = 156.9 (dd$_{sat}$, $^{1}J_{W,P}$ = 275.2 Hz, $^{2}J_{P,H}$ = 12.6 Hz, $^{2}J_{P,H}$ = 4.2 Hz).

***Isomer 2:***

**$^{1}$H NMR (300.1 MHz, $C_6D_6$):** δ = 0.15 (s, 9H, Si(C*H*$_3$)$_3$), 0.32 (s, 9H, Si(C*H*$_3$)$_3$), 1.14 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 2.20 (d, 1H, $^{2}J_{P,H}$ = 18.9 Hz, P-C*H*), 2.49 (dd, 1H, $^{2}J_{H,H}$ = 13.4 Hz, $^{2}J_{P,H}$ = 11.3 Hz, C*H*$_2$), 2.95 (d, 1H, $^{2}J_{H,H}$ = 13.4 Hz, C*H*$_2$).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $C_6D_6$):** δ = 2.2 (d, $^{3}J_{P,C}$ = 3.9 Hz, Si(*C*H$_3$)$_3$), 2.6 (d, $^{3}J_{P,C}$ = 3.1 Hz, Si(*C*H$_3$)$_3$), 32.0 (d, $^{3}J_{P,C}$ = 3.9 Hz, *C*H$_3$), 34.1 (s, *C*H$_3$), 38.6 (d, $^{1}J_{P,C}$ = 26.8 Hz, P-*C*H), 51.5 (d, $^{1}J_{P,C}$ = 26.9 Hz, *C*H$_2$), 85.5 (d, $^{2}J_{P,C}$ = 12.6 Hz, O-*C*(CH$_3$)$_2$), 197.8 (d$_{sat}$, $^{1}J_{W,C}$ = 125.3 Hz, $^{2}J_{P,C}$ = 7.7 Hz, *cis*-*C*O), 199.2 (d, $^{2}J_{P,C}$ = 24.8 Hz, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (59.6 MHz, $C_6D_6$):** δ = -2.83 (d, $^{2}J_{P,Si}$ = 8.0 Hz, *Si*(CH$_3$)$_3$), -0.01 (d, $^{2}J_{P,Si}$ = 1.5 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P NMR (121.5 MHz, $C_6D_6$):** δ = 150.7 (dd$_{sat}$, $^{1}J_{W,P}$ = 274.0 Hz, $^{2}J_{P,H}$ = 18.9 Hz, $^{2}J_{P,H}$ = 11.3 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 586.1 (30) [M]$^{\bullet+}$, 530.1 (10) [M - 2 CO]$^{+}$, 502.1 (20) [M - 3 CO]$^{+}$, 474.0 (15) [M - 4 CO]$^{+}$, 446.0 (35) [M - 5 CO]$^{+}$, 418.0 (50) [M - 4 CO - $C_4H_8$]$^{+}$, 390.0 (100) [M - 5 CO - $C_4H_8$]$^{+}$, 73.1 (70) [$SiMe_3$]$^{+}$.

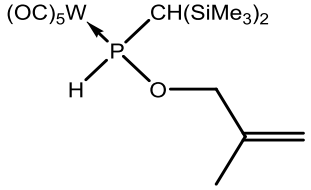
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2071 (s, ν(CO)), 1998 (w, ν(CO)), 1905 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 32.77 | H | 4.64 |
| found: | C | 32.64 | H | 4.84 |

**Single crystal measurement:** GSTR390, AKY-469-F2 // GXray3852f

## 11.2.8.12 Pentacarbonyl{[(2-methyl-2-propenyl)oxy][bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [4.1d]




**Purification:** The crude product was separated from the reaction mixture of the synthesis of **25.1a** by column chromatography (ø = 2 cm, h = 6 cm, petroleum ether, - 20 °C, $SiO_2$) after initial removal of all volatiles in *vacuo* (ca. 0.02 mbar). The first yellow fraction using pure petroleum ether was collected. After evaporation of all volatiles in *vacuo* (ca. 0.02 mbar) the product was washed at -100 °C three times with 2 mL of *n*-pentane to yield the product as yellow powder.

**Molecular formula:** $C_{16}H_{27}O_6PSi_2W$

**Molecular weight:** 586.366 g/mol

**Melting point:** 44 °C

**Yield:** 85 mg (0.14 mmol, 14 %)

**$^1$H NMR (300.1 MHz, $C_6D_6$):** δ = 0.01 (s, 9H, Si(C*H*$_3$)$_3$), 0.24 (s, 9H, Si(C*H*$_3$)$_3$), 0.87 (s$_{br}$, 1H, P-C*H*), 1.57 (s$_{br}$, 3H, C*H*$_3$), 4.00 (dd, 1H, $^3J_{P,H}$ = 8.4 Hz, $^2J_{H,H}$ = 11.4 Hz, O-C*H*$_2$), 3.67 (dd, 1H, $^3J_{P,H}$ = 9.0 Hz, $^2J_{H,H}$ = 11.4 Hz, O-C*H*$_2$), 4.76 (s$_{br}$, 1H, C*H*$_2$), 4.93 (s$_{br}$, 1H, C*H*$_2$), 7.69 (dd, 1H, $^1J_{P,H}$ = 322.4 Hz, $^3J_{H,H}$ = 1.1 Hz, P-*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$):** δ = 0.2 (d, $^3J_{P,C}$ = 2.5 Hz, Si(*C*H$_3$)$_3$), 2.1 (d, $^3J_{P,C}$ = 2.9 Hz, Si(*C*H$_3$)$_3$), 19.5 (s, *C*H$_3$), 23.7 (d, $^1J_{P,C}$ = 13.3 Hz, *C*H), 73.7 (d, $^2J_{P,C}$ = 3.6 Hz, *C*H$_2$), 114.4 (s, *C*H$_2$), 140.6 (d, $^3J_{P,C}$ = 8.4 Hz, *C*=CH$_2$), 197.2 (d$_{sat}$, $^1J_{W,C}$ = 125.4 Hz, $^2J_{P,C}$ = 7.4 Hz, *cis-C*O), 199.4 (d, $^2J_{P,C}$ = 24.6 Hz, *trans-C*O).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$):** δ = 0.05 (d, $^2J_{P,Si}$ = 5.7 Hz, *Si*(CH$_3$)$_3$), 1.72 (d, $^2J_{P,Si}$ = 9.0 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P NMR (121.5 MHz, $C_6D_6$):** δ = 103.6 (ddd$_{sat}$, $^1J_{W,P}$ = 268.1 Hz, $^1J_{P,H}$ = 322.3 Hz, $^3J_{P,H}$ = 9.0 Hz, $^3J_{P,H}$ = 8.4 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 586.1 (55) $[M]^{\bullet+}$, 558.1 (5) $[M - CO]^+$, 530.1 (20) $[M - 2\ CO]^+$, 500.1 (85) $[M - 2\ CO - C_2H_6]^+$, 474.0 (15) $[M - 4\ CO]^+$, 444.1 (65) $[M - 4\ CO - C_2H_6]^+$, 73.1 (100) $[SiMe_3]^+$.

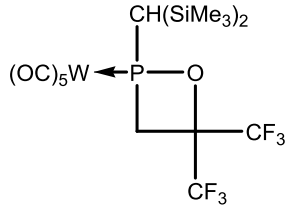
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2276 (w, ν(PH)), 2070 (s, ν(CO)), 1982 (m, ν(CO)), 1907 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 32.77 | H | 4.64 |
| found: | C | 32.87 | H | 4.70 |

**Single crystal measurement:** GSTR388, AKY-469-F1 // GXray3851f

## 11.2.8.13 Pentacarbonyl{4,4-bis(trifluoromethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [25.1b]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was extracted with diethyl ether (two times 15 mL) and the solvent was removed in *vacuo* (ca. 0.02 mbar). The product was obtained via precipitation from *n*-pentane at -100 °C and removing the supernatant solution by filtration, which was repeated three times. The product was obtained as mixture of two isomers (ratio (isomer 1 : isomer 2) 96:4) and all data are given for the mixture.

**Thermal isomerization:** 50 mg of the 96:4 mixture of **25.1[1]** and **25.1[2]** were dissolved in 0.5 mL of toluene-$d_8$ and heated in a closed NMR tube with Young valve to 85 °C for 3 days. The ratio between the two isomers changed slowly to finally yield a mixture of 7:93 (**25.1[1]**:**25.1[2]**) together with some unidentified impurities.

| | |
|---|---|
| **Molecular formula:** | $C_{16}H_{21}F_6O_6PSi_2W$ |
| **Molecular weight:** | 694.310 g/mol |
| **Melting point:** | 83 °C |
| **Yield:** | 257 mg (0.37 mmol, 37 %) |

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.30 (s, 9H, Si(C$H_3$)$_3$), 0.34 (s, 9H, Si(C$H_3$)$_3$), 2.25 (d, 1H, $^2J_{P,H}$ = 4.0 Hz, C*H*), 3.57 (d, 1H, $^2J_{H,H}$ = 15.0 Hz, C$H_2$), 3.85 (dd, 1H, $^2J_{H,H}$ = 15.0 Hz, $^2J_{P,H}$ = 11.3 Hz, C$H_2$).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.6 (d, $^3J_{P,C}$ = 3.2 Hz, Si(*C*H$_3$)$_3$), 2.9 (d, $^3J_{P,C}$ = 1.9 Hz, Si(*C*H$_3$)$_3$), 35.0 (d, $^1J_{P,C}$ = 26.5 Hz, P-*C*H$_2$), 43.3 (d, $^1J_{P,C}$ = 12.9 Hz, P-*C*H), 79.0 – 82.0 (m, O-*C*(CF$_3$)$_2$), 121.7 (q, $^1J_{F,C}$ = 284.5 Hz, *C*F$_3$), 122.1 (qd, $^1J_{F,C}$ = 285.5 Hz, $^3J_{P,C}$ = 4.5 Hz, *C*F$_3$), 196.2 (dq$_{sat}$, $^1J_{W,C}$ = 126.1 Hz, $^2J_{P,C}$ = 7.8 Hz, $^6J_{F,C}$ = 1.5 Hz, *cis*-*C*O), 199.0 (d, $^2J_{P,C}$ = 31.0 Hz, *trans*-*C*O).

**$^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$):** δ = -77.8 (qd, $^4J_{F,F}$ = 9.9 Hz, $^4J_{P,F}$ = 1.9 Hz, C*F*$_3$), -76.3 (qd, $^4J_{F,F}$ = 9.9 Hz, $^4J_{P,F}$ = 3.4 Hz, C*F*$_3$).

**$^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$):** δ = -0.07 (d, $^2J_{P,Si}$ = 7.6 Hz, *Si*(CH$_3$)$_3$), 2.81 (d, $^2J_{P,Si}$ = 6.8 Hz, *Si*(CH$_3$)$_3$).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** δ = 198.2 ($s_{sat}$, $^1J_{W,P}$ = 297.6 Hz).

***Isomer 2:***

**$^1H$ NMR (300.1 MHz, toluene-$d_8$):** δ = 0.05 (s, 9H, Si(C*H*$_3$)$_3$), 0.22 (s, 9H, Si(C*H*$_3$)$_3$), 2.70 (d, 1H, $^2J_{P,H}$ = 19.5 Hz, P-C*H*), 2.85 (dd, 1H, $^2J_{H,H}$ = 15.2 Hz, $^2J_{P,H}$ = 10.5 Hz, P-C*H*$_2$), 3.11 (d, 1H, $^2J_{H,H}$ = 15.2 Hz, P-C*H*$_2$).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, toluene-$d_8$):** δ = 1.9 (d, $^3J_{P,C}$ = 4.2 Hz, Si(*C*H$_3$)$_3$), 2.3 (d, $^3J_{P,C}$ = 3.6 Hz, Si(*C*H$_3$)$_3$), 38.4 (d, $^1J_{P,C}$ = 27.5 Hz, P-*C*H), 40.0 (d, $^1J_{P,C}$ = 28.1 Hz, P-*C*H$_2$), 80 – 83 (m, *C*(CF$_3$)$_2$), 122.0 (q, $^1J_{F,C}$ = 284.8 Hz, *C*F$_3$), 122.6 (q, $^1J_{F,C}$ = 289.0 Hz, *C*F$_3$), 196.1 ($dq_{sat}$, $^1J_{W,C}$ = 125.7 Hz, $^2J_{P,C}$ = 7.5 Hz, $^6J_{F,C}$ = 0.4 Hz, *cis*-*C*O), 197.5 (d, $^2J_{P,C}$ = 29.4 Hz, *trans*-*C*O).

**$^{19}F\{^1H\}$ NMR (282.4 MHz, toluene-$d_8$):** δ = -77.4 (q, $^4J_{F,F}$ = 10.1 Hz, C*F*$_3$), -76.6 (qd, $^4J_{F,F}$ = 10.1 Hz, $^4J_{P,F}$ = 2.1 Hz, C*F*$_3$).

**$^{29}Si\{^1H\}$ NMR (59.6 MHz, toluene-$d_8$):** δ = -1.60 (d, $^2J_{P,Si}$ = 9.1 Hz, *Si*(CH$_3$)$_3$), 1.46 (s, *Si*(CH$_3$)$_3$).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-$d_8$):** δ = 191.5 ($s_{sat}$, $^1J_{W,P}$ = 295.0 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 694.0 (50) $[M]^{\bullet+}$, 638.0 (20) $[M - 2\ CO]^+$, 610.0 (100) $[M- 3\ CO]^+$, 554.0 (15) $[M - 5\ CO]^+$, 474.0 (5) $[M - 1\ CO - C_4H_2F_6]^+$, 446.0 (5) $[M - 2\ CO - C_4H_2F_6]^+$, 446.0 (10) $[M - 3\ CO - C_4H_2F_6]^+$, 418.0 (10) $[M - 4\ CO - C_4H_2F_6]^+$, 390.0 (30) $[M - 5\ CO - C_4H_2F_6]^+$, 73.1 (100) $[SiMe_3]^+$.

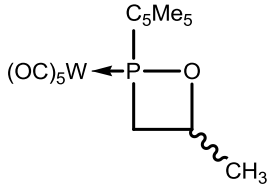
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2077 (s, ν(CO)), 1996 (w, ν(CO)), 1910 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 27.68 | H | 3.05 |
| found: | C | 27.69 | H | 3.28 |

**Single crystal measurement:** GSTR378, 3684f

## 11.2.8.14 Pentacarbonyl[4-methyl-2-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.2a]




**Analysis:** After reaching ambient temperature the reaction mixture was analysed by $^{31}P\{^{1}H\}$ NMR. The spectrum showed two isomeric 1,2-oxaphosphetane complexes.

**Isomeric ratio:** 53 : 47

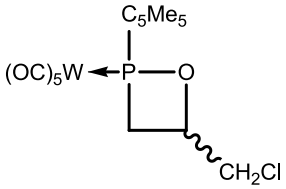
***Isomer 1:***

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 184.8 ($s_{sat}$, $^{1}J_{W,P}$ = 279.5 Hz).

***Isomer 2:***

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 174.0 ($s_{sat}$, $^{1}J_{W,P}$ = 273.6 Hz).

## 11.2.8.15 Pentacarbonyl[4-chloromethyl-2-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.2e]




**Analysis:** After reaching ambient temperature the reaction mixture was analysed by $^{31}P\{^{1}H\}$ NMR. The spectrum showed two isomeric 1,2-oxaphosphetane complexes.

**Isomeric ratio:** 53 : 47

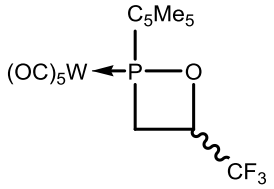
***Isomer 1:***

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 189.6 ($s_{sat}$, $^{1}J_{W,P}$ = 283.6 Hz).

***Isomer 2:***

**$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 178.4 ($s_{sat}$, $^{1}J_{W,P}$ = 280.0 Hz).

### 11.2.8.16 Pentacarbonyl[4-(trifluoromethyl)-2-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.2g]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was extracted from the formed salt with three times 20 mL of diethyl ether and the solvent was removed in *vacuo* (ca. 0.02 mbar). The product was purified via precipitation from 2 mL of *n*-pentane at -100 °C and filtering off the supernatant solution, which was repeated three times. A mixture of two isomers was obtained and all data are given for the mixture.

**Molecular formula:** $C_{18}H_{18}F_3O_6PW$

**Molecular weight:** 602.145 g/mol

**Melting point:** 93 °C

**Yield:** 214 mg (0.36 mmol, 36 %)

**Isomeric ratio:** 73 : 27

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $C_6D_6$):** δ = 1.73 (d, 3H, $J_{P,H}$ = 11.0 Hz, $C_5Me_5$), 1.79 (s, 3H, $C_5Me_5$), 1.80 - 1.85 (m, 6H, $C_5Me_5$), 1.96 (s, 3H, $C_5Me_5$), 3.51 (dd, 1H, $^2J_{H,H}$ = 14.5 Hz, $^3J_{H,H}$ = 7.0 Hz, P-C$H_2$), 3.56 (ddd, 1H, $^2J_{P,H}$ = 8.5 Hz, $^2J_{H,H}$ = 14.5 Hz, $^3J_{H,H}$ = 8.5 Hz, P-C$H_2$), 5.20 - 5.32 (m, 1H, O-C*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$):** δ = 11.7 - 11.9 (m, 3 times $C_5Me_5$), 11.96 (d, $J_{P,C}$ = 2 Hz, $C_5Me_5$), 14.18 (d, $J_{P,C}$ = 5.2 Hz, $C_5Me_5$), 30.4 (dq, $^1J_{P,C}$ = 24.1 Hz, $^3J_{F,C}$ = 1 Hz, P-*C*H$_2$), 65.7 (d, $J_{P,C}$ = 1.6 Hz, *C*$_5$Me$_5$), 78.6 (qd, $^2J_{F,C}$ = 37.0 Hz, $^2J_{P,C}$ = 11.9 Hz, O-*C*H), 123.2 (qd, $^1J_{F,C}$ = 279.8 Hz, $^3J_{P,C}$ = 5.0 Hz, *C*F$_3$), 132.5 (d, $J_{P,C}$ = 7.8 Hz, *C*=C), 138. 8 (d, $J_{P,C}$ = 2.2 Hz, *C*=C), 142.2 (d, $J_{P,C}$ = 6.2 Hz, *C*=C), 144.1 (d, $J_{P,C}$ = 7.2 Hz, *C*=C), 195.0 (d$_{sat}$, $^1J_{W,C}$ = 125.7 Hz, $^2J_{P,C}$ = 7.6 Hz, *cis-C*O), 198.2 (d, $^2J_{P,C}$ = 30.9 Hz, *trans-C*O).

**$^{19}$F{$^1$H} NMR (282.4 MHz, $C_6D_6$):** δ = -81.3 (s, C*F*$_3$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $C_6D_6$):** δ = 200.8 (s$_{sat}$, $^1J_{W,P}$ = 292.3 Hz).

***Isomer 2:***

**$^1$H NMR (300.1 MHz, $C_6D_6$):** δ = 1.61 (d, 3H, $J_{P,H}$ = 12.1 Hz, $C_5Me_5$), 1.73 (s, 3H, $C_5Me_5$), 1.80 - 1.85 (m, 6H, 2 times $C_5Me_5$), 1.92 (s, 3H, $C_5Me_5$), 3.09 (ddd, 1H, $^2J_{P,H}$ = 3.1 Hz, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 7.1 Hz, P-C$H_2$), 3.90 (ddd, 1H, $^2J_{P,H}$ = 11.8 Hz, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 8.8 Hz, P-C$H_2$), 5.28 - 5.42 (m, 1H, O-C*H*).

**$^{13}C\{^1H\}$ NMR (75.5 MHz, $C_6D_6$):** δ = 11.3 (d, $J_{P,C}$ = 2.8 Hz, $C_5Me_5$), 11.7 (d, $J_{P,C}$ = 1.5 Hz, $C_5Me_5$) 11.7 - 11.9 (m, 2 times $C_5Me_5$), 13.8 (dq, $J_{P,C}$ = 5.2 Hz, $J_{F,C}$ = 2.6 Hz, $C_5Me_5$), 32.8 (dq, $^1J_{P,C}$ = 20.3 Hz, $^3J_{F,C}$ = 1.1 Hz, P-$CH_2$), 65.5 (d, $J_{P,C}$ = 4.7 Hz, $C_5Me_5$), 75.0 (qd, $^2J_{F,C}$ = 37.8 Hz, $^2J_{P,C}$ = 12.0 Hz, O-CH), 123.1 (qd, $^1J_{F,C}$ = 279.9 Hz, $^3J_{P,C}$ = 6.4 Hz, $CF_3$), 132.3 (d, $J_{P,C}$ = 8.0 Hz, C=C), 138.5 (d, $J_{P,C}$ = 2.5 Hz, C=C), 142.7 (d, $J_{P,C}$ = 6.4 Hz, C=C), 144.8 (d, $J_{P,C}$ = 7.5 Hz, C=C), 195.5 ($d_{sat}$, $^1J_{W,C}$ = 125.3 Hz, $^2J_{P,C}$ = 7.5 Hz, *cis*-CO), 197.9 (d, $^2J_{P,C}$ = 30.0 Hz, *trans*-CO).

**$^{19}F\{^1H\}$ NMR (282.4 MHz, $C_6D_6$):** δ = -79.5 (s, $CF_3$).

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $C_6D_6$):** δ = 186.1 ($s_{sat}$ $^1J_{W,P}$ = 284.0 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 601.9 (50) $[M]^{\bullet+}$, 517.9 (15) $[M - 3\ CO]^+$, 466.8 (50) $[M - C_5Me_5]^+$, 438.8 (100) $[M - C_5Me_5 - CO]^+$, 410.8 (20) $[M - C_5Me_5 - 2\ CO]^+$, 135.1 (15) $[C_5Me_5]^+$.

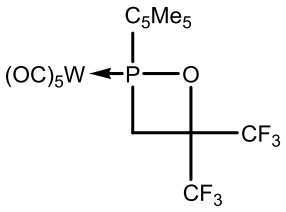
**IR (ATR Diamond; $\tilde{\nu}$[$cm^{-1}$], selected data):** 2074 (s, ν(CO)), 2000 (w, ν(CO)), 1902 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 35.90 | H | 3.01 |
| found: | C | 35.78 | H | 3.28 |

**Single crystal measurement:** GSTR406, AKY-490 // GXray3961g

## 11.2.8.17 Pentacarbonyl[4,4-bis(trifluoromethyl)-2-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [25.2b]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude mixture was extracted from the formed salt with diethyl ether and the solvent was removed in *vacuo* (ca. 0.02 mbar). The pure product was obtained via precipitation from *n*-pentane at -100 °C and filtering off the supernatant solution, which was repeated three times.

**Molecular formula:** $C_{19}H_{17}F_6O_6PW$

**Molecular weight:** 670.139 g/mol

**Melting point:** 90 °C

**Yield:** 303 mg (0.45 mmol, 45 %)

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 1.58 (qd, 3H, $J_{P,H}$ = 11.5 Hz, $J$ = 2.2 Hz, $C_5Me_5$), 1.76 (s, 3H, $C_5Me_5$), 1.80 (d, 3H, $J_{P,H}$ = 2.8 Hz, $C_5Me_5$), 1.82 (dd, 3H, $J_{P,H}$ = 1.98 Hz, $J_{H,H}$ = 1.0 Hz, $C_5Me_5$), 1.96 (s, 3H, $C_5Me_5$), 3.47 (dd, 1H, $^{2}J_{H,H}$ = 15.0 Hz, $^{2}J_{P,H}$ = 2.2 Hz, C$H_2$), 4.04 (dd, 1H, $^{2}J_{H,H}$ = 15.0 Hz, $^{2}J_{P,H}$ = 10.7 Hz, C$H_2$).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 11.8 (d, $J_{P,C}$ = 2.7 Hz, $C_5Me_5$) 12,0 (s, $C_5Me_5$), 12,0 (d, $J_{P,C}$ = 2.1 Hz, $C_5Me_5$), 12.0 (d, $J_{P,C}$ = 1.8 Hz, $C_5Me_5$), 16.3 (dq, $J_{P,C}$ = 6.1 Hz, $J_{F,C}$ = 6.1 Hz, $C_5Me_5$), 32.0 (d, $^{1}J_{P,C}$ = 21.8 Hz, P-$C$H$_2$), 66.8 (d, $^{1}J_{P,C}$ = 6.0 Hz, P-$C$), 82.5 - 85.0 (m, $C(CF_3)_2$), 121.7 (q, $^{1}J_{F,C}$ = 284.9 Hz, $C$F$_3$), 122.4 (qd, $^{1}J_{F,C}$ = 287.3 Hz, $^{3}J_{P,C}$ = 2.7 Hz, $C$F$_3$), 134.4 (d, $J_{P,C}$ = 10.1 Hz, $C$=C), 139.7 (d, $J_{P,C}$ = 4.5 Hz, $C$=C), 143.1 (d, $J_{P,C}$ = 6.9 Hz, $C$=C), 144.0 (d, $J_{P,C}$ = 8.0 Hz, $C$=C), 196.6 (dq$_{sat}$, $^{1}J_{W,C}$ = 126.0 Hz, $^{2}J_{P,C}$ = 7.8 Hz, $^{6}J_{F,C}$ = 2.6 Hz *cis-C*O), 197.2 (d, $^{2}J_{P,C}$ = 33.1 Hz, *trans-C*O).

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, $CDCl_3$):** $\delta$ = -74.6 (qd, $^{4}J_{F,F}$ = 11.4 Hz, $^{4}J_{P,F}$ = 3.8 Hz, C$F_3$), -73.5 (qd, $^{4}J_{F,F}$ = 11.4 Hz, $^{4}J_{P,F}$ = 0.4 Hz, C$F_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 199.0 (s$_{sat}$, $^{1}J_{W,P}$ = 295.1 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 670.1 (40) $[M]^{\bullet+}$, 586.0 (300) $[M - 3\ CO]^{+}$, 535.0 (40) $[M - C_5Me_5]^{+}$, 507.0 (70) $[M - C_5Me_5 - CO]^{+}$, 479.0 (20) $[M - C_5Me_5 - 2\ CO]^{+}$, 464.0 (60) $[M - 5\ CO - C_3F_6O]^{+}$, 135.1 (100) $[C_5Me_5]^{+}$.

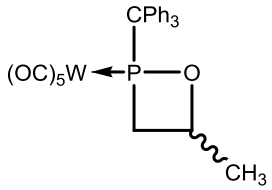
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2077 (s, $\nu$(CO)), 1991 (w, $\nu$(CO)), 1917 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 34.05 | H | 2.56 |
| found: | C | 34.25 | H | 2.84 |

**Single crystal measurement:** GSTR380, 3707f

## 11.2.8.18 Pentacarbonyl[4-methyl-2-(triphenylmethyl)-1,2-oxaphosphetane-$\kappa P$]tungsten(0) [21.3a]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was extracted from the formed salt with four times 20 mL of diethyl ether. Subsequent removal of the solvent in *vacuo* (ca. 0.02 mbar) and washing of the product with three times 3 mL of *n*-pentane at 0 °C yielded the product as slightly yellow powder. A mixture of two isomers was obtained and all data are given for the mixture.

**Molecular formula:** $C_{27}H_{21}O_6PW$

**Molecular weight:** 656.058 g/mol

**Melting point:** 151 °C

**Yield:** 150 mg (0.23 mmol, 46 %)

**Isomeric ratio:** 47 : 53

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 1.62 (d, 3H, $^3J_{H,H}$ = 6.4 Hz, C*H*$_3$), 3.08 (ddd, 1H, $^3J_{P,H}$ = 2.1 Hz, $^2J_{H,H}$ = 13.6 Hz, $^3J_{H,H}$ = 6.3 Hz, C*H*$_2$), 3.36 (ddd, 1H, $^3J_{P,H}$ = 11.0 Hz, $^2J_{H,H}$ = 13.6 Hz, $^3J_{H,H}$ = 8.6 Hz, C*H*$_2$), 4.86 - 4.82 (dm, 1H, $^4J_{P,H}$ = 2.2 Hz, C*H*), 7.18 - 7.58 (m, 15H, $CPh_3$).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 24.7 (d, $^3J_{P,C}$ = 4.2 Hz, *C*H$_3$), 40.4 (d, $^1J_{P,C}$ = 25.5 Hz, P-*C*H$_2$), 67.3 (d, $^1J_{P,C}$ = 3.1 Hz, *C*Ph$_3$), 81.5 (d, $^2J_{P,C}$ = 12.6 Hz, O-*C*H), 127.8 (s$_{br}$, *para-C*H$_{Ar}$), 128.6 (s, *C*H$_{Ar}$), 131.4 (d, $J_{P,C}$ = 7.1 Hz, *C*H$_{Ar}$), 140 - 142 (s$_{br}$, *ipso-C*), 196.5 (d$_{sat}$, $^1J_{W,C}$ = 126.4 Hz, $^2J_{P,C}$ = 7.8 Hz, *cis-C*O), 199.1 (d, $^2J_{P,C}$ = 31.0 Hz, *trans-C*O).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 180.2 (s$_{sat}$, $^1J_{W,P}$ = 283.1 Hz).

***Isomer 2:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 1.16 (d, 3H, $^3J_{H,H}$ = 6.2 Hz, C*H*$_3$), 3.10 - 3.16 (m, 2H, C*H*$_2$), 5.26 - 5.41 (dm, 1H, $^4J_{P,H}$ = 1.8 Hz, C*H*), 7.18 - 7.58 (m, 15H, $CPh_3$).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 23.4 (d, $^3J_{P,C}$ = 4.0 Hz, *C*H$_3$), 42.6 (d, $^1J_{P,C}$ = 22.5 Hz, P-*C*H$_2$), 68.0 (d, $^1J_{P,C}$ = 4.4 Hz, *C*Ph$_3$), 77.8 (d, $^2J_{P,C}$ = 12.6 Hz, O-*C*H), 127.6 (s$_{br}$, *para-C*H$_{Ar}$), 128.6 (s, *C*H$_{Ar}$), 131.0 (d, $J_{P,C}$ = 7.0 Hz, *C*H$_{Ar}$), 140 - 142 (s$_{br}$, *ipso-C*), 196.4 (d$_{sat}$, $^1J_{W,C}$ = 126.6 Hz, $^2J_{P,C}$ = 7.3 Hz, *cis-C*O), 199.3 (d, $^2J_{P,C}$ = 31.3 Hz, *trans-C*O).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 161.0 (s$_{sat}$, $^1J_{W,P}$ = 278.3 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 656.0 (0.2) $[M]^{\bullet+}$, 572.0 (0.1) $[M - 3\ CO]^+$, 529.9 (5) $[M - 3\ CO - C_3H_6]^+$, 474.0 (5) $[M - 5\ CO - C_3H_6]^+$, 412.9 (10) $[M - CPh_3]^+$, 370.8 (25) $[M - CPh_3 - C_3H_6]^+$, 342.8 (10) $[M- CO - CPh_3 - C_3H_6]^+$, 314.8 (5) $[M - 2\ CO - CPh_3 - C_3H_6]^+$, 243.0 (100) $[CPh_3]^+$, 165.0 (60) $[CPh_3 - C_6H_6]^+$.

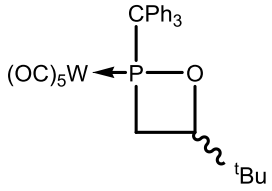
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2072 (s, $\nu$(CO)), 1995 (w, $\nu$(CO)), 1904 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 49.41 | H | 3.23 |
| found: | C | 49.90 | H | 3.55 |

**Single crystal measurement:** GSTR399, AKY-484 // GXray3939f

## 11.2.8.19 Attempted synthesis of pentacarbonyl[4-(1,1-dimethylethyl)-2-(triphenylmethyl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.3d]



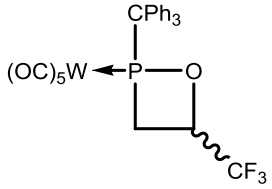

The synthesis of the complex was attempted as described in the general procedure. The reaction mixture was submitted for $^{31}P\{^{1}H\}$ NMR measurement. The NMR spectrum revealed full conversion to **21.3d** after 24 h as a mixture of two isomers.

**Isomeric ratio:** 52 : 48

***Isomer 1:* $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 181.0 ($s_{sat}$, $^{1}J_{W,P}$ = 285.2 Hz).

***Isomer 2:* $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $Et_2O$):** $\delta$ = 155.2 ($s_{sat}$, $^{1}J_{W,P}$ = 279.9 Hz).

## 11.2.8.20 Pentacarbonyl[4-(trifluoromethyl)-2-(triphenylmethyl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.3g]




**Purification:** After the reaction was completed (checked by $^{31}P$ NMR spectroscopy), all volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was extracted from the formed salt with 4 times 20 mL of diethyl ether and the solvent was removed in *vacuo* (ca. 0.02 mbar). The pure product was obtained by washing with *n*-pentane at 0° (two times 4 mL and two times 2 mL) and filtering off the supernatant solution, which was repeated three times. A mixture of two isomers was obtained and all data are given for the mixture.

| | |
|---|---|
| **Molecular formula:** | $C_{27}H_{18}F_3O_6PW$ |
| **Molecular weight:** | 710.237 g/mol |
| **Melting point:** | 169 °C |
| **Yield:** | 224 mg (0.32 mmol, 32 %) |

**Isomeric ratio:** 42: 58

***Isomer 1:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 3.23 - 3.36 (m, 1H, C*H*$_2$), 3.43 - 3.53 (m,1 H, C*H*$_2$), 4.50 - 4.65 (m, 1H, C*H*), 7.10 - 7.70 (m, 15H, C*Ph*$_3$).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 33.3 (d, $^{1}J_{P,C}$ = 27.2 Hz, P-*C*H$_2$), 67.9 (d, $^{1}J_{P,C}$ = 1.8 Hz, *C*Ph$_3$), 77.7 (qd, $^{2}J_{F,C}$ = 37.5 Hz, $^{2}J_{P,C}$ = 12.1 Hz, O-*C*H), 123.2 (qd, $^{1}J_{F,C}$ = 279.8 Hz, $^{3}J_{P,C}$ = 5.1 Hz, *C*F$_3$), 128.0 - 128.2 (m, *para-C*H$_{Ar}$), 128.9 (s, *C*H$_{Ar}$), 131.0 (d, $J_{P,C}$ = 6.8 Hz, *C*H$_{Ar}$), 140.7 (s$_{br}$, *ipso-C*), 195.3 (d$_{sat}$, $^{1}J_{W,C}$ = 126.3 Hz, $^{2}J_{P,C}$ = 7.4 Hz, *cis-C*O), 198.3 (d, $^{2}J_{P,C}$ = 34.3 Hz, *trans-C*O).

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, $CDCl_3$):** $\delta$ = -79.7 (d, $^{4}J_{P,F}$ = 0.7 Hz, C*F*$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 194.3 (s$_{sat}$, $^{1}J_{W,P}$ = 295.3 Hz).

***Isomer 2:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 2.98 - 3.07 (m, 1H, C*H*$_2$), 3.65 - 3.80 (m, 1H, C*H*$_2$), 5.15 - 5.29 (m, 1H, C*H*), 7.18 - 7.58 (m, 15H, C*Ph*$_3$).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 36.1 (d, $^{1}J_{P,C}$ = 24.2 Hz, P-*C*H$_2$), 69.4 (d, $^{1}J_{P,C}$ = 5.5 Hz, *C*Ph$_3$), 73.3 (qd, $^{2}J_{F,C}$ = 38.8 Hz, $^{2}J_{P,C}$ = 11.6 Hz, O-*C*H), 122.1 (qd, $^{1}J_{F,C}$ = 280.8 Hz, $^{3}J_{P,C}$ = 8.5 Hz, *C*F$_3$), 128.0 - 128.2 (m, *para-C*H$_{Ar}$), 128.9 (s, *C*H$_{Ar}$), 131.2 (d, $J_{P,C}$ = 7.3 Hz, *C*H$_{Ar}$), 139.3 (s$_{br}$, *ipso-C*), 195.5 (d$_{sat}$, $^{1}J_{W,C}$ = 126.5 Hz, $^{2}J_{P,C}$ = 7.1 Hz, *cis-C*O), 197.9 (d, $^{2}J_{P,C}$ = 33.3 Hz, *trans-C*O).

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, $CDCl_3$):** $\delta$ = -77.3 (d, $^{4}J_{P,F}$ = 0.9 Hz, C*F*$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 167.5 (s$_{sat}$, $^{1}J_{W,P}$ = 287.1 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 710.2 (0.02) $[M]^{\bullet+}$, 628.0 (0.02) $[M - 3\ CO]^{+}$, 530.0 (0.01) $[M - 3\ CO - C_3H_3F_3]^{+}$, 474.0 (0.3) $[M - 4\ CO - C_3H_3F_3]^{+}$, 438.9 (0.5) $[M - CPh_3 - CO]^{+}$, 243.1 (100) $[CPh_3]^{+}$.

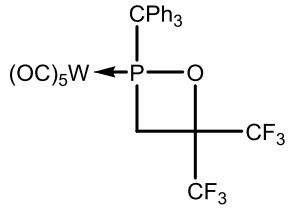
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2075 (s, $\nu$(CO)), 1995 (w, $\nu$(CO)), 1909 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 45.66 | H | 2.55 |
| found: | C | 46.01 | H | 3.07 |

**Single crystal measurement:** GSTR398, AKY-487 // GXray3940f

## 11.2.8.21 Pentacarbonyl[4,4-bis(trifluoromethyl)-2-(triphenylmethyl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [25.3b]




**Purification:** After the reaction solution reached – 10 °C (ca. 105 min.), the solvent was removed in *vacuo* (ca. 0.02 mbar). The crude product was extracted with diethyl ether (three times 20 mL) and the extract, after evaporation of all volatiles in *vacuo* (ca. 0.02 mbar), subjected to column chromatography ($Al_2O_3$, ø= 2 cm, h = 7 cm, petroleum ether 40/60, -20 °C). After 60 mL of petroleum ether were added a fraction using petroleum ether/toluene (5:1, 120 mL) and one fraction using petroleum ether/toluene (5:2, 135 mL) were collected. After combining, the solvent of the petroleum ether/toluene fractions was removed in *vacuo* (ca. 0.02 mbar) to yield the product as colourless foam that was washed once with 4 mL of petroleum ether at -25 °C. Final drying at ca. 0.02 mbar yielded the product as white powder.

**Molecular formula:** $C_{28}H_{17}F_6O_6PW$

**Molecular weight:** 778.235 g/mol

**Melting point:** 147 °C

**Yield:** 188 mg (0.24 mmol, 32 %)

**$^1$H NMR (500.17 MHz, $CDCl_3$):** δ = 3.62 (dd, 1H, $^2J_{H,H}$ = 15.2 Hz, $^2J_{P,H}$ = 3.4 Hz, C$H_2$), 4.26 (dd, 1H, $^2J_{H,H}$ = 15.2 Hz, $^2J_{P,H}$ = 11.3 Hz, C$H_2$), 7.30 - 7.56 (m, 15H, C$Ph_3$).

**$^{13}$C{$^1$H} NMR (125.78 MHz, $CDCl_3$):** δ = 36.3 (d, $^1J_{P,C}$ = 24.4 Hz, P-$C$H$_2$), 70.6 (d, $^1J_{P,C}$ = 6.4 Hz, $C$Ph$_3$), 81.6 - 83.3 (m, $C$(CF$_3$)$_2$), 120.4 (q, $^1J_{F,C}$ = 287.2 Hz, $C$F$_3$), 122.3 (q, $^1J_{P,C}$= 287.2 Hz, CF$_3$), 128.2 (s, *para*-$C$H$_{Ar}$), 128.9 (s, $C$H$_{Ar}$), 131.8 (d, $J_{P,C}$ = 7.06 Hz, $C$H$_{Ar}$), 139.4 (s$_{br}$, *ipso*-$C$), 195.3 (d$_{sat,br}$, $^2J_{P,C}$ = 4.6 Hz, $^1J_{W,C}$ = 127.0 Hz, *cis*-$C$O), 197.8 (d$_{sat}$, $^2J_{P,C}$ = 36.9 Hz, $^1J_{W,C}$ = 136.7 Hz, *trans*-$C$O).

**$^{19}$F{$^1$H} NMR (282.4 MHz, $CDCl_3$):** δ = -72.6 (qd, $^4J_{P,F}$ = 3.6 Hz, $^4J_{F,F}$ = 10.7 Hz, C$F_3$), -74.3 (q, $^4J_{F,F}$ = 10.7 Hz, C$F_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 190.7 (s$_{sat}$, $^1J_{W,P}$ = 299.0 Hz).

**LIFDI-MS:** m/z (%) = 778.0 (100) $[M]^{+\cdot}$, 243.1 (15) $[CPh_3]^+$.

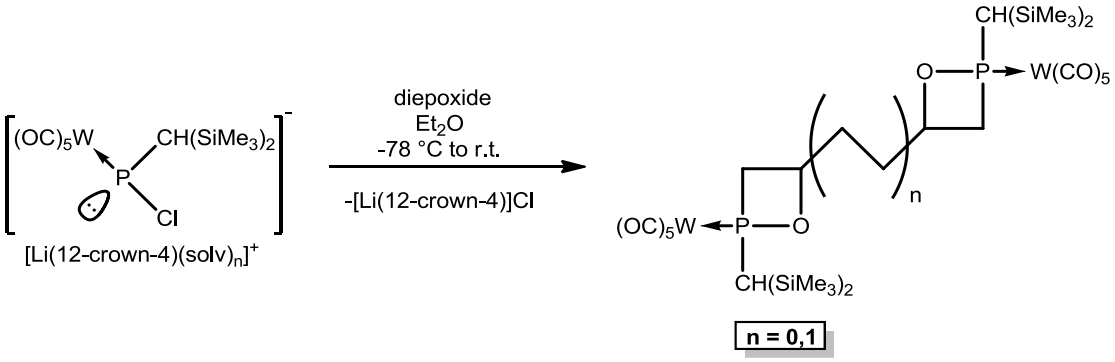
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2076 (s, ν(CO)), 1996 (m, ν(CO)), 1951 (w, ν(CO)), 1922 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 43.21 | H | 2.20 |
| found: | C | 43.23 | H | 2.46 |

**Single crystal measurement:** GSTR494, PB-13 // GXraymo_4641f

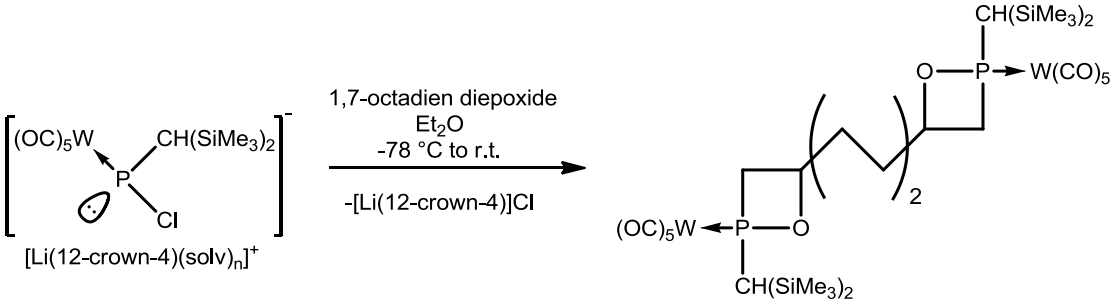
## 11.2.9 Attempted reactions of Li/Cl phosphinidenoid complex 2.1 with 1,3-butadiene diepoxide and 1,5-hexadiene diepoxide




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.1** was prepared as described, starting from 117 mg (0.2 mmol) of $[(OC)_5W\{P(CH(SiMe_3)_2)Cl_2\}]$ (**1.1**) and either 9 µL (0.1 mmol, 0.5 eq.) of 1,3-butadiene diepoxide (**20f, n = 0**) or 11 µL (0.1 mmol, 0.5 eq.) of 1,5-hexadiene diepoxide (**28a, n = 1**) was added. The solution was allowed warming up to ambient temperature and during the warming up period formation of a white precipitate was observed.

Both reaction mixtures were subsequently analysed by $^{31}P\{^1H\}$ NMR measurement.

## 11.2.10 Synthesis of 1,4-bis[(pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-4-yl}-κ*P*)tungsten(0)]butane [29.1c]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.1** was prepared as described, starting from 585 mg (1.0 mmol) of $[(OC)_5W\{P(CH(SiMe_3)_2)Cl_2\}]$ (**1.1**) and 71 µL (0.50 mmol, 0.5 eq.) of 1,7-octadien diepoxide (**28b**) was added. The solution was allowed warming up to ambient temperature and during the warming up period formation of a white precipitate was observed.

**Purification:** All volatiles were removed in *vacuo* (ca 0.02 mbar). The product was purified by extraction with *n*-pentane (3 times 20 mL) and subsequent recrystallization from a saturated *n*-pentane solution at 4 °C. Complex **29.1c** was obtained as colorless crystals after drying in *vacuo* (ca. 0.02 mbar) and as a mixture of isomers. All data are given for the isomeric mixture.

**Molecular formula:** $C_{32}H_{52}O_{12}P2Si_4W_2$

**Molecular weight:** 1170.724 g/mol

**Yield:** 180 mg (0.154 mmol, 31 %)

**$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$):** Three sets of signals between 165 - 168 ppm, 171 - 172 ppm and 177 - 180 ppm were observed. No further NMR distinguishing was possible due to the high amount of signals present.

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 1170.1 (30) $[M]^{\bullet+}$, 1086.0 (5) [M - 3 CO]$^+$, 974.1 (5) [M - 7 CO]$^+$, 945.9 (5) [M - 8 CO]$^+$, 890.1 (20) [M - 10 CO]$^+$, 640.2 (40) [M - $(OC)_5WP(O)(CH(SiMe_3)_2)]^+$, 530.0 (20) $[(OC)_5WP(O)(CH(SiMe_3)_2)]^+$, 502.1 (40) $[(OC)_5WP(O)(CH(SiMe_3)_2)$ - CO$]^+$, 474.0 (30) $[(OC)_5WP(O)(CH(SiMe_3)_2)$ - 2 CO$]^+$, 446.0 (40) $[(OC)_5WP(O)(CH(SiMe_3)_2)$ - 3 CO$]^+$, 418.0 (40) $[(OC)_5WP(O)(CH(SiMe_3)_2)$ - 4 CO$]^+$, 390.0 (80) $[(OC)_5WP(O)(CH(SiMe_3)_2)$ - 5 CO$]^+$, 73.1 (100) $[Me_3Si]^+$.

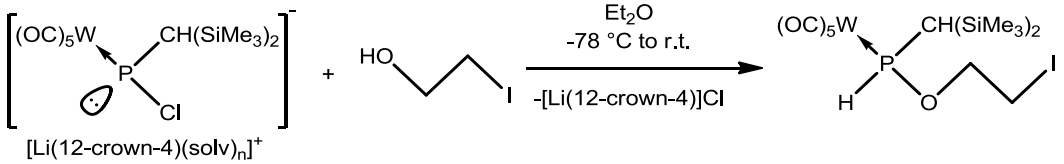
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2069 (s, $\nu$(CO)), 1978 (w, $\nu$(CO)), 1895 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 32.83 | H | 4.48 |
| found: | C | 33.08 | H | 4.56 |

**Single crystal measurement:** GSTR348, 3322f

## 11.2.11 Synthesis of pentacarbonyl{(2-iodoethoxy)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [33.1$_W$]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.1** was prepared as described, starting from 585 mg (1.0 mmol) of [$(OC)_5W\{P(CH(SiMe_3)_2)Cl_2\}$] (**1.1**) and 0.08 mL (1.03 mmol, 1.03 eq.) of 2-iodoethanol (**35a**) was added. The solution was allowed warming up to ambient temperature and during the warming up period formation of a white precipitate was observed.

**Purification:** After the reaction was completed (checked by $^{31}$P NMR), all volatiles were removed in *vacuo* (ca. 0.02 mbar).The product was extracted from the formed salt with three times 20 mL of *n*-pentane and the solvent was removed in *vacuo* (ca. 0.02 mbar) to yield **33.1$_W$** as yellow oil.

**Molecular formula:** $C_{14}H_{24}IO_6PSi_2W$

**Molecular weight:** 686.226 g/mol

**Yield:** 624 mg (0.91 mmol, 91 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.22 (s, 9H, Si(C*H*$_3$)$_3$), 0.30 (s, 9H, Si(C*H*$_3$)$_3$), 0.95 (s, 1H, P-C*H*), 3.30 (dd, 2H, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 6.0 Hz, C*H*$_2$-I), 3.73 - 3.91 (m, 1H, P-OC*H*$_2$), 4.00 - 4.18 (m, 1H, P-O-C*H*$_2$), 7.96 (dd, 1H, $^1J_{P,H}$ = 321.4 Hz, $^3J_{H,H}$ = 1.2 Hz, P-*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 0.4 (d, $^3J_{P,C}$ = 2.3 Hz, Si(*C*H$_3$)$_3$), 1.3 (d, $^3J_{P,C}$ = 9.1 Hz, *C*H$_2$-I), 2.4 (d, $^3J_{P,C}$ = 3.2 Hz, Si(*C*H$_3$)$_3$), 23.7 (d, $^1J_{P,C}$ = 13.6 Hz, P-*C*H), 70.0 (d, $^2J_{P,C}$ = 2.6 Hz, P-O*C*H$_2$), 196.6 (d$_{sat}$, $^1J_{W,C}$ = 125.1 Hz, $^2J_{P,C}$ = 7.4 Hz, *cis*-*C*O), 199.1 (d, $^2J_{P,C}$ = 25.2 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $CDCl_3$):** δ = 0.89 (d, $^2J_{P,Si}$ = 5.8 Hz, *Si*(CH$_3$)$_3$), 2.61 (d, $^2J_{P,Si}$ = 9.2 Hz, *Si*(CH$_3$)$_3$).

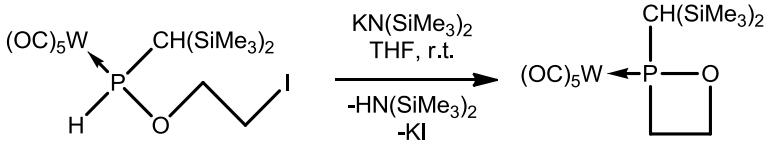
**$^{31}$P NMR (121.5 MHz, $CDCl_3$):** δ = 106.7 (dm$_{sat}$, $^1J_{W,P}$ = 270.3 Hz, $^1J_{P,H}$ = 321.4 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 686.0 (15) [M]$^{\bullet+}$, 657.9 (10) [M - CO]$^+$, 602.0 (20) [M - 3 CO]$^+$, 574.0 (30) [M - 4 CO]$^+$, 546.0 (25) [M - 5 CO]$^+$, 73.1 (100) [SiMe$_3$]$^+$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2263 (w, ν(PH)), 2071 (s, ν(CO)), 1981 (w, ν(CO)), 1904 (vs, ν(CO)).

**Single crystal measurement:** GSTR383, AKY-424 // GXray3760f

## 11.2.12 Synthesis of pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [34.1$_W$]




**Synthesis:** In a 50 mL Schlenk tube, 687.5 mg (1.26 mmol) of complex **33.1$_W$** were dissolved in 30 mL of THF. To it 315 mg (1.58 mmol, 1.25 eq.) of potassium hexamethyldisilazide in 3 mL of THF were added dropwise at room temperature. During addition a rapid formation of a precipitate and a change of the colour to yellow-brown was observed. The solution was kept on stirring for additional 60 minutes.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was purified by extraction from the formed salt with *n*-pentane (4 times 20 mL), followed by removal of all volatiles. Subsequent precipitation from 5 mL of *n*-pentane at -100 °C and filtering off the supernatant solution, which was repeated four times, yielded complex **34.1$_W$** as white powder, after drying in *vacuo* (ca. 0.02 mbar).

| | |
|---|---|
| **Molecular formula:** | $C_{14}H_{23}O_6PSi_2W$ |
| **Molecular weight:** | 558.314 g/mol |
| **Melting point:** | 77 °C |
| **Yield:** | 457 mg (0.819 mmol, 65 %) |

***Measurement in $C_6D_6$:***

**$^1$H NMR (300.1 MHz, $C_6D_6$):** δ = 0.08 (d, $^4J_{P,H}$ = 0.4 Hz, 9H, Si(C$H_3$)$_3$), 0.16 (s, 9H, Si(C$H_3$)$_3$), 2.00 (d, 1H, $^2J_{P,H}$ = 8.8 Hz, P-C*H*), 2.64 (ddd, 1H, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 5.0 Hz, P-C$H_2$), 2.98 (dddd, 1H, $^2J_{P,H}$ = 13.0 Hz, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 8.2 Hz, P-C$H_2$), 4.04 (dddd, 1H, $^3J_{P,H}$ = 10.5 Hz, $^3J_{H,H}$ = 10.2 Hz, $^2J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 5.0 Hz, O-C$H_2$), 4.48 (dddd, 1H, $^3J_{P,H}$ = 4.5 Hz, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 8.2 Hz, $^2J_{H,H}$ = 7.5 Hz, O-C$H_2$).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$):** δ = 1.7 (d, $^3J_{P,C}$ = 4.2 Hz, Si(*C*H$_3$)$_3$), 2.1 (d, $^3J_{P,C}$ = 2.6 Hz, Si(*C*H$_3$)$_3$), 35.4 (d$_{br}$, P-*C*H$_2$), 38.5 (d, $^1J_{P,C}$ = 14.6 Hz, P-*C*H), 68.9 (d, $^2J_{P,C}$ = 15.2 Hz, O-*C*H$_2$), 197.5 (d$_{sat}$, $^1J_{W,C}$ = 125.8 Hz, $^2J_{P,C}$ = 7.8 Hz, *cis*-*C*O), 200.7 (d, $^2J_{P,C}$ = 25.2 Hz, *trans*-*CO*).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$):** δ = -2.52 (s, *Si*(CH$_3$)$_3$), 0.05 (d, $^2J_{P,Si}$ = 6.0 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $C_6D_6$):** δ = 190.3 (s$_{sat}$, $^1J_{W,P}$ = 267.7 Hz).

***Measurement in $CDCl_3$:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.32 (d, $^4J_{P,H}$ = 0.4 Hz, 9H, Si(C$H_3$)$_3$), 0.32 (s, 9H, Si(C$H_3$)$_3$), 2.10 (d, 1H, $^2J_{P,H}$ = 8.7 Hz, P-C*H*), 3.21 (ddd, 1H, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 5.0 Hz, P-C$H_2$), 3.60

(dddd, 1H, $^{2}J_{P,H}$ = 13.3 Hz, $^{2}J_{H,H}$ = 13.2 Hz, $^{3}J_{H,H}$ = 10.2 Hz, $^{3}J_{H,H}$ = 8.0 Hz, P-C$H_2$), 4.71 (dddd, 1H, $^{3}J_{P,H}$ = 10.3 Hz, $^{3}J_{H,H}$ = 10.2 Hz, $^{2}J_{H,H}$ = 7.4 Hz, $^{3}J_{H,H}$ = 5.0 Hz, O-C$H_2$), 5.00 (dddd, 1H, $^{3}J_{P,H}$ = 4.6 Hz, $^{3}J_{H,H}$ = 8.2 Hz, $^{3}J_{H,H}$ = 8.0Hz, $^{2}J_{H,H}$ = 7.4 Hz, O-C$H_2$).

**$^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.0 (d, $^{3}J_{P,C}$ = 4.1 Hz, Si(*C*$H_3$)$_3$), 2.3 (d, $^{3}J_{P,C}$ = 2.1 Hz, Si(*C*$H_3$)$_3$), 35.4 ($d_{br}$, P-*C*$H_2$), 38.7 (d, $^{1}J_{P,C}$ = 14.2 Hz, P-*C*H), 69.0 (d, $^{2}J_{P,C}$ = 15.3 Hz, O-*C*$H_2$), 197.2 ($d_{sat}$, $^{1}J_{W,C}$ = 125.9 Hz, $^{2}J_{P,C}$ = 7.9 Hz, *cis-CO*), 200.6 ($d_{sat}$, $^{1}J_{W,C}$ = 137.7 Hz, $^{2}J_{P,C}$ = 26.0 Hz, *trans-CO*).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 191.4 ($s_{sat}$, $^{1}J_{W,P}$ = 268.5 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 558.1 (50) $[M]^{\bullet+}$, 502.1 (20) $[M - 2\ CO]^{+}$, 474.1 (30) $[M - 3\ CO]^{+}$, 446.0 (20) $[M - 4\ CO]^{+}$, 418.0 (40) $[M - 5\ CO]^{+}$, 390.0 (100) $[M - 5\ CO - C_2H_4]^{+}$, 73.1 (70) $[SiMe_3]^{+}$.

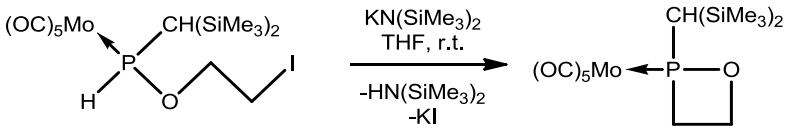
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2071 (s, ν(CO)), 1992 (w, ν(CO)), 1908 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 30.12 | H | 4.15 |
| found: | C | 30.23 | H | 4.30 |

**Single crystal measurement:** GSTR389, AKY-466 // GXray3853f

## 11.2.13 Synthesis of pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}molybdenum(0) [34.1$_{Mo}$]




**Synthesis:** In a 50 mL Schlenk tube 522 mg (0.87 mmol) of complex **33.1$_{Mo}$** were dissolved in 10 mL of THF. To it 184 mg (0.92 mmol, 1.06 eq.) of potassium hexamethyldisilazide in 5 mL of THF were added dropwise at room temperature. The solution was kept on stirring for 30 minutes. During addition a rapid formation of a precipitate and a change of the colour to red-brown was observed.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar), yielding a red oil. This crude material was further purified by low temperature column chromatography (ø = 2 cm, h = 10 cm, $SiO_2$, petroleum ether 40/60, -20 °C).

The product was obtained in the third, orange fraction using petroleum ether and diethyl ether (ratio PE/DE 50:2), after separation of the acyclic side products using pure petroleum ether (200 mL) and separating a yellow fraction using petroleum ether/diethyl ether mixture (50:2) (250 mL).

After evaporation of the solvent in *vacuo* (ca. 0.02 mbar) an orange oil was obtained. The final product was obtained by dissolving the oil in *n*-pentane and precipitation at -100 °C, followed by filtration and drying of the solid in *vacuo* (ca. 0.02 mbar).

**Molecular formula:** $C_{14}H_{23}MoO_6PSi_2$

**Molecular weight:** 470.433 g/mol

**Melting point:** 64 - 65 °C

**Yield:** 162 mg (0.34 mmol), 39 %

**$^1$H NMR (500.1 MHz, $CDCl_3$):** $\delta$ = 0.26 (s, 9H, Si(C$H_3$)$_3$), 0.31 (s, 9H, Si(C$H_3$)$_3$), 1.97 (d, 1H, $^2J_{P,H}$ = 7.6 Hz, P-C*H*), 3.11 (ddd, 1H, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 5.0 Hz, P-C$H_2$), 3.45 (dddd, 1H, $^2J_{P,H}$ = 12.5 Hz, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 8.5 Hz, P-C$H_2$), 4.73 (dddd, 1H, $^3J_{P,H}$ = 9.8 Hz, $^3J_{H,H}$ = 10.3 Hz, $^2J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 5.0 Hz, O-C$H_2$), 5.05 (dddd, 1H, $^3J_{P,H}$ = 4.3 Hz, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 8.2 Hz, $^2J_{H,H}$ = 7.5 Hz, O-C$H_2$).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 2.0 (d, $^3J_{P,C}$ = 4.2 Hz, Si(*C*H$_3$)$_3$), 2.3 (d, $^3J_{P,C}$ = 2.2 Hz, Si(*C*H$_3$)$_3$), 35.1 (s$_{br}$, P-*C*H$_2$), 38.7 (d, $^1J_{P,C}$ = 19.8 Hz, P-*C*H), 69.3 (d, $^2J_{P,C}$ = 14.2 Hz, O-*C*H$_2$), 205.5 (d$_{sat}$, $^1J_{Mo,C}$ = 68.2 Hz, $^2J_{P,C}$ = 10.4 Hz, *cis*-*C*O), 210.8 (d, $^2J_{P,C}$ = 27.5 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** $\delta$ = -2.6 (s, *Si*(CH$_3$)$_3$), -0.26 (d, $^2J_{P,Si}$ = 5.4 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 225.0 (s$_{sat}$, $^1J_{Mo,P}$ = 151.7 Hz).

**MS (EI, 70 eV, $^{98}$Mo, selected data):** m/z (%) = 471.9 (35) $[M]^{\cdot+}$, 443.9 (2) $[M - CO]^+$, 415.9 (28) $[M - 2\ CO]^+$, 387.9 (91) $[M - 3\ CO]^+$, 359.9 (26) $[M - 4\ CO]^+$, 331.9 (65) $[M - 5\ CO]^+$, 301.9 (100) $[M - 5\ CO - C_2H_6]^+$, 271.9 (42) $[M - 5\ CO - 2\ C_2H_6]^+$, 269.9 (56) $[M - 5\ CO - 2\ C_2H_6 - H_2]^+$, 75.0 (16) $[POC_2H_4]^+$, 73.0 (71) $[SiMe_3]^+$.

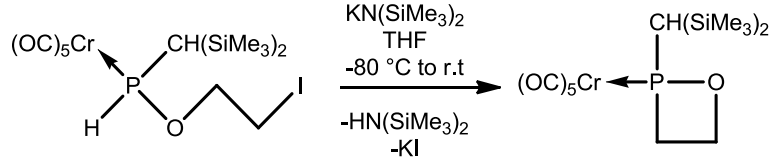
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 1996 (s, $\nu$(CO)), 1983 (s, $\nu$(CO)), 1913 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 35.74 | H | 4.98 |
| found: | C | 35.73 | H | 5.04 |

**Single crystal measurement:** GSTR493, FG-oxa // GXray4661f

## 11.2.14 Synthesis of pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}chromium(0) [34.1$_{Cr}$]




**Synthesis:** In a 100 mL Schlenk tube 1.108 g (2.0 mmol) of complex **33.1$_{Cr}$** were dissolved in 60 mL of THF. To it 439 mg (2.2 mmol, 1.1 eq.) of potassium hexamethyldisilazide were added as a solid at -80 °C. During addition a rapid formation of precipitate and a change of the colour to yellow-brown was observed. The solution was allowed to slowly warm up to ambient temperature overnight.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude material was subjected to low temperature column chromatography (ø = 3 cm, h = 5 cm, $SiO_2$, PE, - 20 °C). A first fraction using petroleum ether (200 mL) was discarded and a fraction using a mixture of petroleum ether and diethyl ether (40 : 1) was collected. All volatiles were removed from the second fraction in *vacuo* (ca. 0.02 mbar) and the formed solid was four times washed with 3 mL of *n*-pentane at - 100 °C. Drying of the product in *vacuo* (ca. 0.02 mbar) yielded **34.1$_{Cr}$** as white solid.

| | |
|---|---|
| **Molecular formula:** | $C_{14}H_{23}CrO_6PSi_2$ |
| **Molecular weight:** | 426.470 g/mol |
| **Melting point:** | 91 °C |
| **Yield:** | 270 mg (0.63 mmol, 32 %) |

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.26 (s, 9H, Si(C*H*$_3$)$_3$), 0.32 (s, 9H, Si(C*H*$_3$)$_3$), 1.99 (d, 1H, $^2J_{P,H}$ = 8.2 Hz, P-C*H*), 3.10 - 3.25 (m, 1H, P-C*H*$_2$), 3.35 - 3.57 (m, 1H, P-C*H*$_2$), 4.65 - 4.80 (m, 1H, O-C*H*$_2$), 4.96 - 5.11 (m, 1H, O-C*H*$_2$).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 1.9 (d, $^3J_{P,C}$ = 4.0 Hz, Si(*C*H$_3$)$_3$), 2.3 (d, $^3J_{P,C}$ = 1.9 Hz, Si(*C*H$_3$)$_3$), 34.6 (d$_{br}$, P-*C*H$_2$), 39.0 (d, $^1J_{P,C}$ = 18.6 Hz, P-*C*H), 69.3 (d, $^2J_{P,C}$ = 14.6 Hz, O-*C*H$_2$), 216.2 (d, $^2J_{P,C}$ = 15.2 Hz, *cis*-*C*O), 221.3 (d, $^2J_{P,C}$ = 6.6 Hz, *trans*-*CO*).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 250.2 (s).

**MS (EI, 70 eV, $^{52}$Cr, selected data):** m/z (%) = 426.0 (20) $[M]^{\bullet+}$, 370.0 (10) $[M - 2\ CO]^+$, 342.0 (50) $[M - 3\ CO]^+$, 314.0 (35) $[M - 4\ CO]^+$, 286.0 (100) $[M - 5\ CO]^+$, 258.0 (80) $[M - 5\ CO - C_2H_4]^+$, 73.0 (25) $[SiMe_3]^+$.

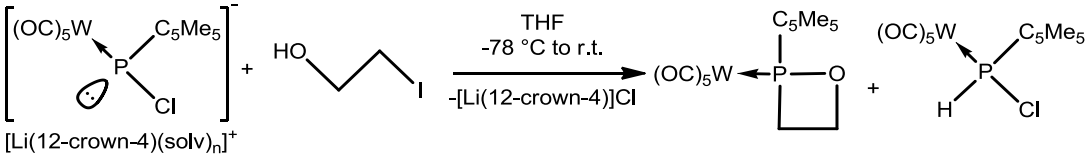
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2063 (s, ν(CO)), 1993 (w, ν(CO)), 1906 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 39.43 | H | 5.44 |
| found: | C | 39.21 | H | 5.51 |

**Single crystal measurement:** GSTR461, AKY-526 // GXraymo_4477f

## 11.2.15 Synthesis of pentacarbonyl[2-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [34.2]




**Synthesis:** A solution of the Li/Cl phosphinidenoid complex **2.2** was prepared as described, starting from 841.5 mg (1.5 mmol) of dichlorophosphane complex $[(OC)_5W\{PCl_2(C_5Me_5)\}]$ (**2.2**), but using THF as solvent under otherwise similar conditions. 0.2 mL (2.58 mmol, 1.7 eq.) of 2-iodoethanol (**35a**) was added. The solution was allowed warming up to ambient temperature and during the warming up period formation of a white precipitate was observed.

**Purification:** After the reaction was completed (checked by $^{31}P$ NMR spectroscopy), a small amount of $SiO_2$ was added and all volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was subjected to column chromatography (ø = 2 cm, h = 5 cm, petroleum ether, - 20 °C, $SiO_2$). The first fraction using pure petroleum ether contained acyclic side products. The second fraction using petroleum ether and diethyl ether (ratio 50:0.5) contained the product and **XXXVIII** as impurity. The solvent was removed in *vacuo* (ca. 0.02 mbar), the product was sublimed at 110 °C and 2.6 $\cdot 10^{-2}$ mbar over one hour and obtained as slightly orange solid.

**Molecular formula:** $C_{17}H_{19}O_6PW$

**Molecular weight:** 534.143 g/mol

**Melting point:** 59-60 °C

**Yield:** 160 mg (0.30 mmol, 20 %)

**$^1$H NMR (400.1 MHz, $CDCl_3$):** $\delta$ = 1.74 (d, 3H, $J_{P,H}$ = 11.0 Hz, $C_5Me_5$), 1.75 (s, 3H, $C_5Me_5$), 1.80 (dq, 3H, $J_{P,H}$ = 5.0 Hz, $J_{H,H}$ = 1 Hz, $C_5Me_5$), 1.82 (dq, 3H, $J_{P,H}$ = 4.3 Hz, $J_{H,H}$ = 1.0 Hz, $C_5Me_5$), 1.93 (s, 3H, $C_5Me_5$), 3.34 (dddd, 1H, $^2J_{P,H}$ = 0.4 Hz, $^2J_{H,H}$ = 13.8 Hz, $^3J_{H,H}$ = 9.2 Hz, $^3J_{H,H}$ = 6.6 Hz, P-C$H_2$), 3.63 (dddd, 1H, $^2J_{P,H}$ = 5.3 Hz, $^2J_{H,H}$ = 13.8 Hz, $^3J_{H,H}$ = 9.7 Hz, $^3J_{H,H}$ = 6.5 Hz, P-C$H_2$), 5.05 (dddd, 1H, $^3J_{P,H}$ = 2.2 Hz, $^2J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 9.7 Hz, $^3J_{H,H}$ = 6.6 Hz, O-C$H_2$), 5.16 (dddd, 1H, $^3J_{P,H}$ = 3.3 Hz, $^2J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 9.2 Hz,$^3J_{H,H}$ = 6.5 Hz, O-C$H_2$).

**$^{13}C\{^1H\}$ NMR (100.7 MHz, $CDCl_3$):** $\delta$ = 11.5 (d, $J_{P,C}$ = 2.8 Hz, $C_5Me_5$), 11.5 (d, $J_{P,C}$ = 1.5 Hz, $C_5Me_5$), 11.7 (d, $J_{P,C}$ = 1.5 Hz, $C_5Me_5$), 11.8 (d, $J_{P,C}$ = 2.0 Hz, $C_5Me_5$), 13.2 (d, $J_{P,C}$ = 4.8 Hz, $C_5Me_5$), 32.2 (d, $^1J_{P,C}$ = 23.5 Hz, P-$CH_2$), 65.4 (d, $^1J_{P,C}$ = 2.9 Hz, P-$C_5Me_5$), 73.1 (d, $^2J_{P,C}$ = 13.7 Hz, O-$CH_2$), 132.7 (d, $J_{P,C}$ = 7.3 Hz, $C_5Me_5$), 138.9 (d, $J_{P,C}$ = 1.7 Hz, $C_5Me_5$), 141.4 (d, $J_{P,C}$ = 5.9 Hz, $C_5Me_5$), 143.4 (d, $J_{P,C}$ = 7.0 Hz, $C_5Me_5$), 196.1 ($d_{sat}$, $^1J_{W,C}$ = 125.6 Hz, $^2J_{P,C}$ = 7.8 Hz, *cis*-CO), 199.4 ($d_{sat}$, $^1J_{W,C}$ = 139.2 Hz, $^2J_{P,C}$ = 28.0 Hz, *trans*-CO).

**$^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$):** $\delta$ = 204.8 ($s_{sat}$, $^1J_{W,P}$ = 275.5 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 534.0 (40) $[M]^{\bullet+}$, 450.0 (5) $[M - 3\ CO]^+$, 398.8 (65) $[M - C_5Me_5]^+$, 370.8 (100) $[M - C_5Me_5 - CO]^+$, 342.8 (30) $[M - C_5Me_5 - 2\ CO]^+$, 314.8 (20) $[M - C_5Me_5 - 3\ CO]^+$, 286.8 (20) $[M - C_5Me_5 - 4\ CO]^+$, 258.9 (10) $[M - C_5Me_5 - 5\ CO]^+$, 135.1 (70) $[C_5Me_5]^+$, 119.0 (50) $[C_5Me_5 - CH_4]^+$, 105.0 (40) $[C_5Me_5 - C_2H_6]^+$, 91.0 (20) $[C_5Me_5 - C_3H_8]^+$.

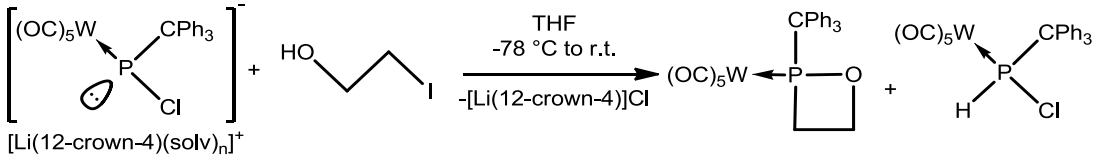
HR-MS: calculated for $C_{17}H_{19}O_6PW$: 532.0402 found: 532.0404 (standard deviation: 0.35 ppm).

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selection):** 2069 (s, $\nu$(CO)), 1977 (w, $\nu$(CO)), 1896 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 38.23 | H | 3.59 |
| found: | C | 38.68 | H | 3.74 |

## 11.2.16 Attempted synthesis of pentacarbonyl[2-(triphenylmethyl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [34.3]

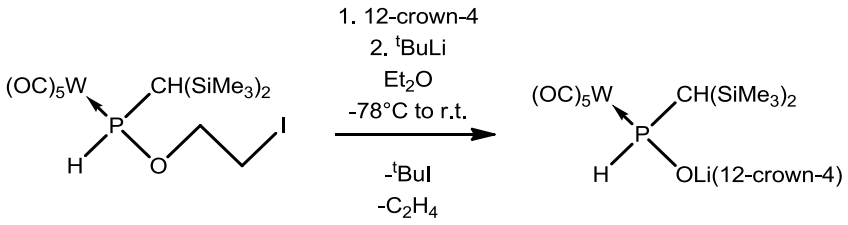



**Synthesis:** A solution of the Li/Cl phosphinidenoid complex **2.3** was prepared as described, starting from 334.5 mg (0.5 mmol) of dichlorophosphane complex $[(OC)_5W\{PCl_2(CPh_3)\}]$ (**2.3**). 39 µL (0.50 mmol, 1 eq.) of 2-iodoethanol (**35a**) was added. The solution was allowed warming up to ambient temperature and during the warming up period formation of a white precipitate was observed. The $^{31}P\{^1H\}$ spectrum showed the resonance signals for 1,2-oxaphosphetane complex **34.3** and the chloro(organo)phosphane complex **10.3** as main products.

**34.3:**

**$^{31}P\{^1H\}$ NMR (121.5 MHz, THF):** $\delta$ = 193.4 ($s_{sat}$, $^1J_{W,P}$ = 277.8 Hz).

## 11.2.17 Synthesis of lithium(1,4,7,10-tetraoxacyclododecane) pentacarbonyl{[bis(trimethylsilyl)methyl]phosphanoxido-κ*P*}tungsten(0) [36.1]




**Synthesis:** In a 100 mL Schlenk tube, 643.2 mg (0.924 mmol) of complex **33.1$_W$** were dissolved in 30 mL of diethyl ether. To it 148 µL (0.925 mmol, 1 eq.) of 12-crown-4 was added at ambient temperature and the mixture was cooled to -78 °C. Then 0.55 mL (0.93 mmol, 1.7 M in *n*-pentane, 1.0 eq.) of $^t$BuLi was added upon which a change to a light yellow colour and the formation of a yellow precipitate was observed. The reaction mixture was kept on stirring while slowly warming up to ambient temperature.

**Purification:** After the reaction was completed (checked by $^{31}$P NMR), all volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was purified by washing it three times with 5 mL of *n*-pentane and drying it in *vacuo* (ca. 0.02 mbar), yielding a slightly yellow solid.

**Molecular formula:** $C_{20}H_{36}LiO_{10}PSi_2W$

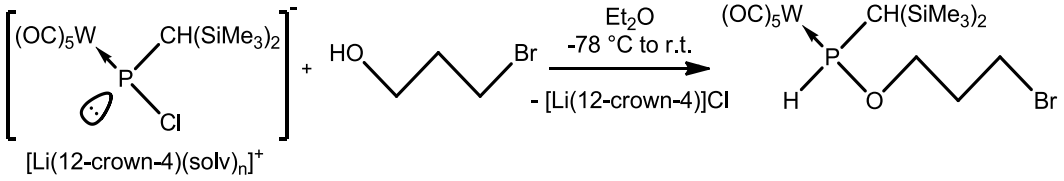
**Molecular weight:** 714.420 g/mol

**Yield:** 547 mg (0.77 mmol, 83 %)

All data are in good accordance to previously reported values.[132]

**$^{31}$P{$^1$H} NMR (121.5 MHz, THF-d$_8$):** $\delta$ = 46.0 ($s_{sat}$, $^1J_{W,P}$ = 244.1 Hz, $^1J_{P,H}$ = 302.6 Hz).

## 11.2.18 Synthesis of {(4-bromopropoxy)[bis(trimethylsilyl)methyl]phosphane-κ*P*}pentacarbonyltungsten(0) [39.1]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.1** was prepared as described, starting from 877.5 mg (1.5 mmol) of [(OC)$_5$W{P(CH(SiMe$_3$)$_2$)Cl$_2$}] (**1.1**) and 0.14 mL (1.6 mmol, 1.06 eq.) of 3-bromopropane-1-ol (**38**) was added. The solution was allowed warming up to ambient temperature overnight and during warming up formation of a white precipitate was observed.

**Purification:** After the reaction was completed (checked by $^{31}$P NMR), all volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude mixture was extracted from the formed salt with *n*-pentane (3 times 40 mL) and the solvent was removed in *vacuo* (ca. 0.02 mbar). The crude product was subsequently placed in a sublimation flask and heated for 1.5 h (130 °C, $2 \cdot 10^{-2}$ mbar) to remove all volatile material and complexes with a lower molecular weight. The product was obtained as yellow-brownish oil.

**Molecular formula:** $C_{15}H_{26}O_6BrPSi_2W$

**Molecular weight:** 653.252 g/mol

**Yield:** 604 mg (0.930 mmol, 62 %)

**$^1$H NMR (500.2 MHz, $CDCl_3$):** $\delta$ = 0.21 (s, 9H, Si(C$H_3$)$_3$), 0.27 (s, 9H, Si(C$H_3$)$_3$), 0.93 (s, 1H, P-C*H*), 2.12 - 2.56 (m, 2H, C$H_2$), 3.46 - 3.51 (m, 2H, C$H_2$), 3.66 - 3.74 (m, 1H, $CH_2$), 3.87 - 3.96 (m, 1H, $CH_2$), 7.87 (dd, 1H, $^1J_{P,H}$ = 321.5 Hz, $^3J_{P,H}$ = 0.8 Hz, P-*H*).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 0.3 (d, $^3J_{P,C}$ = 2.2 Hz, Si(*C*H$_3$)$_3$), 2.2 (d, $^3J_{P,C}$ = 3.3 Hz, Si(*C*H$_3$)$_3$), 23.5 (d, $^1J_{P,C}$ = 13.1 Hz, P-*C*H), 29.4 (s, *C*H$_2$), 33.3 (d, $^1J_{P,C}$ = 8.7 Hz, *C*H$_2$), 67.1 (d, $^2J_{P,C}$ = 3.5 Hz, O-*C*H$_2$), 196.7 (d$_{sat}$, $^1J_{W,C}$ = 125.6 Hz, $^2J_{P,C}$ = 7.4 Hz, *cis*-*C*O), 199.3 (d$_{sat}$, $^1J_{W,C}$ = 140.3 Hz, $^2J_{P,C}$ = 25.1 Hz, *trans*-*C*O).

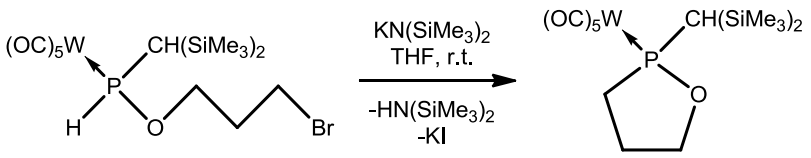
**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** $\delta$ = 1.12 (d, $^2J_{P,Si}$ = 5.5 Hz, *Si*(CH$_3$)$_3$), 2.97 (d, $^2J_{P,Si}$ = 9.1 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 104.7 (d$_{sat}$, $^1J_{W,P}$ = 268.1 Hz, $^1J_{P,H}$ = 321.5 Hz).

**pos. ESI-MS:** calculated for $(C_{15}H_{26}O_6BrPSi_2W)^+$: 651.970; found: 651.946 $[M]^+$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2262 (w, $\nu$(PH)), 2071 (s, $\nu$(CO)), 1981 (w, $\nu$(CO)), 1906 (vs, $\nu$(CO)).

## 11.2.19 Synthesis of pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphospholane-κ*P*}tungsten(0) [19.1]




**Synthesis:** In a 50 mL Schlenk tube, 514 mg (0.787 mmol) of complex **39.1** were dissolved in 25 mL of THF. To it 164 mg (0.82 mmol, 1.04 eq.) of potassium hexamethyldisilazide, dissolved in 10 mL of THF, were added dropwise at ambient temperature. During the addition a rapid formation of precipitate and a change of the color to yellow-orange was observed. The solution was kept on stirring for 1h.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was purified by extraction from the formed salt with *n*-pentane (4 times 20 mL), subsequent precipitation from *n*-pentane at -100 °C and filtering off the supernatant solution. This was repeated four times (once 5 mL and three times 2 mL) to yield the product as white powder after drying in *vacuo* (ca. 0.02 mbar).

| | |
|---|---|
| **Molecular formula:** | $C_{15}H_{25}O_6PSi_2W$ |
| **Molecular weight:** | 572.340 g/mol |
| **Melting point:** | 85 °C |
| **Yield:** | 102.5 mg (0.180 mmol, 23 %) |

**Isomeric ratio:** 99.5 : 0.5

***Isomer 1:***

**$^1$H NMR (500.1 MHz, $CDCl_3$):** δ = 0.24 (s, 9H, Si(C*H*$_3$)$_3$), 0.28 (s, 9H, Si(C*H*$_3$)$_3$), 1.64 (d, 1H, $^2J_{P,H}$ = 12.8 Hz, P-C*H*), 2.05 - 2.25 (m, 2H, C*H*$_2$), 2.50 - 2.64 (m, 2H, C*H*$_2$), 4.01 - 4.10 (m, 1H, C*H*$_2$), 4.11 - 4.20 (m, 1H, C*H*$_2$).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.6 (d, $^3J_{P,C}$ = 3.3 Hz, Si(*C*H$_3$)$_3$), 2.8 (d, $^3J_{P,C}$ = 2.2 Hz, Si(*C*H$_3$)$_3$), 25.3 (s, *C*H$_2$), 31.7 (s$_{br}$, P-*C*H), 37.2 (s$_{br}$, *C*H$_2$), 70.9 (d, $^2J_{P,C}$ = 5.7 Hz, O-*C*H$_2$), 197.6 (d$_{sat}$, $^1J_{W,C}$ = 126.2 Hz, $^2J_{P,C}$ = 8.2 Hz, *cis*-*C*O), 200.3 (d, $^2J_{P,C}$ = 24.8 Hz, *trans*-*C*O).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 139.5 (s$_{br}$, full-width at half-intensity (FWHI, $h_{1/2}$) = 760 Hz).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$, 60 °C):** δ = 138.4 ($^1J_{W,P}$ = 275.5 Hz).

***Isomer 2:***

No resonance signals except in the $^{31}$P NMR could be observed due to the isomers low percentage of the mixture.

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 125.2 (s$_{sat}$, $^1J_{W,P}$ = 267.1 Hz).

**pos. ESI-MS:** calculated for $(C_{15}H_{25}O_6PSi_2W)^+$: 572.04, found: 572.03 $[M]^+$, 287.11 [M - $W(CO)_5$ + Na + O]$^+$, 265.13 [M - $W(CO)_5$ + H + O]$^+$, 249.14 [M - $W(CO)_5$ + H]$^+$.

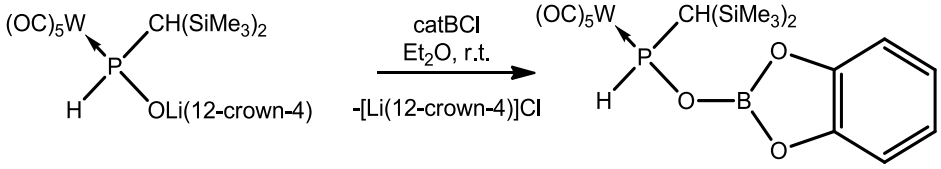
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2066 (s, $\nu$(CO)), 1981 (w, $\nu$(CO)), 1898 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 31.48 | H | 4.40 |
| found: | C | 31.41 | H | 4.34 |

**Single crystal measurement:** GSTR485, AKY-554 // GXraymo_4626f

## 11.2.20 Synthesis of pentacarbonyl{catecholboranoxo[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [41.1]




**Synthesis:** In a 10 mL Schlenk tube, 357.2 mg (0.5 mmol) of phosphinito complex **36.1** were dissolved in 2 mL of diethyl ether and a solution of 77.18 mg (0.5 mmol, 1.0 eq.) catechol(chloro)borane in 2 mL of diethyl ether was added dropwise.

**Purification:** After the reaction was completed (checked by $^{31}$P NMR) all volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude mixture was extracted from the formed salt with four times 1 mL of *n*-pentane and the solvent was removed in *vacuo* (ca. 0.02 mbar) to yield the product as white powder.

**Molecular formula:** $C_{18}H_{24}BO_8PSi_2W$

**Molecular weight:** 650.174 g/mol

**Yield:** 255 mg (0.39 mmol, 78 %)

**$^1$H NMR (300.1 MHz, $C_6D_6$):** $\delta$ = -0.03 (d, 9H, $^4J_{P,H}$ = 0.4 Hz, Si(C*H*$_3$)$_3$), 0.28 (s, 9H, Si(C*H*$_3$)$_3$), 0.98 (dd, 1H, $^2J_{P,H}$ = 3.2 Hz, $^3J_{H,H}$ = 2.3 Hz, P-C*H*), 6.66 - 6.72 (m, 2H, C*H*$_{Ar}$), 6.87 - 6.94 (m, 2H, C*H*$_{Ar}$), 8.46 (dd, 1H, $^1J_{P,H}$ = 341.8 Hz, $^3J_{H,H}$ = 2.3 Hz, P-*H*).

**$^{11}$B{$^1$H} NMR (96.3 MHz, $C_6D_6$):** $\delta$ = 21.7 (s).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$):** $\delta$ = 0.0 (d, $^3J_{P,C}$ = 2.9 Hz, Si(*C*H$_3$)$_3$), 2.2 (d, $^3J_{P,C}$ = 3.2 Hz, Si(*C*H$_3$)$_3$), 25.2 (d, $^1J_{P,C}$ = 11.0 Hz, P-*C*H), 112.7 (s, *C*H$_{Ar}$), 123.3 (s, *C*H$_{Ar}$), 148.0 (s, O-*C*), 196.6 (d$_{sat}$, $^1J_{W,C}$ = 126.1 Hz, $^2J_{P,C}$ = 7.4 Hz, *cis*-CO), 199.2 (d, $^2J_{P,C}$ = 27.8 Hz, *trans*-CO).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$):** $\delta$ = 1.0 (d, $^2J_{P,Si}$ = 6.1 Hz), 1.9 (d, $^2J_{P,Si}$ = 8.7 Hz).

**$^{31}$P NMR (121.5 MHz, $C_6D_6$):** $\delta$ = 97.7 ($d_{sat}$, $^1J_{W,P}$ = 277.1 Hz, $^1J_{P,H}$ = 331.6 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 650.0 (15) $[M]^{\bullet+}$, 622.0 (5) [M - 1 CO]$^+$, 594.0 (55) [M - 2 CO]$^+$, 73.1 (100) $[SiMe_3]^+$.

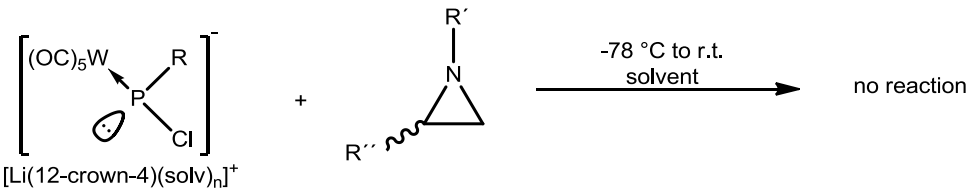
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2300 (w, $\nu$(PH)), 2075 (m, $\nu$(CO)), 1986 (w, $\nu$(CO)), 1944 (w, $\nu$(CO)) 1912 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 33.25 | H | 3.72 |
| found: | C | 33.49 | H | 3.97 |

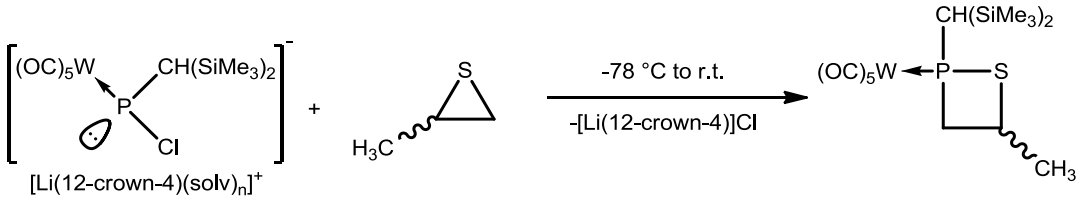
**Single crystal measurement:** GSTR385, AKY-458 // GXray3821

## 11.2.21 Attempted reactions of Li/Cl phosphinidenoid complexes 2.1 and 2.3 with aziridines 42a or 42b



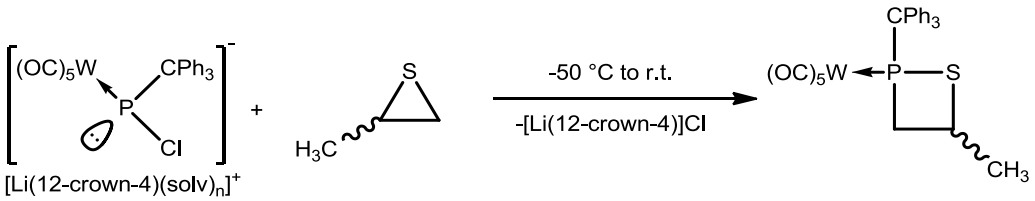

A solution of the Li/Cl phosphinidenoid complexes **2.1** or **2.3** was prepared starting from complexes **1.1** or **1.3**, respectively, as described in chapter 11.2.1. The corresponding aziridine (**42a** (R´= $^i$Pr, R´´ = Ph) or **42b** (R´ = $PhCH_2$, R´´ = $CF_3$)) was added in a two times excess via syringe and the solution was allowed slowly warming up to ambient temperature. The reaction mixtures were analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. No reaction was observed between the Li/Cl phosphinidenoid complexes and the used aziridines.

## 11.2.22 Attempted synthesis of pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-thiaphosphetane-κ*P*}tungsten(0) [46.1]




A solution of Li/Cl phosphinidenoid complex **2.1** was prepared as described, starting from 58.5 mg (0.1 mmol) of **1.1**, and 8 µL (0.102 mmol, 1.02 equivalents) of propylene sulfide (**45**) was added dropwise. The solution was allowed slowly warming up to ambient temperature and subsequently analysed by $^{31}P\{^1H\}$ NMR measurement. The NMR showed several resonance signals that could not be assigned to any desired or known product.

## 11.2.23 Synthesis of pentacarbonyl[4-methyl-2-(triphenylmethyl)-1,2-thiaphosphetane-κ*P*]tungsten(0) [46.3]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.3** was prepared as described, starting from 1.004 g (1.5 mmol) of [$(OC)_5W\{PCl_2(CPh_3)\}$] (**1.3**) and 0.2 mL (2.55 mmol, 1.7 equivalents) of propylene sulfide (**45**) was added dropwise. The solution was kept on stirring for 12 h, while being allowed slowly warming up to ambient temperature.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was purified by dissolving in diethyl ether and filtration over $Al_2O_3$ (ø = 2 cm, h = 5 cm). After removing of all volatiles in *vacuo* (ca. 0.02 mbar) the product was washed with three times 5 mL of petroleum ether 40/60 at -50 °C. Drying of the solid in *vacuo* (ca. 0.02 mbar) yielded the product as white solid.

| | |
|---|---|
| **Molecular formula:** | $C_{27}H_{21}O_5PSW$ |
| **Molecular weight:** | 672.331 g/mol |
| **Melting point:** | 138 °C |
| **Yield:** | 390 mg (0.58 mmol, 39 %) |

**Isomeric ratio:** 44 : 56

***Isomer 1:***

**$^1$H NMR (400.1 MHz, $CDCl_3$):** δ = 1.43 (d, 3H, $^3J_{H,H}$ = 6.6 Hz, C*H*$_3$), 3.15 - 3.25 (m, 1H, *CH*$_2$), 3.15 - 3.25 (m, 1H, C*H*$_2$), 3.39 - 3.50 (m, 1H, S-C*H*), 7.3 - 7.45 (m, 15H, C*Ph*$_3$).

**$^{13}$C{$^1$H} NMR (100.7 MHz, $CDCl_3$):** δ = 25.7 ($s_{br}$, *C*H$_3$), 39.1 (d, $^2J_{P,C}$ = 5.2 Hz, S-*C*H), 42.1 (d, $^1J_{P,C}$ = 29.7 Hz, P-*C*H$_2$), 65.3 (d, $^1J_{P,C}$ = 8.6 Hz, *C*Ph$_3$), 127.8 ($s_{br}$, *para-C*H$_{Ar}$), 128.4 ($s_{br}$, *C*H$_{Ar}$), 130.8 ($s_{br}$, *C*H$_{Ar}$), 142.3 (s, *ipso-C*), 197.5 ($dq_{sat}$, $^1J_{W,C}$ = 127.6 Hz, $^2J_{P,C}$ = 6.5 Hz, *cis-C*O), 200.0 (d, $^2J_{P,C}$ = 31.5 Hz, *trans-C*O).

**$^{31}$P{$^1$H} NMR (162.0 MHz, $CDCl_3$):** δ = 50.5 ($s_{sat}$, $^1J_{W,P}$ = 254.6 Hz).

***Isomer 2:***

**$^1$H NMR (400.1 MHz, $CDCl_3$):** δ = 1.05 (d, 3H, $J_{H,H}$ = 6.6 Hz, C*H*$_3$), 2.80 - 2.90 (m, 1H, P-*CH*$_2$), 3.10 - 3.15 (m, 1H, P-C*H*$_2$), 4.15 - 4.28 (m, 1H, S-C*H*), 7.3 - 7.45 (m, 15H, CPh$_3$).

**$^{13}$C{$^1$H} NMR (100.7 MHz, $CDCl_3$):** δ = 25.7 ($s_{br}$, *C*H$_3$), 35.6 (d, $^2J_{P,C}$ = 4.5 Hz, S-*C*H), 42.6 (d, $^1J_{P,C}$ = 24.6 Hz, P-*C*H$_2$), 66.3 (d, $^1J_{P,C}$ = 9.3 Hz, *C*Ph$_3$), 128.0 ($s_{br}$, *para-C*H$_{Ar}$), 128.4 ($s_{br}$, *C*H$_{Ar}$), 131.1 (d, $J_{P,C}$

= 7.7 Hz, *C*H$_{Ar}$), 141.6 (d, $^2J_{P,C}$ = 2.7 Hz, *ipso-C*), 197.2 (dq$_{sat}$, $^1J_{W,C}$ = 127.4 Hz, $^2J_{P,C}$ = 6.5 Hz, *cis-C*O), 199.5 (d, $^2J_{P,C}$ = 31.7 Hz, *trans-C*O).

**$^{31}$P{$^1$H} NMR (162.0 MHz, CDCl$_3$):** $\delta$ = 65.3 (s$_{sat}$, $^1J_{W,P}$ = 256.7 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 672.1 (2) $[M]^{\bullet+}$, 546.0 (8) $[M - 3\ CO - C_3H_6]^+$, 490.0 (65) $[M - 5\ CO - C_3H_6]^+$, 243.1 (100) $[CPh_3]^+$, 165.0 (30) $[CPh_3 - C_6H_6]^+$.

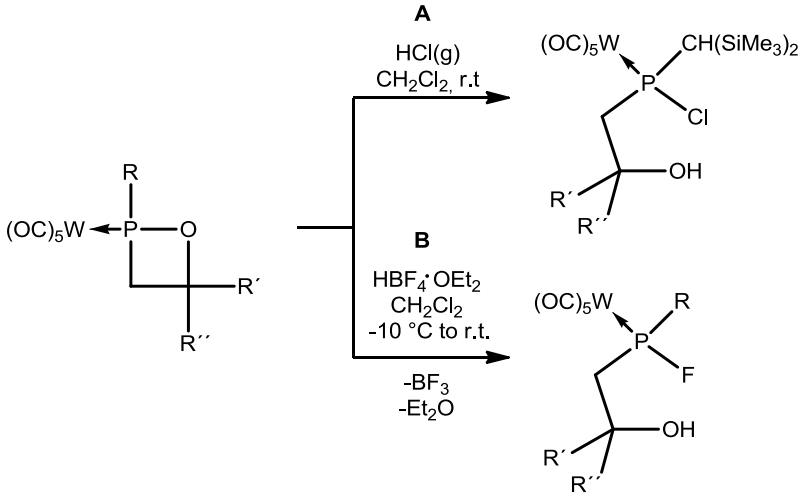
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2070 (s, $\nu$(CO)), 1984 (w, $\nu$(CO)), 1910 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 48.23 | H | 3.15 | S | 4.77 |
| found: | C | 48.54 | H | 3.20 | S | 4.79 |

**Single crystal measurement:** GSTR523, AKY-583 // GXray4889af

## 11.2.24 Acid induced ring opening reactions of 1,2-oxaphosphetane complexes




**A: Ring opening reactions using HCl$_{(g)}$**

**Syntheses:** In a 10 mL Schlenk tube the 1,2-oxaphosphetane complex was dissolved in $CH_2Cl_2$. A stream of $HCl_{(g)}$ (prepared by dropping concentrated hydrochloric acid on anhydrous $CaCl_2$) and argon was bubbled through the solution for $t^1$ minutes. The solution was subsequently stirred for additional $t^2$ hours (see table 11.3 for details).

***Table 11.3:*** Reaction conditions for the syntheses of **47.1a-c**.

| | R | R´ | R´´ | 1,2-oxaphopsphetane complex / m [mg] (n [mmol]) | V ($CH_2Cl_2$) [mL] | $t^1$ [min] | $t^2$ [h] |
|---|---|---|---|---|---|---|---|
| **47.1a** | $CH(SiMe_3)_2$ | H | H | **34.1$_W$** / 250 (0.45) | 4 | 30 | 1 |
| **47.1b** | $CH(SiMe_3)_2$ | H | $CH_3$ | **21.1a$_W$** / 300 (0.54) | 5 | 60 | 2 |
| **47.1c** | $CH(SiMe_3)_2$ | H | $CF_3$ | **21.1g** / 200 (0.32) | 5 | 180 | 12 |

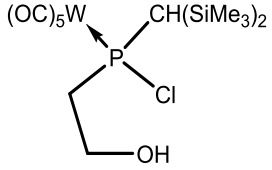
**B: Ring opening reactions using $HBF_4 \cdot OEt_2$**

**Syntheses:** In a 10 mL Schlenk tube the 1,2-oxaphosphetane complex was dissolved in $CH_2Cl_2$. The mixture was cooled to -10 °C and $HBF_4 \cdot OEt_2$ was added via syringe. The mixture was stirred and allowed slowly warming to ambient temperature (see table 11.4 for details).

***Table 11.4:*** Reaction conditions for the syntheses of **48.1a,b** and **48.2b**.

| | R | R´ | R´´ | 1,2-oxaphosphetane complex / m [mg] (n [mmol] | $HBF_4 \cdot OEt_2$ V in µL (n [mmol]) | V ($CH_2Cl_2$) [mL] |
|---|---|---|---|---|---|---|
| **48.1a** | $CH(SiMe_3)_2$ | H | $CF_3$ | **21.1g** / 200 (0.32) | 44 (0.32) | 5 |
| **48.1b** | $CH(SiMe_3)_2$ | $CF_3$ | $CF_3$ | **25.1b** / 137 (0.20) | 27 (0.20) | 5 |
| **48.2b** | $C_5Me_5$ | $CF_3$ | $CF_3$ | **25.2b** / 142 (0.21) | 29 (0.21) | 5 |

## 11.2.24.1 Pentacarbonyl{chloro(2-hydroxyethyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [47.1a]




**Purification:** The colour of the solution changed to slightly blue during the reaction before all volatiles were removed in *vacuo* (ca. 0.02 mbar). The residue was extracted with *n*-pentane (two times 5 mL) to yield a clear yellow solution. The product was then crystallized by slow evaporation of this solution at 4 °C.

**Molecular formula:** $C_{14}H_{24}ClO_6PSi_2W$

**Molecular weight:** 594.775 g/mol

**Melting point:** 84 °C

**Yield:** 189.6 mg (0.319 mmol, 71 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.36 (s, 9H, Si(C*H*$_3$)$_3$), 0.38 (s, 9H, Si(C*H*$_3$)$_3$), 1.92 (d, 1H, $^2J_{P,H}$ = 11.2 Hz, P-C*H*), 1.90 - 2.20 (s$_{br}$, 1H, O*H*), 2.62 (dddd, 1H, $^2J_{H,H}$ = 14.0 Hz, $^2J_{P,H}$ = 9.3 Hz, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 7.1 Hz, P-C*H*$_2$), 2.92 (dddd, 1H, $^2J_{H,H}$ = 14.0 Hz, $^2J_{P,H}$ = 12.7 Hz, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 7.1 Hz, P-C*H*$_2$), 4.17 (ddd, 2H, $^3J_{P,H}$ = 10.1 Hz, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 7.1 Hz, O-C*H*$_2$).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 3.2 (d, $^3J_{P,C}$ = 3.8 Hz, Si(*C*H$_3$)$_3$), 4.0 (d, $^3J_{P,C}$ = 2.5 Hz, Si(*C*H$_3$)$_3$), 32.0 (d, $^1J_{P,C}$ = 13.1 Hz, P-*C*H), 42.6 (d, $^1J_{P,C}$ = 14.4 Hz, P-*C*H$_2$), 59.8 (d, $^2J_{P,C}$ = 6.5 Hz, *C*H$_2$), 197.2 (d$_{sat}$, $^1J_{W,C}$ = 127.0 Hz, $^2J_{P,C}$ = 7.1 Hz, *cis*-*C*O), 199.3 (d$_{sat}$, $^1J_{W,C}$ = 141.4 Hz, $^2J_{P,C}$ = 30.0 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $CDCl_3$):** $\delta$ = -0.12 (s, *Si*(CH$_3$)$_3$), 3.10 (d, $^2J_{P,Si}$ = 6.7 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 111.5 (s$_{sat}$, $^1J_{W,P}$ = 272.9 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 594.0 (1) $[M]^{\bullet+}$, 566.0 (6) $[M - CO]^+$, 585.1 (5) $[M - HCl]^+$, 510.0 (30) $[M - 3\ CO]^+$, 235.1 (50) $[M - W(CO)_5 - Cl]^+$, 73.1 (100) $[SiMe_3]^+$.

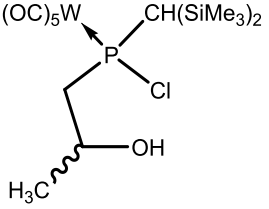
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3298 (s, $\nu$(OH)), 2072 (m, $\nu$(CO)), 1995 (w, $\nu$(CO)), 1901 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 28.27 | H | 4.07 |
| found: | C | 28.49 | H | 4.26 |

**Single crystal measurement:** GSTR488, AKY-546 // GXraymo_4589f

### 11.2.24.2 Pentacarbonyl{chloro(2-hydroxypropyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [47.1b]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude, oily product was dissolved in *n*-pentane and the product was obtained in form of big crystal needles after slow evaporation of the solvent at 4 °C.

**Molecular formula:** $C_{15}H_{26}ClO_6PSi_2W$

**Molecular weight:** 608.801 g/mol

**Melting point:** 91-92 °C

**Yield:** 319 mg (0.524 mmol, 100 %)

**Isomeric ratio:** 25 : 75

***Isomer 1:***

**$^1$H NMR (300.1 MHz, $CDCl_3$):** $\delta$ = 0.36 (s, 18H, Si(C$H_3$)$_3$), 1.43 (dd, 3H, $^4J_{P,H}$ = 1.5 Hz, $^3J_{H,H}$ = 6.3 Hz, $CH_3$), 1.88 ($s_{br}$, 1H, O*H*), 2.19 (d, 1H, $^2J_{P,H}$ = 12.8 Hz, P-C*H*), 2.48 (ddd, 1H, $^2J_{P,H}$ = 12.6 Hz, $^3J_{H,H}$ = 14.5 Hz, $^2J_{H,H}$ = 8.1 Hz, P-C$H_2$), 2.83 (ddd, 1H, $^2J_{P,H}$ = 7.9 Hz, $^3J_{H,H}$ = 15.0 Hz, $^2J_{H,H}$ = 8.1 Hz, P-C$H_2$), 4.37 - 4.57 (m, 1H, O-C*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** $\delta$ = 3.2 (d, $^2J_{P,C}$ = 3.6 Hz, Si(*C*H$_3$)$_3$), 3.8 (d, $^2J_{P,C}$ = 2.9 Hz, Si(*C*H$_3$)$_3$), 25.9 (d, $^3J_{P,C}$ = 12.6 Hz, *C*H$_3$), 31.2 (d, $^1J_{P,C}$ = 16.8 Hz, P-*C*H), 49.7 (d, $^1J_{P,C}$ = 13.9 Hz, P-*C*H$_2$), 66.1 (s, O-*C*H), 197.0 ($d_{sat}$, $^2J_{P,C}$ = 7.1 Hz, $^1J_{W,C}$ = 126.7 Hz, *cis*-*C*O), 198.8 (d, $^2J_{P,C}$ = 30.4 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $CDCl_3$):** $\delta$ = 0.45 (s, *Si*(CH$_3$)$_3$), 2.74 (d, $^2J_{P,Si}$ = 2.86 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 119.8 ($s_{br}$, $^1J_{W,P}$ = 276.0 Hz).

***Isomer 2:***

**$^{1}$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.35 (s, 9H, Si(C*H*$_3$)$_3$), 0.38 (s, 9H, Si(C*H*$_3$)$_3$), 1.40 (dd, 3H, $^{4}J_{P,H}$ = 1.4 Hz, $^{3}J_{H,H}$ = 6.2 Hz, C*H*$_3$), 1.88 (s$_{br}$, 1H, O*H*), 1.90 (d, 1H, $^{2}J_{P,H}$ = 10.2 Hz, P-C*H*), 2.42 (ddd, 1H, $^{2}J_{P,H}$ = 8.5 Hz, $^{3}J_{H,H}$ = 14.9 Hz, $^{2}J_{H,H}$ = 2.0 Hz, P-C*H*$_2$), 2.70 (ddd, 1H, $^{2}J_{P,H}$ = 14.2 Hz, $^{3}J_{H,H}$ = 14.4 Hz, $^{2}J_{H,H}$ = 2.0 Hz, P-C*H*$_2$), 4.37 - 4.57 (m, 1H, O-C*H*).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$):** δ = 3.1 (d, $^{2}J_{P,C}$ = 3.6 Hz, Si(*C*H$_3$)$_3$), 3.8 (d, $^{2}J_{P,C}$ = 2.6 Hz, Si(*C*H$_3$)$_3$), 26.7 (d, $^{3}J_{P,C}$ = 9.7 Hz, *C*H$_3$), 32.3 (d, $^{1}J_{P,C}$ = 12.6 Hz, P-*C*H), 48.0 (d, $^{1}J_{P,C}$ = 13.9 Hz, P-*C*H$_2$), 64.8 (s, O-*C*H), 197.5 (d$_{sat}$, $^{1}J_{W,C}$ = 127.4 Hz, $^{2}J_{P,C}$ = 7.4 Hz, *cis*-*C*O), 199.7 (d, $^{2}J_{P,C}$ = 31.4, *trans*-*C*O).

**$^{29}$Si{$^{1}$H} NMR (59.6 MHz, $CDCl_3$):** δ = -0.50 (s, *Si*(CH$_3$)$_3$), 3.07 (d, $^{2}J_{P,Si}$ = 7.3 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** δ = 115.1 (s$_{sat}$, $^{1}J_{W,P}$ = 274.2 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 608.1 (1) $[M]^{\bullet+}$, 580.0 (10) $[M - CO]^+$, 524.0 (60) [M - 3 CO]$^+$, 488.0 (2) [M - 3 CO - HCl]$^+$, 466.0 (5) [M - 3 CO - HCl - $C_3H_6$]$^+$, 390.0 (15) [M - 4 CO - HCl - $C_3H_6$]$^+$, 249.1 (25) [M - $W(CO)_5$ - Cl]$^+$, 207.0 (30) $[HP(O)CH(SiMe_3)_2]^+$, 147.0 (45) $[C_3H_6OPSi_2]^+$, 73.0 (100) $[SiMe_3]^+$.

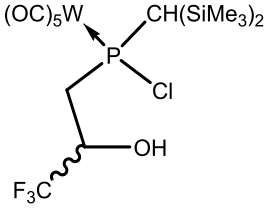
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2074 (m, ν(CO)), 1987 (w, ν(CO)), 1933 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 29.59 | H | 4.30 |
| found: | C | 29.63 | H | 4.57 |

**Single crystal measurement:** GSTR337, 3181

## 11.2.24.3 Pentacarbonyl{chloro(3,3,3-trifluoro-2-hydroxypropyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [47.1c]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was recrystallized by slow evaporation of a concentrated *n*-pentane solution at 4°C.

**Molecular formula:** $C_{15}H_{23}ClF_3O_6PSi_2W$

**Molecular weight:** 662.772 g/mol

**Melting point:** 106 °C

**Yield:** 70 mg (0.106 mmol, 33 %)

**Isomeric ratio:** 12 : 88

***Isomer 1:***

**$^{1}$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.37 (s, 9H, Si(C*H*$_3$)$_3$), 0.38 (s, 9H, Si(C*H*$_3$)$_3$), 2.30 (d, 1H, $^{2}J_{P,H}$ = 13.7 Hz, P-C*H*), 2.50 - 2.68 (s, 1H, O*H*), 2.64 (ddd, 1H, $^{2}J_{H,H}$ = 15.4 Hz, $^{2}J_{P,H}$ = 2.1 z, $^{3}J_{H,H}$ = 0.9 Hz, P-C*H*$_2$), 2.88 (ddd, 1H, $^{2}J_{H,H}$ = 15.4 Hz, $^{3}J_{H,H}$ = 9.9 Hz, $^{2}J_{P,H}$ = 3.8 z, P-C*H*$_2$), 4.57 - 4.68 (m, 1H, O-C*H*).

**$^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$):** δ = 3.4 (d, $^{3}J_{P,C}$ = 3.8 Hz, Si(*C*H$_3$)$_3$), 3.7 (d, $^{3}J_{P,C}$ = 3.0 Hz, Si(*C*H$_3$)$_3$), 31.2 (d, $^{1}J_{P,C}$ = 19.6 Hz, P-*C*H), 41.8 (d, $^{1}J_{P,C}$ = 16.0 Hz, P-*C*H$_2$), 69.5 (q, $^{2}J_{F,C}$ = 32.6 Hz, O-*C*H), 124.4 (qd, $^{1}J_{F,C}$ = 282.2 Hz, $^{4}J_{P,C}$ = 15.4 Hz, *C*F$_3$), 196.7 (d$_{sat}$, $^{1}J_{W,C}$ = 126.7 Hz, $^{2}J_{P,C}$ = 7.1 Hz, *cis*-*C*O), 198.2 (d, $^{2}J_{P,C}$ = 31.3 Hz, *trans*-*C*O).

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, $CDCl_3$):** δ = -80.7 (s, C*F*$_3$).

**$^{29}$Si{$^{1}$H} NMR (99.4 MHz, $CDCl_3$):** δ = -0.43 (d, $^{2}J_{P,Si}$ = 1.3 Hz, *Si*(CH$_3$)$_3$), 3.58 (d, $^{2}J_{P,Si}$ = 8.3 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (202.5 MHz, $CDCl_3$):** δ = 113.4 (s$_{br}$, FWHI, $h_{1/2}$ = 26 Hz).

***Isomer 2:***

**$^{1}$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.36 (s, 9H, Si(C*H*$_3$)$_3$), 0.39 (s, 9H, Si(C*H*$_3$)$_3$), 1.91 (d, 1H, $^{2}J_{P,H}$ = 9.0 Hz, P-C*H*), 2.50 – 2.68 (s, 1H, O*H*), 2.57 (ddd, 1H, $^{2}J_{H,H}$ = 14.3 Hz, $^{2}J_{P,H}$ = 12.9 Hz, $^{3}J_{H,H}$ = 10.1 Hz, P-C*H*$_2$), 2.93 (ddd, 1H, $^{2}J_{P,H}$ = 14.5 z, $^{2}J_{H,H}$ = 14.3 Hz, $^{3}J_{H,H}$ = 1.1 Hz, P-C*H*$_2$), 4.53 – 4.63 (m, 1H, O-C*H*).

**$^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$):** δ = 3.2 (d, $^{3}J_{P,C}$ = 3.8 Hz, Si(*C*H$_3$)$_3$), 3.9 (d, $^{3}J_{P,C}$ = 2.2 Hz, Si(*C*H$_3$)$_3$), 33.1 (d, $^{1}J_{P,C}$ = 11.2 Hz, P-*C*H), 38.5 (d, $^{1}J_{P,C}$ = 15.3 Hz, P-*C*H$_2$), 67.9 (q, $^{2}J_{F,C}$ = 32.4 Hz, O-*C*H), 124.7 (qd, $^{1}J_{F,C}$ = 282.3 Hz, $^{4}J_{P,C}$ = 14.3 Hz, *C*F$_3$), 197.4 (d$_{sat}$, $^{1}J_{W,C}$ = 127.8 Hz, $^{2}J_{P,C}$ = 7.4 Hz, *cis*-*C*O), 199.4 (d$_{sat}$, $^{1}J_{W,C}$ = 142.0 Hz, $^{2}J_{P,C}$ = 32.7 Hz, *trans*-*C*O).

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, $CDCl_3$):** δ = -81.1 (s, C*F*$_3$).

**$^{29}$Si{$^{1}$H} NMR (99.4 MHz, $CDCl_3$):** δ = -0.43 (d, $^{2}J_{P,Si}$ = 1.3 Hz, *Si*(CH$_3$)$_3$), 3.58 (d, $^{2}J_{P,Si}$ = 8.3 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (202.5 MHz, $CDCl_3$):** δ = 110.6 (s$_{sat}$, $^{1}J_{W,P}$ = 281.3 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 662.0 (35) $[M]^{\bullet+}$, 634.0 (30) $[M - CO]^{+}$, 606.0 (5) [M - 2 CO]$^{+}$, 578.0 (30) [M - 3 CO]$^{+}$, 542.0 (5) [M - 3 CO - HCl]$^{+}$, 73.0 (100) $[SiMe_3]^{+}$.

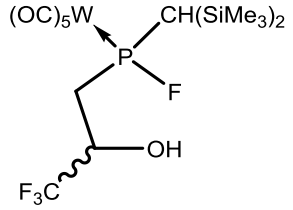
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3598 (m, ν(OH)), 2074 (m, ν(CO)), 1984 (w, ν(CO)), 1906 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 27.18 | H | 3.50 |
| found: | C | 27.36 | H | 3.69 |

**Single crystal measurement:** GSTR419, AKY-505 // GXray4067f

## 11.2.24.4 Pentacarbonyl{fluoro(3,3,3-trifluoro-2-hydroxypropyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [48.1a]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was recrystallized by slow evaporation of a concentrated *n*-pentane solution at 4°C.

**Molecular formula:** $C_{15}H_{23}F_4O_6PSi_2W$

**Molecular weight:** 646.318 g/mol

**Melting point:** 99 °C

**Yield:** 81 mg (0.126 mmol, 39 %)

**Isomeric ratio:** 26 : 74

***Isomer 1:***

**$^1$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.28 (s, 9H, Si(C*H*$_3$)$_3$), 0.28 (s, 9H, Si(C*H*$_3$)$_3$), 2.11 (d, 1H, $^2J_{P,H}$ = 12.2 Hz, P-C*H*), 2.44 (s, 1H, O*H*), 2.70 - 2.81 (m, 1H, P-C*H*$_2$), 2.75 (dddd, 1H, $^2J_{P,H}$ = 13.5 Hz, *J* = 15.1 Hz, *J* = 10.5 Hz, *J* = 6.0 Hz, P-C*H*$_2$), 4.54 - 4.65 (m, 1H, O-C*H*).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.4 (d, $^3J_{P,C}$ = 2.7 Hz, Si(*C*H$_3$)$_3$), 2.8 (dd, *J* = 2.7 Hz, *J* = 1.9 Hz, Si(*C*H$_3$)$_3$), 34.1 (d, $^1J_{P,C}$ = 13.3 Hz, P-*C*H), 38.2 (dd, *J* = 19.5 Hz, *J* = 15.0 Hz, P-*C*H$_2$), 69.3 (q, $^2J_{F,C}$ = 32.7 Hz, O-*C*H), 124.4 (qd, $^1J_{C,F}$ = 282.0 Hz, *J* = 17.7 Hz, *C*F$_3$), 196.0 (dd$_{sat}$, $^1J_{W,C}$ = 125.7 Hz, $^2J_{P,C}$ = 7.9 Hz, $^3J_{F,C}$ = 2.9 Hz, *cis*-*C*O), 198.3 (d$_{sat}$, $^1J_{W,C}$ = 137.2 Hz, $^2J_{P,C}$ = 29.4 Hz, *trans*-*C*O).

**$^{19}$F{$^1$H} NMR (282.4 MHz, $CDCl_3$):** δ = -111.0 (d, 1F, $^1J_{P,F}$ = 823.0 Hz, P-*F*), -80.7 (s, 3F, C*F*$_3$).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** δ = -3.3 (d, *J* = 4.4 Hz, *Si*(CH$_3$)$_3$), 1.90 (dd, J = 14.2, *J* = 7.0, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 194.0 (d$_{sat,br}$ full-width at half-intensity (FWHI, $h_{1/2}$) = 60 Hz, $^1J_{P,F}$ = 823.0 Hz, $^1J_{W,P}$ = ca. 290 Hz).

***Isomer 2:***

**$^{1}$H NMR (500.1 MHz, $CDCl_3$):** $\delta$ = 0.31 (s, 9H, Si(C*H*$_3$)$_3$), 0.32 (s, 9H, Si(C*H*$_3$)$_3$), 2.06 (d, 1H, $^{2}J_{P,H}$ = 11.0 Hz, P-C*H*), 2.54 (s, 1H, O*H*), 2.70 - 2.81 (m, 1H, P-C*H*$_2$), 2.88 (ddd, 1H, $^{2}J_{P,H}$ = 15.0 Hz, *J* = 15.0 Hz, *J* = 2.7 Hz, P-C*H*$_2$), 4.34 - 4.48 (m, 1H, O-C*H*).

**$^{13}$C{$^{1}$H} NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 2.5 (d, $^{3}J_{P,C}$ = 3.2 Hz, Si(*C*H$_3$)$_3$), 2.7 (dd, *J* = 3.0 Hz, *J* = 1.7 Hz, Si(*C*H$_3$)$_3$), 34.9 (d, $^{1}J_{P,C}$ = 13.9 Hz, P-*C*H), 37.0 (dd, *J* = 20.7 Hz, *J* = 15.8 Hz, P-*C*H$_2$), 66.8 (qd, $^{2}J_{F,C}$ = 32.8 Hz, *J* = 2.2 Hz, O-*C*H), 124.6 (qd, $^{1}J_{C,F}$ = 282.2 Hz, *J* = 12.8 Hz, *C*F$_3$), 196.7 (dd$_{sat}$, $^{1}J_{W,C}$ = 126.4 Hz, $^{2}J_{P,C}$ = 8.1 Hz, $^{3}J_{F,C}$ = 2.8 Hz, *cis*-*C*O), 199.1 (d$_{sat}$, $^{1}J_{W,C}$ = 138.1 Hz, $^{2}J_{P,C}$ = 29.2 Hz, *trans*-*C*O).

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, $CDCl_3$):** $\delta$ = -81.2 (s, 3F, C*F*$_3$), -115.9 (d, 1F, $^{1}J_{P,F}$ = 821.8 Hz, P-*F*).

**$^{29}$Si{$^{1}$H} NMR (99.4 MHz, $CDCl_3$):** $\delta$ = -3.3 (d, *J* = 4.4 Hz, *Si*(CH$_3$)$_3$), 1.90 (dd, J = 14.2, *J* = 7.0, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^{1}$H} NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 185.6 (d$_{sat}$, $^{1}J_{P,F}$ = 821.8 Hz, $^{1}J_{W,P}$ = 294.0 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 654.9 (30) [M]$^{\bullet+}$, 617.9 (60) [M - CO]$^{+}$, 589.9 (100) [M - 2 CO]$^{+}$, 561.9 (40) [M - 3 CO]$^{+}$, 543.9 (75) [M - 4 CO]$^{+}$, 73.1 (85) [SiMe$_3$]$^{+}$.

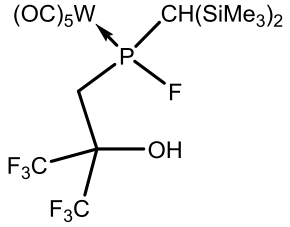
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3607 (m, $\nu$(OH)), 2075 (m, $\nu$(CO)), 1985 (w, $\nu$(CO)), 1904 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 27.87 | H | 3.59 |
| found: | C | 27.87 | H | 3.71 |

**Single crystal measurement:** GSTR418, AKY-506 // GXray4066

## 11.2.24.5 Pentacarbonyl{[3,3,3-trifluoro-2-(trifluoromethyl)-2-hydroxypropyl][bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [48.1b]




**Purification:** The mixture turned slightly blue during the reaction. All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was recrystallized by slow evaporation of a concentrated *n*-pentane solution at 4°C to yield colourless crystals.

**Molecular formula:** $C_{16}H_{22}F_7O_6PSi_2W$

**Molecular weight:** 714.316 g/mol

**Melting point:** 110 °C

**Yield:** 98 mg (0.137 mmol, 70 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.30 (d, 9H, $^4J_{P,H}$ = 1.5 Hz, Si(C*H*$_3$)$_3$), 0.33 (s, 9H, Si(C*H*$_3$)$_3$), 2.08 (d$_{br}$, 1H, $^2J_{P,H}$ = 5.7 Hz, P-C*H*), 2.41 - 2.67 (m, 1H, P-C*H*$_2$), 3.03 - 3.26 (m, 1H, P-C*H*$_2$), 3.41 (s, 1H, O*H*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.5 (d, $^3J_{P,C}$ = 2.9 Hz, Si(*C*H$_3$)$_3$), 2.65 - 2.79 (m, Si(*C*H$_3$)$_3$), 34.8 - 35.8 (m, *C*H$_2$), 36.0 - 36.9 (m, P-*C*H), *C*(CF$_3$)$_2$ not observed due to low intensity, 122.5 (q, $^1J_{C,F}$ = 286.3 Hz, *C*F$_3$), 123.0 (qd, $^1J_{C,F}$ = 287.5 Hz, $^1J_{P,C}$ = 6.8 Hz, *C*F$_3$), 196.4 (dd$_{sat}$, $^1J_{W,C}$ = 125.5 Hz, $^2J_{P,C}$ = 8.1 Hz, $^3J_{F,C}$ = 2.9 Hz, *cis*-*C*O), 198.7 (dm, $^2J_{P,C}$ = 31.6 Hz, *trans*-*C*O).

**$^{19}$F{$^1$H} NMR (282.4 MHz, $CDCl_3$):** δ = -110.5 (dq, 1F, $^1J_{P,F}$ = 851.8 Hz, $^5J_{F,F}$ = 17.4 Hz, P-*F*), -79.2 - -79.5 (m, 3F, C*F*$_3$), -76.6 - -77.0 (m, 3F, C*F*$_3$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 180.4 (d$_{sat}$, $^1J_{P,F}$ = 852.4 Hz, $^1J_{W,P}$ = 302.1 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 714.0 (25) $[M]^{\cdot+}$, 686.0 (30) $[M - CO]^+$, 658.0 (60) $[M - 2\ CO]^+$, 610.0 (100) $[M - 3\ CO - HF]^+$, 554.0 (20) $[M - 5\ CO - HF]^+$, 73.1 (70) $[SiMe_3]^+$.

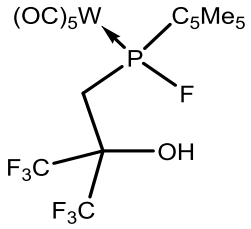
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3533 (m, ν(OH)), 2077 (m, ν(CO)), 1990 (w, ν(CO)), 1908 (vs, ν(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 26.90 | H | 3.10 |
| found: | C | 27.02 | H | 3.17 |

**Single crystal measurement:** GSTR413, AKY-499A // GXray4033f

## 11.2.24.6 Pentacarbonyl{fluoro[3,3,3-trifluoro-2-(trifluoromethyl)-2-hydroxypropyl](1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)phosphane-κ*P*}tungsten(0) [48.2b]




**Purification:** The mixture turned yellow during the reaction. All volatiles were removed in *vacuo* (ca 0.02 mbar) to yield the product as slightly yellow solid.

**Molecular formula:** $C_{19}H_{18}F_7O_6PW$

**Molecular weight:** 690.145 g/mol

**Yield:** 146.3 mg (0.212 mmol, 100 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 1.46 (d, 3H, $J_{P,H}$ = 14.3 Hz, $C_5\mathit{Me}_5$), 1.84 (s, 6H, $C_5\mathit{Me}_5$), 1.85 (s, 3H, $C_5\mathit{Me}_5$), 1.93 (s, 3H, $C_5\mathit{Me}_5$), 2.30 - 2.58 (m, 1H, P-C$\mathit{H}_2$), 2.90 - 3.35 (m, 1H, P-C$\mathit{H}_2$), 3.54 (s, 1H, OH).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 11.6 (s, $C_5\mathit{Me}_5$), 11.8 (s, $C_5\mathit{Me}_5$), 12.4 (d, *J* = 2.8 Hz, $C_5\mathit{Me}_5$), 12.5 (dd, *J* = 3.9 Hz, *J* = 1.3 Hz, $C_5\mathit{Me}_5$), 15.4 ($s_{br}$, $C_5\mathit{Me}_5$), 33.8 ($s_{br}$, P-$\mathit{C}H_2$), 64.8 (dd, *J* = 10.5 Hz, *J* = 8.7 Hz, P-$\mathit{C}_5Me_5$ ), 76.0 - 78.0 (m, $\mathit{C}(CF_3)_2$), 122.6 (qd, $^1J_{F,C}$ = 287.4 Hz, $^4J_{P,C}$ = 1.9 Hz, C$\mathit{F}_3$), 123.0 (qd, $^1J_{F,C}$ = 287.3 Hz, $^4J_{P,C}$ = 5.2 Hz, C$\mathit{F}_3$), 142.5 ($s_{br}$, C=C), 144.5 ($s_{br}$, C=C), 195.6 ($d_{sat}$, $^1J_{W,C}$ = 126.2 Hz, $^2J_{P,C}$ = 6.9 Hz, *cis-CO*), 197.5 (d, $^2J_{P,C}$ = 33.0 Hz, *trans-CO*).

**$^{19}$F{$^1$H} NMR (282.4 MHz, $CDCl_3$):** δ = -144.1 (d, 1F, $^1J_{P,F}$ = 830 Hz, P-*F*), - 78.5 (s, 3F, C$\mathit{F}_3$), -77.5 (s, 3F, C$\mathit{F}_3$).

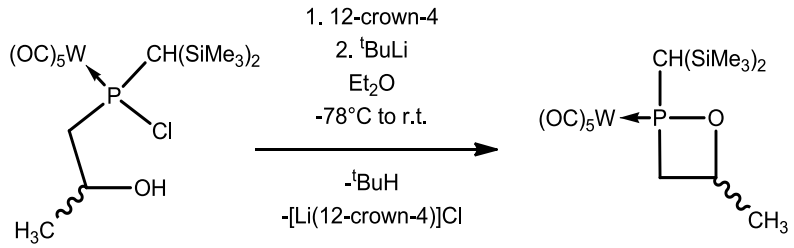
**$^{31}$P{$^1$H} NMR (121.5 MHz, $CDCl_3$):** δ = 190.3 ($d_{br}$, $^1J_{P,F}$ = 830 Hz, full-width at half-intensity (FWHI, $h_{1/2}$) = 440 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 690.1 (10) $[M]^{\bullet+}$, 634.0 (5) $[M - 2\ CO]^+$, 606.1 (40) $[M - 3\ CO]^+$, 554.9 (15) $[M - C_5Me_5]^+$, 526.9 (40) $[M - C_5Me_5 - CO]^+$, 498.9 (40) $[M - C_5Me_5 - 2\ CO]^+$, 470.9 (10) $[M - C_5Me_5 - 3\ CO]^+$, 135.1 (100) $[C_5Me_5]^+$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3557 (m, ν(OH)), 2078 (m, ν(CO)), 1990 (w, ν(CO)), 1917 (vs, ν(CO)).

**Single crystal measurement:** GSTR392, AKY-476 // GXray3908f

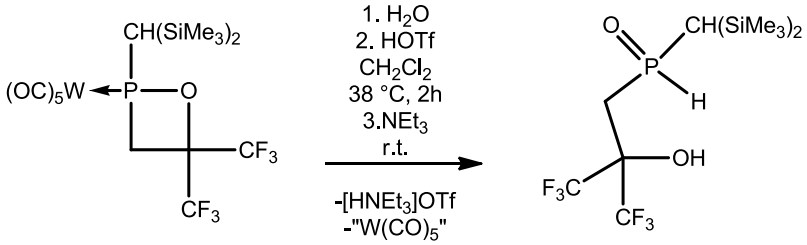
## 11.2.25 Synthesis of 1,2-oxaphosphetane complex (21.1a$_W$) from pentacarbonyl{chloro(2-hydroxypropyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) (47.1b)




**Synthesis:** In a 10 mL Schlenk tube, 22.7 mg (0.038 mmol) of chlorophosphane complex **47.1b** were dissolved in 1 mL of diethyl ether and 6 µL (0,033 mmol) of 12-crown-4 were added. The solution was cooled to -78 °C and 0.025 mL (0.042 mmol, 1.1 eq., 1.7 M in *n*-pentane) of *tert*-butyllithium was added. The solution was allowed slowly warming up to ambient temperature. Formation of a white salt was observed and the reaction mixture subsequently analysed by $^{31}P\{^1H\}$ NMR.

The $^{31}P\{^1H\}$ NMR spectrum showed the selective conversion to **21.1a$_W$**[1-4]. A mixture of the isomers that were described before was observed (ratio: 10:0:60:30).

## 11.2.26 Synthesis of [3,3,3-trifluoro-2-(trifluoromethyl)-2-hydroxypropyl][bis(trimethylsilyl)methyl]phosphane-oxide [52]




**Synthesis:** In a 50 mL Schlenk tube, 300 mg (0.432 mmol) of 1,2-oxaphosphetane complex **25.1b** were dissolved in 20 mL of $CH_2Cl_2$ and 10 µL of $H_2O$ (0.556 mmol, 1.29 eq.) were added. The mixture was treated with 0.1 mL of TfOH (1.130 mmol, 2.6 eq.) and heated to 38 °C for 2 h. After cooling to ambient temperature 0.4 mL of $Net_3$ (2.867 mmol, 6.6 eq.) were added, which led to a colour change of the solution to brown.

**Purification:** The solution was acidified with conc. HCl and the yellow organic phase separated from the violet inorganic phase. All volatiles were evaporated from the organic phase in *vacuo* (ca. 0.02 mbar) and the product was subsequently extracted with five times 10 mL of *n*-pentane. All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product purified by subliming off the remaining $W(CO)_6$ at 55 °C/1.4 ·$10^{-2}$ mbar for 6 h. The progress was checked by IR spectroscopy and stopped after vanishing of all signals for the CO-vibration.

**Molecular formula:** $C_{11}H_{23}F_6O_2PSi_2$

**Molecular weight:** 388.434 g/mol

**Melting point:** 134 °C

**Yield:** 76.7 mg (0.197 mmol, 46 %)

**$^1$H NMR (500.2 MHz, $CDCl_3$):** $\delta$ = 0.27 (s, 9H, Si(C$H_3$)$_3$), 0.30 (s, 9H, Si(C$H_3$)$_3$), 0.7 (d, 1H, $^2J_{P,H}$ = 18.2 Hz, P-C*H*), 2.12 (dd, 1H, $^2J_{H,H}$ = 15.9 Hz, $^2J_{P,H}$ = 5.0 Hz, P-C$H_2$), 2.52 (ddd, 1H, $^2J_{H,H}$ = 15.9 Hz, $^3J_{H,H}$ = 7.1 Hz, $^2J_{F,H}$ = 17.3 Hz, P-C$H_2$), 7.50 (d, 1H, $^1J_{P,H}$ = 485.6 Hz, P-*H*), 7.53 ($s_{br}$, 1H, OH).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 1.2 ($d_{sat}$, $^3J_{P,C}$ = 4.0 Hz, $^1J_{Si,C}$ = 53.2 Hz, Si(*C*H$_3$)$_3$), 2.0 ($d_{sat}$, $^3J_{P,C}$ = 3.2 Hz, $^1J_{Si,C}$ = 53.4 Hz, Si(*C*H$_3$)$_3$), 20.0 ($d_{sat}$, $^1J_{P,C}$ = 41.8 Hz, $^1J_{Si,C}$ = 32.0 Hz, P-*C*H), 27.9 (d, $^1J_{P,C}$ = 60.0 Hz, P-*C*H$_2$), 75.6 - 77.3 (dm, $^2J_{P,C}$ = 5.7 Hz, *C*(CF$_3$)$_2$), 122.4 (qd, $^1J_{F,C}$ = 285.6 Hz, $^3J_{P,C}$ = 12.2 Hz, *C*F$_3$), 123.5 (q, $^1J_{F,C}$ = 288.1 Hz, *C*F$_3$).

**$^{19}$F{$^1$H} NMR (469.7 MHz, $CDCl_3$):** $\delta$ = -79.9 (q, $^4J_{F,F}$ = 10.0 Hz, C*F*$_3$), -76.4 (qd, $^4J_{F,F}$ = 10.0 Hz, $^4J_{P,F}$ = 8.6 Hz, C*F*$_3$).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** $\delta$ = 1.46 (d, $^2J_{P,Si}$ = 4.0 Hz, *Si*(CH$_3$)$_3$), 1.58 (d, $^2J_{P,Si}$ = 6.8 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 34.3 (d, $^1J_{P,H}$ = 485.6 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 388.1 (10) $[M]^{\bullet+}$, 373.1 (100) $[M - CH_3]^+$, 319.1 (45) $[M - CF_3]^+$, 73.1 (50) $[SiMe_3]^+$.

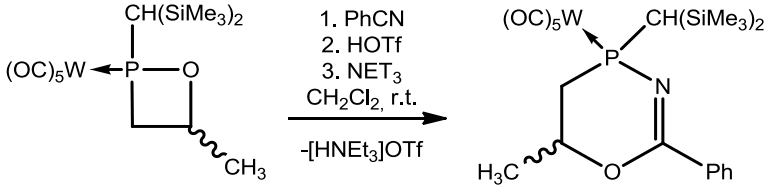
**HR-MS:** calculated for $C_{11}H_{23}F_6O_2PSi_2$: 388.0878, found: 388.0876 (+/- 0.47 ppm)

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2961 (m, $\nu$(OH)), 2366 (w, $\nu$(PH)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 34.01 | H | 5.97 |
| found: | C | 34.34 | H | 6.07 |

## 11.2.27 Synthesis of pentacarbonyl{6-methyl-4-[bis(trimethylsilyl)methyl]-2-phenyl-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [54.1]




**Synthesis:** In a 50 mL Schlenk tube, 572 mg (1.0 mmol) of the 1,2-oxaphosphetane complex **21.1a$_W$** were dissolved in 20 mL of $CH_2Cl_2$. Then 0.11 mL (1.1 mmol, 1.1 eq.) of PhCN and, subsequently, 0.13 mL (1.5 mmol, 1.5 eq.) of HOTf was added. The mixture was stirred for 30 minutes at ambient temperature, cooled to 0 °C and 0.21 mL (1.5 mmol, 1.5 eq.) of triethylamine was added.

**Purification:** After 20 min of stirring the solvent was removed in *vacuo* (ca. 0.02 mbar). The residue was purified by column chromatography ($SiO_2$, -20 °C, eluent: petroleum ether, petroleum ether/diethyl ether 10 : 0.1). The product was obtained as a yellow solid after evaporation of the second yellow fraction in *vacuo* (ca. 0.02 mbar) and recrystallization by slow evaporation of a saturated diethyl ether solution at 4 °C.

**Molecular formula:** $C_{22}H_{30}NO_6PSi_2W$

**Molecular weight:** 675.461 g/mol

**Melting point:** 143 - 144 °C

**Yield:** 375.6 mg (0.560 mmol, 56 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.20 (s, 9H, Si(C*H*$_3$)$_3$), 0.34 (s, 9H, Si(C*H*$_3$)$_3$), 1.50 (d$_{sat}$, 1H, $^2J_{P,H}$ = 12.2 Hz, $^2J_{Si,H}$ = 9.4 Hz, P-C*H*), 1.63 (dd, 3H, $^4J_{P,H}$ = 2.0 Hz, $^3J_{H,H}$ = 6.2 Hz, C*H*$_3$), 2.28 (ddd, 1H, $^2J_{P,H}$ = 12.0 Hz, $^2J_{H,H}$ = 13.6 Hz, $^3J_{H,H}$ = 12.1 Hz, P-C*H*$_2$), 2.50 (dd, 1H, $^2J_{H,H}$ = 13.6 Hz, $^3J_{H,H}$ = 2.2 Hz, P-C*H*$_2$), 4.84 (dddq, 1H, $^3J_{P,H}$ = 12.0 Hz, $^3J_{H,H}$ = 12.1 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 2.2 Hz, O-C*H*), 7.36 - 7.52 (m, 3H, *Ph*), 7.95 - 8.01 (m, 2H, *Ph*).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 2.8 (d, $^2J_{P,C}$ = 6.5 Hz, Si(*C*H$_3$)$_3$), 2.9 (d, $^2J_{P,C}$ = 4.5 Hz, Si(*C*H$_3$)$_3$), 23.5 (d, $^3J_{P,C}$ = 10.0 Hz, *C*H$_3$), 24.9 (d, $^1J_{P,C}$ = 10.7 Hz, P-*C*H), 33.3 (d, $^1J_{P,C}$ = 19.4 Hz, P-*C*H$_2$), 71.1 (s, O-*C*H), 128.1 (s, *C*H$_{Ar}$), 128.3 (d, $J_{P,C}$ = 1.0 Hz, *C*H$_{Ar}$), 131.5 (s, *C*H$_{Ar}$) 133.3 (d, $^3J_{P,C}$ = 10.0 Hz, *ipso-C*), 157.0 (d, $^2J_{P,C}$ = 12.9 Hz, *C*=N), 197.9 (d$_{sat}$, $^1J_{W,C}$ = 126.4 Hz, $^2J_{P,C}$ = 7.8 Hz, *cis-C*O), 200.5 (d, $^2J_{P,C}$ = 22.6, *trans-C*O).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $CDCl_3$):** δ = -2.50 (s, *Si*(CH$_3$)$_3$), -0.08 (d, $^2J_{P,Si}$ = 9.4 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P NMR (121.5 MHz, $CDCl_3$):** δ = 40.0 (ddd$_{sat}$, $^1J_{W,P}$ = 258.8 Hz, $^2J_{P,H}$ = 12 Hz, $^2J_{P,H}$ = 12 Hz, $^3J_{P,H}$ = 12 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 675.0 (40) $[M]^{\bullet+}$, 647.1 (60) $[M - CO]^+$, 619.1 (40) $[M - 2\ CO]^+$, 591.1 (40) $[M - 3\ CO]^+$, 577.0 (10) $[M - C_3H_6 - 2\ CO]^+$, 549.0 (10) $[M - C_3H_6 - 3\ CO]^+$, 535.1 (20) $[M - 5\ CO]^+$, 493.0 (90) $[M - C_3H_6 - 5\ CO]^+$, 488.0 (20) $[M - PhCN - 3\ CO]^+$, 432.0 (10) $[M - PhCN - 5\ CO]^+$, 73.1 (100) $[SiMe_3]^+$.

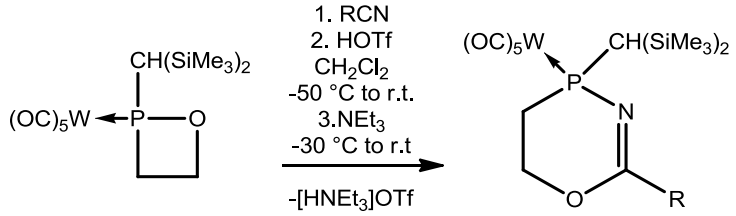
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2067 (m, $\nu$(CO)), 1974 (w, $\nu$(CO)), 1898 (s, $\nu$(CO)), 1618 (m, $\nu$(C=N)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 39.12 | H | 4.48 | N | 2.07 |
| found: | C | 39.08 | H | 4.60 | N | 2.13 |

**Single crystal measurement:** GSTR345, 3334

## 11.2.28 Optimized synthetic protocol for the acid induced ring expansion with nitriles:

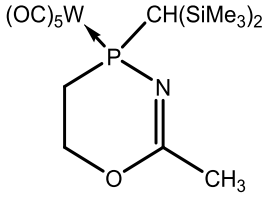



**Synthesis:** In a 20 mL Schlenk tube, 1,2-oxaphosphetane complex **34.1$_W$** was dissolved in 10 mL of $CH_2Cl_2$ and an excess of the corresponding nitrile was added. The mixture was cooled to -50 °C and TfOH was added dropwise. The solution was allowed warming up to -30 °C, then the cooling bath was removed and stirring was continued for further 30 minutes at ambient temperature. The solution was again cooled to -30 °C and triethylamine was added. The reaction mixture was allowed to slowly warm up to ambient temperature overnight.

***Table 11.5:*** Used amounts of 1,2-oxaphosphetane complex **34.1$_W$** and reagents for the acid induced ring expansion reaction with nitriles.

| | R | m (**34.1$_W$**) [mg] | n (**34.1$_W$**) [mmol] | V (RCN) [mL] | V (HOTf) [mL] | V ($NEt_3$) [mL] |
|---|---|---|---|---|---|---|
| **55.1a** | $CH_3$ | 140 | 0.25 | 0.5 | 0.1 | 0.5 |
| **55.1b** | Ph | 140 | 0.25 | 0.5 | 0.1 | 0.5 |
| **55.1c** | $^t$Bu | 167.5 | 0.3 | 0.25 | 0.1 | 0.25 |

## 11.2.28.1 Pentacarbonyl{2-methyl-4-[bis(trimethylsilyl)methyl]-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [55.1a]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude material was purified by filtration over $SiO_2$ (ø = 2 cm, h = 3 cm) using a mixture of petroleum ether 40/60 and diethyl ether in a ratio of 10 : 1. The product was obtained as white powder after removing of all volatiles in *vacuo* (ca. 0.02 mbar).

**Molecular formula:** $C_{16}H_{24}NO_6PSi_2W$

**Molecular weight:** 599.366 g/mol

**Melting point:** 153 °C

**Yield:** 149 mg (0.248 mmol, 99 %)

**$^1$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.24 (s, 9H, Si(C$H_3$)$_3$), 0.30 (s, 9H, Si(C$H_3$)$_3$), 1.36 (d, 1H, $^2J_{P,H}$ = 12.1 Hz, P-C*H*), 2.01 (d, 3H, $^4J_{P,H}$ = 1.25 Hz, $CH_3$), 2.26 - 2.33 (m, 1H, P-C$H_2$), 2.40 - 2.52 (m, 1H, P-C$H_2$), 4.42 - 4.61 (m, 2H, O-C$H_2$).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.9 (d, $^3J_{P,C}$ = 3.7 Hz, Si(*C*H$_3$)$_3$), 3.1 (d, $^3J_{P,C}$ = 1.7 Hz, Si(*C*H$_3$)$_3$), 23.5 (d, $^3J_{P,C}$ = 8.8 Hz, *C*H$_3$), 25.3 (d, $^1J_{P,C}$ = 11.3 Hz, P-*C*H), 26.2 (d, $^1J_{P,C}$ = 19.6 Hz, P-*C*H$_2$), 63.7 (d, $^2J_{P,C}$ = 1.7 Hz, O-*C*H$_2$), 160.0 (d, $^2J_{P,C}$ = 13.7 Hz, *C*=N), 198.0 (d$_{sat}$, $^1J_{W,C}$ = 126.5 Hz, $^2J_{P,C}$ = 7.6 Hz, *cis*-*C*O), 200.6 (d$_{sat}$, $^1J_{W,C}$ = 143.0 Hz, $^2J_{P,C}$ = 22.9 Hz, *trans*-*CO*).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** δ = -1.94 (s, *Si*(CH$_3$)$_3$), 0.59 (d, $^2J_{P,Si}$ = 9.3 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 34.1 (s$_{sat}$, $^1J_{W,P}$ = 259.2 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 599.0 (30) $[M]^{\bullet+}$, 570.9 (60) $[M - CO]^+$, 558.0 (5) $[M - CH_3CN]^+$, 543.0 (75) $[M - 2\ CO]^+$, 515.0 (60) $[M - 3\ CO]^+$, 502.0 (10) $[M - CH_3CN - 2\ CO]^+$, 486.9 (15) $[M - 4\ CO]^+$, 474.0 (10) $[M - CH_3CN - 3\ CO]^+$, 459.0 (50) $[M - 5\ CO]^+$, 446.0 (5) $[M - CH_3CN - 4\ CO]^+$, 418.0 (55) $[M - CH_3CN - 5\ CO]^+$, 390.0 (100) $[M - CH_3CN - 5\ CO - C_2H_4]^+$, 73.1 (50) $[SiMe_3]^+$.

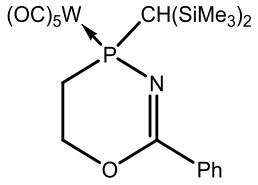
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2068 (s, ν(CO)), 1987 (w, ν(CO)), 1975 (w, ν(CO)), 1934 (w, ν(CO)), 1894 (vs, ν(CO)), 1642 (m, ν(C=N)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 32.06 | H | 4.37 | N | 2.34 |
| found: | C | 31.98 | H | 4.36 | N | 2.35 |

**Single crystal measurement:** GSTR510, AKY-569 // GXray4796

## 11.2.28.2 Pentacarbonyl{4-[bis(trimethylsilyl)methyl]-2-phenyl-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [55.1b]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude material was purified by filtration over $SiO_2$ (ø = 2 cm, h = 3 cm) using a mixture of petroleum ether 40/60 and diethyl ether in a ratio of 10 : 1. The product was obtained as yellow foam after removing of all volatiles in *vacuo* (ca. 0.02 mbar). It could be recrystallized by slow evaporation of a saturated diethyl ether solution at 4 °C to solidify it.

**Molecular formula:** $C_{21}H_{28}NO_6PSi_2W$

**Molecular weight:** 661.435 g/mol

**Melting point:** 154 °C

**Yield:** 165 mg (0,248 mmol, 99 %)

**$^1$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.22 (s, 9H, Si(C*H*$_3$)$_3$), 0.34 (s, 9H, Si(C*H*$_3$)$_3$), 1.51 (d, 1H, $^2J_{P,H}$ = 12.0 Hz, P-C*H*), 2.41 - 2.47 (m, 1H, P-C*H*$_2$), 2.60 - 2.71 (m, 1H, P-C*H*$_2$), 4.69 - 4.84 (m, 2H, O-C*H*$_2$), 7.37 - 7.43 (m, 2H, C*H*$_{Ar}$), 7.45 - 7.50 (m, 1H, *para*-C*H*$_{Ar}$), 7.92 - 7.96 (m, 2H, C*H*$_{Ar}$).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** δ = 2.9 (d, $^3J_{P,C}$ = 3.8 Hz, Si(*C*H$_3$)$_3$), 3.1 (d, $^3J_{P,C}$ = 1.7 Hz, Si(*C*H$_3$)$_3$), 25.2 (d, $^1J_{P,C}$ = 10.2 Hz, P-*C*H), 26.8 (d, $^2J_{P,C}$ = 19.6 Hz, P-*C*H$_2$), 64.3 (d, $^1J_{P,C}$ = 1.8 Hz, O-*C*H$_2$), 128.3 (s, *ortho*-*C*H$_{Ar}$ + *meta*-*C*H$_{Ar}$), 131.7 (s, *para*-*C*H$_{Ar}$), 133.5 (d, $^3J_{P,C}$ = 9.6 Hz, *ipso*-C), 156.9 (d, $^2J_{P,C}$ = 12.6 Hz, *C*=N), 198.0 (d$_{sat}$, $^1J_{W,C}$ = 126.5 Hz, $^2J_{P,C}$ = 7.5 Hz, *cis*-*C*O), 200.6 (d$_{sat}$, $^1J_{W,C}$ = 143.0 Hz, $^2J_{P,C}$ = 22.9 Hz, *trans*-*CO*).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** δ = -1.74 (s, *Si*(CH$_3$)$_3$), 0.59 (d, $^2J_{P,Si}$ = 9.1 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 36.1 (s$_{sat}$, $^1J_{W,P}$ = 259.6 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 661.1 (25) $[M]^{\bullet+}$, 633.1 (80) $[M - CO]^+$, 605.1 (70) [M - 2 CO]$^+$ 577.1 (80) $[M - 3 CO]^+$, 549.1 (5) $[M - 4 CO]^+$, 521.1 (70) $[M - 5 CO]^+$, 493.1 (100) [M - 5 CO - $C_2H_4]^+$, 390.0 (70) [M - 5 CO - PhCN - $C_2H_4]^+$, 73.1 (70) $[SiMe_3]^+$.

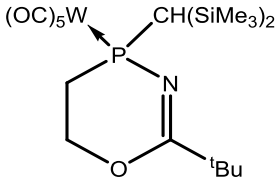
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2067 (s, $\nu$(CO)), 1974 (w, $\nu$(CO)), 1900 (vs, $\nu$(CO)), 1626 (m, $\nu$(C=N)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 38.13 | H | 4.27 | N | 2.12 |
| found: | C | 38.32 | H | 4.32 | N | 2.17 |

**Single crystal measurement:** GSTR509, AKY-570 // GXray4797

## 11.2.28.3 Pentacarbonyl{2-(1,1-dimethylethyl)-4-[bis(trimethylsilyl)methyl]-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [55.1c]




**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The product was purified by filtration over $SiO_2$ (ø = 2 cm, h = 3 cm) using diethyl ether. The crude yellow product, obtained as an oil in almost quantitative yield (99%) after removal of all volatiles in *vacuo* (ca. 0.02 mbar), was then recrystallized by slow evaporation of a saturated diethyl ether solution at 4 °C.

**Molecular formula:** $C_{19}H_{32}NO_6PSi_2W$

**Molecular weight:** 641.445 g/mol

**Melting point:** 138 - 139 °C

**Yield:** 82 mg (0.13 mmol, 43 %)

**$^1$H NMR (500.2 MHz, $CDCl_3$):** δ = 0.27 (s, 9H, Si(C*H*$_3$)$_3$), 0.31 (s, 9H, Si(C*H*$_3$)$_3$), 1.16 (s, 9H, C(C*H*$_3$)$_3$), 1.40 (d, 1H, $^2J_{P,H}$ = 12.1 Hz, P-C*H*), 2.26 - 2.33 (m, 1H, P-C*H*$_2$), 2.40 - 2.52 (m, 1H, P-C*H*$_2$), 4.48 - 4.67 (m, 2H, O-C*H*$_2$).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** δ = 3.0 (d, $^3J_{P,C}$ = 3.5 Hz, Si(*C*H$_3$)$_3$), 3.4 (d, $^3J_{P,C}$ = 1.6 Hz, Si(*C*H$_3$)$_3$), 25.0 (d, $^1J_{P,C}$ = 10.1 Hz, P-*C*H), 26.3 (d, $^1J_{P,C}$ = 20.2 Hz, P-*C*H$_2$), 28.1 (s, C(*C*H$_3$)$_3$), 40.1 (d, $^2J_{P,C}$ = 7.6 Hz, *C*(CH$_3$)$_3$), 64.3 (d, $^2J_{P,C}$ = 1.6 Hz, P-*C*H$_2$), 168.8 (d, $^2J_{P,C}$ = 14.7 Hz, *C*=N), 198.1 (d$_{sat}$, $^1J_{W,C}$ = 126.7 Hz, $^2J_{P,C}$ = 7.6 Hz, *cis*-*C*O), 200.6 (d$_{sat}$, $^1J_{W,C}$ = 142.8 Hz, $^2J_{P,C}$ = 22.9 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (99.4 MHz, $CDCl_3$):** δ = -1.84 (s, *Si*(CH$_3$)$_3$), 0.75 (d, $^2J_{P,Si}$ = 9.3 Hz, *Si*(CH$_3$)$_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** δ = 34.2 (s$_{sat}$, $^1J_{W,P}$ = 260.9 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 641.2 (40) $[M]^{\bullet+}$, 613.2 (20) $[M - CO]^+$, 585.2 (10) $[M - 2\ CO]^+$ 557.2 (75) $[M - 3\ CO]^+$, 501.1 (55) $[M - 5\ CO]^+$, 473.1 (100) $[M - 4\ CO - C_4H_8]^+$, 260.0 (20) $[M - W(CO)_5 - C_4H_8]^+$, 73.1 (50) $[SiMe_3]^+$.

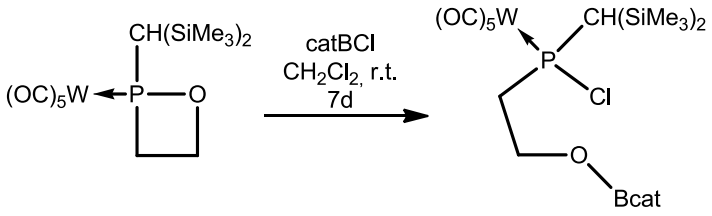
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2067 (s, ν(CO)), 1987 (w, ν(CO)), 1978 (w, ν(CO)), 1928 (s, ν(CO)), 1895 (vs, ν(CO)), 1631 (m, ν(C=N)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 35.58 | H | 5.03 | N | 2.18 |
| found: | C | 35.61 | H | 5.17 | N | 2.12 |

**Single crystal measurement:** GSTR529, AKY-599 // GXraymo_4925f

## 11.2.29 Synthesis of pentacarbonyl{[2-(catecholboranoxo)ethyl]chloro[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [56.1]




**Synthesis:** In a 10 mL Schlenk tube, 111.7 mg (0.2 mmol) of 1,2-oxaphosphetane complex **34.1$_W$** were dissolved in 3 mL of $CH_2Cl_2$. To it 30.9 mg (0.2 mmol, 1 eq.) of catechol(chloro)borane were added at room temperature and the solution was kept on stirring for 7 days. During this time a colour change to slightly yellow brown was observed.

**Purification:** After the reaction was completed (checked by $^{31}P\{^1H\}$ NMR) all volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was obtained as a yellow oil.

**Molecular formula:** $C_{20}H_{27}BO_8PSi_2W$

**Molecular weight:** 712.672 g/mol

**Yield:** 142.5 mg (0.2 mmol, 100 %)

**$^1$H NMR (300.1 MHz, $CDCl_3$):** δ = 0.39 (s, 9H, Si(C*H*$_3$)$_3$), 0.40 (s, 9H, Si(C*H*$_3$)$_3$), 1.96 (d, 1H, $^2J_{P,H}$ = 11.0 Hz, P-C*H*), 2.73 - 2.88 (m, 1H, P-C*H*$_2$), 2.98 - 3.16 (m, 1H, P-C*H*$_2$), 4.56 - 4.75 (m, 2H, O-C*H*$_2$), 6.98 - 7.17 (m, 4H, *Ph*).

**$^{11}$B{$^1$H} NMR (96.3 MHz, $CDCl_3$):** δ = 23.3 (s).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$):** δ = 3.2 (d, $^3J_{P,C}$ = 3.8 Hz, Si(*C*H$_3$)$_3$), 3.9 (d, $^3J_{P,C}$ = 2.6 Hz, Si(*C*H$_3$)$_3$), 32.1 (d, $^1J_{P,C}$ = 13.1 Hz, P-*C*H), 41.5 (d, $^1J_{P,C}$ = 14.2 Hz, P-*C*H$_2$), 63.1 (d, $^2J_{P,C}$ = 7.7 Hz, O-*C*H$_2$), 112.3

(s, *C*$H_{Ar}$), 122.6 (s,*C*$H_{Ar}$), 148.0 (s, O-*C*), 197.0 ($d_{sat}$, $^{1}J_{W,C}$ = 126.9 Hz, $^{2}J_{P,C}$ = 7.2 Hz, *cis-C*O), 199.1 (d, $^{2}J_{P,C}$ = 30.8 Hz, *trans-CO*).

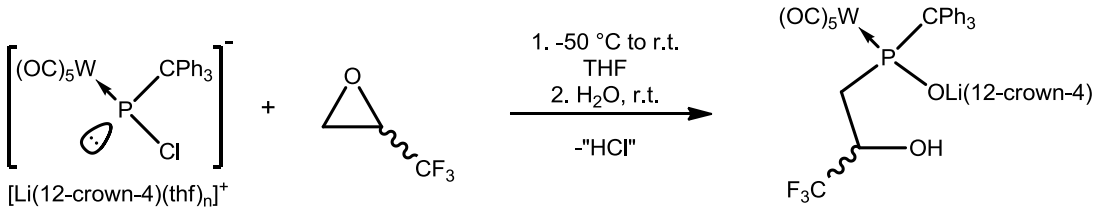
**$^{29}$Si{$^{1}$H} NMR (59.6 MHz, $CDCl_3$):** $\delta$ = 0.06 (s), 3.18 (d, $^{2}J_{P,Si}$ = 6.3 Hz).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, $CDCl_3$):** $\delta$ = 108.9 ($s_{sat}$, $^{1}J_{W,P}$ = 274.3 Hz).

**MS (EI, 70 eV, $^{184}$W, selected data):** m/z (%) = 712.0 (40) $[M]^{\bullet+}$, 684.0 (50) $[M - CO]^{+}$, 628.0 (45) [M - 3 CO]$^{+}$, 572.0 (5) [M - 5 CO]$^{+}$, 325.1 (80) [M - $W(CO)_5$ - Cl - $C_2H_4$]$^{+}$, 254.1 (100) [catBOBcat]$^{+}$, 73.1 (70) $[SiMe_3]^{+}$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2074 (s, $\nu$(CO)), 1987 (w, $\nu$(CO)), 1911 (vs, $\nu$(CO)).

## 11.2.30 Synthesis of lithium(1,4,7,10-tetraoxacyclododecane) pentacarbonyl{[3,3,3-trifluoro-2-hydroxypropyl](triphenylmethyl)phosphanoxido-κ*P*}tungsten(0) [57.3a]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.3** was prepared as described, starting from 133.8 mg (0.2 mmol) of [$(OC)_5W\{PCl_2(CPh_3)\}$] (**1.3**). 16 µL of 1,1,1-trifluoro-2,3-propylene oxide (0.2 mmol, 1.0 eq.) were added and the solution allowed slow warming up to ambient temperature overnight. Subsequently 10 µL of $H_2O$ (0.556 mmol, 2.8 eq) were added and the reaction mixture was stirred for one more hour.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was purified by washing with *n*-pentane (once with 3 mL and once with 2 mL). The product was obtained as slightly yellow powder after drying in *vacuo* (ca. 0.02 mbar).

| | |
|---|---|
| **Molecular formula:** | $C_{35}H_{35}F_3LiO_{11}PW$ |
| **Molecular weight:** | 910.396 g/mol |
| **Melting point:** | 185 °C (dec.) |
| **Yield:** | 145.5 mg (0.156 mmol, 79.9 %) |

**Isomeric ratio:** 47:53

***Isomer 1:***

**$^{1}$H NMR (300.1 MHz, THF-$d_8$):** δ = 1.44 - 1.54 (m, 1H, C*H*$_2$), 2.37 – 2.57 (m, 1H, P-C*H*$_2$), 3.63 (s, 16H, 12-crown-4), 4.67 – 4.84 (m, 1H, O-C*H*), 6.15 (s, 1H, O*H*), 7.03 - 7.85 (m, 15H, C*Ph*$_3$).

**$^{7}$Li NMR (116.6 MHz, THF-$d_8$):** δ = -0.18 (s, *Li*(12-crown-4)).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, THF-$d_8$):** δ = 38.9 (d, $^{1}J_{P,C}$ = 10.7 Hz, P-*C*H$_2$), 70.2 (q, 2JF,C = 31.5 Hz, O-*C*H), 68.6 (s, 12-crown-4), 71.4 (s, *C*Ph$_3$), 126.3 (s, *para-C*H$_{Ar}$), 126.7 (d, $^{5}J_{P,C}$ = 1.6 Hz, *para-C*H$_{Ar}$), 127.3 (d, $^{5}J_{P,C}$ = 1.9 Hz, *para-C*H$_{Ar}$), 127.7 – 128.6 (m, *C*H$_{Ar}$), 131.3 – 128.8 (m, *C*H$_{Ar}$), 144.5 (d, $^{2}J_{P,C}$ = 4.8 Hz, *ipso-C*), 145.9 (d, $^{2}J_{P,C}$ = 4.2 Hz, *ipso-C*), 149.2 (d, $^{2}J_{P,C}$ = 6.1 Hz, *ipso-C*), 200.4 (d, $^{2}J_{P,C}$ = 8.4 Hz, *cis-C*O), 202.3 (d, $^{2}J_{P,C}$ = 22.3 Hz, *trans-CO*).

The signal for the $CF_3$-carbon could not be detected due to a low signal to noise ratio.

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, THF-$d_8$):** δ = -80.8 (s, C*F*$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, THF-$d_8$):** δ = 116.7 (s$_{sat}$, $^{1}J_{W,P}$ = 283.7.0 Hz).

***Isomer 2:***

**$^{1}$H NMR (300.1 MHz, THF-$d_8$):** δ = 2.25 – 2.51 (m, 2H, P-C*H*$_2$), 3.63 (s, 16H, 12-crown-4), 3.80 – 3.90 (m, 1H, O-C*H*), 5.13 (d, 1H, $J_{P,H}$ = 3.7 Hz, O*H*), 7.03 - 7.85 (m, 15H, C*Ph*$_3$).

**$^{7}$Li NMR (116.6 MHz, THF-$d_8$):** δ = -0.18 (s, *Li*(12-crown-4)).

**$^{13}$C{$^{1}$H} NMR (75.5 MHz, THF-$d_8$):** δ = 42.5 (d, $^{1}J_{P,C}$ = 7.1 Hz, P-*C*H$_2$), 70.2 (q, 2JF,C = 31.5 Hz, O-*C*H), 68.6 (s, 12-crown-4), 71.5 (s, *C*Ph$_3$), 126.3 (s, *para-C*H$_{Ar}$), 126.6 (s, *para-C*H$_{Ar}$), 127.0 (s, *para-C*H$_{Ar}$), 127.7 – 128.6 (m, *C*H$_{Ar}$), 131.3 – 128.8 (m, *C*H$_{Ar}$), 145.2 (d, $^{2}J_{P,C}$ = 9.1 Hz, *ipso-C*), 146.5 (d, $^{2}J_{P,C}$ = 4.2 Hz, *ipso-C*), 148.4 (d, $^{2}J_{P,C}$ = 3.2 Hz, *ipso-C*), 200.8 (d, $^{2}J_{P,C}$ = 8.7 Hz, *cis-C*O), 203.3 (d, $^{2}J_{P,C}$ = 22.3 Hz, *trans-CO*).

The signal for the $CF_3$-carbon could not be detected due to a low signal to noise ratio.

**$^{19}$F{$^{1}$H} NMR (282.4 MHz, THF-$d_8$):** δ = -81.3 (s, C*F*$_3$).

**$^{31}$P{$^{1}$H} NMR (121.5 MHz, THF-$d_8$):** δ = 109.2 (s$_{sat}$, $^{1}J_{W,P}$ = 284.9 Hz).

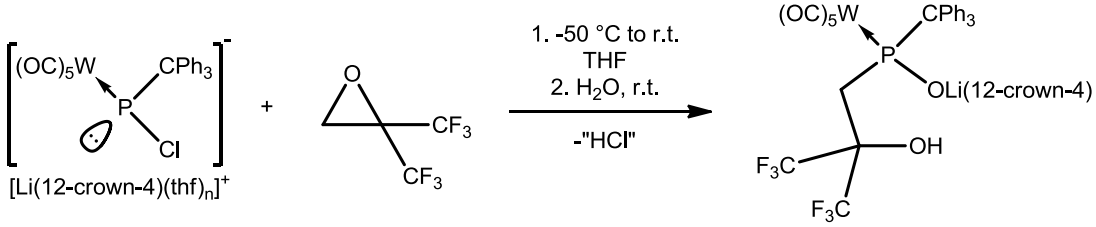
**pos. ESI-MS:** calculated for (Li(12-crown-4)$^{+}$: 183.121, found: 183.121.

**neg. ESI-MS:** calculated for ($C_{27}H_{19}F_3O_7PW)^{+}$: 727.03, found: 727.1.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2061 (m, ν(CO)), 1973 (w, ν(CO)), 1905 (vs, ν(CO)).

**Single crystal measurement:** GSTR505, PB-12 // GXraycu_4642g

## 11.2.31 Synthesis of lithium(1,4,7,10-tetraoxacyclododecane) pentacarbonyl{[3,3,3-trifluoro-2-(trifluoromethyl)-2-hydroxypropyl](triphenylmethyl)phosphanoxido-κ*P*}tungsten(0) [57.3b]




**Synthesis:** A solution of Li/Cl phosphinidenoid complex **2.3** was prepared as described, starting from 334.5 mg (0.5 mmol) of [(OC)$_5$W{PCl$_2$(CPh$_3$)}] (**1.3**). 0.1 mL of hexafluoroisobutene oxide (0.85 mmol, 1.7 eq.) were added and the solution allowed slow warming up to ambient temperature overnight. Subsequently 10 μL of $H_2O$ (0.556 mmol, 1.1 eq) were added and the reaction mixture was stirred for one more hour.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar). The crude product was purified by washing with a mixture of *n*-pentane and diethyl ether (10:1, 2 times 3 mL) and once with 3 mL of *n*-pentane. The product was obtained as white powder after drying in *vacuo* (ca. 0.02 mbar).

**Molecular formula:** $C_{36}H_{34}F_6LiO_{11}PW$

**Molecular weight:** 978.394 g/mol

**Melting point:** 140 °C (dec.)

**Yield:** 323 mg (0.33 mmol, 66 %)

**$^1$H NMR (300.1 MHz, THF-d$_8$):** δ = 1.82 (dd, 1H, $^2J_{H,H}$ = 16.0 Hz, $^2J_{P,H}$ = 7.5 Hz, C*H*$_2$), 2.89 (dd, 1H, $^2J_{H,H}$ = 16.0 Hz, $^2J_{P,H}$ = 9.7 Hz, P-C*H*$_2$), 3.64 (s, 16H, 12-crown-4), 7.04 - 7.74 (m, 15H, C*Ph*$_3$), 9.41 (s$_{br}$, 1H, O*H*).

**$^7$Li NMR (116.6 MHz, THF-d$_8$):** δ = 0.00 (s, *Li*(12-crown-4)).

**$^{13}$C{$^1$H} NMR (75.5 MHz, THF-d$_8$):** δ = 31.6 (s, P-*C*H$_2$), 68.8 (s, 12-crown-4), 70.4 (s, *C*Ph$_3$), 77.0 - 81.0 (m, *C*(CF$_3$)$_2$), 124.8 (q, $^1J_{F,C}$ = 293.0 Hz, *C*F$_3$), 124.8 (q, $^1J_{F,C}$ = 310.8 Hz, *C*F$_3$), 126.5 (s, *para-C*H$_{Ar}$), 126.8 (d, $^5J_{P,C}$ = 2.4 Hz, *para-C*H$_{Ar}$), 127.5 (d, $^5J_{P,C}$ = 2.1 Hz, *para-C*H$_{Ar}$), 128.2 (s, *C*H$_{Ar}$), 128.5 (s, *C*H$_{Ar}$), 128.6 (s, *C*H$_{Ar}$), 131.9 (d, $^2J_{P,C}$ = 6.0 Hz, *C*H$_{Ar}$), 132.6 (d, $J_{P,C}$ = 1.2 Hz, *C*H$_{Ar}$), 132.7 (d, $J_{P,C}$ = 7.2 Hz, *C*H$_{Ar}$), 144.4 (d, $^2J_{P,C}$ = 5.9 Hz, *ipso-C*), 145.5 (d, $^2J_{P,C}$ = 4.2 Hz, *ipso-C*), 148.4 (d, $^2J_{P,C}$ = 7.5 Hz, *ipso-C*), 200.3 (dq$_{sat}$, $^1J_{W,C}$ = 125.5 Hz, $^2J_{P,C}$ = 8.2 Hz, $^6J_{F,C}$ = 1.7 Hz, *cis-C*O), 202.3 (d, $^2J_{P,C}$ = 25.6 Hz, *trans-CO*).

**$^{19}$F{$^1$H} NMR (282.4 MHz, THF-d$_8$):** δ = -79.6 (q, $^4J_{F,F}$ = 11.0 Hz, C*F*$_3$), -76.7 (q, $^4J_{F,F}$ = 11.0 Hz, C*F*$_3$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, THF-d$_8$):** δ = 123.8 (s$_{sat}$, $^1J_{W,P}$ = 295.0 Hz).

**pos. ESI-MS:** calculated for $(C_{36}H_{34}F_6LiO_{11}PW)^+$: 978.14, found: 1611.1 $[Li_3(C_{28}H_{18}F_6O_7PW)_2]^+$, 985.1 $[Li_2(12\text{-crown-4})(C_{28}H_{18}F_6O_7PW)]^+$, 809.0 $[Li_2(C_{28}H_{18}F_6O_7PW)]^+$, 375.2 $[Na(12\text{-crown-4})_2]^+$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2063 (s, ν(CO)), 1971 (w, ν(CO)), 1923 (w, ν(CO)), 1911 (s, ν(CO)), 1890 (vs, ν(CO)).

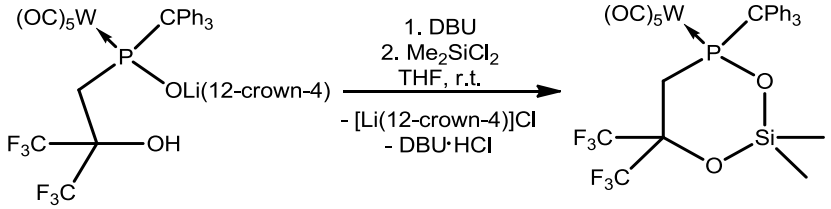
**Elemental analysis:**

**calculated for:** $C_{36}H_{34}F_6LiO_{11}PW + 2\ H_2O$

| | | | | |
|---|---|---|---|---|
| calc.: | C | 42.62 | H | 3.78 |
| found: | C | 42.55 | H | 3.89 |

**Single crystal measurement:** GSTR410, AKY-488-2 // GXray4012f

## 11.2.32 Synthesis of pentacarbonyl[6,6-bis(trifluoromethyl)-2,2-dimethyl-4-triphenylmethyl-1,3,4,2-dioxaphosphasilinan-κ*P*]tungsten(0) [60.3a]




**Synthesis:** In a 20 mL Schlenk tube 250 mg (0.26 mmol) of phosphinito complex **57.3b** were suspended in 10 mL of THF, then 59.4 mg DBU (0.38 mmol, 1.46 eq.), dissolved in 1 mL of THF, were added while stirring. The mixture was stirred for additional ten minutes and 42.3 mg (0.33 mmol 1.27 eq.) $Me_2SiCl_2$, dissolved in 2 mL of THF, were added slowly.

**Purification:** The solvent was removed in *vacuo* (ca. 0.02 mbar) after 24 h to give a greenish brown solid. The crude material was filtered over $SiO_2$ (ø = 1 cm, h = 3 cm, $Et_2O$, r.t.) using 60 mL of $Et_2O$. The solvent was then removed in *vacuo* (ca. 0.02 mbar) and the crude product recrystallized from 2 mL of diethyl ether at 4 °C to yield a white solid.

**Molecular formula:** $C_{30}H_{23}F_6O_7PSiW$

**Molecular weight:** 852.389 g/mol

**Melting point:** 178 °C

**Yield:** 120 mg (0.14 mmol, 54 %).

**$^1$H NMR (500.2 MHz, $CDCl_3$):** δ = -0.16 (s, 3H, Si(C$H_3$)$_2$), 0.53 (s, 3H, Si(C$H_3$)$_2$), 2.55 (dd, 1H, $^2J_{H,H}$ = 16.0 Hz, $^2J_{P,H}$ = 9.7 Hz, P-C$H_2$), 3.40 (dd, 1H, $^2J_{H,H}$ = 16.0 Hz, $^2J_{P,H}$ = 12.5 Hz, P-C$H_2$), 7.27 - 7.48 (m, 15H, C$Ph_3$).

**$^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 0.4 (q, $^5J_{F,C}$ = 3.4 Hz, Si($CH_3$)$_2$), 0.8 (s, Si($CH_3$)$_2$), 29.4 (d, $^1J_{P,C}$ = 2.0 Hz, P-$CH_2$), 70.8 (d, $^1J_{P,C}$ = 10.4 Hz, $CPh_3$), 77.0 - 78.2 (m, $C(CF_3)_2$), 122.7 (q, $^1J_{F,C}$ = 287.1 Hz, $CF_3$ (only one set of signals was observed for both in the $^{13}C$ NMR)), 127.9 (s, 2 times *para*-$CH_{Ar}$), 128.2 (s, $CH_{Ar}$), 128.3 (s, $CH_{Ar}$), 128.4 (s, *para*-$CH_{Ar}$), 128.7 (s, $CH_{Ar}$), 131.6 (d, $J_{P,C}$ = 1.3 Hz, $CH_{Ar}$), 131.8 (d, $^3J_{P,C}$ = 9.5 Hz, $CH_{Ar}$), 132.0 ppm (d, $^3J_{P,C}$ = 7.9 Hz, $CH_{Ar}$), 139.6 (d, $^2J_{P,C}$ = 6.3 Hz, *ipso*-*C*), 140.0 (d, $^2J_{P,C}$ = 7.1 Hz, *ipso*-*C*), 142.8 (d, $^2J_{P,C}$ = 7.1 Hz, *ipso*-*C*), 197.4 ($dq_{sat}$, $^6J_{F,C}$ = 1.9 Hz, $^2J_{P,C}$ = 7.0 Hz, $^1J_{W,C}$ = 127.6 Hz, *cis*-*C*O), 198.2 ($d_{sat}$, $^1J_{W,C}$ = 136.4 Hz, $^2J_{P,C}$ = 33.4 Hz, *trans*-*C*O).

**$^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$):** $\delta$ = -76.9 (q, $^4J_{F,F}$ = 11.5 Hz, $CF_3$), -76.0 (q, $^4J_{F,F}$ = 11.5 Hz, $CF_3$).

**$^{29}Si\{^1H\}$ NMR (99.4 MHz, $CDCl_3$):** $\delta$ = 3.0 (d, $^2J_{P,Si}$ = 9.6 Hz, *Si*($CH_3$)$_2$).

**$^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 125.6 ($s_{sat}$, $^1J_{W,P}$ = 300.9 Hz).

**MS (EI, 70 eV, $^{184}W$, selected data):** m/z (%) = 768.0 (15) $[M - 3\ CO]^+$, 608.9 (45) $[M - CPh_3]^+$, 580.9 (70) $[M - CPh_3 - CO]^+$, 552.9 (20) $[M - CPh_3 - 2\ CO]^+$, 243.1 (100) $[CPh_3]^+$, 165.1 (25) $[CPh_3 - C_6H_6]^+$.

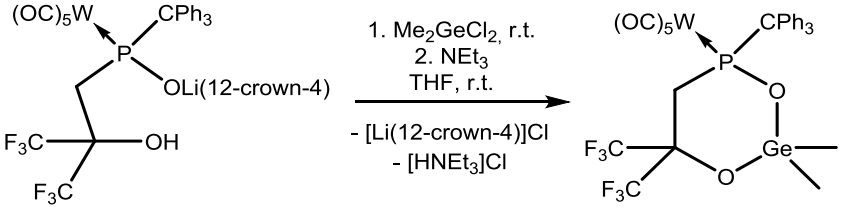
**IR (ATR Diamond; $\tilde{\nu}$[$cm^{-1}$], selected data):** 2074 (s, $\nu$(CO)), 1995 (m, $\nu$(CO)), 1916 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 42.27 | H | 2.27 |
| found: | C | 42.35 | H | 2.79 |

**Single crystal measurement:** GSTR504, PB-35 // GXray4737

## 11.2.33 Synthesis of pentacarbonyl[6,6-bis(trifluoromethyl)-2,2-dimethyl-4-triphenylmethyl-1,3,4,2-dioxaphosphagerminan-κ*P*]tungsten(0) [60.3b]




**Synthesis:** In a 20 mL Schlenk tube 250 mg (0.26 mmol) of phosphinito complex **57.3b** were suspended in 10 mL of THF, then 44 mg of $Me_2GeCl_2$ (0.26 mmol, 1.0 eq.), dissolved in 1 mL of THF, were added while stirring. The mixture was stirred for additional 2.5 h and 0.12 mL of $NEt_3$ (0.91 mmol, 3.5 eq.) were added dropwise.

**Purification:** The solvent was removed at elevated temperature in *vacuo* (ca. 0.02 mbar, 45 °C) after stirring for additional 80 minutes at ambient temperature. The brownish material was filtered over $SiO_2$ (ø = 2 cm, h = 2 cm, $Et_2O$, r.t.). The crude product was obtained as white, sticky solid after removing all volatiles in *vacuo* (ca. 0.02 mbar) and subsequently washed two times with 5 mL of petroleum ether (40/60) at ambient temperature. The product was dried in *vacuo* (ca. 0.02 mbar, 45 °C) for 5 h to yield a white solid.

**Molecular formula:** $C_{30}H_{23}F_6GeO_7PW$

**Molecular weight:** 896.943 g/mol

**Melting point:** 173 °C

**Yield:** 60 mg (0.065 mmol, 25 %)

**$^1$H NMR (500.2 MHz, $CDCl_3$):** $\delta$ = 0.44 (q, 3H, $^6J_{F,H}$ = 1.7 Hz, Ge(C$H_3$)$_2$), 1.04 (s, 3H, Ge(C$H_3$)$_2$), 2.41 (dd, 1H, $^2J_{H,H}$ = 16.0 Hz, $^2J_{P,H}$ = 8.3 Hz, P-C$H_2$), 3.28 (dd, 1H, $^2J_{H,H}$ = 16.0 Hz, $^2J_{P,H}$ = 12.3 Hz, P-C$H_2$), 7.27-7.52 (m, 15H, C$Ph_3$).

**$^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$):** $\delta$ = 4.8 (q, $^5J_{F,C}$ = 4.6 Hz, Ge($C$H$_3$)$_2$), 4.9 (s, Ge($C$H$_3$)$_2$), 30.4 (s, P-$C$H$_2$), 71.0 (d, $^1J_{P,C}$ = 10.2 Hz, $C$Ph$_3$), 77.7 - 79.0 (m, $C$(CF$_3$)$_2$), 123.0 (q, $^1J_{F,C}$ = 285.3 Hz, $C$F$_3$), 123.3 (q, $^1J_{F,C}$ = 289.1 Hz, $C$F$_3$), 127.6 (d, $^5J_{P,C}$ = 1.6 Hz, *para*-CH$_{Ar}$), 127.7 (d, $^5J_{P,C}$ = 1.6 Hz, *para*-CH$_{Ar}$), 128.0 (d, $J_{P,C}$ = 1.1 Hz, $C$H$_{Ar}$), 128.2 (d, $J_{P,C}$ = 1.9 Hz, $C$H$_{Ar}$), 128.2 (s, *para*-$C$H$_{Ar}$), 128.7 (s, $C$H$_{Ar}$), 131.6 (d, $J_{P,C}$ = 2.5 Hz, $C$H$_{Ar}$), 131.8 (d, $^3J_{P,C}$ = 8.7 Hz, $C$H$_{Ar}$), 132.1 ppm (d, $^3J_{P,C}$ = 7.9 Hz, $C$H$_{Ar}$), 140.2 (d, $^2J_{P,C}$ = 6.5 Hz, *ipso*-C), 140.3 (d, $^2J_{P,C}$ = 6.0 Hz, *ipso*-$C$), 143.5 (d, $^2J_{P,C}$ = 7.1 Hz, *ipso*-$C$), 197.7 (dq$_{sat}$, $^2J_{P,C}$ = 7.4 Hz, $^6J_{F,C}$ = 1.9 Hz, $^1J_{W,C}$ = 126.8 Hz, *cis*-$C$O), 198.8 (d, $^2J_{P,C}$ = 32.3 Hz, *trans*-$C$O).

**$^{19}$F{$^1$H} NMR (282.4 MHz, $CDCl_3$):** $\delta$ = -78.7 (q, $^4J_{F,F}$ = 11.3 Hz, C$F_3$), -78.2 (q, $^4J_{F,F}$ = 11.3 Hz, C$F_3$).

**$^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$):** $\delta$ = 126.2 (s$_{sat}$, $^1J_{W,P}$ = 299.0 Hz).

**LIFDI-MS:** m/z (%) = 896 (25) $[M]^{\cdot+}$, 243.1 (100) $[CPh_3]^+$.

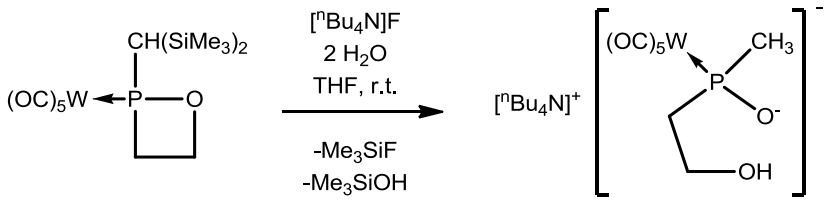
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 2073 (s, $\nu$(CO)), 1994 (m, $\nu$(CO)), 1944 (w, $\nu$(CO)), 1916 (vs, $\nu$(CO)).

**Elemental analysis:**

| | | | | |
|---|---|---|---|---|
| calc.: | C | 40.17 | H | 2.58 |
| found: | C | 39.63 | H | 2.86 |

**Single crystal measurement:** GSTR507, PB-47 // GXray4813

## 11.2.34 Synthesis of tetrabutylammonium pentacarbonyl[(2-hydroxyethyl)methylphosphanoxido-κ*P*]tungsten(0) [61]




**Synthesis:** In a 10 mL Schlenk tube were dissolved 279.2 mg (0.5 mmol) of 1,2-oxaphosphetane complex **34.1$_W$** in 5 mL of THF and 0.5 mL of an $^nBu_4NF$ solution (0.5 mmol, 1 M in THF, 1.0 eq.) were added. The mixture was stirred overnight at ambient temperature and a change of the colour to yellow was observed.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the product was dried for 8 h at the same pressure. The product was obtained as yellow oil, which crystallized over time to yield a yellow solid.

**Molecular formula:** $C_{24}H_{44}NO_7PW$

**Molecular weight:** 673.422 g/mol

**Yield:** 336.7 mg (0.5 mmol, 100 %)

**$^1$H NMR (300.1 MHz, THF-d$_8$):** δ = 1.00 (d, 12H, $^3J_{H,H}$ = 7.3 Hz, $CH_2$-C$H_3$), 1.34 - 1.49 (m, 8H, C$H_2$-$CH_3$), 1.62 - 1.76 (m, 8H, $CH_2$-C$H_2$-$CH_2$), 1.62 - 1.76 (m, 1H, C$H_2$), 1.68 (d, 3H, $^2J_{P,H}$ = 6.5 Hz, P-C$H_3$), 2.10 - 2.25 (m, 2H, P-C$H_2$), 3.31 - 3.41 (m, 8H, N-C$H_2$), 3.86 - 4.18 (m, 2H, O-C$H_2$), 6.43 ($s_{br}$, 1H, OH).

**$^{13}$C{$^1$H} NMR (75.5 MHz, THF-d$_8$):** δ = 13.9 (s, *C*$H_3$), 20.4 (s, *C*$H_2$), 24.5 (s, *C*$H_2$), 29.9 (d, $^1J_{P,C}$ = 17.8 Hz, P-*C*$H_3$), 44.7 (d, $^1J_{P,C}$ = 23.3 Hz, P-*C*$H_2$), 59.0 (s, *C*$H_2$), 61.4 (d, $^2J_{P,C}$ = 4.9 Hz, O-*C*$H_2$), 201.9 ($d_{sat}$, $^1J_{W,C}$ = 125.6 Hz, $^2J_{P,C}$ = 9.5 Hz, *cis*-*C*O), 205.5 (d, $^2J_{P,C}$ = 10.7 Hz, *trans*-*CO*).

**$^{31}$P{$^1$H} NMR (121.5 MHz, THF-d$_8$):** δ = 67.2 ($s_{sat}$, $^1J_{W,P}$ = 233.9 Hz).

**pos. ESI-MS:** calculated for $(^nBu_4N)^+$: 242.285, found: 242.284 $(^nBu_4N)^+$.

**neg. ESI-MS:** calculated for $(C_8H_8O_7PW)^-$: 430.952, found: 430.952 $[M]^-$, 402.957 $[M - CO]^-$, 374.962 $[M - 2 CO]^-$, 346.965 $[M - 3 CO]^-$.

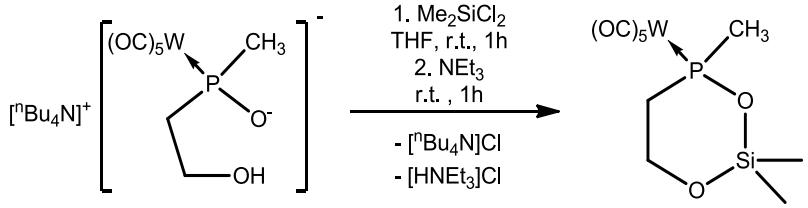
**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selected data):** 3203 (w, ν(OH)), 2051 (m, ν(CO)), 1955 (w, ν(CO)), 1898 (s, ν(CO)), 1865 (vs, ν(CO)).

**Elemental analysis:**

| | | | | | | |
|---|---|---|---|---|---|---|
| calc.: | C | 42.80 | H | 6.59 | N | 2.08 |
| found: | C | 42.28 | H | 6.52 | N | 2.06 |

**Single crystal measurement:** GSTR545, AKY-610 // GXrayneu

## 11.2.35 Synthesis of pentacarbonyl(2,2-dimethyl-4-methyl-1,3,4,2-dioxaphosphasilinan-κ*P*)tungsten(0) [66]




**Synthesis:** In a 10 mL Schlenk tube, 54 mg (0.08 mmol) of phosphinito complex **61** were dissolved in 3 mL of THF, then 0.02 mL of $Me_2SiCl_2$ (0.16 mmol, 2 eq.) were added while stirring. The mixture was stirred for an additional hour at ambient temperature, then 0.05 mL of $Net_3$ (0.36 mmol, 4.5 eq.) were added slowly. Formation of a white solid was observed and the solution was kept stirring for an additional hour.

**Purification:** All volatiles were removed in *vacuo* (ca. 0.02 mbar) and the crude material was filtered over $SiO_2$ (ø = 1 cm, h = 2 cm, $Et_2O$, r.t.) using 50 mL of diethyl ether. The solvent was then removed in *vacuo* (ca. 0.02 mbar) to yield the product as white, oily material.

**Molecular formula:** $C_{10}H_{13}O_7PSiW$

**Molecular weight:** 488.105 g/mol

**Yield:** 33.1 mg (0.068 mmol, 85 %)

**$^1$H NMR (300.1 MHz, $C_6D_6$):** δ = -0.11 ($s_{sat}$, 3H, $^2J_{Si,H}$ = 6.8 Hz, Si(C*H*$_3$)$_2$), 0.10 ($s_{sat}$, 3H, $^2J_{Si,H}$ = 7.2 Hz, Si(C*H*$_3$)$_2$), 1.13 (dddd, 1H, $^2J_{H,H}$ = 15.4 Hz, $^3J_{H,H}$ = 4.7 Hz, $^3J_{H,H}$ = 2.9 Hz, $^2J_{P,H}$ = 2.5 Hz, P-C*H*$_2$), 2.15 (dddd, 1H, $^2J_{H,H}$ = 15.4 Hz, $^3J_{H,H}$ = 9.3 Hz, $^3J_{H,H}$ = 4.6 Hz, $^2J_{P,H}$ = 1.3 Hz, P-C*H*$_2$), 3.63 (dddd, 1H, $^3J_{P,H}$ = 14.2 Hz, $^2J_{H,H}$ = 12.0 Hz, $^3J_{H,H}$ = 9.3 Hz, $^3J_{H,H}$ = 2.9 Hz, O-C*H*$_2$), 3.71 (dddd, 1H, $^3J_{P,H}$ = 12.7 Hz, $^2J_{H,H}$ = 12.0 Hz, $^3J_{H,H}$ = 4.7 Hz, $^3J_{H,H}$ = 4.6 Hz, O-C*H*$_2$).

**$^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$):** δ = -0.6 (d, $^3J_{P,C}$ = 0.6 Hz, Si(*C*H$_3$)$_2$), -0.3 (s, Si(*C*H$_3$)$_2$), 25.5 (d, $^1J_{P,C}$ = 23.3 Hz, P-*C*H$_3$), 39.3 (d, $^1J_{P,C}$ = 23.3 Hz, P-*C*H$_2$), 58.7 (d, $^2J_{P,C}$ = 6.1 Hz, O-*C*H$_2$), 197.0 ($d_{sat}$, $^2J_{P,C}$ = 8.4 Hz, $^1J_{W,C}$ = 125.1 Hz, *cis*-*C*O), 200.2 ($d_{sat}$, $^1J_{W,C}$ = 139.7 Hz, $^2J_{P,C}$ = 24.2 Hz, *trans*-*C*O).

**$^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$):** δ = -0.3 (d, $^2J_{P,Si}$ = 12.1 Hz, *Si*(CH$_3$)$_2$).

**$^{31}$P{$^1$H} NMR (121.5 MHz, $C_6D_6$):** δ = 105.2 ($s_{sat}$, $^1J_{W,P}$ = 279.6 Hz).

**MS (EI, 70 eV, $^{184}$W, selection):** m/z (%) = 505.9 (5) [M + $H_2O$]$^{\bullet+}$, 487.9 (30) [M]$^{\bullet+}$, 451.9 (20) [M + $H_2O$ - 2 CO]$^+$, 431.9 (25) [M - 2 CO]$^+$, 404.0 (10) [M - 3 CO]$^+$, 375.9 (100) [M - 4 CO]$^+$, 348.0 (60) [M - 5 CO]$^+$.

**IR (ATR Diamond; $\tilde{\nu}$[cm$^{-1}$], selection):** 2072 (s, ν(CO)), 1981(m, ν(CO)), 1901 (vs, ν(CO)).

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# 12 X-ray crystallographic data

## 12.1 Pentacarbonyl[diethylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [6.3a]

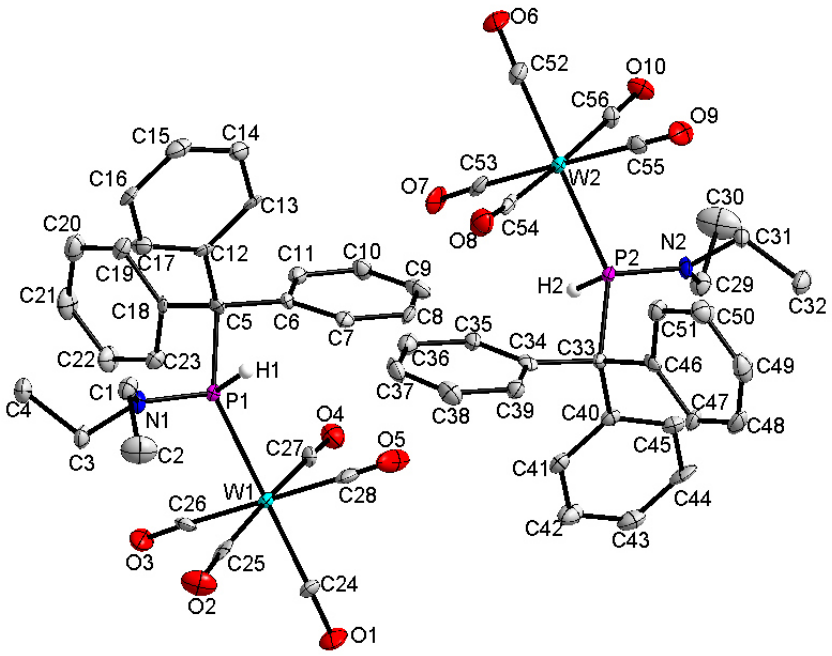


***Table 1:*** Crystal data and structure refinement for **6.3a**.

| | |
|---|---|
| Identification code | GSTR317, AKY-280 // GXraytwin5-merg |
| Crystal Habitus | pale yellow plate |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{28}H_{26}NO_5PW$ |
| Moiety formula | C28 H26 N O5 P W |
| Formula weight | 671.32 |
| Temperature/K | 100(2) |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 10.7367(7) |
| b/Å | 15.677o0(10) |
| c/Å | 17.4538(10) |
| α/° | 104.204(3) |
| β/° | 98.484(3) |
| γ/° | 104.184(3) |
| Volume/Å$^3$ | 2692.9(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.656 |
| μ/mm$^{-1}$ | 4.386 |
| F(000) | 1320.0 |
| Crystal size/mm$^3$ | 0.35 × 0.20 × 0.10 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.3090; 0.6681 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.46 to 50.5° |

| | |
|---|---|
| Completeness to theta | 0.950 |
| Index ranges | -12 ≤ h ≤ 0, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20 |
| Reflections collected | 11119 |
| Independent reflections | 11139 [$R_{int}$ = 0.0700] |
| Data/restraints/parameters | 11139/102/660 |
| Goodness-of-fit on $F^2$ | 1.046 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0419, $wR_2$ = 0.0975 |
| Final R indexes [all data] | $R_1$ = 0.0538, $wR_2$ = 0.1052 |
| Largest diff. peak/hole / e $Å^{-3}$ | 2.07/-1.62 |

***Table 2:*** Bond lengths for **6.3a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | N1 | 1.467(9) | C31 | N2 | 1.482(8) |
| C1 | C2 | 1.517(10) | C31 | C32 | 1.505(10) |
| C3 | N1 | 1.477(8) | C33 | C34 | 1.539(9) |
| C3 | C4 | 1.525(10) | C33 | C46 | 1.540(9) |
| C5 | C6 | 1.524(9) | C33 | C40 | 1.551(9) |
| C5 | C18 | 1.543(9) | C33 | P2 | 1.954(6) |
| C5 | C12 | 1.555(9) | C34 | C39 | 1.382(10) |
| C5 | P1 | 1.957(7) | C34 | C35 | 1.411(10) |
| C6 | C7 | 1.399(9) | C35 | C36 | 1.382(10) |
| C6 | C11 | 1.399(10) | C36 | C37 | 1.396(10) |
| C7 | C8 | 1.386(10) | C37 | C38 | 1.376(11) |
| C8 | C9 | 1.388(10) | C38 | C39 | 1.394(10) |
| C9 | C10 | 1.387(10) | C40 | C41 | 1.390(9) |
| C10 | C11 | 1.394(10) | C40 | C45 | 1.402(10) |
| C12 | C13 | 1.383(9) | C41 | C42 | 1.392(10) |
| C12 | C17 | 1.387(10) | C42 | C43 | 1.382(11) |
| C13 | C14 | 1.400(10) | C43 | C44 | 1.395(11) |
| C14 | C15 | 1.385(11) | C44 | C45 | 1.383(10) |
| C15 | C16 | 1.384(10) | C46 | C51 | 1.398(10) |
| C16 | C17 | 1.393(10) | C46 | C47 | 1.398(9) |
| C18 | C23 | 1.400(9) | C47 | C48 | 1.385(10) |
| C18 | C19 | 1.401(9) | C48 | C49 | 1.399(11) |
| C19 | C20 | 1.393(10) | C49 | C50 | 1.379(11) |
| C20 | C21 | 1.392(11) | C50 | C51 | 1.391(10) |
| C21 | C22 | 1.386(11) | C52 | O6 | 1.137(9) |
| C22 | C23 | 1.377(10) | C52 | W2 | 2.024(8) |
| C24 | O1 | 1.137(8) | C53 | O7 | 1.132(8) |
| C24 | W1 | 2.017(7) | C53 | W2 | 2.065(8) |
| C25 | O2 | 1.144(9) | C54 | O8 | 1.145(9) |
| C25 | W1 | 2.046(8) | C54 | W2 | 2.044(8) |
| C26 | O3 | 1.154(8) | C55 | O9 | 1.144(8) |
| C26 | W1 | 2.033(7) | C55 | W2 | 2.048(8) |
| C27 | O4 | 1.148(8) | C56 | O10 | 1.146(8) |
| C27 | W1 | 2.038(7) | C56 | W2 | 2.039(7) |
| C28 | O5 | 1.142(9) | N1 | P1 | 1.673(6) |
| C28 | W1 | 2.047(8) | N2 | P2 | 1.678(6) |
| C29 | N2 | 1.465(9) | P1 | W1 | 2.5540(18) |
| C29 | C30 | 1.507(10) | P2 | W2 | 2.5509(17) |

***Table 3:*** Bond angles for **6.3a**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N1 | C1 | C2 | 113.1(6) | C42 | C43 | C44 | 118.7(7) |
| N1 | C3 | C4 | 113.4(6) | C45 | C44 | C43 | 120.8(8) |
| C6 | C5 | C18 | 111.0(5) | C44 | C45 | C40 | 120.7(7) |
| C6 | C5 | C12 | 112.0(5) | C51 | C46 | C47 | 117.4(6) |
| C18 | C5 | C12 | 111.5(6) | C51 | C46 | C33 | 120.0(6) |
| C6 | C5 | P1 | 106.2(4) | C47 | C46 | C33 | 122.3(6) |
| C18 | C5 | P1 | 108.5(4) | C48 | C47 | C46 | 120.7(7) |
| C12 | C5 | P1 | 107.3(4) | C47 | C48 | C49 | 120.6(7) |
| C7 | C6 | C11 | 117.1(6) | C50 | C49 | C48 | 119.6(7) |
| C7 | C6 | C5 | 121.4(6) | C49 | C50 | C51 | 119.3(7) |
| C11 | C6 | C5 | 121.5(6) | C50 | C51 | C46 | 122.3(7) |
| C8 | C7 | C6 | 121.8(7) | O6 | C52 | W2 | 177.3(7) |
| C7 | C8 | C9 | 120.1(7) | O7 | C53 | W2 | 177.7(6) |
| C10 | C9 | C8 | 119.6(7) | O8 | C54 | W2 | 175.6(6) |
| C9 | C10 | C11 | 119.8(7) | O9 | C55 | W2 | 178.6(7) |
| C10 | C11 | C6 | 121.6(7) | O10 | C56 | W2 | 177.9(6) |
| C13 | C12 | C17 | 118.8(6) | C1 | N1 | C3 | 116.0(6) |
| C13 | C12 | C5 | 121.0(6) | C1 | N1 | P1 | 122.0(5) |
| C17 | C12 | C5 | 120.1(6) | C3 | N1 | P1 | 121.0(5) |
| C12 | C13 | C14 | 119.7(7) | C29 | N2 | C31 | 115.8(6) |
| C15 | C14 | C13 | 121.4(7) | C29 | N2 | P2 | 124.2(5) |
| C16 | C15 | C14 | 118.6(7) | C31 | N2 | P2 | 119.6(5) |
| C15 | C16 | C17 | 120.1(7) | N1 | P1 | C5 | 109.7(3) |
| C12 | C17 | C16 | 121.3(7) | N1 | P1 | W1 | 115.9(2) |
| C23 | C18 | C19 | 117.1(6) | C5 | P1 | W1 | 123.1(2) |
| C23 | C18 | C5 | 120.7(6) | N2 | P2 | C33 | 110.3(3) |
| C19 | C18 | C5 | 121.9(6) | N2 | P2 | W2 | 115.6(2) |
| C20 | C19 | C18 | 121.0(7) | C33 | P2 | W2 | 123.1(2) |
| C21 | C20 | C19 | 120.5(7) | C24 | W1 | C26 | 89.2(3) |
| C22 | C21 | C20 | 118.9(7) | C24 | W1 | C27 | 89.2(3) |
| C23 | C22 | C21 | 120.5(7) | C26 | W1 | C27 | 88.0(3) |
| C22 | C23 | C18 | 121.9(7) | C24 | W1 | C25 | 87.1(3) |
| O1 | C24 | W1 | 178.9(7) | C26 | W1 | C25 | 89.6(3) |
| O2 | C25 | W1 | 175.4(6) | C27 | W1 | C25 | 175.6(3) |
| O3 | C26 | W1 | 177.3(6) | C24 | W1 | C28 | 90.6(3) |
| O4 | C27 | W1 | 175.4(6) | C26 | W1 | C28 | 178.9(3) |
| O5 | C28 | W1 | 177.8(7) | C27 | W1 | C28 | 91.0(3) |
| N2 | C29 | C30 | 113.8(6) | C25 | W1 | C28 | 91.5(3) |
| N2 | C31 | C32 | 113.6(6) | C24 | W1 | P1 | 173.1(2) |
| C34 | C33 | C46 | 110.3(5) | C26 | W1 | P1 | 94.9(2) |
| C34 | C33 | C40 | 111.3(5) | C27 | W1 | P1 | 96.5(2) |
| C46 | C33 | C40 | 111.9(5) | C25 | W1 | P1 | 87.31(19) |
| C34 | C33 | P2 | 106.8(4) | C28 | W1 | P1 | 85.5(2) |
| C46 | C33 | P2 | 108.6(4) | C52 | W2 | C56 | 86.9(3) |
| C40 | C33 | P2 | 107.8(4) | C52 | W2 | C54 | 88.9(3) |
| C39 | C34 | C35 | 118.5(7) | C56 | W2 | C54 | 174.1(3) |
| C39 | C34 | C33 | 121.4(6) | C52 | W2 | C55 | 90.0(3) |
| C35 | C34 | C33 | 120.0(6) | C56 | W2 | C55 | 88.4(3) |
| C36 | C35 | C34 | 120.2(7) | C54 | W2 | C55 | 87.4(3) |
| C35 | C36 | C37 | 120.8(7) | C52 | W2 | C53 | 90.7(3) |
| C38 | C37 | C36 | 118.8(7) | C56 | W2 | C53 | 92.3(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C37 | C38 | C39 | 121.0(7) | C54 | W2 | C53 | 91.9(3) |
| C34 | C39 | C38 | 120.6(7) | C55 | W2 | C53 | 179.0(3) |
| C41 | C40 | C45 | 118.0(6) | C52 | W2 | P2 | 172.0(2) |
| C41 | C40 | C33 | 121.8(6) | C56 | W2 | P2 | 86.7(2) |
| C45 | C40 | C33 | 120.1(6) | C54 | W2 | P2 | 97.76(19) |
| C40 | C41 | C42 | 121.0(7) | C55 | W2 | P2 | 94.7(2) |
| C43 | C42 | C41 | 120.7(7) | C53 | W2 | P2 | 84.7(2) |

***Table 4:*** Torsion angles for **6.3a**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| C18 | C5 | C6 | C7 | -161.7(6) | C32 | C31 | N2 | P2 | 123.4(6) |
| C12 | C5 | C6 | C7 | 72.9(8) | C1 | N1 | P1 | C5 | -98.7(5) |
| P1 | C5 | C6 | C7 | -43.9(7) | C3 | N1 | P1 | C5 | 93.4(5) |
| C18 | C5 | C6 | C11 | 20.4(8) | C1 | N1 | P1 | W1 | 116.4(5) |
| C12 | C5 | C6 | C11 | -105.0(7) | C3 | N1 | P1 | W1 | -51.6(5) |
| P1 | C5 | C6 | C11 | 138.2(5) | C6 | C5 | P1 | N1 | 178.5(4) |
| C11 | C6 | C7 | C8 | -1.2(10) | C18 | C5 | P1 | N1 | -62.1(5) |
| C5 | C6 | C7 | C8 | -179.2(6) | C12 | C5 | P1 | N1 | 58.5(5) |
| C6 | C7 | C8 | C9 | 1.1(10) | C6 | C5 | P1 | W1 | -39.6(5) |
| C7 | C8 | C9 | C10 | -0.2(10) | C18 | C5 | P1 | W1 | 79.9(5) |
| C8 | C9 | C10 | C11 | -0.6(10) | C12 | C5 | P1 | W1 | -159.5(3) |
| C9 | C10 | C11 | C6 | 0.5(10) | C29 | N2 | P2 | C33 | 96.4(6) |
| C7 | C6 | C11 | C10 | 0.4(10) | C31 | N2 | P2 | C33 | -91.0(5) |
| C5 | C6 | C11 | C10 | 178.4(6) | C29 | N2 | P2 | W2 | -118.3(5) |
| C6 | C5 | C12 | C13 | 1.7(9) | C31 | N2 | P2 | W2 | 54.3(5) |
| C18 | C5 | C12 | C13 | -123.4(6) | C34 | C33 | P2 | N2 | -179.3(4) |
| P1 | C5 | C12 | C13 | 117.9(6) | C46 | C33 | P2 | N2 | 61.8(5) |
| C6 | C5 | C12 | C17 | 178.4(6) | C40 | C33 | P2 | N2 | -59.6(5) |
| C18 | C5 | C12 | C17 | 53.3(8) | C34 | C33 | P2 | W2 | 38.5(5) |
| P1 | C5 | C12 | C17 | -65.4(7) | C46 | C33 | P2 | W2 | -80.4(5) |
| C17 | C12 | C13 | C14 | 1.1(10) | C40 | C33 | P2 | W2 | 158.2(4) |
| C5 | C12 | C13 | C14 | 177.8(6) | O1 | C24 | W1 | C26 | -65(35) |
| C12 | C13 | C14 | C15 | 1.6(11) | O1 | C24 | W1 | C27 | -152(35) |
| C13 | C14 | C15 | C16 | -2.9(11) | O1 | C24 | W1 | C25 | 25(35) |
| C14 | C15 | C16 | C17 | 1.6(11) | O1 | C24 | W1 | C28 | 117(35) |
| C13 | C12 | C17 | C16 | -2.3(10) | O1 | C24 | W1 | P1 | 62(35) |
| C5 | C12 | C17 | C16 | -179.1(6) | O3 | C26 | W1 | C24 | -11(13) |
| C15 | C16 | C17 | C12 | 1.0(11) | O3 | C26 | W1 | C27 | 78(13) |
| C6 | C5 | C18 | C23 | 68.6(8) | O3 | C26 | W1 | C25 | -98(13) |
| C12 | C5 | C18 | C23 | -165.7(6) | O3 | C26 | W1 | C28 | 67(21) |
| P1 | C5 | C18 | C23 | -47.8(7) | O3 | C26 | W1 | P1 | 174(100) |
| C6 | C5 | C18 | C19 | -105.9(7) | O4 | C27 | W1 | C24 | 34(8) |
| C12 | C5 | C18 | C19 | 19.8(9) | O4 | C27 | W1 | C26 | -55(8) |
| P1 | C5 | C18 | C19 | 137.7(6) | O4 | C27 | W1 | C25 | 1(10) |
| C23 | C18 | C19 | C20 | 2.7(10) | O4 | C27 | W1 | C28 | 125(8) |
| C5 | C18 | C19 | C20 | 177.4(6) | O4 | C27 | W1 | P1 | -150(8) |
| C18 | C19 | C20 | C21 | -0.7(11) | O2 | C25 | W1 | C24 | -21(8) |
| C19 | C20 | C21 | C22 | -0.9(12) | O2 | C25 | W1 | C26 | 69(8) |
| C20 | C21 | C22 | C23 | 0.4(12) | O2 | C25 | W1 | C27 | 13(11) |
| C21 | C22 | C23 | C18 | 1.8(11) | O2 | C25 | W1 | C28 | -111(8) |
| C19 | C18 | C23 | C22 | -3.3(10) | O2 | C25 | W1 | P1 | 164(8) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C5 | C18 | C23 | C22 | -178.1(6) | O5 | C28 | W1 | C24 | -151(18) |
| C46 | C33 | C34 | C39 | -22.3(8) | O5 | C28 | W1 | C26 | 131(19) |
| C40 | C33 | C34 | C39 | 102.5(7) | O5 | C28 | W1 | C27 | 120(18) |
| P2 | C33 | C34 | C39 | -140.1(6) | O5 | C28 | W1 | C25 | -63(18) |
| C46 | C33 | C34 | C35 | 161.3(6) | O5 | C28 | W1 | P1 | 24(18) |
| C40 | C33 | C34 | C35 | -73.9(8) | N1 | P1 | W1 | C24 | -70.3(18) |
| P2 | C33 | C34 | C35 | 43.5(7) | C5 | P1 | W1 | C24 | 149.8(18) |
| C39 | C34 | C35 | C36 | 2.2(10) | N1 | P1 | W1 | C26 | 55.5(3) |
| C33 | C34 | C35 | C36 | 178.6(6) | C5 | P1 | W1 | C26 | -84.4(3) |
| C34 | C35 | C36 | C37 | -1.4(10) | N1 | P1 | W1 | C27 | 144.0(3) |
| C35 | C36 | C37 | C38 | -0.6(11) | C5 | P1 | W1 | C27 | 4.1(3) |
| C36 | C37 | C38 | C39 | 1.8(11) | N1 | P1 | W1 | C25 | -33.9(3) |
| C35 | C34 | C39 | C38 | -1.0(10) | C5 | P1 | W1 | C25 | -173.7(3) |
| C33 | C34 | C39 | C38 | -177.4(6) | N1 | P1 | W1 | C28 | -125.6(3) |
| C37 | C38 | C39 | C34 | -1.0(11) | C5 | P1 | W1 | C28 | 94.6(3) |
| C34 | C33 | C40 | C41 | -0.2(9) | O6 | C52 | W2 | C56 | 8(15) |
| C46 | C33 | C40 | C41 | 123.7(7) | O6 | C52 | W2 | C54 | -176(100) |
| P2 | C33 | C40 | C41 | -117.0(6) | O6 | C52 | W2 | C55 | 97(15) |
| C34 | C33 | C40 | C45 | -178.9(6) | O6 | C52 | W2 | C53 | -84(15) |
| C46 | C33 | C40 | C45 | -54.9(8) | O6 | C52 | W2 | P2 | -29(16) |
| P2 | C33 | C40 | C45 | 64.3(7) | O10 | C56 | W2 | C52 | 48(17) |
| C45 | C40 | C41 | C42 | -0.6(10) | O10 | C56 | W2 | C54 | 4(19) |
| C33 | C40 | C41 | C42 | -179.3(6) | O10 | C56 | W2 | C55 | -42(17) |
| C40 | C41 | C42 | C43 | -1.5(11) | O10 | C56 | W2 | C53 | 139(17) |
| C41 | C42 | C43 | C44 | 1.4(12) | O10 | C56 | W2 | P2 | -137(17) |
| C42 | C43 | C44 | C45 | 0.8(11) | O8 | C54 | W2 | C52 | -35(8) |
| C43 | C44 | C45 | C40 | -3.0(11) | O8 | C54 | W2 | C56 | 9(10) |
| C41 | C40 | C45 | C44 | 2.8(10) | O8 | C54 | W2 | C55 | 55(8) |
| C33 | C40 | C45 | C44 | -178.4(6) | O8 | C54 | W2 | C53 | -126(8) |
| C34 | C33 | C46 | C51 | -65.2(8) | O8 | C54 | W2 | P2 | 149(8) |
| C40 | C33 | C46 | C51 | 170.3(6) | O9 | C55 | W2 | C52 | 50(26) |
| P2 | C33 | C46 | C51 | 51.5(7) | O9 | C55 | W2 | C56 | 137(26) |
| C34 | C33 | C46 | C47 | 109.7(7) | O9 | C55 | W2 | C54 | -39(26) |
| C40 | C33 | C46 | C47 | -14.8(9) | O9 | C55 | W2 | C53 | -87(32) |
| P2 | C33 | C46 | C47 | -133.5(6) | O9 | C55 | W2 | P2 | -137(26) |
| C51 | C46 | C47 | C48 | -1.3(10) | O7 | C53 | W2 | C52 | -171(17) |
| C33 | C46 | C47 | C48 | -176.4(6) | O7 | C53 | W2 | C56 | 102(17) |
| C46 | C47 | C48 | C49 | -0.4(11) | O7 | C53 | W2 | C54 | -82(17) |
| C47 | C48 | C49 | C50 | 1.2(12) | O7 | C53 | W2 | C55 | -35(30) |
| C48 | C49 | C50 | C51 | -0.2(11) | O7 | C53 | W2 | P2 | 15(17) |
| C49 | C50 | C51 | C46 | -1.6(11) | N2 | P2 | W2 | C52 | 68.6(16) |
| C47 | C46 | C51 | C50 | 2.3(10) | C33 | P2 | W2 | C52 | -151.0(15) |
| C33 | C46 | C51 | C50 | 177.5(6) | N2 | P2 | W2 | C56 | 30.9(3) |
| C2 | C1 | N1 | C3 | 78.0(8) | C33 | P2 | W2 | C56 | 171.3(3) |
| C2 | C1 | N1 | P1 | -90.5(7) | N2 | P2 | W2 | C54 | -145.3(3) |
| C4 | C3 | N1 | C1 | 77.5(8) | C33 | P2 | W2 | C54 | -4.9(3) |
| C4 | C3 | N1 | P1 | -113.9(6) | N2 | P2 | W2 | C55 | -57.2(3) |
| C30 | C29 | N2 | C31 | -61.0(9) | C33 | P2 | W2 | C55 | 83.2(3) |
| C30 | C29 | N2 | P2 | 111.8(7) | N2 | P2 | W2 | C53 | 123.5(3) |
| C32 | C31 | N2 | C29 | -63.5(8) | C33 | P2 | W2 | C53 | -96.1(3) |

## 12.2 Pentacarbonyl[cyclohexylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [9.3a]

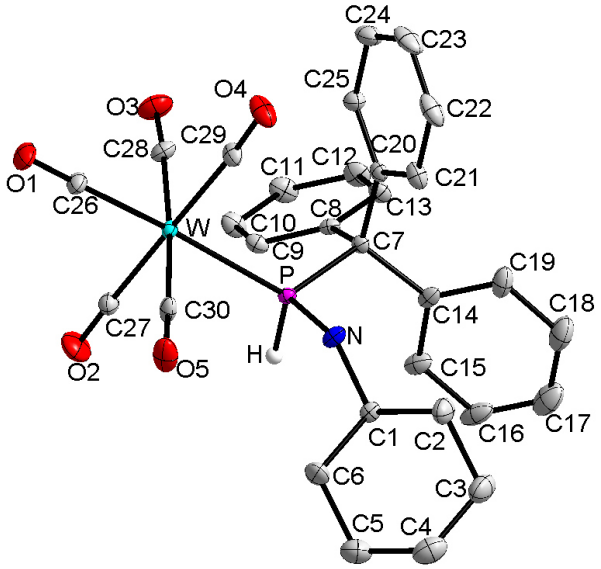


***Table 1:*** Crystal data and structure refinement for **9.3a**.

| | |
|---|---|
| Identification code | GSTR450, AKY-Cy // GXraymo_4395f |
| Crystal Habitus | clear colourless block |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{30}H_{28}NO_5PW$ |
| Moiety formula | C30 H28 N O5 P W |
| Formula weight | 697.35 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 9.5897(3) |
| b/Å | 27.4801(8) |
| c/Å | 11.3823(3) |
| α/° | 90 |
| β/° | 111.0141(9) |
| γ/° | 90 |
| Volume/Å$^3$ | 2800.04(14) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.654 |
| μ/mm$^{-1}$ | 4.222 |
| F(000) | 1376.0 |
| Crystal size/mm$^3$ | 0.25 × 0.24 × 0.23 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4113; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.786 to 55.996° |
| Completeness to theta | 0.999 |
| Index ranges | -12 ≤ h ≤ 12, -36 ≤ k ≤ 36, -15 ≤ l ≤ 14 |
| Reflections collected | 111139 |
| Independent reflections | 6760 [$R_{int}$ = 0.0385, $R_{sigma}$ = 0.0134] |
| Data/restraints/parameters | 6760/145/346 |
| Goodness-of-fit on $F^2$ | 1.085 |

| | |
|---|---|
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0184, $wR_2$ = 0.0403 |
| Final R indexes [all data] | $R_1$ = 0.0205, $wR_2$ = 0.0410 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.05/-0.96 |

***Table 2:*** Bond lengths for **9.3a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5210(5) | C7 | C14 | 1.544(3) |
| W | C26 | 1.996(2) | C7 | C20 | 1.537(3) |
| W | C27 | 2.035(2) | C8 | C9 | 1.391(3) |
| W | C28 | 2.047(2) | C8 | C13 | 1.403(3) |
| W | C29 | 2.061(2) | C9 | C10 | 1.398(3) |
| W | C30 | 2.055(2) | C10 | C11 | 1.387(3) |
| P | N | 1.6652(18) | C11 | C12 | 1.389(3) |
| P | C7 | 1.912(2) | C12 | C13 | 1.388(3) |
| O1 | C26 | 1.150(3) | C14 | C15 | 1.406(3) |
| O2 | C27 | 1.143(3) | C14 | C19 | 1.394(3) |
| O3 | C28 | 1.142(3) | C15 | C16 | 1.389(3) |
| O4 | C29 | 1.136(3) | C16 | C17 | 1.383(4) |
| O5 | C30 | 1.138(3) | C17 | C18 | 1.377(4) |
| N | C1 | 1.470(3) | C18 | C19 | 1.401(3) |
| C1 | C2 | 1.518(3) | C20 | C21 | 1.406(3) |
| C1 | C6 | 1.523(3) | C20 | C25 | 1.393(3) |
| C2 | C3 | 1.529(3) | C21 | C22 | 1.388(3) |
| C3 | C4 | 1.508(4) | C22 | C23 | 1.382(4) |
| C4 | C5 | 1.527(4) | C23 | C24 | 1.386(4) |
| C5 | C6 | 1.536(3) | C24 | C25 | 1.397(3) |
| C7 | C8 | 1.540(3) | | | |

***Table 3:*** Bond angles for **9.3a**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C26 | W | P | 174.72(7) | C20 | C7 | C8 | 112.09(16) |
| C26 | W | C27 | 92.77(9) | C20 | C7 | C14 | 114.48(17) |
| C26 | W | C28 | 88.48(9) | C9 | C8 | C7 | 124.93(18) |
| C26 | W | C29 | 87.74(9) | C9 | C8 | C13 | 118.01(19) |
| C26 | W | C30 | 88.64(9) | C13 | C8 | C7 | 117.05(18) |
| C27 | W | P | 87.49(6) | C8 | C9 | C10 | 120.9(2) |
| C27 | W | C28 | 90.00(9) | C11 | C10 | C9 | 120.2(2) |
| C27 | W | C29 | 179.47(9) | C10 | C11 | C12 | 119.5(2) |
| C27 | W | C30 | 87.23(9) | C13 | C12 | C11 | 120.1(2) |
| C28 | W | P | 96.79(6) | C12 | C13 | C8 | 121.2(2) |
| C28 | W | C29 | 90.15(9) | C15 | C14 | C7 | 118.05(19) |
| C28 | W | C30 | 175.91(9) | C19 | C14 | C7 | 124.4(2) |
| C29 | W | P | 91.99(6) | C19 | C14 | C15 | 117.5(2) |
| C30 | W | P | 86.11(6) | C16 | C15 | C14 | 121.7(2) |
| C30 | W | C29 | 92.65(9) | C17 | C16 | C15 | 119.8(3) |
| N | P | W | 111.49(6) | C18 | C17 | C16 | 119.7(2) |
| N | P | C7 | 106.64(9) | C17 | C18 | C19 | 120.8(3) |
| C7 | P | W | 121.53(6) | C14 | C19 | C18 | 120.5(2) |
| C1 | N | P | 126.12(14) | C21 | C20 | C7 | 120.85(19) |
| N | C1 | C2 | 110.37(17) | C25 | C20 | C7 | 121.32(19) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N | C1 | C6 | 111.65(17) | C25 | C20 | C21 | 117.7(2) |
| C2 | C1 | C6 | 110.97(19) | C22 | C21 | C20 | 120.9(2) |
| C1 | C2 | C3 | 110.9(2) | C23 | C22 | C21 | 120.5(2) |
| C4 | C3 | C2 | 111.6(2) | C22 | C23 | C24 | 119.7(2) |
| C3 | C4 | C5 | 110.8(2) | C23 | C24 | C25 | 119.9(2) |
| C4 | C5 | C6 | 110.5(2) | C20 | C25 | C24 | 121.2(2) |
| C1 | C6 | C5 | 110.5(2) | O1 | C26 | W | 178.3(2) |
| C8 | C7 | P | 111.39(14) | O2 | C27 | W | 178.3(2) |
| C8 | C7 | C14 | 105.69(16) | O3 | C28 | W | 176.2(2) |
| C14 | C7 | P | 108.96(13) | O4 | C29 | W | 175.79(19) |
| C20 | C7 | P | 104.33(13) | O5 | C30 | W | 177.7(2) |

***Table 4:*** Torsion angles for **9.3a**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | N | C1 | 138.94(15) | C8 | C7 | C20 | C25 | 12.3(3) |
| P | N | C1 | C2 | 143.27(17) | C8 | C9 | C10 | C11 | 0.8(3) |
| P | N | C1 | C6 | -92.8(2) | C9 | C8 | C13 | C12 | 1.4(3) |
| P | C7 | C8 | C9 | 1.7(3) | C9 | C10 | C11 | C12 | 0.7(4) |
| P | C7 | C8 | C13 | -176.70(15) | C10 | C11 | C12 | C13 | -1.2(4) |
| P | C7 | C14 | C15 | 65.9(2) | C11 | C12 | C13 | C8 | 0.1(3) |
| P | C7 | C14 | C19 | -117.7(2) | C13 | C8 | C9 | C10 | -1.9(3) |
| P | C7 | C20 | C21 | 67.7(2) | C14 | C7 | C8 | C9 | 119.9(2) |
| P | C7 | C20 | C25 | -108.32(19) | C14 | C7 | C8 | C13 | -58.5(2) |
| N | C1 | C2 | C3 | -179.61(19) | C14 | C7 | C20 | C21 | -51.3(3) |
| N | C1 | C6 | C5 | 179.57(19) | C14 | C7 | C20 | C25 | 132.7(2) |
| C1 | C2 | C3 | C4 | -55.9(3) | C14 | C15 | C16 | C17 | -0.2(4) |
| C2 | C1 | C6 | C5 | -56.8(3) | C15 | C14 | C19 | C18 | -3.4(3) |
| C2 | C3 | C4 | C5 | 56.1(3) | C15 | C16 | C17 | C18 | -2.0(4) |
| C3 | C4 | C5 | C6 | -56.5(3) | C16 | C17 | C18 | C19 | 1.4(4) |
| C4 | C5 | C6 | C1 | 56.8(3) | C17 | C18 | C19 | C14 | 1.4(4) |
| C6 | C1 | C2 | C3 | 56.1(3) | C19 | C14 | C15 | C16 | 2.8(3) |
| C7 | P | N | C1 | -86.30(18) | C20 | C7 | C8 | C9 | -114.7(2) |
| C7 | C8 | C9 | C10 | 179.7(2) | C20 | C7 | C8 | C13 | 66.8(2) |
| C7 | C8 | C13 | C12 | 180.0(2) | C20 | C7 | C14 | C15 | -177.74(18) |
| C7 | C14 | C15 | C16 | 179.5(2) | C20 | C7 | C14 | C19 | -1.3(3) |
| C7 | C14 | C19 | C18 | -179.8(2) | C20 | C21 | C22 | C23 | 1.6(3) |
| C7 | C20 | C21 | C22 | -179.0(2) | C21 | C20 | C25 | C24 | 1.9(3) |
| C7 | C20 | C25 | C24 | 178.1(2) | C21 | C22 | C23 | C24 | 0.6(4) |
| C8 | C7 | C14 | C15 | -53.9(2) | C22 | C23 | C24 | C25 | -1.5(4) |
| C8 | C7 | C14 | C19 | 122.5(2) | C23 | C24 | C25 | C20 | 0.2(4) |
| C8 | C7 | C20 | C21 | -171.62(18) | C25 | C20 | C21 | C22 | -2.8(3) |

## 12.3 Pentacarbonyl[1-methylethylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [9.3b]

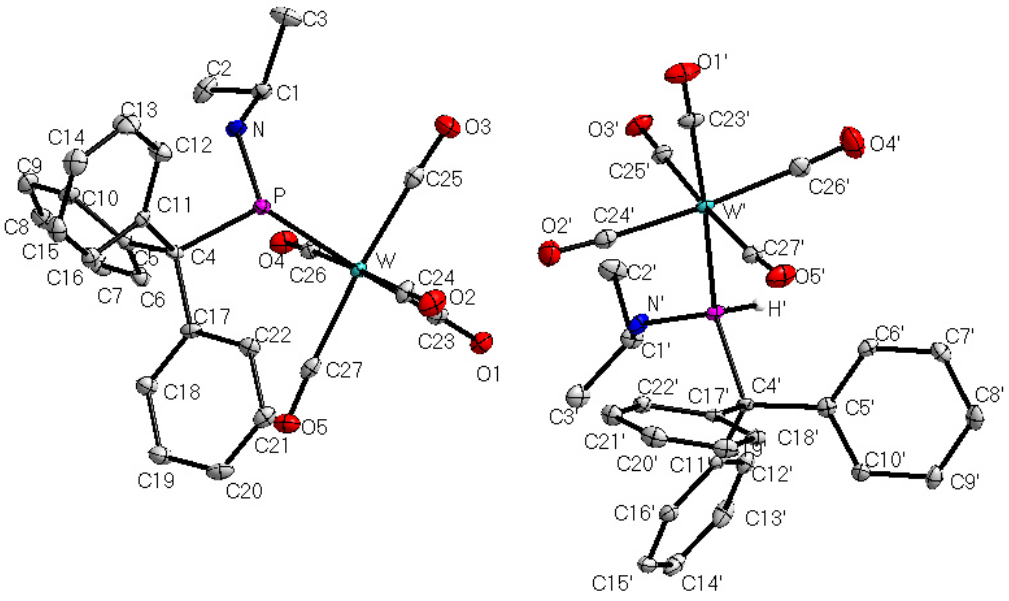


***Table 1:*** Crystal data and structure refinement for **9.3b**.

| | |
|---|---|
| Identification code | GSTR449, AKY-iPr // GXraymo_4396f |
| Crystal Habitus | clear colourless block |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{27}H_{24}NO_5PW$ |
| Moiety formula | C27 H24 N O5 P W |
| Formula weight | 657.29 |
| Temperature/K | 100.01 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 10.2830(5) |
| b/Å | 12.3871(6) |
| c/Å | 20.1318(9) |
| α/° | 93.1130(15) |
| β/° | 99.9351(15) |
| γ/° | 90.4631(16) |
| Volume/Å$^3$ | 2521.7(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.731 |
| μ/mm$^{-1}$ | 4.682 |
| F(000) | 1288.0 |
| Crystal size/mm$^3$ | 0.24 × 0.22 × 0.18 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.3187; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.824 to 55.998° |
| Completeness to theta | 0.999 |
| Index ranges | -13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26 |
| Reflections collected | 132861 |
| Independent reflections | 12179 [$R_{int}$ = 0.0688, $R_{sigma}$ = 0.0300] |
| Data/restraints/parameters | 12179/0/642 |
| Goodness-of-fit on F$^2$ | 1.070 |

| | |
|---|---|
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0258, $wR_2$ = 0.0630 |
| Final R indexes [all data] | $R_1$ = 0.0320, $wR_2$ = 0.0671 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.07/-2.35 |

***Table 2:*** Bond lengths for **9.3b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5361(8) | W' | P' | 2.5344(8) |
| W | C23 | 1.996(3) | W' | C23' | 2.009(3) |
| W | C24 | 2.054(3) | W' | C24' | 2.049(3) |
| W | C25 | 2.035(3) | W' | C25' | 2.042(3) |
| W | C26 | 2.042(3) | W' | C26' | 2.037(3) |
| W | C27 | 2.063(3) | W' | C27' | 2.069(3) |
| P | N | 1.663(3) | P' | N' | 1.674(3) |
| P | C4 | 1.924(3) | P' | C4' | 1.927(3) |
| O1 | C23 | 1.154(4) | O1' | C23' | 1.147(4) |
| O2 | C24 | 1.136(4) | O2' | C24' | 1.142(4) |
| O3 | C25 | 1.150(4) | O3' | C25' | 1.137(4) |
| O4 | C26 | 1.137(4) | O4' | C26' | 1.140(4) |
| O5 | C27 | 1.141(4) | O5' | C27' | 1.135(4) |
| N | C1 | 1.474(4) | N' | C1' | 1.483(4) |
| C1 | C2 | 1.528(5) | C1' | C2' | 1.526(4) |
| C1 | C3 | 1.526(4) | C1' | C3' | 1.521(5) |
| C4 | C5 | 1.537(4) | C4' | C5' | 1.537(4) |
| C4 | C11 | 1.546(4) | C4' | C11' | 1.546(4) |
| C4 | C17 | 1.534(4) | C4' | C17' | 1.536(4) |
| C5 | C6 | 1.400(4) | C5' | C6' | 1.396(4) |
| C5 | C10 | 1.393(4) | C5' | C10' | 1.396(4) |
| C6 | C7 | 1.393(4) | C6' | C7' | 1.391(4) |
| C7 | C8 | 1.386(5) | C7' | C8' | 1.391(5) |
| C8 | C9 | 1.383(5) | C8' | C9' | 1.387(5) |
| C9 | C10 | 1.397(4) | C9' | C10' | 1.397(4) |
| C11 | C12 | 1.400(4) | C11' | C12' | 1.401(4) |
| C11 | C16 | 1.400(4) | C11' | C16' | 1.393(4) |
| C12 | C13 | 1.397(5) | C12' | C13' | 1.389(5) |
| C13 | C14 | 1.379(5) | C13' | C14' | 1.384(5) |
| C14 | C15 | 1.391(5) | C14' | C15' | 1.390(5) |
| C15 | C16 | 1.392(5) | C15' | C16' | 1.397(4) |
| C17 | C18 | 1.396(4) | C17' | C18' | 1.396(4) |
| C17 | C22 | 1.397(4) | C17' | C22' | 1.399(4) |
| C18 | C19 | 1.395(4) | C18' | C19' | 1.395(4) |
| C19 | C20 | 1.386(5) | C19' | C20' | 1.383(5) |
| C20 | C21 | 1.389(5) | C20' | C21' | 1.393(5) |
| C21 | C22 | 1.393(4) | C21' | C22' | 1.390(4) |

***Table 3:*** Bond angles for **9.3b**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C23 | W | P | 177.52(9) | C23' | W' | P' | 176.43(9) |
| C23 | W | C24 | 92.10(12) | C23' | W' | C24' | 87.86(14) |
| C23 | W | C25 | 88.48(13) | C23' | W' | C25' | 91.16(13) |
| C23 | W | C26 | 88.46(12) | C23' | W' | C26' | 89.42(14) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C23 | W | C27 | 86.17(12) | C23' | W' | C27' | 87.49(13) |
| C24 | W | P | 87.65(9) | C24' | W' | P' | 89.96(9) |
| C24 | W | C27 | 91.35(12) | C24' | W' | C27' | 93.13(13) |
| C25 | W | P | 89.04(9) | C25' | W' | P' | 86.01(9) |
| C25 | W | C24 | 88.60(13) | C25' | W' | C24' | 90.07(13) |
| C25 | W | C26 | 92.93(13) | C25' | W' | C27' | 176.47(12) |
| C25 | W | C27 | 174.65(12) | C26' | W' | P' | 92.59(10) |
| C26 | W | P | 91.85(9) | C26' | W' | C24' | 175.79(12) |
| C26 | W | C24 | 178.38(12) | C26' | W' | C25' | 86.76(13) |
| C26 | W | C27 | 87.16(12) | C26' | W' | C27' | 89.96(13) |
| C27 | W | P | 96.30(9) | C27' | W' | P' | 95.46(9) |
| N | P | W | 116.54(10) | N' | P' | W' | 109.73(10) |
| N | P | C4 | 104.13(13) | N' | P' | C4' | 107.54(13) |
| C4 | P | W | 122.83(9) | C4' | P' | W' | 122.75(9) |
| C1 | N | P | 128.1(2) | C1' | N' | P' | 125.7(2) |
| N | C1 | C2 | 111.4(3) | N' | C1' | C2' | 110.7(3) |
| N | C1 | C3 | 109.4(3) | N' | C1' | C3' | 110.7(3) |
| C3 | C1 | C2 | 111.7(3) | C3' | C1' | C2' | 111.3(3) |
| C5 | C4 | P | 104.41(19) | C5' | C4' | P' | 109.63(19) |
| C5 | C4 | C11 | 111.0(2) | C5' | C4' | C11' | 109.2(2) |
| C11 | C4 | P | 112.04(19) | C11' | C4' | P' | 108.16(19) |
| C17 | C4 | P | 108.1(2) | C17' | C4' | P' | 107.13(19) |
| C17 | C4 | C5 | 113.6(2) | C17' | C4' | C5' | 111.0(2) |
| C17 | C4 | C11 | 107.8(2) | C17' | C4' | C11' | 111.6(2) |
| C6 | C5 | C4 | 119.9(3) | C6' | C5' | C4' | 122.5(3) |
| C10 | C5 | C4 | 121.7(3) | C6' | C5' | C10' | 118.0(3) |
| C10 | C5 | C6 | 118.2(3) | C10' | C5' | C4' | 119.3(3) |
| C7 | C6 | C5 | 120.8(3) | C7' | C6' | C5' | 121.3(3) |
| C8 | C7 | C6 | 120.4(3) | C8' | C7' | C6' | 120.1(3) |
| C9 | C8 | C7 | 119.3(3) | C9' | C8' | C7' | 119.2(3) |
| C8 | C9 | C10 | 120.5(3) | C8' | C9' | C10' | 120.6(3) |
| C5 | C10 | C9 | 120.8(3) | C5' | C10' | C9' | 120.7(3) |
| C12 | C11 | C4 | 124.4(3) | C12' | C11' | C4' | 119.3(3) |
| C12 | C11 | C16 | 117.3(3) | C16' | C11' | C4' | 122.9(3) |
| C16 | C11 | C4 | 118.3(3) | C16' | C11' | C12' | 117.7(3) |
| C13 | C12 | C11 | 121.1(3) | C13' | C12' | C11' | 121.3(3) |
| C14 | C13 | C12 | 120.7(3) | C14' | C13' | C12' | 120.4(3) |
| C13 | C14 | C15 | 119.2(3) | C13' | C14' | C15' | 119.0(3) |
| C14 | C15 | C16 | 120.2(3) | C14' | C15' | C16' | 120.6(3) |
| C15 | C16 | C11 | 121.5(3) | C11' | C16' | C15' | 120.9(3) |
| C18 | C17 | C4 | 122.5(3) | C18' | C17' | C4' | 122.0(3) |
| C18 | C17 | C22 | 118.0(3) | C18' | C17' | C22' | 118.0(3) |
| C22 | C17 | C4 | 119.3(3) | C22' | C17' | C4' | 120.0(3) |
| C19 | C18 | C17 | 120.9(3) | C19' | C18' | C17' | 120.5(3) |
| C20 | C19 | C18 | 120.2(3) | C20' | C19' | C18' | 120.9(3) |
| C19 | C20 | C21 | 119.8(3) | C19' | C20' | C21' | 119.1(3) |
| C20 | C21 | C22 | 119.7(3) | C22' | C21' | C20' | 120.1(3) |
| C21 | C22 | C17 | 121.4(3) | C21' | C22' | C17' | 121.3(3) |
| O1 | C23 | W | 177.6(3) | O1' | C23' | W' | 178.0(3) |
| O2 | C24 | W | 178.7(3) | O2' | C24' | W' | 176.4(3) |
| O3 | C25 | W | 177.6(3) | O3' | C25' | W' | 179.5(3) |
| O4 | C26 | W | 177.2(3) | O4' | C26' | W' | 177.5(3) |
| O5 | C27 | W | 174.3(3) | O5' | C27' | W' | 174.8(3) |

***Table 4:*** Torsion angles for **9.3b**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | N | C1 | 1.7(3) | W' | P' | N' | C1' | 134.0(2) |
| P | N | C1 | C2 | 109.9(3) | P' | N' | C1' | C2' | -100.0(3) |
| P | N | C1 | C3 | -126.1(3) | P' | N' | C1' | C3' | 136.1(3) |
| P | C4 | C5 | C6 | 67.9(3) | P' | C4' | C5' | C6' | 31.7(3) |
| P | C4 | C5 | C10 | -107.2(3) | P' | C4' | C5' | C10' | -152.7(2) |
| P | C4 | C11 | C12 | 18.4(4) | P' | C4' | C11' | C12' | 67.5(3) |
| P | C4 | C11 | C16 | -163.4(2) | P' | C4' | C11' | C16' | -115.5(3) |
| P | C4 | C17 | C18 | -138.9(3) | P' | C4' | C17' | C18' | -130.3(3) |
| P | C4 | C17 | C22 | 46.4(3) | P' | C4' | C17' | C22' | 50.9(3) |
| C4 | P | N | C1 | -136.9(3) | C4' | P' | N' | C1' | -90.3(3) |
| C4 | C5 | C6 | C7 | -175.6(3) | C4' | C5' | C6' | C7' | 175.8(3) |
| C4 | C5 | C10 | C9 | 176.4(3) | C4' | C5' | C10' | C9' | -175.8(3) |
| C4 | C11 | C12 | C13 | 177.6(3) | C4' | C11' | C12' | C13' | 178.6(3) |
| C4 | C11 | C16 | C15 | -177.7(3) | C4' | C11' | C16' | C15' | -177.8(3) |
| C4 | C17 | C18 | C19 | -175.5(3) | C4' | C17' | C18' | C19' | -178.5(3) |
| C4 | C17 | C22 | C21 | 177.4(3) | C4' | C17' | C22' | C21' | 179.1(3) |
| C5 | C4 | C11 | C12 | -97.9(3) | C5' | C4' | C11' | C12' | -51.7(3) |
| C5 | C4 | C11 | C16 | 80.3(3) | C5' | C4' | C11' | C16' | 125.3(3) |
| C5 | C4 | C17 | C18 | -23.5(4) | C5' | C4' | C17' | C18' | -10.7(4) |
| C5 | C4 | C17 | C22 | 161.7(3) | C5' | C4' | C17' | C22' | 170.5(3) |
| C5 | C6 | C7 | C8 | -0.8(5) | C5' | C6' | C7' | C8' | 0.1(5) |
| C6 | C5 | C10 | C9 | 1.1(5) | C6' | C5' | C10' | C9' | 0.0(5) |
| C6 | C7 | C8 | C9 | 1.1(5) | C6' | C7' | C8' | C9' | -0.5(5) |
| C7 | C8 | C9 | C10 | -0.2(5) | C7' | C8' | C9' | C10' | 0.7(5) |
| C8 | C9 | C10 | C5 | -0.9(5) | C8' | C9' | C10' | C5' | -0.4(5) |
| C10 | C5 | C6 | C7 | -0.3(5) | C10' | C5' | C6' | C7' | 0.2(5) |
| C11 | C4 | C5 | C6 | -171.2(3) | C11' | C4' | C5' | C6' | 150.1(3) |
| C11 | C4 | C5 | C10 | 13.7(4) | C11' | C4' | C5' | C10' | -34.4(4) |
| C11 | C4 | C17 | C18 | 99.8(3) | C11' | C4' | C17' | C18' | 111.4(3) |
| C11 | C4 | C17 | C22 | -74.9(3) | C11' | C4' | C17' | C22' | -67.3(3) |
| C11 | C12 | C13 | C14 | 0.3(6) | C11' | C12' | C13' | C14' | -1.1(5) |
| C12 | C11 | C16 | C15 | 0.6(5) | C12' | C11' | C16' | C15' | -0.8(4) |
| C12 | C13 | C14 | C15 | 0.0(6) | C12' | C13' | C14' | C15' | 0.1(5) |
| C13 | C14 | C15 | C16 | 0.0(5) | C13' | C14' | C15' | C16' | 0.6(5) |
| C14 | C15 | C16 | C11 | -0.3(5) | C14' | C15' | C16' | C11' | -0.2(5) |
| C16 | C11 | C12 | C13 | -0.6(5) | C16' | C11' | C12' | C13' | 1.4(4) |
| C17 | C4 | C5 | C6 | -49.6(4) | C17' | C4' | C5' | C6' | -86.4(3) |
| C17 | C4 | C5 | C10 | 135.3(3) | C17' | C4' | C5' | C10' | 89.1(3) |
| C17 | C4 | C11 | C12 | 137.1(3) | C17' | C4' | C11' | C12' | -174.9(3) |
| C17 | C4 | C11 | C16 | -44.7(3) | C17' | C4' | C11' | C16' | 2.1(4) |
| C17 | C18 | C19 | C20 | -1.4(5) | C17' | C18' | C19' | C20' | -0.6(5) |
| C18 | C17 | C22 | C21 | 2.4(4) | C18' | C17' | C22' | C21' | 0.3(4) |
| C18 | C19 | C20 | C21 | 1.8(5) | C18' | C19' | C20' | C21' | 0.4(5) |
| C19 | C20 | C21 | C22 | -0.1(5) | C19' | C20' | C21' | C22' | 0.1(5) |
| C20 | C21 | C22 | C17 | -2.0(5) | C20' | C21' | C22' | C17' | -0.5(5) |
| C22 | C17 | C18 | C19 | -0.7(5) | C22' | C17' | C18' | C19' | 0.2(4) |

# 12.4 Pentacarbonyl[1,1-dimethylethylamino(triphenylmethyl)phosphane-κ*P*]tungsten(0) [9.3c]

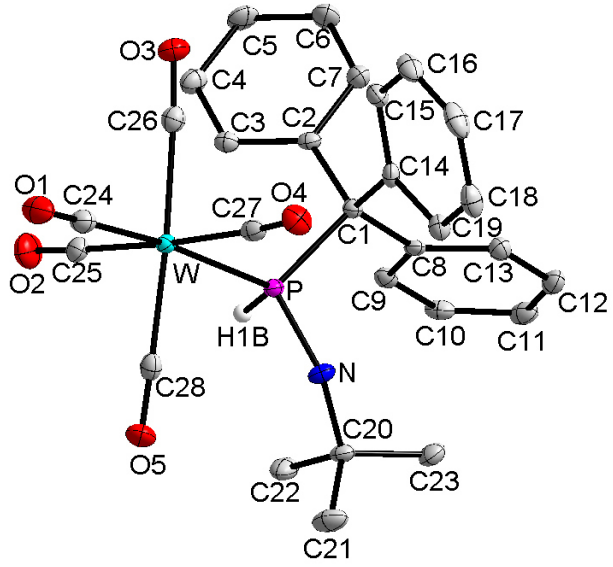


***Table 1:*** Crystal data and structure refinement for **9.3c**.

| | |
|---|---|
| Identification code | GSTR332, AKY-324 // GXray3182f |
| Crystal Habitus | pale yellow plate |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{28}H_{26}NO_5PW$ |
| Moiety formula | C28 H26 N O5 P W |
| Formula weight | 671.32 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 9.5189(6) |
| b/Å | 28.8723(17) |
| c/Å | 10.3507(6) |
| α/° | 90.00 |
| β/° | 110.8730(10) |
| γ/° | 90.00 |
| Volume/Å$^3$ | 2658.0(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.678 |
| μ/mm$^{-1}$ | 4.444 |
| F(000) | 1320.0 |
| Crystal size/mm$^3$ | 0.11 × 0.10 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.6406; 0.8423 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 8.04 to 56° |
| Completeness to theta | 0.990 |
| Index ranges | -12 ≤ h ≤ 12, -38 ≤ k ≤ 36, -10 ≤ l ≤ 13 |
| Reflections collected | 17604 |
| Independent reflections | 6352 [$R_{int}$ = 0.0257] |
| Data/restraints/parameters | 6352/5/334 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.052 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0205, $wR_2$ = 0.0437 |
| Final R indexes [all data] | $R_1$ = 0.0237, $wR_2$ = 0.0449 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.84/-0.56 |

***Table 2:*** Bond lengths for **9.3c**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | C14 | 1.529(3) | C16 | C17 | 1.382(4) |
| C1 | C8 | 1.541(3) | C17 | C18 | 1.390(4) |
| C1 | C2 | 1.543(3) | C18 | C19 | 1.388(3) |
| C1 | P | 1.918(2) | C20 | N | 1.497(3) |
| C2 | C3 | 1.392(3) | C20 | C22 | 1.527(3) |
| C2 | C7 | 1.400(3) | C20 | C23 | 1.531(3) |
| C3 | C4 | 1.395(3) | C20 | C21 | 1.531(3) |
| C4 | C5 | 1.386(3) | C24 | O1 | 1.152(3) |
| C5 | C6 | 1.391(4) | C24 | W | 2.003(2) |
| C6 | C7 | 1.384(3) | C25 | O2 | 1.138(3) |
| C8 | C13 | 1.398(3) | C25 | W | 2.046(3) |
| C8 | C9 | 1.403(3) | C26 | O3 | 1.139(3) |
| C9 | C10 | 1.389(3) | C26 | W | 2.054(3) |
| C10 | C11 | 1.390(3) | C27 | O4 | 1.134(3) |
| C11 | C12 | 1.387(4) | C27 | W | 2.057(2) |
| C12 | C13 | 1.393(3) | C28 | O5 | 1.144(3) |
| C14 | C15 | 1.395(3) | C28 | W | 2.046(3) |
| C14 | C19 | 1.414(3) | N | P | 1.670(2) |
| C15 | C16 | 1.391(3) | P | W | 2.5324(6) |

***Table 3:*** Bond angles for **9.3c**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C14 | C1 | C8 | 114.15(18) | N | C20 | C22 | 110.63(19) |
| C14 | C1 | C2 | 112.58(19) | N | C20 | C23 | 111.83(19) |
| C8 | C1 | C2 | 104.77(17) | C22 | C20 | C23 | 110.0(2) |
| C14 | C1 | P | 103.76(14) | N | C20 | C21 | 105.83(19) |
| C8 | C1 | P | 111.30(15) | C22 | C20 | C21 | 109.1(2) |
| C2 | C1 | P | 110.43(14) | C23 | C20 | C21 | 109.3(2) |
| C3 | C2 | C7 | 117.4(2) | O1 | C24 | W | 176.4(2) |
| C3 | C2 | C1 | 124.7(2) | O2 | C25 | W | 178.2(2) |
| C7 | C2 | C1 | 117.7(2) | O3 | C26 | W | 176.3(2) |
| C2 | C3 | C4 | 121.3(2) | O4 | C27 | W | 174.2(2) |
| C5 | C4 | C3 | 120.2(2) | O5 | C28 | W | 178.6(2) |
| C4 | C5 | C6 | 119.5(2) | C20 | N | P | 133.43(16) |
| C7 | C6 | C5 | 119.9(2) | N | P | C1 | 110.24(10) |
| C6 | C7 | C2 | 121.8(2) | N | P | W | 110.99(7) |
| C13 | C8 | C9 | 117.9(2) | C1 | P | W | 119.08(7) |
| C13 | C8 | C1 | 123.5(2) | C24 | W | C25 | 92.57(10) |
| C9 | C8 | C1 | 118.4(2) | C24 | W | C28 | 87.87(10) |
| C10 | C9 | C8 | 121.2(2) | C25 | W | C28 | 90.12(10) |
| C9 | C10 | C11 | 120.3(2) | C24 | W | C26 | 89.30(10) |
| C12 | C11 | C10 | 118.9(2) | C25 | W | C26 | 87.82(10) |
| C11 | C12 | C13 | 121.1(2) | C28 | W | C26 | 176.42(9) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C12 | C13 | C8 | 120.5(2) | C24 | W | C27 | 86.02(10) |
| C15 | C14 | C19 | 116.8(2) | C25 | W | C27 | 176.56(9) |
| C15 | C14 | C1 | 123.3(2) | C28 | W | C27 | 92.96(10) |
| C19 | C14 | C1 | 119.7(2) | C26 | W | C27 | 89.03(10) |
| C16 | C15 | C14 | 121.8(2) | C24 | W | P | 173.38(7) |
| C17 | C16 | C15 | 120.4(2) | C25 | W | P | 90.04(7) |
| C16 | C17 | C18 | 119.3(2) | C28 | W | P | 86.04(7) |
| C19 | C18 | C17 | 120.3(2) | C26 | W | P | 96.88(7) |
| C18 | C19 | C14 | 121.3(2) | C27 | W | P | 91.70(7) |

***Table 4:*** Torsion angles for **9.3c**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| C14 | C1 | C2 | C3 | -121.8(2) | C21 | C20 | N | P | -142.1(2) |
| C8 | C1 | C2 | C3 | 113.6(2) | C20 | N | P | C1 | -93.5(2) |
| P | C1 | C2 | C3 | -6.3(3) | C20 | N | P | W | 132.4(2) |
| C14 | C1 | C2 | C7 | 63.3(3) | C14 | C1 | P | N | -75.64(16) |
| C8 | C1 | C2 | C7 | -61.3(3) | C8 | C1 | P | N | 47.56(18) |
| P | C1 | C2 | C7 | 178.73(17) | C2 | C1 | P | N | 163.49(15) |
| C7 | C2 | C3 | C4 | -0.9(3) | C14 | C1 | P | W | 54.29(16) |
| C1 | C2 | C3 | C4 | -175.8(2) | C8 | C1 | P | W | 177.49(12) |
| C2 | C3 | C4 | C5 | 0.0(4) | C2 | C1 | P | W | -66.58(16) |
| C3 | C4 | C5 | C6 | 0.9(4) | O1 | C24 | W | C25 | 161(4) |
| C4 | C5 | C6 | C7 | -0.9(4) | O1 | C24 | W | C28 | 71(4) |
| C5 | C6 | C7 | C2 | 0.0(4) | O1 | C24 | W | C26 | -111(4) |
| C3 | C2 | C7 | C6 | 0.9(4) | O1 | C24 | W | C27 | -22(4) |
| C1 | C2 | C7 | C6 | 176.2(2) | O1 | C24 | W | P | 48(4) |
| C14 | C1 | C8 | C13 | -3.6(3) | O2 | C25 | W | C24 | 93(7) |
| C2 | C1 | C8 | C13 | 120.0(2) | O2 | C25 | W | C28 | -179(100) |
| P | C1 | C8 | C13 | -120.7(2) | O2 | C25 | W | C26 | 3(7) |
| C14 | C1 | C8 | C9 | -177.7(2) | O2 | C25 | W | C27 | 27(8) |
| C2 | C1 | C8 | C9 | -54.1(2) | O2 | C25 | W | P | -93(7) |
| P | C1 | C8 | C9 | 65.2(2) | O5 | C28 | W | C24 | 63(10) |
| C13 | C8 | C9 | C10 | 2.1(3) | O5 | C28 | W | C25 | -29(10) |
| C1 | C8 | C9 | C10 | 176.5(2) | O5 | C28 | W | C26 | 25(11) |
| C8 | C9 | C10 | C11 | 0.2(4) | O5 | C28 | W | C27 | 149(10) |
| C9 | C10 | C11 | C12 | -1.7(4) | O5 | C28 | W | P | -119(10) |
| C10 | C11 | C12 | C13 | 0.9(4) | O3 | C26 | W | C24 | -12(3) |
| C11 | C12 | C13 | C8 | 1.4(4) | O3 | C26 | W | C25 | 81(3) |
| C9 | C8 | C13 | C12 | -2.9(3) | O3 | C26 | W | C28 | 26(4) |
| C1 | C8 | C13 | C12 | -177.0(2) | O3 | C26 | W | C27 | -98(3) |
| C8 | C1 | C14 | C15 | 128.7(2) | O3 | C26 | W | P | 171(3) |
| C2 | C1 | C14 | C15 | 9.4(3) | O4 | C27 | W | C24 | -18(2) |
| P | C1 | C14 | C15 | -110.0(2) | O4 | C27 | W | C25 | 48(3) |
| C8 | C1 | C14 | C19 | -54.7(3) | O4 | C27 | W | C28 | -106(2) |
| C2 | C1 | C14 | C19 | -174.00(19) | O4 | C27 | W | C26 | 71(2) |
| P | C1 | C14 | C19 | 66.6(2) | O4 | C27 | W | P | 168(2) |
| C19 | C14 | C15 | C16 | 0.2(3) | N | P | W | C24 | -9.1(6) |
| C1 | C14 | C15 | C16 | 176.9(2) | C1 | P | W | C24 | -138.7(6) |
| C14 | C15 | C16 | C17 | -0.7(4) | N | P | W | C25 | -122.37(10) |
| C15 | C16 | C17 | C18 | 1.0(4) | C1 | P | W | C25 | 108.04(11) |
| C16 | C17 | C18 | C19 | -0.8(4) | N | P | W | C28 | -32.25(10) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C17 | C18 | C19 | C14 | 0.3(4) | C1 | P | W | C28 | -161.85(11) |
| C15 | C14 | C19 | C18 | 0.0(3) | N | P | W | C26 | 149.82(10) |
| C1 | C14 | C19 | C18 | -176.8(2) | C1 | P | W | C26 | 20.23(11) |
| C22 | C20 | N | P | -24.1(3) | N | P | W | C27 | 60.60(10) |
| C23 | C20 | N | P | 98.9(2) | C1 | P | W | C27 | -68.99(10) |

## 12.5 Pentacarbonyl[chloro(triphenylmethyl)phosphane-κ*P*]tungsten(0) [10.3]

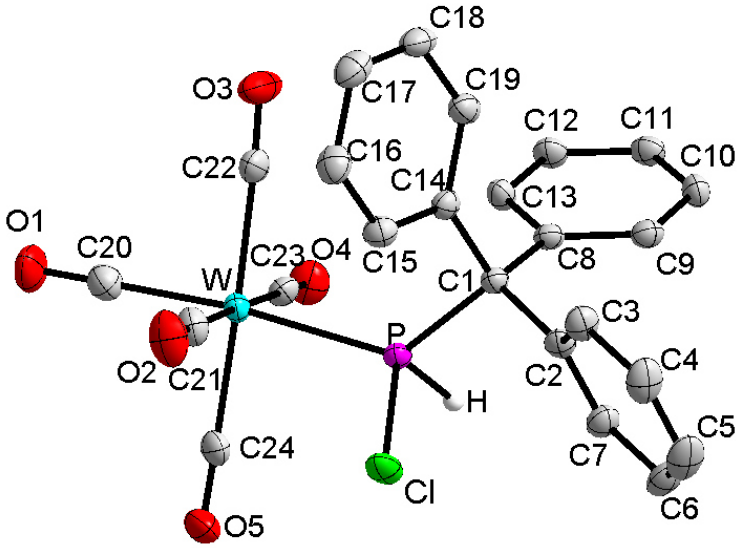


***Table 1:*** Crystal data and structure refinement for **10.3**.

| | |
|---|---|
| Identification code | GSTR534, AKY-602 // GXray4926 |
| Crystal Habitus | clear colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{24}H_{16}ClO_5PW$ |
| Moiety formula | C24 H16 Cl O5 P W |
| Formula weight | 634.64 |
| Temperature/K | 123 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.6102(3) |
| b/Å | 10.5151(4) |
| c/Å | 11.6195(4) |
| α/° | 90.127(2) |
| β/° | 82.603(2) |
| γ/° | 85.552(2) |
| Volume/Å$^3$ | 1160.81(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.816 |
| μ/mm$^{-1}$ | 5.192 |
| F(000) | 612.0 |
| Crystal size/mm$^3$ | 1.6 × 0.6 × 0.12 |
| Absorption correction | multi-scan |
| Tmin; Tmax | 0.1892; 0.3187 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.288 to 55.998° |
| Completeness to theta | 0.999 |

| | |
|---|---|
| Index ranges | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15 |
| Reflections collected | 23636 |
| Independent reflections | 5598 [$R_{int}$ = 0.0554, $R_{sigma}$ = 0.0337] |
| Data/restraints/parameters | 5598/0/292 |
| Goodness-of-fit on $F^2$ | 1.052 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0322, $wR_2$ = 0.0842 |
| Final R indexes [all data] | $R_1$ = 0.0343, $wR_2$ = 0.0862 |
| Largest diff. peak/hole / e $Å^{-3}$ | 2.66/-2.40 |

***Table 2:*** Bond lengths for **10.3**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4868(9) | O1 | C20 | 1.142(5) |
| W | C23 | 2.035(4) | C8 | C13 | 1.401(4) |
| W | C24 | 2.048(4) | C8 | C9 | 1.397(5) |
| W | C22 | 2.062(4) | C14 | C19 | 1.396(5) |
| W | C21 | 2.043(4) | C14 | C15 | 1.403(5) |
| W | C20 | 2.012(4) | C2 | C7 | 1.401(5) |
| P | Cl | 2.0596(11) | C24 | O5 | 1.134(5) |
| P | C1 | 1.917(3) | C22 | O3 | 1.129(5) |
| O4 | C23 | 1.150(5) | C7 | C6 | 1.394(5) |
| O2 | C21 | 1.145(6) | C13 | C12 | 1.397(5) |
| C11 | C12 | 1.388(5) | C9 | C10 | 1.386(5) |
| C11 | C10 | 1.388(5) | C19 | C18 | 1.396(5) |
| C1 | C8 | 1.546(4) | C15 | C16 | 1.392(5) |
| C1 | C14 | 1.531(5) | C4 | C5 | 1.377(6) |
| C1 | C2 | 1.539(4) | C6 | C5 | 1.391(6) |
| C3 | C2 | 1.386(5) | C18 | C17 | 1.380(6) |
| C3 | C4 | 1.402(5) | C16 | C17 | 1.391(6) |

***Table 3:*** Bond angles for **10.3**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C23 | W | P | 89.72(11) | C13 | C8 | C1 | 120.8(3) |
| C23 | W | C24 | 89.98(15) | C9 | C8 | C1 | 121.0(3) |
| C23 | W | C22 | 91.05(16) | C9 | C8 | C13 | 118.1(3) |
| C23 | W | C21 | 178.59(12) | C19 | C14 | C1 | 122.5(3) |
| C24 | W | P | 85.28(11) | C19 | C14 | C15 | 117.9(3) |
| C24 | W | C22 | 178.24(13) | C15 | C14 | C1 | 119.6(3) |
| C22 | W | P | 96.14(11) | C3 | C2 | C1 | 122.1(3) |
| C21 | W | P | 89.06(12) | C3 | C2 | C7 | 118.4(3) |
| C21 | W | C24 | 89.22(16) | C7 | C2 | C1 | 119.4(3) |
| C21 | W | C22 | 89.77(17) | O5 | C24 | W | 178.5(4) |
| C20 | W | P | 174.11(11) | O3 | C22 | W | 176.7(4) |
| C20 | W | C23 | 89.34(16) | O2 | C21 | W | 178.8(4) |
| C20 | W | C24 | 88.91(16) | C6 | C7 | C2 | 120.8(4) |
| C20 | W | C22 | 89.69(16) | C12 | C13 | C8 | 121.0(3) |
| C20 | W | C21 | 91.80(17) | C11 | C12 | C13 | 119.8(3) |
| Cl | P | W | 107.55(5) | C10 | C9 | C8 | 120.8(3) |
| C1 | P | W | 128.54(10) | C9 | C10 | C11 | 120.6(3) |
| C1 | P | Cl | 104.19(10) | C14 | C19 | C18 | 120.6(4) |
| O4 | C23 | W | 179.3(4) | C16 | C15 | C14 | 121.1(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C10 | C11 | C12 | 119.6(3) | C5 | C4 | C3 | 120.3(4) |
| C8 | C1 | P | 105.6(2) | C5 | C6 | C7 | 119.9(4) |
| C14 | C1 | P | 107.1(2) | C4 | C5 | C6 | 119.9(4) |
| C14 | C1 | C8 | 111.7(3) | O1 | C20 | W | 178.5(4) |
| C14 | C1 | C2 | 112.7(3) | C17 | C18 | C19 | 120.9(4) |
| C2 | C1 | P | 109.5(2) | C17 | C16 | C15 | 120.2(4) |
| C2 | C1 | C8 | 110.1(3) | C18 | C17 | C16 | 119.3(4) |
| C2 | C3 | C4 | 120.7(4) | | | | |

***Table 4:*** Torsion angles for **10.3**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| P | C1 | C8 | C13 | 47.1(4) | C14 | C1 | C2 | C3 | -9.1(4) |
| P | C1 | C8 | C9 | -136.3(3) | C14 | C1 | C2 | C7 | 174.1(3) |
| P | C1 | C14 | C19 | -126.3(3) | C14 | C19 | C18 | C17 | 0.4(6) |
| P | C1 | C14 | C15 | 54.1(4) | C14 | C15 | C16 | C17 | -0.5(6) |
| P | C1 | C2 | C3 | -128.1(3) | C2 | C1 | C8 | C13 | 165.1(3) |
| P | C1 | C2 | C7 | 55.1(4) | C2 | C1 | C8 | C9 | -18.2(4) |
| C1 | C8 | C13 | C12 | 178.1(3) | C2 | C1 | C14 | C19 | 113.3(4) |
| C1 | C8 | C9 | C10 | -176.8(3) | C2 | C1 | C14 | C15 | -66.2(4) |
| C1 | C14 | C19 | C18 | 179.5(3) | C2 | C3 | C4 | C5 | 0.2(6) |
| C1 | C14 | C15 | C16 | -179.5(3) | C2 | C7 | C6 | C5 | -0.5(6) |
| C1 | C2 | C7 | C6 | 178.1(3) | C7 | C6 | C5 | C4 | -0.4(6) |
| C3 | C2 | C7 | C6 | 1.2(5) | C13 | C8 | C9 | C10 | -0.1(5) |
| C3 | C4 | C5 | C6 | 0.5(6) | C12 | C11 | C10 | C9 | 1.0(5) |
| C8 | C1 | C14 | C19 | -11.2(4) | C9 | C8 | C13 | C12 | 1.4(5) |
| C8 | C1 | C14 | C15 | 169.3(3) | C10 | C11 | C12 | C13 | 0.3(5) |
| C8 | C1 | C2 | C3 | 116.2(4) | C19 | C14 | C15 | C16 | 1.0(5) |
| C8 | C1 | C2 | C7 | -60.5(4) | C19 | C18 | C17 | C16 | 0.1(6) |
| C8 | C13 | C12 | C11 | -1.5(6) | C15 | C14 | C19 | C18 | -1.0(5) |
| C8 | C9 | C10 | C11 | -1.1(5) | C15 | C16 | C17 | C18 | -0.1(7) |
| C14 | C1 | C8 | C13 | -68.9(4) | C4 | C3 | C2 | C1 | -177.8(3) |
| C14 | C1 | C8 | C9 | 107.7(3) | C4 | C3 | C2 | C7 | -1.0(5) |

## 12.6 Pentacarbonyl[1-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-3,4-diphenyl-1*H*-phosphet-2-on-κ*P*]tungsten(0) [14.2]

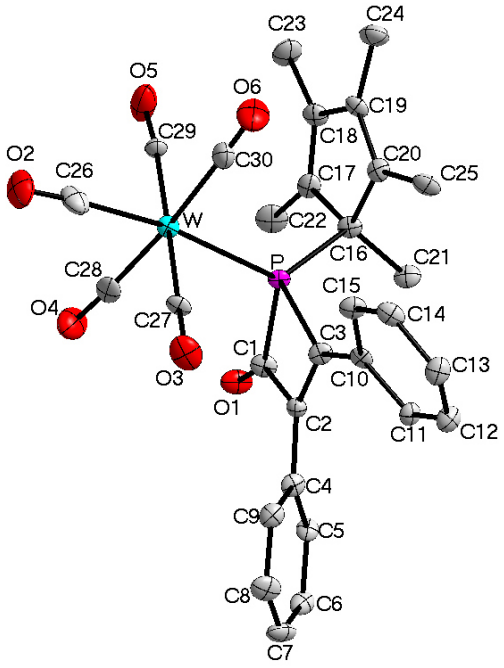


***Table 1:*** Crystal data and structure refinement for **14.2**.

| | |
|---|---|
| Identification code | GSTR466, AKY-536 // GXraycu_4526f |
| Crystal Habitus | clear yellow plate |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{30}H_{25}O_6PW$ |
| Moiety formula | C30 H25 O6 P W |
| Formula weight | 696.32 |
| Temperature/K | 122.99 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 8.8513(3) |
| b/Å | 10.7052(4) |
| c/Å | 14.8284(6) |
| α/° | 92.8570(16) |
| β/° | 99.0783(15) |
| γ/° | 91.9166(15) |
| Volume/Å$^3$ | 1384.52(9) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.670 |
| μ/mm$^{-1}$ | 8.626 |
| F(000) | 684.0 |
| Crystal size/mm$^3$ | 0.3 × 0.2 × 0.05 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.2129; 0.7536 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.046 to 135.482° |
| Completeness to theta | 0.999 |
| Index ranges | -10 ≤ h ≤ 9, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17 |
| Reflections collected | 33677 |
| Independent reflections | 5024 [$R_{int}$ = 0.0730, $R_{sigma}$ = 0.0417] |
| Data/restraints/parameters | 5024/54/348 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.067 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0671, $wR_2$ = 0.1829 |
| Final R indexes [all data] | $R_1$ = 0.0685, $wR_2$ = 0.1853 |
| Largest diff. peak/hole / e $Å^{-3}$ | 5.06/-4.00 |

***Table 2:*** Bond lengths for **14.2**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5004(17) | C5 | C6 | 1.390(10) |
| W | C26 | 2.011(9) | C6 | C7 | 1.392(11) |
| W | C27 | 2.010(7) | C7 | C8 | 1.392(11) |
| W | C28 | 2.041(10) | C8 | C9 | 1.378(10) |
| W | C29 | 2.020(8) | C10 | C11 | 1.408(9) |
| W | C30 | 2.051(9) | C10 | C15 | 1.386(10) |
| P | C1 | 1.905(7) | C11 | C12 | 1.382(10) |
| P | C3 | 1.857(6) | C12 | C13 | 1.369(11) |
| P | C16 | 1.877(7) | C13 | C14 | 1.391(10) |
| O1 | C1 | 1.201(8) | C14 | C15 | 1.407(10) |
| O2 | C26 | 1.146(10) | C16 | C17 | 1.517(9) |
| O3 | C27 | 1.160(10) | C16 | C20 | 1.513(9) |
| O4 | C28 | 1.149(12) | C16 | C21 | 1.535(9) |
| O5 | C29 | 1.154(11) | C17 | C18 | 1.371(10) |
| O6 | C30 | 1.146(12) | C17 | C22 | 1.478(10) |
| C1 | C2 | 1.480(9) | C18 | C19 | 1.466(10) |
| C2 | C3 | 1.362(9) | C18 | C23 | 1.492(10) |
| C2 | C4 | 1.468(9) | C19 | C20 | 1.343(10) |
| C3 | C10 | 1.465(9) | C19 | C24 | 1.506(10) |
| C4 | C5 | 1.397(9) | C20 | C25 | 1.506(10) |
| C4 | C9 | 1.399(9) | | | |

***Table 3:*** Bond angles for **14.2**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C26 | W | P | 171.0(2) | C6 | C7 | C8 | 120.0(6) |
| C26 | W | C28 | 85.5(3) | C9 | C8 | C7 | 120.0(7) |
| C26 | W | C29 | 90.6(3) | C8 | C9 | C4 | 120.8(7) |
| C26 | W | C30 | 92.1(3) | C11 | C10 | C3 | 119.6(6) |
| C27 | W | P | 83.6(2) | C15 | C10 | C3 | 121.5(6) |
| C27 | W | C26 | 88.9(3) | C15 | C10 | C11 | 118.9(6) |
| C27 | W | C28 | 91.6(3) | C12 | C11 | C10 | 120.4(7) |
| C27 | W | C29 | 179.0(2) | C13 | C12 | C11 | 120.5(7) |
| C27 | W | C30 | 92.9(3) | C12 | C13 | C14 | 120.5(7) |
| C28 | W | P | 89.7(2) | C13 | C14 | C15 | 119.4(7) |
| C28 | W | C30 | 174.9(3) | C10 | C15 | C14 | 120.4(7) |
| C29 | W | P | 96.8(2) | C17 | C16 | P | 104.2(4) |
| C29 | W | C28 | 87.5(3) | C17 | C16 | C21 | 113.8(6) |
| C29 | W | C30 | 88.0(3) | C20 | C16 | P | 108.8(4) |
| C30 | W | P | 93.3(2) | C20 | C16 | C17 | 104.4(5) |
| C1 | P | W | 113.9(2) | C20 | C16 | C21 | 113.8(6) |
| C3 | P | W | 116.6(2) | C21 | C16 | P | 111.2(4) |
| C3 | P | C1 | 70.9(3) | C18 | C17 | C16 | 107.5(6) |
| C3 | P | C16 | 109.8(3) | C18 | C17 | C22 | 127.9(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C16 | P | W | 124.8(2) | C22 | C17 | C16 | 124.6(6) |
| C16 | P | C1 | 108.1(3) | C17 | C18 | C19 | 109.3(6) |
| O1 | C1 | P | 135.6(5) | C17 | C18 | C23 | 128.4(7) |
| O1 | C1 | C2 | 133.3(6) | C19 | C18 | C23 | 122.4(7) |
| C2 | C1 | P | 91.1(4) | C18 | C19 | C24 | 123.7(6) |
| C3 | C2 | C1 | 100.3(6) | C20 | C19 | C18 | 110.8(6) |
| C3 | C2 | C4 | 133.3(6) | C20 | C19 | C24 | 125.5(7) |
| C4 | C2 | C1 | 126.0(6) | C19 | C20 | C16 | 108.0(6) |
| C2 | C3 | P | 97.0(4) | C19 | C20 | C25 | 127.6(7) |
| C2 | C3 | C10 | 129.3(6) | C25 | C20 | C16 | 124.4(6) |
| C10 | C3 | P | 133.5(5) | O2 | C26 | W | 176.1(7) |
| C5 | C4 | C2 | 120.3(6) | O3 | C27 | W | 177.4(7) |
| C5 | C4 | C9 | 118.9(6) | O4 | C28 | W | 176.8(8) |
| C9 | C4 | C2 | 120.7(6) | O5 | C29 | W | 174.7(7) |
| C6 | C5 | C4 | 120.4(6) | O6 | C30 | W | 178.7(8) |
| C5 | C6 | C7 | 119.9(7) | | | | |

***Table 4:*** Torsion angles for **14.2**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C3 | C2 | 102.3(4) | C4 | C2 | C3 | C10 | 9.9(12) |
| W | P | C3 | C10 | -73.3(7) | C4 | C5 | C6 | C7 | 0.9(10) |
| W | P | C16 | C17 | -52.3(5) | C5 | C4 | C9 | C8 | 0.6(10) |
| W | P | C16 | C20 | 58.6(5) | C5 | C6 | C7 | C8 | 0.0(11) |
| W | P | C16 | C21 | -175.3(4) | C6 | C7 | C8 | C9 | -0.7(11) |
| P | C1 | C2 | C3 | -6.6(5) | C7 | C8 | C9 | C4 | 0.4(11) |
| P | C1 | C2 | C4 | 167.0(6) | C9 | C4 | C5 | C6 | -1.2(10) |
| P | C3 | C10 | C11 | -153.9(5) | C10 | C11 | C12 | C13 | 2.7(11) |
| P | C3 | C10 | C15 | 26.8(10) | C11 | C10 | C15 | C14 | -1.5(10) |
| P | C16 | C17 | C18 | 115.0(5) | C11 | C12 | C13 | C14 | -3.4(12) |
| P | C16 | C17 | C22 | -66.4(7) | C12 | C13 | C14 | C15 | 1.6(11) |
| P | C16 | C20 | C19 | -110.4(5) | C13 | C14 | C15 | C10 | 0.9(11) |
| P | C16 | C20 | C25 | 72.9(7) | C15 | C10 | C11 | C12 | -0.2(10) |
| O1 | C1 | C2 | C3 | 175.4(8) | C16 | P | C3 | C2 | -108.5(5) |
| O1 | C1 | C2 | C4 | -11.0(12) | C16 | P | C3 | C10 | 75.9(7) |
| C1 | P | C3 | C2 | -5.5(4) | C16 | C17 | C18 | C19 | -1.9(8) |
| C1 | P | C3 | C10 | 178.9(7) | C16 | C17 | C18 | C23 | 177.9(7) |
| C1 | P | C16 | C17 | 85.8(5) | C17 | C16 | C20 | C19 | 0.4(7) |
| C1 | P | C16 | C20 | -163.2(4) | C17 | C16 | C20 | C25 | -176.3(6) |
| C1 | P | C16 | C21 | -37.1(5) | C17 | C18 | C19 | C20 | 2.2(8) |
| C1 | C2 | C3 | P | 6.8(5) | C17 | C18 | C19 | C24 | 179.9(6) |
| C1 | C2 | C3 | C10 | -177.3(7) | C18 | C19 | C20 | C16 | -1.5(8) |
| C1 | C2 | C4 | C5 | 47.7(10) | C18 | C19 | C20 | C25 | 175.0(7) |
| C1 | C2 | C4 | C9 | -129.0(7) | C20 | C16 | C17 | C18 | 1.0(7) |
| C2 | C3 | C10 | C11 | 31.7(10) | C20 | C16 | C17 | C22 | 179.5(6) |
| C2 | C3 | C10 | C15 | -147.6(7) | C21 | C16 | C17 | C18 | -123.7(6) |
| C2 | C4 | C5 | C6 | -178.0(6) | C21 | C16 | C17 | C22 | 54.8(9) |
| C2 | C4 | C9 | C8 | 177.4(6) | C21 | C16 | C20 | C19 | 125.0(6) |
| C3 | P | C16 | C17 | 161.5(4) | C21 | C16 | C20 | C25 | -51.6(9) |
| C3 | P | C16 | C20 | -87.6(5) | C22 | C17 | C18 | C19 | 179.7(7) |
| C3 | P | C16 | C21 | 38.5(5) | C22 | C17 | C18 | C23 | -0.5(13) |
| C3 | C2 | C4 | C5 | -141.0(8) | C23 | C18 | C19 | C20 | -177.6(7) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C3 | C2 | C4 | C9 | 42.2(11) | C23 | C18 | C19 | C24 | 0.0(11) |
| C3 | C10 | C11 | C12 | -179.5(7) | C24 | C19 | C20 | C16 | -179.1(6) |
| C3 | C10 | C15 | C14 | 177.7(6) | C24 | C19 | C20 | C25 | -2.6(11) |
| C4 | C2 | C3 | P | -166.0(7) | | | | | |

## 12.7 Pentacarbonyl{2-[bis(trimethylsilyl)methyl]-3-phenyl-1,2-oxaphosphetane-κ*P*}tungsten(0) [16.1]

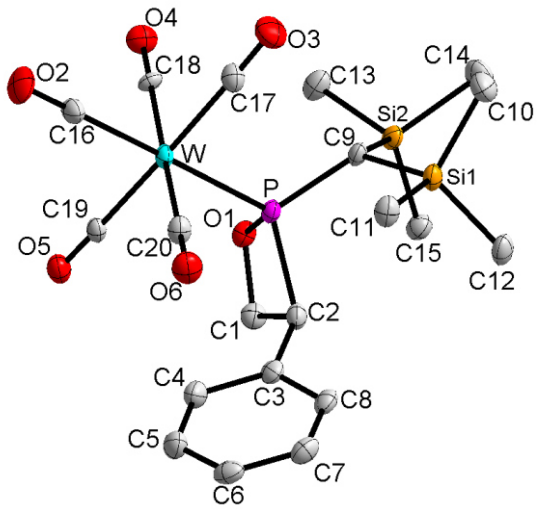


***Table 1:*** Crystal data and structure refinement for **16.1**.

| | |
|---|---|
| Identification code | GSTR314, AKY-276 // GXray2987f |
| Crystal Habitus | colourless plate |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{20}H_{27}O_6PSi_2W$ |
| Moiety formula | C20 H27 O6 P Si2 W |
| Formula weight | 634.42 |
| Temperature/K | 100(2) |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.1581(9) |
| b/Å | 11.1649(9) |
| c/Å | 13.6235(13) |
| α/° | 67.265(4) |
| β/° | 79.233(2) |
| γ/° | 75.176(2) |
| Volume/Å$^3$ | 1235.9(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.705 |
| μ/mm$^{-1}$ | 4.866 |
| F(000) | 624.0 |
| Crystal size/mm$^3$ | 0.40 × 0.18 × 0.10 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.2463; 0.6418 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.32 to 50.5° |

| | |
|---|---|
| Completeness to theta | 0.957 |
| Index ranges | -10 ≤ h ≤ 10, -13 ≤ k ≤ 11, -16 ≤ l ≤ 16 |
| Reflections collected | 7378 |
| Independent reflections | 4271 [$R_{int}$ = 0.0290] |
| Data/restraints/parameters | 4271/0/277 |
| Goodness-of-fit on $F^2$ | 1.065 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0286, $wR_2$ = 0.0740 |
| Final R indexes [all data] | $R_1$ = 0.0299, $wR_2$ = 0.0749 |
| Largest diff. peak/hole / e $Å^{-3}$ | 2.90/-1.70 |

***Table 2:*** Bond lengths for **16.1**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | C16 | 2.020(5) | Si2 | C13 | 1.867(5) |
| W | C18 | 2.034(4) | Si2 | C9 | 1.912(5) |
| W | C17 | 2.037(5) | O1 | C1 | 1.458(5) |
| W | C19 | 2.040(4) | O2 | C16 | 1.145(6) |
| W | C20 | 2.070(5) | O3 | C17 | 1.135(6) |
| W | P | 2.4749(11) | O4 | C18 | 1.141(6) |
| P | O1 | 1.677(3) | O5 | C19 | 1.134(6) |
| P | C9 | 1.820(4) | O6 | C20 | 1.132(6) |
| P | C2 | 1.894(5) | C1 | C2 | 1.537(6) |
| P | C1 | 2.322(5) | C2 | C3 | 1.501(6) |
| Si1 | C10 | 1.866(5) | C3 | C8 | 1.389(6) |
| Si1 | C12 | 1.870(5) | C3 | C4 | 1.414(6) |
| Si1 | C11 | 1.879(5) | C4 | C5 | 1.383(7) |
| Si1 | C9 | 1.906(4) | C5 | C6 | 1.382(7) |
| Si2 | C15 | 1.857(5) | C6 | C7 | 1.394(7) |
| Si2 | C14 | 1.866(5) | C7 | C8 | 1.389(7) |

***Table 3:*** Bond angles for **16.1**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C16 | W | C18 | 90.24(19) | C11 | Si1 | C9 | 110.86(19) |
| C16 | W | C17 | 89.80(19) | C15 | Si2 | C14 | 106.9(2) |
| C18 | W | C17 | 88.45(18) | C15 | Si2 | C13 | 111.0(2) |
| C16 | W | C19 | 91.35(18) | C14 | Si2 | C13 | 107.7(2) |
| C18 | W | C19 | 87.18(17) | C15 | Si2 | C9 | 113.1(2) |
| C17 | W | C19 | 175.48(17) | C14 | Si2 | C9 | 109.6(2) |
| C16 | W | C20 | 89.22(19) | C13 | Si2 | C9 | 108.4(2) |
| C18 | W | C20 | 178.59(16) | C1 | O1 | P | 95.3(3) |
| C17 | W | C20 | 90.24(19) | O1 | C1 | C2 | 99.2(3) |
| C19 | W | C20 | 94.15(18) | O1 | C1 | P | 45.97(19) |
| C16 | W | P | 176.14(15) | C2 | C1 | P | 54.3(2) |
| C18 | W | P | 86.91(12) | C3 | C2 | C1 | 118.6(4) |
| C17 | W | P | 92.73(13) | C3 | C2 | P | 123.1(3) |
| C19 | W | P | 85.89(12) | C1 | C2 | P | 84.5(3) |
| C20 | W | P | 93.68(13) | C8 | C3 | C4 | 117.9(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 | P | C9 | 107.28(18) | C8 | C3 | C2 | 120.1(4) |
| O1 | P | C2 | 79.20(18) | C4 | C3 | C2 | 122.0(4) |
| C9 | P | C2 | 109.76(19) | C5 | C4 | C3 | 120.3(4) |
| O1 | P | C1 | 38.70(16) | C6 | C5 | C4 | 121.2(4) |
| C9 | P | C1 | 120.16(19) | C5 | C6 | C7 | 119.1(4) |
| C2 | P | C1 | 41.23(18) | C8 | C7 | C6 | 120.0(4) |
| O1 | P | W | 111.47(11) | C3 | C8 | C7 | 121.4(4) |
| C9 | P | W | 116.91(15) | P | C9 | Si1 | 114.1(2) |
| C2 | P | W | 124.78(14) | P | C9 | Si2 | 114.8(2) |
| C1 | P | W | 121.41(12) | Si1 | C9 | Si2 | 117.0(2) |
| C10 | Si1 | C12 | 109.8(2) | O2 | C16 | W | 179.3(5) |
| C10 | Si1 | C11 | 106.1(2) | O3 | C17 | W | 177.6(4) |
| C12 | Si1 | C11 | 110.0(2) | O4 | C18 | W | 179.1(4) |
| C10 | Si1 | C9 | 108.1(2) | O5 | C19 | W | 176.9(4) |
| C12 | Si1 | C9 | 111.7(2) | O6 | C20 | W | 177.0(5) |

***Table 4:*** Torsion angles for **16.1**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| C16 | W | P | O1 | -9.8(19) | C4 | C3 | C8 | C7 | -1.8(7) |
| C18 | W | P | O1 | -52.50(17) | C2 | C3 | C8 | C7 | 177.1(4) |
| C17 | W | P | O1 | -140.79(18) | C6 | C7 | C8 | C3 | 1.8(7) |
| C19 | W | P | O1 | 34.89(17) | O1 | P | C9 | Si1 | -139.7(2) |
| C20 | W | P | O1 | 128.79(18) | C2 | P | C9 | Si1 | -55.3(3) |
| C16 | W | P | C9 | 114.1(19) | C1 | P | C9 | Si1 | -99.6(3) |
| C18 | W | P | C9 | 71.4(2) | W | P | C9 | Si1 | 94.3(2) |
| C17 | W | P | C9 | -16.9(2) | O1 | P | C9 | Si2 | -0.7(3) |
| C19 | W | P | C9 | 158.8(2) | C2 | P | C9 | Si2 | 83.7(3) |
| C20 | W | P | C9 | -107.3(2) | C1 | P | C9 | Si2 | 39.4(3) |
| C16 | W | P | C2 | -101.4(19) | W | P | C9 | Si2 | -126.74(18) |
| C18 | W | P | C2 | -144.1(2) | C10 | Si1 | C9 | P | -146.1(3) |
| C17 | W | P | C2 | 127.6(2) | C12 | Si1 | C9 | P | 92.9(3) |
| C19 | W | P | C2 | -56.7(2) | C11 | Si1 | C9 | P | -30.2(3) |
| C20 | W | P | C2 | 37.2(2) | C10 | Si1 | C9 | Si2 | 75.8(3) |
| C16 | W | P | C1 | -51.9(19) | C12 | Si1 | C9 | Si2 | -45.1(3) |
| C18 | W | P | C1 | -94.56(19) | C11 | Si1 | C9 | Si2 | -168.2(2) |
| C17 | W | P | C1 | 177.1(2) | C15 | Si2 | C9 | P | -62.4(3) |
| C19 | W | P | C1 | -7.18(18) | C14 | Si2 | C9 | P | 178.4(2) |
| C20 | W | P | C1 | 86.72(19) | C13 | Si2 | C9 | P | 61.1(3) |
| C9 | P | O1 | C1 | 116.9(3) | C15 | Si2 | C9 | Si1 | 75.3(3) |
| C2 | P | O1 | C1 | 9.4(3) | C14 | Si2 | C9 | Si1 | -43.9(3) |
| W | P | O1 | C1 | -113.9(2) | C13 | Si2 | C9 | Si1 | -161.2(3) |
| P | O1 | C1 | C2 | -11.6(3) | C18 | W | C16 | O2 | 32(32) |
| C9 | P | C1 | O1 | -79.9(3) | C17 | W | C16 | O2 | 121(32) |
| C2 | P | C1 | O1 | -165.9(4) | C19 | W | C16 | O2 | -55(32) |
| W | P | C1 | O1 | 85.6(2) | C20 | W | C16 | O2 | -149(32) |
| O1 | P | C1 | C2 | 165.9(4) | P | W | C16 | O2 | -10(33) |
| C9 | P | C1 | C2 | 86.0(3) | C16 | W | C17 | O3 | -86(10) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | -108.5(2) | C18 | W | C17 | O3 | 4(10) |
| O1 | C1 | C2 | C3 | 135.2(4) | C19 | W | C17 | O3 | 18(12) |
| P | C1 | C2 | C3 | 124.9(4) | C20 | W | C17 | O3 | -176(100) |
| O1 | C1 | C2 | P | 10.2(3) | P | W | C17 | O3 | 91(10) |
| O1 | P | C2 | C3 | -129.6(4) | C16 | W | C18 | O4 | 21(26) |
| C9 | P | C2 | C3 | 125.7(4) | C17 | W | C18 | O4 | -69(26) |
| C1 | P | C2 | C3 | -120.7(5) | C19 | W | C18 | O4 | 112(26) |
| W | P | C2 | C3 | -20.9(4) | C20 | W | C18 | O4 | -47(29) |
| O1 | P | C2 | C1 | -8.9(2) | P | W | C18 | O4 | -162(26) |
| C9 | P | C2 | C1 | -113.6(3) | C16 | W | C19 | O5 | 102(7) |
| W | P | C2 | C1 | 99.8(3) | C18 | W | C19 | O5 | 12(7) |
| C1 | C2 | C3 | C8 | 148.0(4) | C17 | W | C19 | O5 | -3(9) |
| P | C2 | C3 | C8 | -109.0(4) | C20 | W | C19 | O5 | -169(7) |
| C1 | C2 | C3 | C4 | -33.1(6) | P | W | C19 | O5 | -75(7) |
| P | C2 | C3 | C4 | 69.9(5) | C16 | W | C20 | O6 | -43(7) |
| C8 | C3 | C4 | C5 | -0.1(7) | C18 | W | C20 | O6 | 25(12) |
| C2 | C3 | C4 | C5 | -178.9(5) | C17 | W | C20 | O6 | 47(7) |
| C3 | C4 | C5 | C6 | 2.1(8) | C19 | W | C20 | O6 | -135(7) |
| C4 | C5 | C6 | C7 | -2.2(8) | P | W | C20 | O6 | 139(7) |
| C5 | C6 | C7 | C8 | 0.3(7) | | | | | |

## 12.8 Pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1a$_W$]

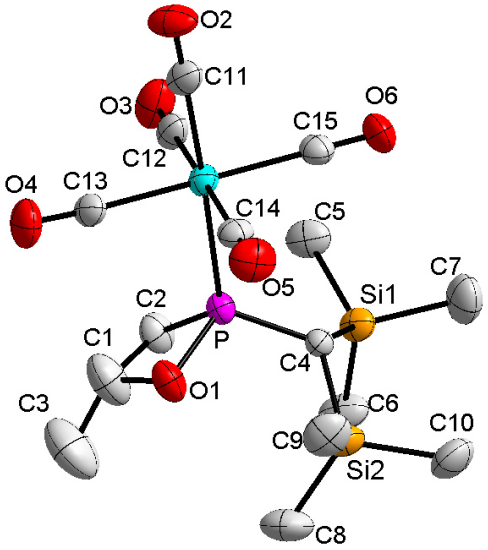


***Table 1:*** Crystal data and structure refinement for **21.1a$_W$**.

| | |
|---|---|
| Identification code | GSTR321, AKY-301 // GXray3087 |
| Crystal Habitus | colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{15}H_{25}O_6PSi_2W$ |
| Moiety formula | C15 H25 O6 P Si2 W |
| Formula weight | 572.35 |
| Temperature/K | 123(2) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |

| | |
|---|---|
| a/Å | 10.5131(4) |
| b/Å | 13.8027(5) |
| c/Å | 15.4963(5) |
| α/° | 90.00 |
| β/° | 90.00 |
| γ/° | 90.00 |
| Volume/Å$^3$ | 2248.66(14) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.691 |
| μ/mm$^{-1}$ | 5.339 |
| F(000) | 1120.0 |
| Crystal size/mm$^3$ | 0.40 × 0.20 × 0.06 |
| Absorption correction | Multi-Scan |
| Tmin; Tmax | 0.2239; 0.7400 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.88 to 55.98° |
| Completeness to theta | 0.995 |
| Index ranges | -13 ≤ h ≤ 12, -17 ≤ k ≤ 18, -20 ≤ l ≤ 20 |
| Reflections collected | 18819 |
| Independent reflections | 5329 [$R_{int}$ = 0.0632] |
| Data/restraints/parameters | 5329/31/234 |
| Goodness-of-fit on $F^2$ | 0.978 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0338, $wR_2$ = 0.0619 |
| Final R indexes [all data] | $R_1$ = 0.0474, $wR_2$ = 0.0654 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.35/-1.87 |
| Flack parameter | 0.467(8) |

***Table 2:*** Bond lengths for **21.1a$_W$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | C3 | 1.375(9) | C10 | Si2 | 1.878(7) |
| C1 | O1 | 1.463(8) | C11 | O2 | 1.144(6) |
| C1 | C2 | 1.545(9) | C11 | W | 2.018(6) |
| C1 | P | 2.298(7) | C12 | O3 | 1.135(7) |
| C2 | P | 1.827(5) | C12 | W | 2.047(6) |
| C4 | P | 1.800(5) | C13 | O4 | 1.134(7) |
| C4 | Si2 | 1.905(5) | C13 | W | 2.036(6) |
| C4 | Si1 | 1.913(5) | C14 | O5 | 1.134(7) |
| C5 | Si1 | 1.859(6) | C14 | W | 2.034(6) |
| C6 | Si1 | 1.863(6) | C15 | O6 | 1.129(7) |
| C7 | Si1 | 1.877(6) | C15 | W | 2.044(6) |
| C8 | Si2 | 1.865(6) | O1 | P | 1.672(4) |
| C9 | Si2 | 1.873(7) | P | W | 2.4846(14) |

***Table 3:*** Bond angles for **21.1a$_W$**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C3 | C1 | O1 | 117.7(7) | C5 | Si1 | C7 | 106.2(3) |
| C3 | C1 | C2 | 122.3(7) | C6 | Si1 | C7 | 110.1(3) |
| O1 | C1 | C2 | 96.5(5) | C5 | Si1 | C4 | 111.1(2) |
| C3 | C1 | P | 150.8(7) | C6 | Si1 | C4 | 112.1(2) |
| O1 | C1 | P | 46.6(2) | C7 | Si1 | C4 | 108.3(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2 | C1 | P | 52.4(3) | C8 | Si2 | C9 | 108.8(3) |
| C1 | C2 | P | 85.5(4) | C8 | Si2 | C10 | 110.1(3) |
| P | C4 | Si2 | 115.9(3) | C9 | Si2 | C10 | 107.8(3) |
| P | C4 | Si1 | 113.9(3) | C8 | Si2 | C4 | 114.0(3) |
| Si2 | C4 | Si1 | 116.5(3) | C9 | Si2 | C4 | 108.3(3) |
| O2 | C11 | W | 178.2(4) | C10 | Si2 | C4 | 107.5(3) |
| O3 | C12 | W | 179.1(6) | C11 | W | C14 | 91.2(2) |
| O4 | C13 | W | 176.9(5) | C11 | W | C13 | 88.8(2) |
| O5 | C14 | W | 177.2(5) | C14 | W | C13 | 89.2(2) |
| O6 | C15 | W | 178.6(6) | C11 | W | C15 | 91.4(2) |
| C1 | O1 | P | 94.0(3) | C14 | W | C15 | 91.5(3) |
| O1 | P | C4 | 108.4(2) | C13 | W | C15 | 179.3(3) |
| O1 | P | C2 | 79.7(2) | C11 | W | C12 | 91.5(2) |
| C4 | P | C2 | 111.5(3) | C14 | W | C12 | 177.3(3) |
| O1 | P | C1 | 39.4(2) | C13 | W | C12 | 91.0(2) |
| C4 | P | C1 | 125.6(3) | C15 | W | C12 | 88.3(2) |
| C2 | P | C1 | 42.1(3) | C11 | W | P | 177.48(16) |
| O1 | P | W | 113.73(16) | C14 | W | P | 88.23(17) |
| C4 | P | W | 118.00(17) | C13 | W | P | 88.79(18) |
| C2 | P | W | 118.9(2) | C15 | W | P | 91.04(17) |
| C1 | P | W | 115.9(2) | C12 | W | P | 89.10(18) |
| C5 | Si1 | C6 | 109.1(3) | | | | |

***Table 4:*** Torsion angles for **21.1a$_W$**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| C3 | C1 | C2 | P | -144.7(8) | O2 | C11 | W | C12 | 138(19) |
| O1 | C1 | C2 | P | -15.9(5) | O2 | C11 | W | P | 34(23) |
| C3 | C1 | O1 | P | 149.3(7) | O5 | C14 | W | C11 | 5(11) |
| C2 | C1 | O1 | P | 17.4(5) | O5 | C14 | W | C13 | -84(11) |
| C1 | O1 | P | C4 | -124.2(5) | O5 | C14 | W | C15 | 96(11) |
| C1 | O1 | P | C2 | -14.8(5) | O5 | C14 | W | C12 | -178(100) |
| C1 | O1 | P | W | 102.4(4) | O5 | C14 | W | P | -173(11) |
| Si2 | C4 | P | O1 | -10.1(4) | O4 | C13 | W | C11 | 34(11) |
| Si1 | C4 | P | O1 | 129.1(3) | O4 | C13 | W | C14 | 125(11) |
| Si2 | C4 | P | C2 | -96.0(3) | O4 | C13 | W | C15 | -70(26) |
| Si1 | C4 | P | C2 | 43.2(3) | O4 | C13 | W | C12 | -58(11) |
| Si2 | C4 | P | C1 | -50.3(4) | O4 | C13 | W | P | -147(11) |
| Si1 | C4 | P | C1 | 88.9(3) | O6 | C15 | W | C11 | -124(21) |
| Si2 | C4 | P | W | 121.0(2) | O6 | C15 | W | C14 | 145(21) |
| Si1 | C4 | P | W | -99.8(3) | O6 | C15 | W | C13 | -19(36) |
| C1 | C2 | P | O1 | 14.0(4) | O6 | C15 | W | C12 | -32(21) |
| C1 | C2 | P | C4 | 119.8(4) | O6 | C15 | W | P | 57(21) |
| C1 | C2 | P | W | -97.6(4) | O3 | C12 | W | C11 | 14(38) |
| C3 | C1 | P | O1 | -67.6(12) | O3 | C12 | W | C14 | -164(35) |
| C2 | C1 | P | O1 | -158.0(7) | O3 | C12 | W | C13 | 103(38) |
| C3 | C1 | P | C4 | 7.3(14) | O3 | C12 | W | C15 | -78(38) |
| O1 | C1 | P | C4 | 74.9(5) | O3 | C12 | W | P | -169(100) |
| C2 | C1 | P | C4 | -83.1(5) | O1 | P | W | C11 | -21(4) |
| C3 | C1 | P | C2 | 90.4(14) | C4 | P | W | C11 | -150(4) |
| O1 | C1 | P | C2 | 158.0(7) | C2 | P | W | C11 | 70(4) |
| C3 | C1 | P | W | -164.2(12) | C1 | P | W | C11 | 22(4) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | P | W | -96.6(4) | O1 | P | W | C14 | 55.2(2) |
| C2 | C1 | P | W | 105.4(4) | C4 | P | W | C14 | -73.4(3) |
| P | C4 | Si1 | C5 | 26.9(4) | C2 | P | W | C14 | 146.4(3) |
| Si2 | C4 | Si1 | C5 | 165.9(3) | C1 | P | W | C14 | 98.8(3) |
| P | C4 | Si1 | C6 | -95.4(3) | O1 | P | W | C13 | -34.0(2) |
| Si2 | C4 | Si1 | C6 | 43.6(4) | C4 | P | W | C13 | -162.6(2) |
| P | C4 | Si1 | C7 | 143.1(3) | C2 | P | W | C13 | 57.1(3) |
| Si2 | C4 | Si1 | C7 | -77.9(4) | C1 | P | W | C13 | 9.5(3) |
| P | C4 | Si2 | C8 | 63.6(4) | O1 | P | W | C15 | 146.7(2) |
| Si1 | C4 | Si2 | C8 | -74.6(4) | C4 | P | W | C15 | 18.1(2) |
| P | C4 | Si2 | C9 | -57.7(4) | C2 | P | W | C15 | -122.2(3) |
| Si1 | C4 | Si2 | C9 | 164.1(3) | C1 | P | W | C15 | -169.8(3) |
| P | C4 | Si2 | C10 | -174.0(3) | O1 | P | W | C12 | -125.0(2) |
| Si1 | C4 | Si2 | C10 | 47.8(4) | C4 | P | W | C12 | 106.4(2) |
| O2 | C11 | W | C14 | -42(19) | C2 | P | W | C12 | -33.8(3) |
| O2 | C11 | W | C13 | 47(19) | C1 | P | W | C12 | -81.5(3) |
| O2 | C11 | W | C15 | -134(19) | | | | | |

## 12.9 Pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}molybdenum(0) [21.1a$_{Mo}$]

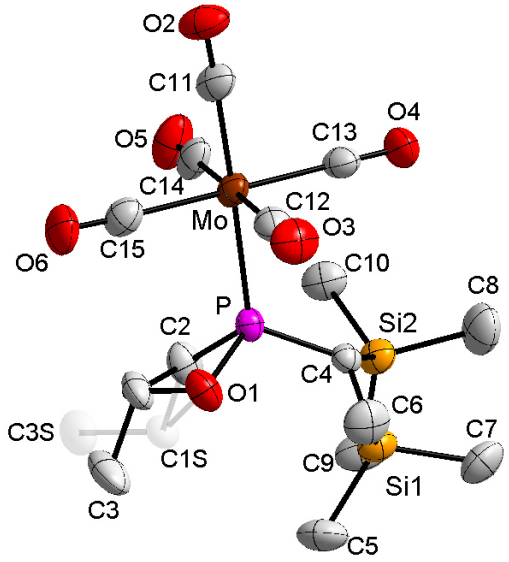


***Table 1:*** Crystal data and structure refinement for **21.1a$_{Mo}$**.

| | |
|---|---|
| Identification code | GSTR370, 3621 |
| Empirical formula | $C_{15}H_{25}MoO_6PSi_2$ |
| Formula weight | 484.44 |
| Temperature/K | 123.15 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 10.5587(3) |
| b/Å | 13.8356(5) |
| c/Å | 15.4608(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2258.61(12) |
| Z | 4 |

| | |
|---|---|
| $\rho_{calc}$g/cm$^3$ | 1.425 |
| μ/mm$^{-1}$ | 0.782 |
| F(000) | 992.0 |
| Crystal size/mm$^3$ | 0.24 × 0.16 × 0.08 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.27 to 55.998 |
| Index ranges | -13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20 |
| Reflections collected | 31032 |
| Independent reflections | 5424 [$R_{int}$ = 0.0529, $R_{sigma}$ = 0.0457] |
| Data/restraints/parameters | 5424/18/257 |
| Goodness-of-fit on F$^2$ | 0.983 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0274, $wR_2$ = 0.0498 |
| Final R indexes [all data] | $R_1$ = 0.0412, $wR_2$ = 0.0527 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.40/-0.70 |
| Flack parameter | 0.51(3) |

***Table 2:*** Bond lengths for **21.1a$_{Mo}$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Mo | P | 2.4883(8) | Si2 | C8 | 1.873(4) |
| Mo | C11 | 2.014(4) | Si2 | C9 | 1.864(3) |
| Mo | C12 | 2.045(4) | Si2 | C10 | 1.863(3) |
| Mo | C13 | 2.042(4) | O1 | C1 | 1.467(7) |
| Mo | C14 | 2.046(4) | O1 | C1S | 1.621(11) |
| Mo | C15 | 2.042(4) | O2 | C11 | 1.149(4) |
| P | O1 | 1.673(2) | O3 | C12 | 1.137(4) |
| P | C2 | 1.817(3) | O4 | C13 | 1.137(4) |
| P | C4 | 1.806(3) | O5 | C14 | 1.145(4) |
| P | C1 | 2.265(6) | O6 | C15 | 1.145(4) |
| Si1 | C4 | 1.907(3) | C2 | C1 | 1.580(8) |
| Si1 | C5 | 1.857(4) | C2 | C1S | 1.544(11) |
| Si1 | C6 | 1.864(4) | C1 | C3 | 1.512(14) |
| Si1 | C7 | 1.875(4) | C1S | C3S | 1.49(2) |
| Si2 | C4 | 1.908(3) | | | |

***Table 3:*** Bond angles for **21.1a$_{Mo}$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C11 | Mo | P | 177.66(9) | C6 | Si1 | C7 | 107.30(19) |
| C11 | Mo | C12 | 90.32(14) | C7 | Si1 | C4 | 107.56(15) |
| C11 | Mo | C13 | 91.48(14) | C8 | Si2 | C4 | 107.77(17) |
| C11 | Mo | C14 | 91.07(15) | C9 | Si2 | C4 | 111.82(14) |
| C11 | Mo | C15 | 88.68(15) | C9 | Si2 | C8 | 110.4(2) |
| C12 | Mo | P | 88.66(10) | C10 | Si2 | C4 | 111.12(14) |
| C12 | Mo | C14 | 178.60(16) | C10 | Si2 | C8 | 106.35(18) |
| C13 | Mo | P | 90.65(10) | C10 | Si2 | C9 | 109.24(17) |
| C13 | Mo | C12 | 91.54(15) | C1 | O1 | P | 92.1(3) |
| C13 | Mo | C14 | 88.43(13) | C1S | O1 | P | 94.9(4) |
| C14 | Mo | P | 89.94(11) | C1 | C2 | P | 83.3(3) |
| C15 | Mo | P | 89.20(11) | C1S | C2 | P | 92.2(4) |
| C15 | Mo | C12 | 89.35(14) | P | C4 | Si1 | 115.85(15) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C15 | Mo | C13 | 179.09(16) | P | C4 | Si2 | 114.15(15) |
| C15 | Mo | C14 | 90.68(15) | Si1 | C4 | Si2 | 116.67(15) |
| O1 | P | Mo | 114.07(10) | O2 | C11 | Mo | 177.9(3) |
| O1 | P | C2 | 80.03(14) | O3 | C12 | Mo | 178.5(3) |
| O1 | P | C4 | 107.99(13) | O4 | C13 | Mo | 178.9(4) |
| O1 | P | C1 | 40.3(2) | O5 | C14 | Mo | 179.0(3) |
| C2 | P | Mo | 119.89(13) | O6 | C15 | Mo | 177.8(3) |
| C2 | P | C1 | 43.9(2) | O1 | C1 | P | 47.58(19) |
| C4 | P | Mo | 117.95(10) | O1 | C1 | C2 | 94.9(4) |
| C4 | P | C2 | 110.41(16) | O1 | C1 | C3 | 107.4(9) |
| C4 | P | C1 | 129.7(3) | C2 | C1 | P | 52.8(2) |
| C1 | P | Mo | 111.8(3) | C3 | C1 | P | 139.7(10) |
| C5 | Si1 | C4 | 114.56(17) | C3 | C1 | C2 | 114.0(8) |
| C5 | Si1 | C6 | 109.1(2) | C2 | C1S | O1 | 90.4(6) |
| C5 | Si1 | C7 | 109.6(2) | C3S | C1S | O1 | 106.7(12) |
| C6 | Si1 | C4 | 108.41(16) | C3S | C1S | C2 | 111.8(12) |

***Table 4:*** Torsion angles for **21.1a$_{Mo}$**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| Mo | P | O1 | C1 | 95.9(4) | C2 | P | C4 | Si1 | -96.27(19) |
| Mo | P | O1 | C1S | 129.5(5) | C2 | P | C4 | Si2 | 43.5(2) |
| Mo | P | C2 | C1 | -91.2(4) | C4 | P | O1 | C1 | -130.9(4) |
| Mo | P | C2 | C1S | -123.7(6) | C4 | P | O1 | C1S | -97.3(6) |
| Mo | P | C4 | Si1 | 120.65(13) | C4 | P | C2 | C1 | 126.6(4) |
| Mo | P | C4 | Si2 | -99.55(14) | C4 | P | C2 | C1S | 94.0(6) |
| P | O1 | C1 | C2 | 25.8(5) | C1 | P | O1 | C1S | 33.6(4) |
| P | O1 | C1 | C3 | 142.9(7) | C1 | P | C2 | C1S | -32.6(4) |
| P | O1 | C1S | C2 | -12.9(6) | C1 | P | C4 | Si1 | -50.0(3) |
| P | O1 | C1S | C3S | -125.8(10) | C1 | P | C4 | Si2 | 89.8(3) |
| P | C2 | C1 | O1 | -23.8(4) | C1 | O1 | C1S | C2 | 73.4(8) |
| P | C2 | C1 | C3 | -135.3(9) | C1 | O1 | C1S | C3S | -39.5(12) |
| P | C2 | C1S | O1 | 11.8(6) | C1 | C2 | C1S | O1 | -62.7(8) |
| P | C2 | C1S | C3S | 120.0(11) | C1 | C2 | C1S | C3S | 45.5(11) |
| O1 | P | C2 | C1 | 21.0(4) | C1S | O1 | C1 | P | -95.8(8) |
| O1 | P | C2 | C1S | -11.6(6) | C1S | O1 | C1 | C2 | -70.0(8) |
| O1 | P | C4 | Si1 | -10.5(2) | C1S | O1 | C1 | C3 | 47.1(10) |
| O1 | P | C4 | Si2 | 129.31(15) | C1S | C2 | C1 | P | 104.1(8) |
| C2 | P | O1 | C1 | -22.5(5) | C1S | C2 | C1 | O1 | 80.4(9) |
| C2 | P | O1 | C1S | 11.1(6) | C1S | C2 | C1 | C3 | -31.1(10) |

## 12.10 Pentacarbonyl{4-methyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}chromium(0) [21.1a$_{Cr}$]

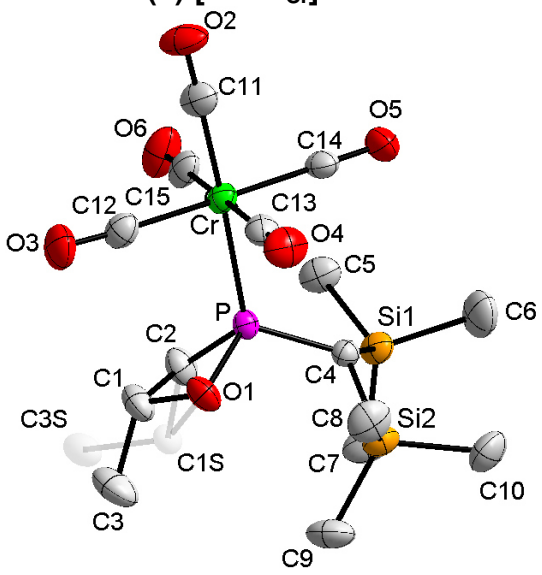


***Table 1:*** Crystal data and structure refinement for **21.1a$_{Cr}$**.

| | |
|---|---|
| Identification code | GSTR369, 3648 |
| Empirical formula | $C_{15}H_{25}CrO_6PSi_2$ |
| Formula weight | 440.50 |
| Temperature/K | 123.15 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 10.4217(3) |
| b/Å | 13.6908(7) |
| c/Å | 15.3565(7) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2191.09(16) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.335 |
| μ/mm$^{-1}$ | 0.729 |
| F(000) | 920.0 |
| Crystal size/mm$^3$ | 0.28 × 0.18 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.724 to 55.982 |
| Index ranges | -10 ≤ h ≤ 13, -13 ≤ k ≤ 18, -20 ≤ l ≤ 19 |
| Reflections collected | 15836 |
| Independent reflections | 5195 [$R_{int}$ = 0.0517, $R_{sigma}$ = 0.0596] |
| Data/restraints/parameters | 5195/0/257 |
| Goodness-of-fit on F$^2$ | 0.974 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0319, $wR_2$ = 0.0659 |
| Final R indexes [all data] | $R_1$ = 0.0430, $wR_2$ = 0.0690 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.23/-0.49 |
| Flack parameter | 0.52(2) |

***Table 2:*** Bond lengths for **21.1a$_{Cr}$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cr | P | 2.3412(8) | Si2 | C8 | 1.862(3) |
| Cr | C11 | 1.878(3) | Si2 | C9 | 1.852(3) |
| Cr | C12 | 1.889(3) | Si2 | C10 | 1.876(3) |
| Cr | C13 | 1.893(3) | O1 | C1 | 1.459(5) |
| Cr | C14 | 1.894(3) | O1 | C1S | 1.632(15) |
| Cr | C15 | 1.896(3) | O2 | C11 | 1.145(3) |
| P | O1 | 1.663(2) | O3 | C12 | 1.147(4) |
| P | C2 | 1.830(3) | O4 | C13 | 1.144(4) |
| P | C4 | 1.807(3) | O5 | C14 | 1.141(4) |
| P | C1 | 2.287(4) | O6 | C15 | 1.146(4) |
| Si1 | C4 | 1.909(3) | C2 | C1 | 1.575(6) |
| Si1 | C5 | 1.852(3) | C2 | C1S | 1.538(13) |
| Si1 | C6 | 1.869(3) | C1 | C3 | 1.502(10) |
| Si1 | C7 | 1.869(3) | C1S | C3S | 1.50(3) |
| Si2 | C4 | 1.911(3) | | | |

***Table 3:*** Bond angles for **21.1a$_{Cr}$**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C11 | Cr | P | 176.98(9) | C7 | Si1 | C4 | 111.62(13) |
| C11 | Cr | C12 | 88.27(13) | C7 | Si1 | C6 | 110.52(18) |
| C11 | Cr | C13 | 90.59(13) | C8 | Si2 | C4 | 108.88(14) |
| C11 | Cr | C14 | 91.30(13) | C8 | Si2 | C10 | 107.48(17) |
| C11 | Cr | C15 | 91.35(14) | C9 | Si2 | C4 | 114.70(15) |
| C12 | Cr | P | 88.96(10) | C9 | Si2 | C8 | 108.90(17) |
| C12 | Cr | C13 | 89.79(13) | C9 | Si2 | C10 | 109.61(17) |
| C12 | Cr | C14 | 178.95(14) | C10 | Si2 | C4 | 107.03(14) |
| C12 | Cr | C15 | 90.75(14) | C1 | O1 | P | 94.0(2) |
| C13 | Cr | P | 88.20(9) | C1S | O1 | P | 94.5(5) |
| C13 | Cr | C14 | 91.17(14) | C1 | C2 | P | 84.1(2) |
| C13 | Cr | C15 | 177.99(13) | C1S | C2 | P | 91.4(5) |
| C14 | Cr | P | 91.49(9) | P | C4 | Si1 | 114.34(14) |
| C14 | Cr | C15 | 88.30(13) | P | C4 | Si2 | 115.72(14) |
| C15 | Cr | P | 89.88(10) | Si1 | C4 | Si2 | 116.28(12) |
| O1 | P | Cr | 114.06(7) | O2 | C11 | Cr | 178.1(3) |
| O1 | P | C2 | 79.90(13) | O3 | C12 | Cr | 177.3(3) |
| O1 | P | C4 | 107.73(12) | O4 | C13 | Cr | 178.0(3) |
| O1 | P | C1 | 39.51(15) | O5 | C14 | Cr | 179.3(3) |
| C2 | P | Cr | 119.59(11) | O6 | C15 | Cr | 179.4(3) |
| C2 | P | C1 | 43.24(16) | O1 | C1 | P | 46.49(14) |
| C4 | P | Cr | 118.22(9) | O1 | C1 | C2 | 95.4(3) |
| C4 | P | C2 | 110.66(13) | O1 | C1 | C3 | 111.1(6) |
| C4 | P | C1 | 127.1(2) | C2 | C1 | P | 52.71(16) |
| C1 | P | Cr | 114.10(19) | C3 | C1 | P | 141.3(7) |
| C5 | Si1 | C4 | 111.54(12) | C3 | C1 | C2 | 115.6(5) |
| C5 | Si1 | C6 | 105.88(16) | C2 | C1S | O1 | 90.2(8) |
| C5 | Si1 | C7 | 109.23(15) | C3S | C1S | O1 | 105.2(15) |
| C6 | Si1 | C4 | 107.90(15) | C3S | C1S | C2 | 111.3(16) |

***Table 4:*** Torsion angles for **21.1a$_{Cr}$**.

| A | B | C | D | Angle/˚ | A | B | C | D | Angle/˚ |
|---|---|---|---|---|---|---|---|---|---|
| Cr | P | O1 | C1 | 99.3(3) | C2 | P | C4 | Si1 | 43.45(19) |
| Cr | P | O1 | C1S | 132.0(7) | C2 | P | C4 | Si2 | -95.78(17) |
| Cr | P | C2 | C1 | -94.7(3) | C4 | P | O1 | C1 | -127.3(3) |
| Cr | P | C2 | C1S | -126.9(8) | C4 | P | O1 | C1S | -94.6(7) |
| Cr | P | C4 | Si1 | -99.82(13) | C4 | P | C2 | C1 | 122.6(3) |
| Cr | P | C4 | Si2 | 120.96(12) | C4 | P | C2 | C1S | 90.5(8) |
| P | O1 | C1 | C2 | 21.6(3) | C1 | P | O1 | C1S | 32.7(5) |
| P | O1 | C1 | C3 | 141.8(5) | C1 | P | C2 | C1S | -32.2(6) |
| P | O1 | C1S | C2 | -16.5(8) | C1 | P | C4 | Si1 | 89.7(2) |
| P | O1 | C1S | C3S | -128.7(13) | C1 | P | C4 | Si2 | -49.5(2) |
| P | C2 | C1 | O1 | -19.6(3) | C1 | O1 | C1S | C2 | 74.0(10) |
| P | C2 | C1 | C3 | -136.2(6) | C1 | O1 | C1S | C3S | -38.3(13) |
| P | C2 | C1S | O1 | 14.9(7) | C1 | C2 | C1S | O1 | -61.9(9) |
| P | C2 | C1S | C3S | 121.3(14) | C1 | C2 | C1S | C3S | 44.6(14) |
| O1 | P | C2 | C1 | 17.3(3) | C1S | O1 | C1 | P | -92.1(9) |
| O1 | P | C2 | C1S | -14.8(8) | C1S | O1 | C1 | C2 | -70.4(9) |
| O1 | P | C4 | Si1 | 129.08(14) | C1S | O1 | C1 | C3 | 49.8(10) |
| O1 | P | C4 | Si2 | -10.14(17) | C1S | C2 | C1 | P | 101.9(9) |
| C2 | P | O1 | C1 | -18.7(3) | C1S | C2 | C1 | O1 | 82.3(10) |
| C2 | P | O1 | C1S | 14.0(7) | C1S | C2 | C1 | C3 | -34.3(10) |

## 12.11 Pentacarbonyl{4-ethyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1b]

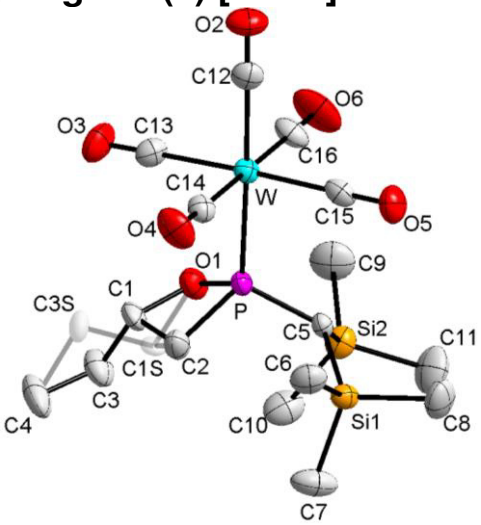


***Table 1:*** Crystal data and structure refinement for **21.1b**.

| | |
|---|---|
| Identification code | GSTR519, AKY-574 // GXray4852f |
| Crystal Habitus | clear colourless plate |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{16}H_{27}O_6Si_2PW$ |
| Moiety formula | C16 H27 O6 P Si2 W |
| Formula weight | 586.37 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 8.8913(4) |

| | |
|---|---|
| b/Å | 10.6987(5) |
| c/Å | 13.6623(7) |
| α/° | 102.842(3) |
| β/° | 94.549(3) |
| γ/° | 113.104(3) |
| Volume/Å$^3$ | 1145.22(10) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.700 |
| μ/mm$^{-1}$ | 5.244 |
| F(000) | 576.0 |
| Crystal size/mm$^3$ | 0.18 × 0.16 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4450; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.226 to 55.998° |
| Completeness to theta | 0.997 |
| Index ranges | -11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18 |
| Reflections collected | 23442 |
| Independent reflections | 5524 [$R_{int}$ = 0.0668, $R_{sigma}$ = 0.0612] |
| Data/restraints/parameters | 5524/0/260 |
| Goodness-of-fit on F$^2$ | 1.039 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0346, $wR_2$ = 0.0773 |
| Final R indexes [all data] | $R_1$ = 0.0478, $wR_2$ = 0.0839 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.60/-1.27 |

***Table 2:*** Bond lengths for **21.1b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4789(12) | Si2 | C10 | 1.864(6) |
| W | C12 | 2.031(5) | Si2 | C11 | 1.863(6) |
| W | C13 | 2.044(5) | O1 | C1 | 1.511(9) |
| W | C14 | 2.042(5) | O1 | C1S | 1.467(16) |
| W | C15 | 2.032(5) | O2 | C12 | 1.133(6) |
| W | C16 | 2.035(6) | O3 | C13 | 1.124(6) |
| P | O1 | 1.668(3) | O4 | C14 | 1.128(6) |
| P | C2 | 1.800(5) | O5 | C15 | 1.145(6) |
| P | C5 | 1.809(4) | O6 | C16 | 1.137(7) |
| Si1 | C5 | 1.914(4) | C1 | C2 | 1.507(9) |
| Si1 | C6 | 1.869(6) | C1 | C3 | 1.499(13) |
| Si1 | C7 | 1.869(5) | C1S | C2 | 1.658(18) |
| Si1 | C8 | 1.863(6) | C1S | C3S | 1.51(3) |
| Si2 | C5 | 1.906(5) | C3 | C4 | 1.494(11) |
| Si2 | C9 | 1.867(6) | C3S | C4 | 1.632(19) |

***Table 3:*** Bond angles for **21.1b**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C12 | W | P | 175.85(13) | C9 | Si2 | C5 | 109.9(3) |
| C12 | W | C13 | 90.0(2) | C10 | Si2 | C5 | 114.4(3) |
| C12 | W | C14 | 89.90(19) | C10 | Si2 | C9 | 108.1(3) |
| C12 | W | C15 | 91.56(19) | C11 | Si2 | C5 | 108.5(3) |
| C12 | W | C16 | 89.8(2) | C11 | Si2 | C9 | 106.2(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C13 | W | P | 86.80(14) | C11 | Si2 | C10 | 109.4(3) |
| C14 | W | P | 92.73(13) | C1 | O1 | P | 92.0(4) |
| C14 | W | C13 | 89.2(2) | C1S | O1 | P | 99.0(7) |
| C15 | W | P | 91.68(13) | C2 | C1 | O1 | 94.9(5) |
| C15 | W | C13 | 177.89(18) | C3 | C1 | O1 | 110.5(8) |
| C15 | W | C14 | 89.44(19) | C3 | C1 | C2 | 116.3(9) |
| C15 | W | C16 | 90.3(2) | O1 | C1S | C2 | 90.5(9) |
| C16 | W | P | 87.60(15) | O1 | C1S | C3S | 106.8(15) |
| C16 | W | C13 | 91.1(2) | C3S | C1S | C2 | 108.5(16) |
| C16 | W | C14 | 179.57(19) | C1 | C2 | P | 87.2(4) |
| O1 | P | W | 114.11(13) | C1S | C2 | P | 87.2(6) |
| O1 | P | C2 | 79.7(2) | C4 | C3 | C1 | 110.7(9) |
| O1 | P | C5 | 108.6(2) | C1S | C3S | C4 | 105.1(15) |
| C2 | P | W | 119.5(2) | P | C5 | Si1 | 113.3(2) |
| C2 | P | C5 | 111.3(2) | P | C5 | Si2 | 116.0(2) |
| C5 | P | W | 117.41(14) | Si2 | C5 | Si1 | 117.2(2) |
| C6 | Si1 | C5 | 111.4(2) | O2 | C12 | W | 178.6(4) |
| C6 | Si1 | C7 | 109.0(3) | O3 | C13 | W | 178.7(5) |
| C7 | Si1 | C5 | 112.3(2) | O4 | C14 | W | 178.5(5) |
| C8 | Si1 | C5 | 108.1(2) | O5 | C15 | W | 179.2(5) |
| C8 | Si1 | C6 | 106.7(3) | O6 | C16 | W | 179.3(5) |
| C8 | Si1 | C7 | 109.2(3) | | | | |

***Table 4:*** Torsion angles for **21.1b**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | -100.3(4) | O1 | C1 | C3 | C4 | -175.7(6) |
| W | P | O1 | C1S | -132.5(9) | O1 | C1S | C2 | P | -14.4(9) |
| W | P | C2 | C1 | 94.4(5) | O1 | C1S | C3S | C4 | -177.4(10) |
| W | P | C2 | C1S | 124.8(8) | C2 | P | O1 | C1 | 17.5(5) |
| W | P | C5 | Si1 | 100.7(2) | C2 | P | O1 | C1S | -14.7(9) |
| W | P | C5 | Si2 | -119.48(19) | C2 | P | C5 | Si1 | -42.1(3) |
| P | O1 | C1 | C2 | -20.8(5) | C2 | P | C5 | Si2 | 97.6(3) |
| P | O1 | C1 | C3 | -141.2(8) | C2 | C1 | C3 | C4 | 77.6(12) |
| P | O1 | C1S | C2 | 15.7(9) | C2 | C1S | C3S | C4 | -81.0(15) |
| P | O1 | C1S | C3S | 125.2(13) | C3 | C1 | C2 | P | 135.0(8) |
| O1 | P | C2 | C1 | -17.6(5) | C3S | C1S | C2 | P | -122.4(13) |
| O1 | P | C2 | C1S | 12.8(8) | C5 | P | O1 | C1 | 126.7(5) |
| O1 | P | C5 | Si1 | -128.0(2) | C5 | P | O1 | C1S | 94.5(9) |
| O1 | P | C5 | Si2 | 11.8(3) | C5 | P | C2 | C1 | -123.6(5) |
| O1 | C1 | C2 | P | 19.2(5) | C5 | P | C2 | C1S | -93.2(8) |

# 12.12 Pentacarbonyl{4-(1-methylethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1c]

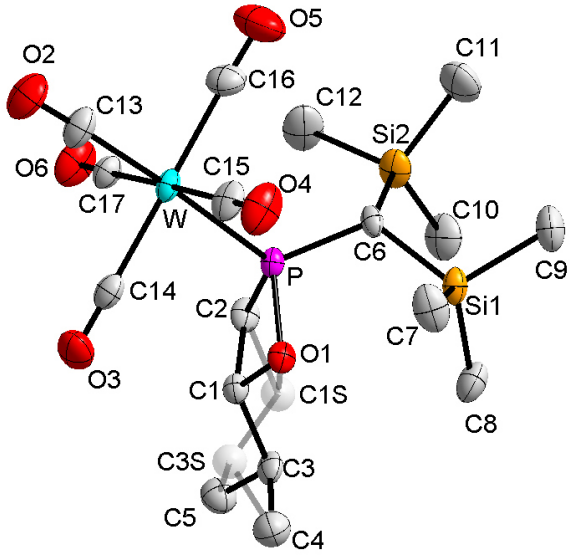


***Table 1:*** Crystal data and structure refinement for **21.1c**.

| | |
|---|---|
| Identification code | GSTR518, AKY-575 // GXray4851f |
| Crystal Habitus | clear colourless plank |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{17}H_{29}O_6Si_2PW$ |
| Moiety formula | C17 H29 O6 P Si2 W |
| Formula weight | 600.40 |
| Temperature/K | 100 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.1548(5) |
| b/Å | 14.3346(8) |
| c/Å | 18.6104(9) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2442.3(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.633 |
| μ/mm$^{-1}$ | 4.920 |
| F(000) | 1184.0 |
| Crystal size/mm$^3$ | 0.32 × 0.21 × 0.18 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4382; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 7.158 to 55.988° |
| Completeness to theta | 0.991 |
| Index ranges | -12 ≤ h ≤ 10, -12 ≤ k ≤ 18, -18 ≤ l ≤ 24 |
| Reflections collected | 12514 |
| Independent reflections | 5861 [$R_{int}$ = 0.0386, $R_{sigma}$ = 0.0528] |
| Data/restraints/parameters | 5861/48/270 |
| Goodness-of-fit on F$^2$ | 1.015 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0302, $wR_2$ = 0.0602 |
| Final R indexes [all data] | $R_1$ = 0.0342, $wR_2$ = 0.0615 |

| | |
|---|---|
| Largest diff. peak/hole / e Å$^{-3}$ | 1.65/-0.57 |
| Flack parameter | 0.398(10) |

***Table 2:*** Bond lengths for **21.1c**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4818(15) | Si2 | C12 | 1.874(9) |
| W | C13 | 2.014(7) | O1 | C1 | 1.475(9) |
| W | C14 | 2.054(8) | O1 | C1S | 1.59(4) |
| W | C15 | 2.053(8) | O2 | C13 | 1.140(8) |
| W | C16 | 2.046(8) | O3 | C14 | 1.130(9) |
| W | C17 | 2.041(6) | O4 | C15 | 1.139(9) |
| P | O1 | 1.668(5) | O5 | C16 | 1.127(9) |
| P | C2 | 1.846(6) | O6 | C17 | 1.137(7) |
| P | C6 | 1.808(6) | C1 | C2 | 1.536(11) |
| Si1 | C6 | 1.907(6) | C1 | C3 | 1.522(13) |
| Si1 | C7 | 1.860(7) | C2 | C1S | 1.54(4) |
| Si1 | C8 | 1.871(8) | C3 | C4 | 1.522(13) |
| Si1 | C9 | 1.863(8) | C3 | C5 | 1.546(12) |
| Si2 | C6 | 1.922(6) | C4 | C3S | 1.64(4) |
| Si2 | C10 | 1.857(8) | C5 | C3S | 1.49(4) |
| Si2 | C11 | 1.852(9) | C1S | C3S | 1.39(6) |

***Table 3:*** Bond angles for **21.1c**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C13 | W | P | 177.1(3) | C11 | Si2 | C6 | 107.5(4) |
| C13 | W | C14 | 89.4(3) | C11 | Si2 | C10 | 111.0(4) |
| C13 | W | C15 | 90.7(3) | C11 | Si2 | C12 | 107.0(5) |
| C13 | W | C16 | 91.2(3) | C12 | Si2 | C6 | 112.3(3) |
| C13 | W | C17 | 89.2(3) | C1 | O1 | P | 93.4(4) |
| C14 | W | P | 87.94(17) | C1S | O1 | P | 95.1(13) |
| C15 | W | P | 90.42(18) | O1 | C1 | C2 | 96.9(6) |
| C15 | W | C14 | 90.0(3) | O1 | C1 | C3 | 111.3(7) |
| C16 | W | P | 91.4(2) | C3 | C1 | C2 | 118.0(7) |
| C16 | W | C14 | 178.0(4) | C1 | C2 | P | 84.8(4) |
| C16 | W | C15 | 91.8(4) | C1S | C2 | P | 89.8(14) |
| C17 | W | P | 89.66(17) | C1 | C3 | C5 | 107.7(8) |
| C17 | W | C14 | 88.9(3) | C4 | C3 | C1 | 110.5(7) |
| C17 | W | C15 | 178.9(4) | C4 | C3 | C5 | 112.3(7) |
| C17 | W | C16 | 89.3(4) | P | C6 | Si1 | 116.0(4) |
| O1 | P | W | 114.59(15) | P | C6 | Si2 | 114.0(3) |
| O1 | P | C2 | 79.6(3) | Si1 | C6 | Si2 | 116.5(3) |
| O1 | P | C6 | 107.0(3) | O2 | C13 | W | 177.4(8) |
| C2 | P | W | 118.7(2) | O3 | C14 | W | 179.5(7) |
| C6 | P | W | 118.6(2) | O4 | C15 | W | 179.4(9) |
| C6 | P | C2 | 111.5(3) | O5 | C16 | W | 178.0(7) |
| C7 | Si1 | C6 | 108.8(3) | O6 | C17 | W | 177.7(7) |
| C7 | Si1 | C8 | 109.2(4) | C2 | C1S | O1 | 92(2) |
| C7 | Si1 | C9 | 106.8(4) | C3S | C1S | O1 | 110(3) |
| C8 | Si1 | C6 | 114.2(3) | C3S | C1S | C2 | 119(4) |
| C9 | Si1 | C6 | 109.4(4) | C5 | C3S | C4 | 109(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C9 | Si1 | C8 | 108.1(4) | C1S | C3S | C4 | 108(3) |
| C10 | Si2 | C6 | 111.7(4) | C1S | C3S | C5 | 113(4) |
| C10 | Si2 | C12 | 107.3(4) | | | | |

***Table 4:*** Torsion angles for **21.1c**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | 100.7(4) | O1 | C1 | C3 | C4 | 57.0(11) |
| W | P | O1 | C1S | 129.9(16) | O1 | C1 | C3 | C5 | 180.0(6) |
| W | P | C2 | C1 | -96.9(4) | O1 | C1S | C3S | C4 | -64(4) |
| W | P | C2 | C1S | -125.8(17) | O1 | C1S | C3S | C5 | 176(2) |
| W | P | C6 | Si1 | 121.5(3) | C2 | P | O1 | C1 | -16.2(4) |
| W | P | C6 | Si2 | -99.1(3) | C2 | P | O1 | C1S | 13.0(17) |
| P | O1 | C1 | C2 | 19.4(5) | C2 | P | C6 | Si1 | -95.2(4) |
| P | O1 | C1 | C3 | 143.1(7) | C2 | P | C6 | Si2 | 44.2(4) |
| P | O1 | C1S | C2 | -15.4(19) | C2 | C1 | C3 | C4 | 167.7(7) |
| P | O1 | C1S | C3S | -137(3) | C2 | C1 | C3 | C5 | -69.4(10) |
| P | C2 | C1S | O1 | 13.8(17) | C2 | C1S | C3S | C4 | -168(2) |
| P | C2 | C1S | C3S | 128(4) | C2 | C1S | C3S | C5 | 72(5) |
| O1 | P | C2 | C1 | 15.6(4) | C3 | C1 | C2 | P | -136.1(8) |
| O1 | P | C2 | C1S | -13.3(17) | C6 | P | O1 | C1 | -125.7(4) |
| O1 | P | C6 | Si1 | -9.9(4) | C6 | P | O1 | C1S | -96.5(17) |
| O1 | P | C6 | Si2 | 129.5(3) | C6 | P | C2 | C1 | 119.9(5) |
| O1 | C1 | C2 | P | -17.5(5) | C6 | P | C2 | C1S | 91.0(17) |

## 12.13 Pentacarbonyl{4-(chloromethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1e]

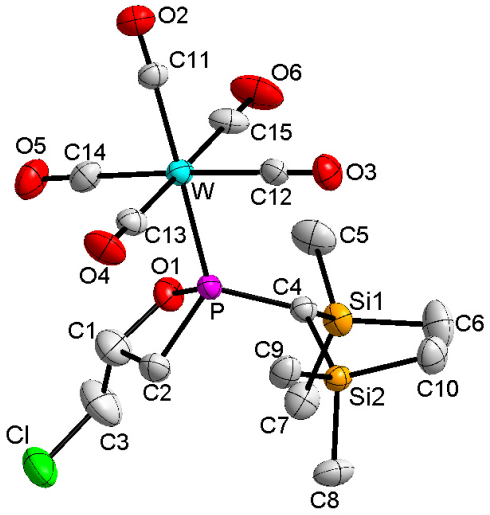


***Table 1:*** Crystal data and structure refinement for **21.1e**.

| | |
|---|---|
| Identification code | GSTR324, AKY-306 // GXray3114 |
| Crystal Habitus | colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{15}H_{24}ClO_6PSi_2W$ |
| Moiety formula | C15 H24 Cl O6 P Si2 W |
| Formula weight | 606.79 |
| Temperature/K | 123(2) |

| | |
|---|---|
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 8.7534(3) |
| b/Å | 10.7464(4) |
| c/Å | 13.5918(5) |
| α/° | 102.8140(18) |
| β/° | 93.438(2) |
| γ/° | 113.6090(18) |
| Volume/Å$^3$ | 1126.40(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.789 |
| μ/mm$^{-1}$ | 5.449 |
| F(000) | 592.0 |
| Crystal size/mm$^3$ | 0.08 × 0.06 × 0.02 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.6697; 0.8988 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.56 to 56° |
| Completeness to theta | 0.998 |
| Index ranges | -11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17 |
| Reflections collected | 37295 |
| Independent reflections | 5438 [$R_{int}$ = 0.0757] |
| Data/restraints/parameters | 5438/5/241 |
| Goodness-of-fit on F$^2$ | 0.993 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0309, $wR_2$ = 0.0658 |
| Final R indexes [all data] | $R_1$ = 0.0427, $wR_2$ = 0.0687 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.44/-1.49 |

***Table 2:*** Bond lengths for **21.1e**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C2 | C1 | 1.527(7) | C10 | Si2 | 1.858(4) |
| C2 | P | 1.835(4) | C11 | O2 | 1.144(5) |
| C1 | C3 | 1.474(7) | C11 | W | 2.027(4) |
| C1 | O1 | 1.527(6) | C12 | O3 | 1.145(5) |
| C1 | P | 2.320(5) | C12 | W | 2.036(4) |
| C3 | Cl | 1.753(6) | C13 | O4 | 1.140(5) |
| C4 | P | 1.813(4) | C13 | W | 2.046(4) |
| C4 | Si1 | 1.906(4) | C14 | O5 | 1.156(5) |
| C4 | Si2 | 1.922(4) | C14 | W | 2.031(5) |
| C5 | Si1 | 1.867(5) | C15 | O6 | 1.148(5) |
| C6 | Si1 | 1.869(5) | C15 | W | 2.035(4) |
| C7 | Si1 | 1.859(5) | O1 | P | 1.693(3) |
| C8 | Si2 | 1.869(4) | P | W | 2.4726(10) |
| C9 | Si2 | 1.880(4) | | | |

***Table 3:*** Bond angles for **21.1e**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C1 | C2 | P | 86.8(3) | C7 | Si1 | C5 | 109.1(2) |
| C3 | C1 | C2 | 118.8(5) | C7 | Si1 | C6 | 109.1(2) |
| C3 | C1 | O1 | 107.9(4) | C5 | Si1 | C6 | 107.3(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2 | C1 | O1 | 96.5(3) | C7 | Si1 | C4 | 113.87(19) |
| C3 | C1 | P | 138.3(4) | C5 | Si1 | C4 | 109.4(2) |
| C2 | C1 | P | 52.2(2) | C6 | Si1 | C4 | 107.8(2) |
| O1 | C1 | P | 46.82(18) | C10 | Si2 | C8 | 109.4(2) |
| C1 | C3 | Cl | 109.6(4) | C10 | Si2 | C9 | 106.7(2) |
| P | C4 | Si1 | 116.6(2) | C8 | Si2 | C9 | 109.5(2) |
| P | C4 | Si2 | 113.28(19) | C10 | Si2 | C4 | 108.00(19) |
| Si1 | C4 | Si2 | 117.1(2) | C8 | Si2 | C4 | 111.91(19) |
| O2 | C11 | W | 177.2(4) | C9 | Si2 | C4 | 111.13(18) |
| O3 | C12 | W | 179.6(4) | C11 | W | C14 | 91.10(17) |
| O4 | C13 | W | 178.2(4) | C11 | W | C15 | 89.70(16) |
| O5 | C14 | W | 179.5(4) | C14 | W | C15 | 91.00(18) |
| O6 | C15 | W | 179.6(5) | C11 | W | C12 | 90.71(16) |
| C1 | O1 | P | 92.0(3) | C14 | W | C12 | 177.95(16) |
| O1 | P | C4 | 108.25(17) | C15 | W | C12 | 89.97(17) |
| O1 | P | C2 | 80.35(18) | C11 | W | C13 | 89.17(16) |
| C4 | P | C2 | 111.42(19) | C14 | W | C13 | 90.03(17) |
| O1 | P | C1 | 41.14(17) | C15 | W | C13 | 178.49(16) |
| C4 | P | C1 | 125.9(2) | C12 | W | C13 | 89.04(16) |
| C2 | P | C1 | 41.1(2) | C11 | W | P | 175.57(11) |
| O1 | P | W | 112.31(11) | C14 | W | P | 85.77(13) |
| C4 | P | W | 117.65(13) | C15 | W | P | 87.22(12) |
| C2 | P | W | 120.31(16) | C12 | W | P | 92.48(12) |
| C1 | P | W | 115.86(15) | C13 | W | P | 93.96(12) |

***Table 4:*** Torsion angles for **21.1e**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| P | C2 | C1 | C3 | 130.7(5) | O2 | C11 | W | C15 | 74(7) |
| P | C2 | C1 | O1 | 16.1(3) | O2 | C11 | W | C12 | 164(7) |
| C2 | C1 | C3 | Cl | 69.8(6) | O2 | C11 | W | C13 | -107(7) |
| O1 | C1 | C3 | Cl | 178.1(4) | O2 | C11 | W | P | 28(8) |
| P | C1 | C3 | Cl | 134.0(5) | O5 | C14 | W | C11 | -92(43) |
| C3 | C1 | O1 | P | -140.7(4) | O5 | C14 | W | C15 | 178(100) |
| C2 | C1 | O1 | P | -17.5(3) | O5 | C14 | W | C12 | 60(44) |
| C1 | O1 | P | C4 | 124.1(3) | O5 | C14 | W | C13 | -3(43) |
| C1 | O1 | P | C2 | 14.6(3) | O5 | C14 | W | P | 91(43) |
| C1 | O1 | P | W | -104.3(2) | O6 | C15 | W | C11 | 119(85) |
| Si1 | C4 | P | O1 | 9.7(3) | O6 | C15 | W | C14 | -150(85) |
| Si2 | C4 | P | O1 | -130.63(19) | O6 | C15 | W | C12 | 28(85) |
| Si1 | C4 | P | C2 | 96.3(3) | O6 | C15 | W | C13 | 77(86) |
| Si2 | C4 | P | C2 | -44.1(3) | O6 | C15 | W | P | -64(85) |
| Si1 | C4 | P | C1 | 52.0(3) | O3 | C12 | W | C11 | 154(65) |
| Si2 | C4 | P | C1 | -88.4(3) | O3 | C12 | W | C14 | 2(68) |
| Si1 | C4 | P | W | -118.89(18) | O3 | C12 | W | C15 | -116(65) |
| Si2 | C4 | P | W | 100.76(18) | O3 | C12 | W | C13 | 65(65) |
| C1 | C2 | P | O1 | -14.6(3) | O3 | C12 | W | P | -29(65) |
| C1 | C2 | P | C4 | -120.6(3) | O4 | C13 | W | C11 | -13(13) |
| C1 | C2 | P | W | 95.6(3) | O4 | C13 | W | C14 | -104(13) |
| C3 | C1 | P | O1 | 65.1(6) | O4 | C13 | W | C15 | 29(17) |
| C2 | C1 | P | O1 | 157.7(4) | O4 | C13 | W | C12 | 78(13) |
| C3 | C1 | P | C4 | -10.9(7) | O4 | C13 | W | P | 170(13) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C2 | C1 | P | C4 | 81.7(4) | O1 | P | W | C11 | -16.5(15) |
| O1 | C1 | P | C4 | -76.0(3) | C4 | P | W | C11 | 110.2(15) |
| C3 | C1 | P | C2 | -92.6(7) | C2 | P | W | C11 | -108.2(15) |
| O1 | C1 | P | C2 | -157.7(4) | C1 | P | W | C11 | -61.6(15) |
| C3 | C1 | P | W | 160.1(6) | O1 | P | W | C14 | 28.56(17) |
| C2 | C1 | P | W | -107.3(3) | C4 | P | W | C14 | 155.22(18) |
| O1 | C1 | P | W | 94.9(2) | C2 | P | W | C14 | -63.2(2) |
| P | C4 | Si1 | C7 | -69.4(3) | C1 | P | W | C14 | -16.5(2) |
| Si2 | C4 | Si1 | C7 | 69.4(3) | O1 | P | W | C15 | -62.65(18) |
| P | C4 | Si1 | C5 | 52.9(3) | C4 | P | W | C15 | 64.01(19) |
| Si2 | C4 | Si1 | C5 | -168.2(2) | C2 | P | W | C15 | -154.4(2) |
| P | C4 | Si1 | C6 | 169.3(3) | C1 | P | W | C15 | -107.8(2) |
| Si2 | C4 | Si1 | C6 | -51.8(3) | O1 | P | W | C12 | -152.50(16) |
| P | C4 | Si2 | C10 | -145.0(2) | C4 | P | W | C12 | -25.83(18) |
| Si1 | C4 | Si2 | C10 | 74.8(3) | C2 | P | W | C12 | 115.8(2) |
| P | C4 | Si2 | C8 | 94.4(3) | C1 | P | W | C12 | 162.39(19) |
| Si1 | C4 | Si2 | C8 | -45.7(3) | O1 | P | W | C13 | 118.29(17) |
| P | C4 | Si2 | C9 | -28.3(3) | C4 | P | W | C13 | -115.04(18) |
| Si1 | C4 | Si2 | C9 | -168.4(2) | C2 | P | W | C13 | 26.6(2) |
| O2 | C11 | W | C14 | -17(7) | C1 | P | W | C13 | 73.18(19) |

## 12.14 Pentacarbonyl{4-epoxy-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1f]

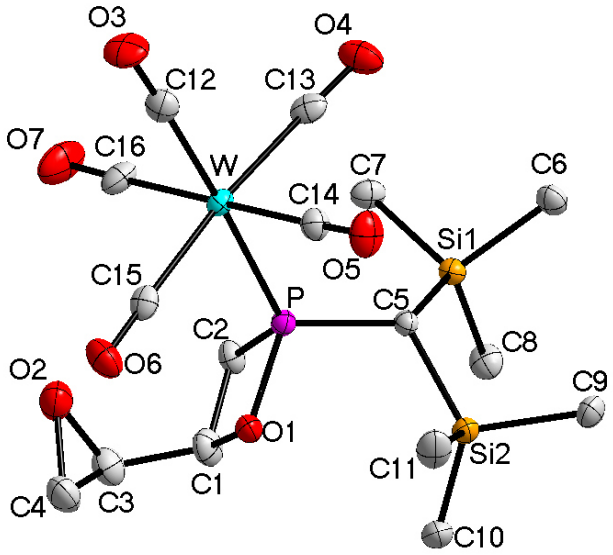


***Table 1:*** Crystal data and structure refinement for **21.1f**.

| | |
|---|---|
| Identification code | GSTR382, AKY-425 // GXraycollect |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{16}H_{25}O_7PSi_2W$ |
| Formula weight | 600.36 |
| Temperature/K | 123.0 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.3903(2) |
| b/Å | 11.0600(2) |
| c/Å | 21.8725(4) |
| α/° | 90.00 |

| | |
|---|---|
| β/° | 90.00 |
| γ/° | 90.00 |
| Volume/Å$^3$ | 2271.61(8) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.755 |
| μ/mm$^{-1}$ | 5.293 |
| F(000) | 1176.0 |
| Crystal size/mm$^3$ | 0.28 × 0.22 × 0.12 |
| Absorption correction | multi-scan |
| Tmin; Tmax | 0.29346; 0.64943 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.7 to 55.98° |
| Completeness to theta | 0.997 |
| Index ranges | -10 ≤ h ≤ 12, -13 ≤ k ≤ 14, -28 ≤ l ≤ 28 |
| Reflections collected | 26317 |
| Independent reflections | 5435 [$R_{int}$ = 0.0630, $R_{sigma}$ = 0.0391] |
| Data/restraints/parameters | 5435/0/250 |
| Goodness-of-fit on F$^2$ | 1.053 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0226, $wR_2$ = 0.0494 |
| Final R indexes [all data] | $R_1$ = 0.0245, $wR_2$ = 0.0499 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.59/-1.32 |
| Flack parameter | -0.005(6) |

***Table 2:*** Bond lengths for **21.1f**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4914(10) | Si2 | C9 | 1.861(4) |
| W | C12 | 2.009(4) | Si2 | C10 | 1.865(4) |
| W | C13 | 2.045(4) | Si2 | C11 | 1.875(4) |
| W | C14 | 2.041(4) | O1 | C1 | 1.474(5) |
| W | C15 | 2.050(4) | O2 | C3 | 1.451(5) |
| W | C16 | 2.054(4) | O2 | C4 | 1.462(5) |
| P | O1 | 1.679(3) | O3 | C12 | 1.145(5) |
| P | C2 | 1.841(4) | O5 | C14 | 1.138(5) |
| P | C5 | 1.809(4) | O4 | C13 | 1.136(5) |
| Si1 | C5 | 1.916(4) | O6 | C15 | 1.142(5) |
| Si1 | C6 | 1.860(4) | O7 | C16 | 1.130(5) |
| Si1 | C7 | 1.877(4) | C2 | C1 | 1.532(6) |
| Si1 | C8 | 1.879(4) | C1 | C3 | 1.487(6) |
| Si2 | C5 | 1.915(4) | C3 | C4 | 1.465(6) |

***Table 3:*** Bond angles for **21.1f**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C12 | W | P | 176.64(13) | C8 | Si1 | C5 | 112.08(18) |
| C12 | W | C13 | 90.28(17) | C9 | Si2 | C5 | 108.67(17) |
| C12 | W | C14 | 90.05(17) | C9 | Si2 | C10 | 109.2(2) |
| C12 | W | C15 | 92.05(16) | C9 | Si2 | C11 | 106.7(2) |
| C12 | W | C16 | 86.91(17) | C10 | Si2 | C5 | 113.42(18) |
| C13 | W | P | 90.99(11) | C10 | Si2 | C11 | 109.7(2) |
| C13 | W | C15 | 173.26(18) | C11 | Si2 | C5 | 108.91(18) |
| C13 | W | C16 | 95.34(18) | C1 | O1 | P | 95.4(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C14 | W | P | 93.13(12) | C3 | O2 | C4 | 60.4(3) |
| C14 | W | C13 | 86.63(17) | C1 | C2 | P | 87.2(3) |
| C14 | W | C15 | 87.04(16) | O1 | C1 | C2 | 97.6(3) |
| C14 | W | C16 | 176.39(17) | O1 | C1 | C3 | 113.1(4) |
| C15 | W | P | 87.04(11) | C3 | C1 | C2 | 114.7(4) |
| C15 | W | C16 | 91.11(17) | O2 | C3 | C1 | 114.9(4) |
| C16 | W | P | 89.87(12) | O2 | C3 | C4 | 60.2(3) |
| O1 | P | W | 114.27(10) | C4 | C3 | C1 | 122.7(4) |
| O1 | P | C2 | 79.79(16) | O2 | C4 | C3 | 59.4(3) |
| O1 | P | C5 | 108.86(15) | P | C5 | Si1 | 115.68(19) |
| C2 | P | W | 123.86(14) | P | C5 | Si2 | 115.00(19) |
| C5 | P | W | 115.35(12) | Si2 | C5 | Si1 | 116.37(18) |
| C5 | P | C2 | 109.03(18) | O3 | C12 | W | 177.4(4) |
| C6 | Si1 | C5 | 106.87(17) | O4 | C13 | W | 175.6(4) |
| C6 | Si1 | C7 | 106.68(18) | O5 | C14 | W | 177.2(4) |
| C6 | Si1 | C8 | 110.73(19) | O6 | C15 | W | 177.4(4) |
| C7 | Si1 | C5 | 112.43(17) | O7 | C16 | W | 176.9(4) |
| C7 | Si1 | C8 | 107.94(19) | | | | |

***Table 4:*** Torsion angles for **21.1f**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | 121.2(2) | C11 | Si2 | C5 | P | -56.6(3) |
| W | P | C2 | C1 | -111.0(2) | C11 | Si2 | C5 | Si1 | 163.5(2) |
| W | P | C5 | Si1 | -102.11(18) | C12 | W | P | O1 | -79(2) |
| W | P | C5 | Si2 | 117.73(16) | C12 | W | P | C2 | 15(2) |
| P | W | C12 | O3 | 1(10) | C12 | W | P | C5 | 154(2) |
| P | W | C13 | O4 | -102(5) | C12 | W | C13 | O4 | 81(5) |
| P | W | C14 | O5 | -178(100) | C12 | W | C14 | O5 | 1(8) |
| P | W | C15 | O6 | 109(8) | C12 | W | C15 | O6 | -75(8) |
| P | W | C16 | O7 | 168(8) | C12 | W | C16 | O7 | -11(8) |
| P | O1 | C1 | C2 | 1.8(3) | C13 | W | P | O1 | 168.86(16) |
| P | O1 | C1 | C3 | -119.3(3) | C13 | W | P | C2 | -97.2(2) |
| P | C2 | C1 | O1 | -1.6(3) | C13 | W | P | C5 | 41.57(18) |
| P | C2 | C1 | C3 | 118.2(4) | C13 | W | C12 | O3 | 113(9) |
| O1 | P | C2 | C1 | 1.4(2) | C13 | W | C14 | O5 | 91(8) |
| O1 | P | C5 | Si1 | 127.92(19) | C13 | W | C15 | O6 | 35(9) |
| O1 | P | C5 | Si2 | -12.2(2) | C13 | W | C16 | O7 | -101(8) |
| O1 | C1 | C3 | O2 | 49.9(5) | C14 | W | P | O1 | 82.19(16) |
| O1 | C1 | C3 | C4 | -19.4(6) | C14 | W | P | C2 | 176.1(2) |
| C2 | P | O1 | C1 | -1.5(2) | C14 | W | P | C5 | -45.10(17) |
| C2 | P | C5 | Si1 | 42.5(3) | C14 | W | C12 | O3 | -161(9) |
| C2 | P | C5 | Si2 | -97.6(2) | C14 | W | C13 | O4 | -9(5) |
| C2 | C1 | C3 | O2 | -60.8(5) | C14 | W | C15 | O6 | 15(8) |
| C2 | C1 | C3 | C4 | -130.1(4) | C14 | W | C16 | O7 | 22(10) |
| C1 | C3 | C4 | O2 | 102.1(5) | C15 | W | P | O1 | -4.69(15) |
| C4 | O2 | C3 | C1 | -114.8(4) | C15 | W | P | C2 | 89.23(19) |
| C5 | P | O1 | C1 | -108.2(2) | C15 | W | P | C5 | -131.98(17) |
| C5 | P | C2 | C1 | 108.0(3) | C15 | W | C12 | O3 | -74(9) |
| C6 | Si1 | C5 | P | 137.3(2) | C15 | W | C13 | O4 | -29(6) |
| C6 | Si1 | C5 | Si2 | -83.1(2) | C15 | W | C14 | O5 | -91(8) |
| C7 | Si1 | C5 | P | 20.6(3) | C15 | W | C16 | O7 | 81(8) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C7 | Si1 | C5 | Si2 | 160.19(19) | C16 | W | P | O1 | -95.80(17) |
| C8 | Si1 | C5 | P | -101.2(2) | C16 | W | P | C2 | -1.9(2) |
| C8 | Si1 | C5 | Si2 | 38.4(3) | C16 | W | P | C5 | 136.91(19) |
| C9 | Si2 | C5 | P | -172.5(2) | C16 | W | C12 | O3 | 17(9) |
| C9 | Si2 | C5 | Si1 | 47.7(3) | C16 | W | C13 | O4 | 168(5) |
| C10 | Si2 | C5 | P | 65.9(3) | C16 | W | C14 | O5 | -32(10) |
| C10 | Si2 | C5 | Si1 | -74.0(2) | C16 | W | C15 | O6 | -162(8) |

## 12.15 Pentacarbonyl{4-(trifluoromethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [21.1g]

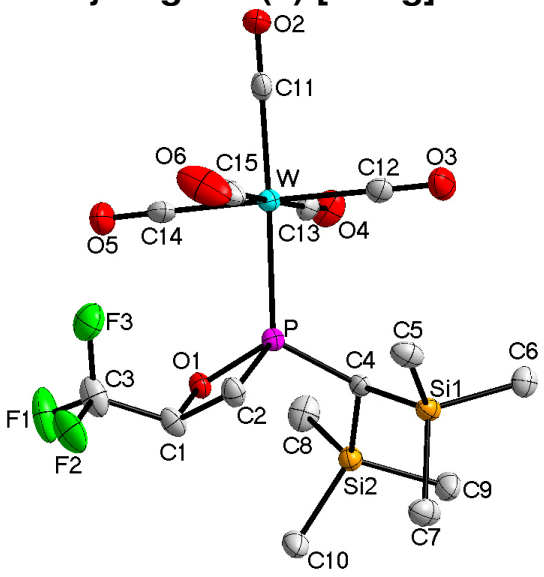


***Table 1:*** Crystal data and structure refinement for **21.1g**.

| | |
|---|---|
| Identification code | GSTR344, AKY-360 //GXRay3313 |
| Crystal Habitus | colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{15}H_{22}F_3O_6PSi_2W$ |
| Moiety formula | C15 H22 F3 O6 P Si2 W |
| Formula weight | 626.33 |
| Temperature/K | 123(2) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.3854(3) |
| b/Å | 11.0383(2) |
| c/Å | 22.0540(6) |
| α/° | 90.00 |
| β/° | 90.00 |
| γ/° | 90.00 |
| Volume/Å$^3$ | 2284.77(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.821 |
| μ/mm$^{-1}$ | 5.281 |
| F(000) | 1216.0 |
| Crystal size/mm$^3$ | 0.28 × 0.18 × 0.06 |
| Absorption correction | Multi-Scan |
| Tmin; Tmax | 0.3194; 0.7423 |
| Radiation | MoKα (λ = 0.71073) |

| | |
|---|---|
| 2Θ range for data collection/° | 5.22 to 56° |
| Completeness to theta | 0.993 |
| Index ranges | -11 ≤ h ≤ 12, -11 ≤ k ≤ 14, -29 ≤ l ≤ 28 |
| Reflections collected | 23791 |
| Independent reflections | 5449 [$R_{int}$ = 0.0529, $R_{sigma}$ = 0.0529] |
| Data/restraints/parameters | 5449/8/260 |
| Goodness-of-fit on $F^2$ | 1.017 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0280, $wR_2$ = 0.0484 |
| Final R indexes [all data] | $R_1$ = 0.0340, $wR_2$ = 0.0500 |
| Largest diff. peak/hole / e $Å^{-3}$ | 1.40/-1.80 |
| Flack parameter | 0.646(6) |

***Table 2:*** Bond lengths for **21.1g**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | O1 | 1.446(5) | C9 | Si2 | 1.859(4) |
| C1 | C3 | 1.499(6) | C10 | Si2 | 1.863(4) |
| C1 | C2 | 1.531(6) | C11 | O2 | 1.150(5) |
| C1 | P | 2.336(4) | C11 | W | 2.017(4) |
| C2 | P | 1.858(4) | C12 | O3 | 1.138(5) |
| C3 | F2 | 1.332(5) | C12 | W | 2.047(4) |
| C3 | F1 | 1.339(5) | C13 | O4 | 1.148(5) |
| C3 | F3 | 1.342(6) | C13 | W | 2.036(5) |
| C4 | P | 1.802(4) | C14 | O5 | 1.145(5) |
| C4 | Si2 | 1.911(4) | C14 | W | 2.046(5) |
| C4 | Si1 | 1.919(4) | C15 | O6 | 1.125(5) |
| C5 | Si1 | 1.875(4) | C15 | W | 2.048(5) |
| C6 | Si1 | 1.854(4) | O1 | P | 1.687(3) |
| C7 | Si1 | 1.872(4) | P | W | 2.4672(11) |
| C8 | Si2 | 1.868(5) | | | |

***Table 3:*** Bond angles for **21.1g**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| O1 | C1 | C3 | 110.7(4) | C2 | P | W | 124.24(15) |
| O1 | C1 | C2 | 98.5(3) | C1 | P | W | 128.06(13) |
| C3 | C1 | C2 | 114.1(4) | C6 | Si1 | C7 | 111.1(2) |
| O1 | C1 | P | 45.92(16) | C6 | Si1 | C5 | 107.6(2) |
| C3 | C1 | P | 124.4(3) | C7 | Si1 | C5 | 107.0(2) |
| C2 | C1 | P | 52.6(2) | C6 | Si1 | C4 | 106.98(19) |
| C1 | C2 | P | 86.6(3) | C7 | Si1 | C4 | 111.86(19) |
| F2 | C3 | F1 | 107.1(4) | C5 | Si1 | C4 | 112.29(18) |
| F2 | C3 | F3 | 107.7(3) | C9 | Si2 | C10 | 110.1(2) |
| F1 | C3 | F3 | 107.3(4) | C9 | Si2 | C8 | 107.3(2) |
| F2 | C3 | C1 | 110.0(4) | C10 | Si2 | C8 | 109.3(2) |
| F1 | C3 | C1 | 111.5(4) | C9 | Si2 | C4 | 107.64(18) |
| F3 | C3 | C1 | 113.0(4) | C10 | Si2 | C4 | 113.16(19) |
| P | C4 | Si2 | 115.9(2) | C8 | Si2 | C4 | 109.2(2) |
| P | C4 | Si1 | 115.2(2) | C11 | W | C13 | 90.98(17) |
| Si2 | C4 | Si1 | 116.6(2) | C11 | W | C14 | 90.84(17) |
| O2 | C11 | W | 178.5(4) | C13 | W | C14 | 88.19(18) |
| O3 | C12 | W | 176.7(4) | C11 | W | C12 | 89.62(17) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O4 | C13 | W | 177.4(4) | C13 | W | C12 | 87.15(18) |
| O5 | C14 | W | 177.4(4) | C14 | W | C12 | 175.32(19) |
| O6 | C15 | W | 178.7(5) | C11 | W | C15 | 88.02(19) |
| C1 | O1 | P | 96.1(2) | C13 | W | C15 | 178.5(2) |
| O1 | P | C4 | 108.24(16) | C14 | W | C15 | 90.8(2) |
| O1 | P | C2 | 78.83(17) | C12 | W | C15 | 93.9(2) |
| C4 | P | C2 | 108.5(2) | C11 | W | P | 177.25(12) |
| O1 | P | C1 | 37.99(14) | C13 | W | P | 91.46(13) |
| C4 | P | C1 | 114.83(18) | C14 | W | P | 87.98(12) |
| C2 | P | C1 | 40.86(17) | C12 | W | P | 91.76(12) |
| O1 | P | W | 114.28(11) | C15 | W | P | 89.52(14) |
| C4 | P | W | 116.32(13) | | | | |

***Table 4:*** Torsion angles for **21.1g**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | C2 | P | 1.4(3) | P | C4 | Si2 | C8 | 55.2(3) |
| C3 | C1 | C2 | P | -115.8(4) | Si1 | C4 | Si2 | C8 | -164.2(2) |
| O1 | C1 | C3 | F2 | 179.5(3) | O2 | C11 | W | C13 | -178(100) |
| C2 | C1 | C3 | F2 | -70.5(5) | O2 | C11 | W | C14 | 94(15) |
| P | C1 | C3 | F2 | -130.5(3) | O2 | C11 | W | C12 | -90(15) |
| O1 | C1 | C3 | F1 | 60.9(5) | O2 | C11 | W | C15 | 3(15) |
| C2 | C1 | C3 | F1 | 170.8(4) | O2 | C11 | W | P | 30(17) |
| P | C1 | C3 | F1 | 110.9(4) | O4 | C13 | W | C11 | -25(8) |
| O1 | C1 | C3 | F3 | -60.2(5) | O4 | C13 | W | C14 | 66(8) |
| C2 | C1 | C3 | F3 | 49.8(5) | O4 | C13 | W | C12 | -115(8) |
| P | C1 | C3 | F3 | -10.2(6) | O4 | C13 | W | C15 | 21(14) |
| C3 | C1 | O1 | P | 118.3(3) | O4 | C13 | W | P | 154(8) |
| C2 | C1 | O1 | P | -1.6(3) | O5 | C14 | W | C11 | 92(9) |
| C1 | O1 | P | C4 | 107.2(3) | O5 | C14 | W | C13 | 1(9) |
| C1 | O1 | P | C2 | 1.3(3) | O5 | C14 | W | C12 | -4(10) |
| C1 | O1 | P | W | -121.4(2) | O5 | C14 | W | C15 | -180(100) |
| Si2 | C4 | P | O1 | 10.3(3) | O5 | C14 | W | P | -90(9) |
| Si1 | C4 | P | O1 | -130.9(2) | O3 | C12 | W | C11 | -77(7) |
| Si2 | C4 | P | C2 | 94.2(3) | O3 | C12 | W | C13 | 14(7) |
| Si1 | C4 | P | C2 | -46.9(3) | O3 | C12 | W | C14 | 19(9) |
| Si2 | C4 | P | C1 | 50.6(3) | O3 | C12 | W | C15 | -165(7) |
| Si1 | C4 | P | C1 | -90.5(2) | O3 | C12 | W | P | 105(7) |
| Si2 | C4 | P | W | -119.99(18) | O6 | C15 | W | C11 | 38(19) |
| Si1 | C4 | P | W | 98.9(2) | O6 | C15 | W | C13 | -8(24) |
| C1 | C2 | P | O1 | -1.2(2) | O6 | C15 | W | C14 | -52(19) |
| C1 | C2 | P | C4 | -106.9(3) | O6 | C15 | W | C12 | 128(19) |
| C1 | C2 | P | W | 110.7(2) | O6 | C15 | W | P | -140(19) |
| C3 | C1 | P | O1 | -86.2(4) | O1 | P | W | C11 | 74(3) |
| C2 | C1 | P | O1 | 178.1(4) | C4 | P | W | C11 | -158(3) |
| O1 | C1 | P | C4 | -88.2(3) | C2 | P | W | C11 | -19(3) |
| C3 | C1 | P | C4 | -174.4(3) | C1 | P | W | C11 | 33(3) |
| C2 | C1 | P | C4 | 89.9(3) | O1 | P | W | C13 | -78.33(16) |
| O1 | C1 | P | C2 | -178.1(4) | C4 | P | W | C13 | 48.98(19) |
| C3 | C1 | P | C2 | 95.7(4) | C2 | P | W | C13 | -171.2(2) |
| O1 | C1 | P | W | 81.1(2) | C1 | P | W | C13 | -120.19(19) |
| C3 | C1 | P | W | -5.0(4) | O1 | P | W | C14 | 9.80(17) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C2 | C1 | P | W | -100.8(3) | C4 | P | W | C14 | 137.1(2) |
| P | C4 | Si1 | C6 | -135.9(2) | C2 | P | W | C14 | -83.1(2) |
| Si2 | C4 | Si1 | C6 | 83.3(2) | C1 | P | W | C14 | -32.1(2) |
| P | C4 | Si1 | C7 | 102.2(3) | O1 | P | W | C12 | -165.53(16) |
| Si2 | C4 | Si1 | C7 | -38.6(3) | C4 | P | W | C12 | -38.21(19) |
| P | C4 | Si1 | C5 | -18.1(3) | C2 | P | W | C12 | 101.6(2) |
| Si2 | C4 | Si1 | C5 | -158.9(2) | C1 | P | W | C12 | 152.6(2) |
| P | C4 | Si2 | C9 | 171.4(2) | O1 | P | W | C15 | 100.59(19) |
| Si1 | C4 | Si2 | C9 | -48.0(3) | C4 | P | W | C15 | -132.1(2) |
| P | C4 | Si2 | C10 | -66.8(3) | C2 | P | W | C15 | 7.7(2) |
| Si1 | C4 | Si2 | C10 | 73.8(3) | C1 | P | W | C15 | 58.7(2) |

## 12.16 Pentacarbonyl{4,4-dimethyl-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [25.1a]

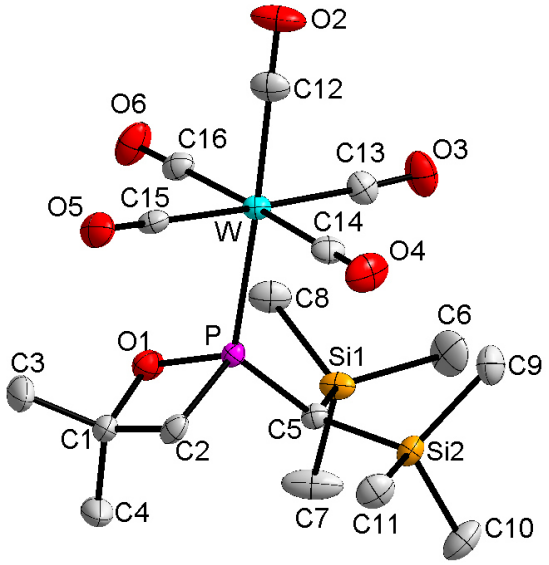


***Table 1:*** Crystal data and structure refinement for **25.1a**.

| | |
|---|---|
| Identification code | GSTR390, AKY-469-F2 // GXray3852f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{16}H_{27}O_6PSi_2W$ |
| Formula weight | 586.37 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 10.3369(6) |
| b/Å | 21.4329(12) |
| c/Å | 10.6585(6) |
| α/° | 90 |
| β/° | 98.7415(18) |
| γ/° | 90 |
| Volume/Å$^3$ | 2334.0(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.669 |
| μ/mm$^{-1}$ | 5.146 |
| F(000) | 1152.0 |
| Crystal size/mm$^3$ | 0.14 × 0.12 × 0.03 |
| Absorption correction | empirical |

| | |
|---|---|
| Tmin; Tmax | 0.5236; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.374 to 55.996° |
| Completeness to theta | 0.993 |
| Index ranges | -13 ≤ h ≤ 13, -28 ≤ k ≤ 28, -14 ≤ l ≤ 14 |
| Reflections collected | 20193 |
| Independent reflections | 5602 [$R_{int}$ = 0.0343, $R_{sigma}$ = 0.0333] |
| Data/restraints/parameters | 5602/1/243 |
| Goodness-of-fit on $F^2$ | 1.051 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0244, $wR_2$ = 0.0423 |
| Final R indexes [all data] | $R_1$ = 0.0318, $wR_2$ = 0.0439 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.60/-0.59 |

***Table 2:*** Bond lengths for **25.1a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W1 | P1 | 2.4879(7) | Si2 | C5 | 1.902(3) |
| W1 | C15 | 2.044(3) | Si2 | C9 | 1.867(3) |
| W1 | C13 | 2.045(3) | Si2 | C11 | 1.866(3) |
| W1 | C16 | 2.060(3) | Si2 | C10 | 1.866(3) |
| W1 | C14 | 2.025(3) | O5 | C15 | 1.136(3) |
| W1 | C12 | 2.017(3) | O1 | C1 | 1.493(4) |
| P1 | C5 | 1.809(3) | C2 | C1 | 1.537(4) |
| P1 | O1 | 1.664(2) | O2 | C12 | 1.141(4) |
| P1 | C2 | 1.804(3) | O4 | C14 | 1.151(4) |
| Si1 | C7 | 1.865(3) | C13 | O3 | 1.133(4) |
| Si1 | C5 | 1.917(3) | C1 | C3 | 1.505(4) |
| Si1 | C8 | 1.857(3) | C1 | C4 | 1.520(4) |
| Si1 | C6 | 1.865(4) | C16 | O6 | 1.134(4) |

***Table 3:*** Bond angles for **25.1a**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C15 | W1 | P1 | 88.90(8) | C8 | Si1 | C6 | 105.65(17) |
| C15 | W1 | C13 | 177.06(11) | C6 | Si1 | C5 | 114.90(15) |
| C15 | W1 | C16 | 89.88(12) | C9 | Si2 | C5 | 114.26(14) |
| C13 | W1 | P1 | 93.80(9) | C11 | Si2 | C5 | 110.38(14) |
| C13 | W1 | C16 | 91.42(12) | C11 | Si2 | C9 | 107.87(15) |
| C16 | W1 | P1 | 87.15(8) | C11 | Si2 | C10 | 108.31(16) |
| C14 | W1 | P1 | 92.06(8) | C10 | Si2 | C5 | 106.85(14) |
| C14 | W1 | C15 | 86.91(12) | C10 | Si2 | C9 | 109.03(17) |
| C14 | W1 | C13 | 91.82(12) | P1 | C5 | Si1 | 115.58(15) |
| C14 | W1 | C16 | 176.72(13) | P1 | C5 | Si2 | 117.59(14) |
| C12 | W1 | P1 | 177.19(10) | Si2 | C5 | Si1 | 116.27(15) |
| C12 | W1 | C15 | 89.76(12) | C1 | O1 | P1 | 94.79(16) |
| C12 | W1 | C13 | 87.59(13) | C1 | C2 | P1 | 87.85(19) |
| C12 | W1 | C16 | 90.38(12) | O5 | C15 | W1 | 177.8(3) |
| C12 | W1 | C14 | 90.33(12) | O3 | C13 | W1 | 177.1(3) |
| C5 | P1 | W1 | 123.37(10) | O1 | C1 | C2 | 96.2(2) |
| O1 | P1 | W1 | 114.34(8) | O1 | C1 | C3 | 109.0(3) |
| O1 | P1 | C5 | 104.47(12) | O1 | C1 | C4 | 108.1(3) |
| O1 | P1 | C2 | 81.08(12) | C3 | C1 | C2 | 114.7(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2 | P1 | W1 | 119.24(10) | C3 | C1 | C4 | 112.7(3) |
| C2 | P1 | C5 | 105.79(13) | C4 | C1 | C2 | 114.5(3) |
| C7 | Si1 | C5 | 104.17(14) | O6 | C16 | W1 | 178.1(3) |
| C7 | Si1 | C6 | 109.15(19) | O4 | C14 | W1 | 177.4(3) |
| C8 | Si1 | C7 | 109.56(16) | O2 | C12 | W1 | 179.4(3) |
| C8 | Si1 | C5 | 113.35(14) | | | | |

***Table 4:*** Torsion angles for **25.1a**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W1 | P1 | C5 | Si1 | -76.74(16) | P1 | C2 | C1 | C4 | 111.6(3) |
| W1 | P1 | C5 | Si2 | 66.76(18) | C5 | P1 | O1 | C1 | 102.66(17) |
| W1 | P1 | O1 | C1 | -119.60(14) | C5 | P1 | C2 | C1 | -101.20(18) |
| W1 | P1 | C2 | C1 | 114.38(15) | O1 | P1 | C5 | Si1 | 56.06(18) |
| P1 | O1 | C1 | C2 | 1.71(19) | O1 | P1 | C5 | Si2 | -160.44(15) |
| P1 | O1 | C1 | C3 | 120.5(2) | O1 | P1 | C2 | C1 | 1.42(16) |
| P1 | O1 | C1 | C4 | -116.6(2) | C2 | P1 | C5 | Si1 | 140.69(15) |
| P1 | C2 | C1 | O1 | -1.57(18) | C2 | P1 | C5 | Si2 | -75.81(19) |
| P1 | C2 | C1 | C3 | -115.9(3) | C2 | P1 | O1 | C1 | -1.46(17) |

## 12.17 Pentacarbonyl{[(2-methyl-2-propenyl)oxy]-[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [4.1d]

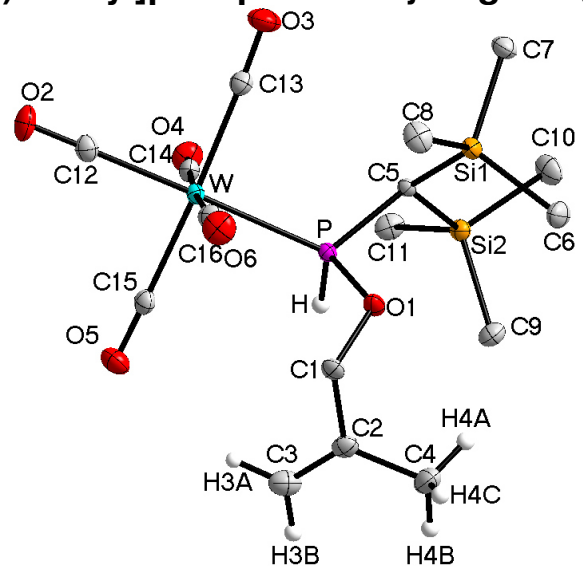


***Table 1:*** Crystal data and structure refinement for **4.1d**.

| | |
|---|---|
| Identification code | GSTR388, AKY-469-F1 // GXray3851f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{16}H_{27}O_6PSi_2W$ |
| Formula weight | 586.37 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 16.7313(8) |
| b/Å | 9.3726(4) |
| c/Å | 14.9852(7) |
| α/° | 90 |

| | |
|---|---|
| β/° | 103.5173(17) |
| γ/° | 90 |
| Volume/Å$^3$ | 2284.82(18) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.705 |
| μ/mm$^{-1}$ | 5.257 |
| F(000) | 1152.0 |
| Crystal size/mm$^3$ | 0.2 × 0.06 × 0.03 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4035; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 7.64 to 55.996° |
| Completeness to theta | 0.993 |
| Index ranges | -22 ≤ h ≤ 14, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19 |
| Reflections collected | 20157 |
| Independent reflections | 5488 [$R_{int}$ = 0.0226, $R_{sigma}$ = 0.0194] |
| Data/restraints/parameters | 5488/0/245 |
| Goodness-of-fit on F$^2$ | 1.138 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0160, w$R_2$ = 0.0392 |
| Final R indexes [all data] | $R_1$ = 0.0165, w$R_2$ = 0.0394 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.00/-1.08 |

***Table 2:*** Bond lengths for **4.1d**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4849(4) | Si2 | C9 | 1.865(2) |
| W | C12 | 2.0155(19) | Si2 | C10 | 1.870(2) |
| W | C13 | 2.037(2) | Si2 | C11 | 1.865(2) |
| W | C14 | 2.031(2) | O1 | C1 | 1.454(2) |
| W | C15 | 2.043(2) | O2 | C12 | 1.139(2) |
| W | C16 | 2.055(2) | O3 | C13 | 1.135(3) |
| P | O1 | 1.6242(13) | O4 | C14 | 1.141(2) |
| P | C5 | 1.8087(18) | O5 | C15 | 1.136(3) |
| Si1 | C5 | 1.9063(18) | O6 | C16 | 1.134(2) |
| Si1 | C6 | 1.863(2) | C1 | C2 | 1.495(3) |
| Si1 | C7 | 1.864(2) | C2 | C3 | 1.323(3) |
| Si1 | C8 | 1.865(2) | C2 | C4 | 1.502(3) |
| Si2 | C5 | 1.8986(18) | | | |

***Table 3:*** Bond angles for **4.1d**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C12 | W | P | 177.67(6) | C7 | Si1 | C8 | 107.37(10) |
| C12 | W | C13 | 88.57(8) | C8 | Si1 | C5 | 113.53(9) |
| C12 | W | C14 | 92.52(7) | C9 | Si2 | C5 | 110.81(9) |
| C12 | W | C15 | 89.20(8) | C9 | Si2 | C10 | 109.20(10) |
| C12 | W | C16 | 90.69(8) | C9 | Si2 | C11 | 110.30(10) |
| C13 | W | P | 92.81(5) | C10 | Si2 | C5 | 112.11(9) |
| C13 | W | C15 | 176.26(7) | C11 | Si2 | C5 | 107.26(8) |
| C13 | W | C16 | 90.01(8) | C11 | Si2 | C10 | 107.08(10) |
| C14 | W | P | 85.65(5) | C1 | O1 | P | 119.57(11) |
| C14 | W | C13 | 88.00(8) | O1 | C1 | C2 | 111.54(15) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C14 | W | C15 | 89.10(8) | C1 | C2 | C4 | 116.24(18) |
| C14 | W | C16 | 176.18(7) | C3 | C2 | C1 | 120.49(18) |
| C15 | W | P | 89.32(5) | C3 | C2 | C4 | 123.2(2) |
| C15 | W | C16 | 93.02(8) | P | C5 | Si1 | 114.51(9) |
| C16 | W | P | 91.20(5) | P | C5 | Si2 | 110.94(9) |
| O1 | P | W | 120.82(5) | Si2 | C5 | Si1 | 116.70(9) |
| O1 | P | C5 | 99.94(7) | O2 | C12 | W | 179.6(2) |
| C5 | P | W | 119.00(6) | O3 | C13 | W | 177.33(17) |
| C6 | Si1 | C5 | 111.02(8) | O4 | C14 | W | 178.56(17) |
| C6 | Si1 | C7 | 111.30(9) | O5 | C15 | W | 177.55(18) |
| C6 | Si1 | C8 | 107.74(10) | O6 | C16 | W | 178.43(18) |
| C7 | Si1 | C5 | 105.86(8) | | | | |

***Table 4:*** Torsion angles for **4.1d**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | 49.91(15) | C5 | P | O1 | C1 | -177.43(13) |
| W | P | C5 | Si1 | 91.80(9) | C9 | Si2 | C5 | P | -52.23(12) |
| W | P | C5 | Si2 | -133.52(6) | C9 | Si2 | C5 | Si1 | 81.36(12) |
| P | O1 | C1 | C2 | 93.19(17) | C10 | Si2 | C5 | P | -174.52(10) |
| O1 | P | C5 | Si1 | -41.98(10) | C10 | Si2 | C5 | Si1 | -40.92(13) |
| O1 | P | C5 | Si2 | 92.70(9) | C11 | Si2 | C5 | P | 68.21(11) |
| O1 | C1 | C2 | C3 | -113.4(2) | C11 | Si2 | C5 | Si1 | -158.19(10) |
| O1 | C1 | C2 | C4 | 68.8(2) | | | | | |

## 12.18 Pentacarbonyl{4,4-bis(trifluoromethyl)-2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [25.1b]

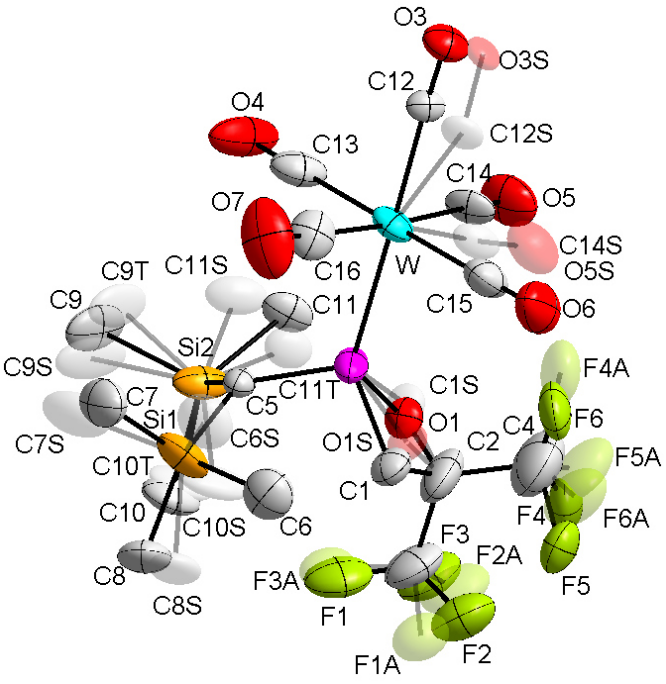

***Table 1:*** Crystal data and structure refinement for **25.1b**.

| | |
|---|---|
| Identification code | GSTR378, 3684f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{16}H_{21}F_6O_6PSi_2W$ |
| Formula weight | 694.33 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 8.9748(9) |
| b/Å | 10.3623(9) |
| c/Å | 15.4170(13) |
| α/° | 70.869(5) |
| β/° | 79.168(6) |
| γ/° | 66.889(5) |
| Volume/Å$^3$ | 1243.0(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.855 |
| μ/mm$^{-1}$ | 4.880 |
| F(000) | 672.0 |
| Crystal size/mm$^3$ | 0.05 × 0.04 × 0.01 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5698; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.52 to 56° |
| Completeness to theta | 0.984 |
| Index ranges | -11 ≤ h ≤ 9, -13 ≤ k ≤ 13, -19 ≤ l ≤ 20 |
| Reflections collected | 12106 |
| Independent reflections | 5889 [$R_{int}$ = 0.0426, $R_{sigma}$ = 0.0712] |
| Data/restraints/parameters | 5889/293/486 |
| Goodness-of-fit on F$^2$ | 1.024 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0464, $wR_2$ = 0.1034 |
| Final R indexes [all data] | $R_1$ = 0.0747, $wR_2$ = 0.1170 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.43/-2.73 |

***Table 2:*** Bond lengths for **25.1b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4562(19) | Si2 | C9T | 1.8100(11) |
| W | C13 | 2.028(10) | Si2 | C10T | 1.8100(11) |
| W | C15 | 2.039(10) | Si2 | C11T | 1.8100(11) |
| W | C16 | 2.039(10) | F1 | C3 | 1.22(2) |
| W | C14 | 2.081(12) | F6 | C4 | 1.23(2) |
| W | C12 | 2.062(10) | F3 | C3 | 1.403(18) |
| W | C12S | 1.87(3) | F4 | C4 | 1.34(4) |
| W | C14S | 1.95(4) | F5 | C4 | 1.76(3) |
| P | C2 | 2.317(9) | F2 | C3 | 1.293(16) |
| P | C5 | 1.805(7) | O4 | C13 | 1.149(11) |
| P | O1 | 1.568(12) | O6 | C15 | 1.148(10) |
| P | C1 | 2.04(2) | O7 | C16 | 1.139(11) |
| P | O1S | 1.579(12) | C2 | C3 | 1.568(15) |
| P | C1S | 1.980(17) | C2 | C4 | 1.531(18) |
| Si1 | C5 | 1.898(7) | C2 | O1 | 1.208(17) |
| Si1 | C6 | 1.968(19) | C2 | C1 | 1.79(2) |

| | | | | | |
|---|---|---|---|---|---|
| Si1 | C7 | 1.750(17) | C2 | O1S | 1.241(16) |
| Si1 | C8 | 1.886(19) | C2 | C1S | 1.72(2) |
| Si1 | C6S | 1.8103(11) | C3 | F2A | 1.20(2) |
| Si1 | C7S | 1.8104(11) | C3 | F3A | 1.384(10) |
| Si1 | C8S | 1.8098(11) | C3 | F1A | 1.51(3) |
| Si2 | C5 | 1.915(7) | C4 | F6A | 1.151(19) |
| Si2 | C9 | 1.90(4) | C4 | F4A | 1.49(2) |
| Si2 | C10 | 1.97(3) | C4 | F5A | 1.36(3) |
| Si2 | C11 | 2.07(3) | O3 | C12 | 1.112(14) |
| Si2 | C11S | 1.8099(11) | O5 | C14 | 1.092(16) |
| Si2 | C9S | 1.8101(11) | C12S | O3S | 1.36(4) |
| Si2 | C10S | 1.8101(11) | C14S | O5S | 1.30(5) |

***Table 3:*** Bond angles for **25.1b**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| C13 | W | P | 91.4(2) | C9T | Si2 | C5 | 106.6(18) |
| C13 | W | C15 | 177.7(4) | C9T | Si2 | C9 | 15(2) |
| C13 | W | C16 | 88.6(4) | C9T | Si2 | C10 | 114(3) |
| C13 | W | C14 | 87.7(6) | C9T | Si2 | C11 | 95(2) |
| C13 | W | C12 | 88.1(4) | C9T | Si2 | C9S | 31.5(18) |
| C15 | W | P | 89.6(2) | C9T | Si2 | C10S | 129.5(19) |
| C15 | W | C16 | 89.3(4) | C9T | Si2 | C10T | 116(4) |
| C15 | W | C14 | 94.3(6) | C9T | Si2 | C11T | 109(2) |
| C15 | W | C12 | 90.8(4) | C10T | Si2 | C5 | 119(3) |
| C16 | W | P | 90.5(3) | C10T | Si2 | C9 | 102(4) |
| C16 | W | C14 | 176.1(6) | C10T | Si2 | C10 | 9(4) |
| C16 | W | C12 | 88.5(4) | C10T | Si2 | C11 | 111(3) |
| C14 | W | P | 91.1(4) | C10T | Si2 | C10S | 16(4) |
| C12 | W | P | 178.9(4) | C10T | Si2 | C11T | 98(3) |
| C12 | W | C14 | 89.8(4) | C11T | Si2 | C5 | 108.3(12) |
| C12S | W | P | 159.5(16) | C11T | Si2 | C9 | 119(2) |
| C12S | W | C13 | 102.6(12) | C11T | Si2 | C10 | 106(2) |
| C12S | W | C15 | 76.9(12) | C11T | Si2 | C11 | 15.1(13) |
| C12S | W | C16 | 104.5(13) | C11T | Si2 | C10S | 84.4(18) |
| C12S | W | C14 | 74.9(12) | C3 | C2 | P | 125.3(7) |
| C12S | W | C12 | 21.5(13) | C3 | C2 | C1 | 102.4(11) |
| C12S | W | C14S | 83.0(15) | C3 | C2 | C1S | 107.3(10) |
| C14S | W | P | 79.9(12) | C4 | C2 | P | 120.8(9) |
| C14S | W | C13 | 100.3(12) | C4 | C2 | C3 | 113.8(9) |
| C14S | W | C15 | 81.9(12) | C4 | C2 | C1 | 113.9(12) |
| C14S | W | C16 | 166.9(14) | C4 | C2 | C1S | 105.7(13) |
| C14S | W | C14 | 16.8(11) | O1 | C2 | P | 38.7(7) |
| C14S | W | C12 | 101.2(11) | O1 | C2 | C3 | 114.5(11) |
| C2 | P | W | 126.2(3) | O1 | C2 | C4 | 114.3(14) |
| C5 | P | W | 116.1(2) | O1 | C2 | C1 | 95.9(10) |
| C5 | P | C2 | 117.8(4) | O1 | C2 | O1S | 78.6(9) |
| C5 | P | C1 | 104.0(7) | O1 | C2 | C1S | 17.8(8) |
| C5 | P | C1S | 106.4(6) | C1 | C2 | P | 57.9(7) |
| O1 | P | W | 123.6(5) | O1S | C2 | P | 39.9(7) |
| O1 | P | C2 | 28.8(6) | O1S | C2 | C3 | 120.1(12) |
| O1 | P | C5 | 111.4(5) | O1S | C2 | C4 | 111.0(12) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 | P | C1 | 76.5(7) | O1S | C2 | C1 | 20.8(9) |
| O1 | P | O1S | 59.1(6) | O1S | C2 | C1S | 96.2(9) |
| O1 | P | C1S | 17.6(7) | C1S | C2 | P | 56.4(6) |
| C1 | P | W | 117.4(6) | C1S | C2 | C1 | 113.7(9) |
| C1 | P | C2 | 48.1(7) | F1 | C3 | F3 | 106.2(14) |
| O1S | P | W | 117.0(4) | F1 | C3 | F2 | 116.1(17) |
| O1S | P | C2 | 30.3(6) | F1 | C3 | C2 | 111.8(13) |
| O1S | P | C5 | 117.7(5) | F1 | C3 | F3A | 15(2) |
| O1S | P | C1 | 19.9(6) | F1 | C3 | F1A | 83.1(15) |
| O1S | P | C1S | 76.6(7) | F3 | C3 | C2 | 110.9(12) |
| C1S | P | W | 116.1(6) | F3 | C3 | F1A | 123.1(11) |
| C1S | P | C2 | 46.4(6) | F2 | C3 | F3 | 107.3(11) |
| C1S | P | C1 | 94.1(7) | F2 | C3 | C2 | 104.4(11) |
| C5 | Si1 | C6 | 106.5(6) | F2 | C3 | F3A | 129.5(18) |
| C7 | Si1 | C5 | 112.0(7) | F2 | C3 | F1A | 33.1(9) |
| C7 | Si1 | C6 | 108.1(10) | F2A | C3 | F1 | 126(2) |
| C7 | Si1 | C8 | 112.6(11) | F2A | C3 | F3 | 26.3(12) |
| C7 | Si1 | C6S | 61.6(11) | F2A | C3 | F2 | 82.2(14) |
| C7 | Si1 | C7S | 35.0(10) | F2A | C3 | C2 | 111.1(15) |
| C7 | Si1 | C8S | 119.2(12) | F2A | C3 | F3A | 117.1(15) |
| C8 | Si1 | C5 | 113.5(9) | F2A | C3 | F1A | 104.7(15) |
| C8 | Si1 | C6 | 103.4(9) | F3A | C3 | F3 | 94.2(16) |
| C6S | Si1 | C5 | 109.2(7) | F3A | C3 | C2 | 109.5(15) |
| C6S | Si1 | C6 | 49.1(9) | F3A | C3 | F1A | 97.0(17) |
| C6S | Si1 | C8 | 134.8(10) | F1A | C3 | C2 | 116.9(11) |
| C6S | Si1 | C7S | 96.7(12) | F6 | C4 | F4 | 144(2) |
| C7S | Si1 | C5 | 101.0(8) | F6 | C4 | F5 | 91.4(18) |
| C7S | Si1 | C6 | 141.6(10) | F6 | C4 | C2 | 109.0(13) |
| C7S | Si1 | C8 | 89.4(11) | F6 | C4 | F4A | 44.0(12) |
| C8S | Si1 | C5 | 123.0(10) | F6 | C4 | F5A | 122(2) |
| C8S | Si1 | C6 | 80.3(10) | F4 | C4 | F5 | 96.6(19) |
| C8S | Si1 | C8 | 23.1(8) | F4 | C4 | C2 | 104.4(16) |
| C8S | Si1 | C6S | 115.7(12) | F4 | C4 | F4A | 111(2) |
| C8S | Si1 | C7S | 106.5(12) | F4 | C4 | F5A | 24.0(16) |
| C5 | Si2 | C10 | 113(2) | C2 | C4 | F5 | 97.3(13) |
| C5 | Si2 | C11 | 107.1(11) | F6A | C4 | F6 | 72.4(17) |
| C9 | Si2 | C5 | 110.6(19) | F6A | C4 | F4 | 102.3(19) |
| C9 | Si2 | C10 | 100(3) | F6A | C4 | F5 | 25.2(11) |
| C9 | Si2 | C11 | 107(2) | F6A | C4 | C2 | 118.7(19) |
| C10 | Si2 | C11 | 119(2) | F6A | C4 | F4A | 108.5(17) |
| C11S | Si2 | C5 | 116.6(7) | F6A | C4 | F5A | 108.5(15) |
| C11S | Si2 | C9 | 82.7(19) | F4A | C4 | F5 | 132.3(15) |
| C11S | Si2 | C10 | 126(2) | F4A | C4 | C2 | 111.1(11) |
| C11S | Si2 | C11 | 24.4(10) | F5A | C4 | F5 | 112.4(14) |
| C11S | Si2 | C9S | 101.1(12) | F5A | C4 | C2 | 118.0(18) |
| C11S | Si2 | C10S | 110.8(17) | F5A | C4 | F4A | 87.6(18) |
| C11S | Si2 | C9T | 71(2) | P | C5 | Si1 | 118.8(4) |
| C11S | Si2 | C10T | 118(3) | P | C5 | Si2 | 114.5(4) |
| C11S | Si2 | C11T | 37.8(13) | Si1 | C5 | Si2 | 117.6(3) |
| C9S | Si2 | C5 | 101.4(9) | O4 | C13 | W | 177.5(9) |
| C9S | Si2 | C9 | 18.4(17) | O6 | C15 | W | 178.8(9) |
| C9S | Si2 | C10 | 90(3) | O7 | C16 | W | 177.7(9) |
| C9S | Si2 | C11 | 125.5(13) | O5 | C14 | W | 177.0(12) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C9S | Si2 | C10S | 110.1(15) | O3 | C12 | W | 177.6(10) |
| C9S | Si2 | C10T | 94(3) | O3S | C12S | W | 158(3) |
| C9S | Si2 | C11T | 137.3(14) | O5S | C14S | W | 177(3) |
| C10S | Si2 | C5 | 115.2(15) | C2 | O1 | P | 112.5(11) |
| C10S | Si2 | C9 | 116.9(19) | C2 | C1 | P | 74.0(9) |
| C10S | Si2 | C10 | 23(2) | C2 | O1S | P | 109.9(11) |
| C10S | Si2 | C11 | 98.4(17) | C2 | C1S | P | 77.2(8) |

***Table 4:*** Torsion angles for **25.1b**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C2 | C3 | 178.6(8) | C14 | W | C12S | O3S | 130(6) |
| W | P | C2 | C4 | -4.2(14) | C14 | W | C14S | O5S | 35(50) |
| W | P | C2 | O1 | -95.5(11) | C12 | W | P | C2 | -149(15) |
| W | P | C2 | C1 | 96.3(9) | C12 | W | P | C5 | 31(15) |
| W | P | C2 | O1S | 82.2(11) | C12 | W | P | O1 | 175(100) |
| W | P | C2 | C1S | -93.2(9) | C12 | W | P | C1 | -93(15) |
| W | P | C5 | Si1 | -109.0(3) | C12 | W | P | O1S | -115(15) |
| W | P | C5 | Si2 | 104.9(3) | C12 | W | P | C1S | 157(15) |
| W | P | O1 | C2 | 105.1(11) | C12 | W | C13 | O4 | -61(17) |
| W | P | C1 | C2 | -115.3(6) | C12 | W | C15 | O6 | 35(41) |
| W | P | O1S | C2 | -116.1(9) | C12 | W | C16 | O7 | 1(21) |
| W | P | C1S | C2 | 116.2(6) | C12 | W | C14 | O5 | -165(27) |
| P | W | C13 | O4 | 118(17) | C12 | W | C12S | O3S | -3(5) |
| P | W | C15 | O6 | -144(41) | C12 | W | C14S | O5S | -13(53) |
| P | W | C16 | O7 | -178(100) | C12S | W | P | C2 | 10(2) |
| P | W | C14 | O5 | 14(27) | C12S | W | P | C5 | -170(2) |
| P | W | C12 | O3 | 115(26) | C12S | W | P | O1 | -25(2) |
| P | W | C12S | O3S | 179(5) | C12S | W | P | C1 | 66(2) |
| P | W | C14S | O5S | 167(53) | C12S | W | P | O1S | 44(2) |
| P | C2 | C3 | F1 | -12.6(19) | C12S | W | P | C1S | -44(2) |
| P | C2 | C3 | F3 | 105.8(13) | C12S | W | C13 | O4 | -77(17) |
| P | C2 | C3 | F2 | -138.9(13) | C12S | W | C15 | O6 | 52(41) |
| P | C2 | C3 | F2A | 134.0(18) | C12S | W | C16 | O7 | 16(21) |
| P | C2 | C3 | F3A | 3(2) | C12S | W | C14 | O5 | 179(100) |
| P | C2 | C3 | F1A | -105.9(16) | C12S | W | C12 | O3 | -45(23) |
| P | C2 | C4 | F6 | 31(2) | C12S | W | C14S | O5S | -24(53) |
| P | C2 | C4 | F4 | -136.4(19) | C14S | W | P | C2 | 43.6(12) |
| P | C2 | C4 | F5 | 124.7(10) | C14S | W | P | C5 | -136.1(12) |
| P | C2 | C4 | F6A | 110.5(17) | C14S | W | P | O1 | 8.4(13) |
| P | C2 | C4 | F4A | -16(2) | C14S | W | P | C1 | 100.1(13) |
| P | C2 | C4 | F5A | -115.0(17) | C14S | W | P | O1S | 77.7(13) |
| C2 | P | C5 | Si1 | 71.3(6) | C14S | W | P | C1S | -10.0(13) |
| C2 | P | C5 | Si2 | -74.8(5) | C14S | W | C13 | O4 | -162(17) |
| C3 | C2 | C4 | F6 | -151.8(19) | C14S | W | C15 | O6 | 136(41) |
| C3 | C2 | C4 | F4 | 41(2) | C14S | W | C16 | O7 | 140(21) |
| C3 | C2 | C4 | F5 | -57.8(15) | C14S | W | C14 | O5 | 62(26) |
| C3 | C2 | C4 | F6A | -72(2) | C14S | W | C12 | O3 | -78(24) |
| C3 | C2 | C4 | F4A | 161.3(14) | C14S | W | C12S | O3S | 145(6) |
| C3 | C2 | C4 | F5A | 62(2) | O1 | P | C2 | C3 | -85.9(14) |
| C3 | C2 | O1 | P | 116.6(11) | O1 | P | C2 | C4 | 91.3(17) |
| C3 | C2 | C1 | P | -124.1(8) | O1 | P | C2 | C1 | -168.2(15) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C3 | C2 | O1S | P | -110.3(11) | O1 | P | C2 | O1S | 177.6(17) |
| C3 | C2 | C1S | P | 121.3(8) | O1 | P | C2 | C1S | 2.3(15) |
| C4 | C2 | C3 | F1 | 170.1(17) | O1 | P | C5 | Si1 | 102.3(6) |
| C4 | C2 | C3 | F3 | -71.6(17) | O1 | P | C5 | Si2 | -43.8(6) |
| C4 | C2 | C3 | F2 | 43.7(18) | O1 | P | C1 | C2 | 5.8(7) |
| C4 | C2 | C3 | F2A | -43(2) | O1 | P | O1S | C2 | -1.3(10) |
| C4 | C2 | C3 | F3A | -174.3(19) | O1 | P | C1S | C2 | -4(2) |
| C4 | C2 | C3 | F1A | 76.7(19) | O1 | C2 | C3 | F1 | -56(2) |
| C4 | C2 | O1 | P | -109.6(13) | O1 | C2 | C3 | F3 | 62.5(16) |
| C4 | C2 | C1 | P | 112.6(11) | O1 | C2 | C3 | F2 | 177.8(15) |
| C4 | C2 | O1S | P | 113.4(12) | O1 | C2 | C3 | F2A | 91(2) |
| C4 | C2 | C1S | P | -116.9(10) | O1 | C2 | C3 | F3A | -40(2) |
| C5 | P | C2 | C3 | -1.7(12) | O1 | C2 | C3 | F1A | -149.2(17) |
| C5 | P | C2 | C4 | 175.5(12) | O1 | C2 | C4 | F6 | 74(2) |
| C5 | P | C2 | O1 | 84.2(12) | O1 | C2 | C4 | F4 | -93(2) |
| C5 | P | C2 | C1 | -84.0(9) | O1 | C2 | C4 | F5 | 168.1(12) |
| C5 | P | C2 | O1S | -98.2(11) | O1 | C2 | C4 | F6A | 153.9(17) |
| C5 | P | C2 | C1S | 86.5(9) | O1 | C2 | C4 | F4A | 27(2) |
| C5 | P | O1 | C2 | -109.0(11) | O1 | C2 | C4 | F5A | -72(2) |
| C5 | P | C1 | C2 | 114.9(7) | O1 | C2 | C1 | P | -7.4(9) |
| C5 | P | O1S | C2 | 98.2(10) | O1 | C2 | O1S | P | 1.5(11) |
| C5 | P | C1S | C2 | -113.0(7) | O1 | C2 | C1S | P | 5(3) |
| C13 | W | P | C2 | 143.8(5) | C1 | P | C2 | C3 | 82.3(14) |
| C13 | W | P | C5 | -35.8(4) | C1 | P | C2 | C4 | -100.5(15) |
| C13 | W | P | O1 | 108.6(7) | C1 | P | C2 | O1 | 168.2(15) |
| C13 | W | P | C1 | -159.7(7) | C1 | P | C2 | O1S | -14.1(14) |
| C13 | W | P | O1S | 177.9(6) | C1 | P | C2 | C1S | 170.5(13) |
| C13 | W | P | C1S | 90.3(7) | C1 | P | C5 | Si1 | 21.6(7) |
| C13 | W | C15 | O6 | -26(46) | C1 | P | C5 | Si2 | -124.6(6) |
| C13 | W | C16 | O7 | -87(21) | C1 | P | O1 | C2 | -9.0(12) |
| C13 | W | C14 | O5 | -77(27) | C1 | P | O1S | C2 | 148(3) |
| C13 | W | C12 | O3 | -178(100) | C1 | P | C1S | C2 | -7.1(10) |
| C13 | W | C12S | O3S | 46(6) | C1 | C2 | C3 | F1 | 46.6(17) |
| C13 | W | C14S | O5S | 77(53) | C1 | C2 | C3 | F3 | 165.0(13) |
| C15 | W | P | C2 | -38.2(5) | C1 | C2 | C3 | F2 | -79.7(15) |
| C15 | W | P | C5 | 142.1(4) | C1 | C2 | C3 | F2A | -166.7(18) |
| C15 | W | P | O1 | -73.4(7) | C1 | C2 | C3 | F3A | 62.3(18) |
| C15 | W | P | C1 | 18.2(7) | C1 | C2 | C3 | F1A | -46.7(17) |
| C15 | W | P | O1S | -4.2(6) | C1 | C2 | C4 | F6 | -35(2) |
| C15 | W | P | C1S | -91.8(7) | C1 | C2 | C4 | F4 | 158(2) |
| C15 | W | C13 | O4 | 0(23) | C1 | C2 | C4 | F5 | 59.2(14) |
| C15 | W | C16 | O7 | 92(21) | C1 | C2 | C4 | F6A | 45(2) |
| C15 | W | C14 | O5 | 104(27) | C1 | C2 | C4 | F4A | -81.8(18) |
| C15 | W | C12 | O3 | 4(24) | C1 | C2 | C4 | F5A | 179.4(17) |
| C15 | W | C12S | O3S | -132(6) | C1 | C2 | O1 | P | 10.0(13) |
| C15 | W | C14S | O5S | -102(53) | C1 | C2 | O1S | P | -144(3) |
| C16 | W | P | C2 | -127.5(5) | C1 | C2 | C1S | P | 8.8(12) |
| C16 | W | P | C5 | 52.8(4) | O1S | P | C2 | C3 | 96.4(15) |
| C16 | W | P | O1 | -162.7(6) | O1S | P | C2 | C4 | -86.4(15) |
| C16 | W | P | C1 | -71.1(7) | O1S | P | C2 | O1 | -177.6(17) |
| C16 | W | P | O1S | -93.4(6) | O1S | P | C2 | C1 | 14.1(14) |
| C16 | W | P | C1S | 178.9(7) | O1S | P | C2 | C1S | -175.4(14) |
| C16 | W | C13 | O4 | 27(17) | O1S | P | C5 | Si1 | 37.0(7) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C16 | W | C15 | O6 | -53(41) | O1S | P | C5 | Si2 | -109.1(6) |
| C16 | W | C14 | O5 | -100(26) | O1S | P | O1 | C2 | 1.4(10) |
| C16 | W | C12 | O3 | 93(24) | O1S | P | C1 | C2 | -21(2) |
| C16 | W | C12S | O3S | -46(6) | O1S | P | C1S | C2 | 2.4(7) |
| C16 | W | C14S | O5S | -150(50) | O1S | C2 | C3 | F1 | 35(2) |
| C9 | Si2 | C5 | P | -141.1(16) | O1S | C2 | C3 | F3 | 153.2(14) |
| C9 | Si2 | C5 | Si1 | 72.3(16) | O1S | C2 | C3 | F2 | -91.5(16) |
| C10 | Si2 | C5 | P | 108(3) | O1S | C2 | C3 | F2A | -178.5(19) |
| C10 | Si2 | C5 | Si1 | -39(3) | O1S | C2 | C3 | F3A | 51(2) |
| C11 | Si2 | C5 | P | -24.7(11) | O1S | C2 | C3 | F1A | -58.5(19) |
| C11 | Si2 | C5 | Si1 | -171.3(11) | O1S | C2 | C4 | F6 | -13(2) |
| C11S | Si2 | C5 | P | -49.0(10) | O1S | C2 | C4 | F4 | -180(2) |
| C11S | Si2 | C5 | Si1 | 164.4(10) | O1S | C2 | C4 | F5 | 81.5(14) |
| C9S | Si2 | C5 | P | -157.7(9) | O1S | C2 | C4 | F6A | 67(2) |
| C9S | Si2 | C5 | Si1 | 55.7(9) | O1S | C2 | C4 | F4A | -60(2) |
| C10S | Si2 | C5 | P | 83.5(14) | O1S | C2 | C4 | F5A | -158.3(17) |
| C10S | Si2 | C5 | Si1 | -63.1(14) | O1S | C2 | O1 | P | -1.5(11) |
| C9T | Si2 | C5 | P | -125.7(17) | O1S | C2 | C1 | P | 26(3) |
| C9T | Si2 | C5 | Si1 | 87.7(18) | O1S | C2 | C1S | P | -3.0(9) |
| C10T | Si2 | C5 | P | 102(3) | C1S | P | C2 | C3 | -88.2(13) |
| C10T | Si2 | C5 | Si1 | -45(3) | C1S | P | C2 | C4 | 89.0(15) |
| C11T | Si2 | C5 | P | -8.9(12) | C1S | P | C2 | O1 | -2.3(15) |
| C11T | Si2 | C5 | Si1 | -155.5(12) | C1S | P | C2 | C1 | -170.5(13) |
| C6 | Si1 | C5 | P | 1.0(7) | C1S | P | C2 | O1S | 175.4(14) |
| C6 | Si1 | C5 | Si2 | 146.1(7) | C1S | P | C5 | Si1 | 120.2(7) |
| C7 | Si1 | C5 | P | 119.0(9) | C1S | P | C5 | Si2 | -26.0(7) |
| C7 | Si1 | C5 | Si2 | -95.8(9) | C1S | P | O1 | C2 | 175(4) |
| C8 | Si1 | C5 | P | -112.1(9) | C1S | P | C1 | C2 | 6.9(9) |
| C8 | Si1 | C5 | Si2 | 33.1(9) | C1S | P | O1S | C2 | -3.4(11) |
| C6S | Si1 | C5 | P | 52.7(9) | C1S | C2 | C3 | F1 | -73.3(17) |
| C6S | Si1 | C5 | Si2 | -162.2(9) | C1S | C2 | C3 | F3 | 45.0(14) |
| C7S | Si1 | C5 | P | 153.8(10) | C1S | C2 | C3 | F2 | 160.3(14) |
| C7S | Si1 | C5 | Si2 | -61.0(10) | C1S | C2 | C3 | F2A | 73.3(19) |
| C8S | Si1 | C5 | P | -88.0(11) | C1S | C2 | C3 | F3A | -57.7(19) |
| C8S | Si1 | C5 | Si2 | 57.1(11) | C1S | C2 | C3 | F1A | -166.7(15) |
| C14 | W | P | C2 | 56.1(7) | C1S | C2 | C4 | F6 | 91(2) |
| C14 | W | P | C5 | -123.6(6) | C1S | C2 | C4 | F4 | -76(2) |
| C14 | W | P | O1 | 20.9(8) | C1S | C2 | C4 | F5 | -175.3(10) |
| C14 | W | P | C1 | 112.5(8) | C1S | C2 | C4 | F6A | 170.5(16) |
| C14 | W | P | O1S | 90.2(7) | C1S | C2 | C4 | F4A | 43.7(18) |
| C14 | W | P | C1S | 2.5(8) | C1S | C2 | C4 | F5A | -55(2) |
| C14 | W | C13 | O4 | -151(17) | C1S | C2 | O1 | P | -174(4) |
| C14 | W | C15 | O6 | 125(41) | C1S | C2 | C1 | P | -8.6(12) |
| C14 | W | C16 | O7 | -64(23) | C1S | C2 | O1S | P | 3.9(12) |
| C14 | W | C12 | O3 | -90(24) | | | | | |

# 12.19 Pentacarbonyl[4-(trifluoromethyl)-2-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.2g]

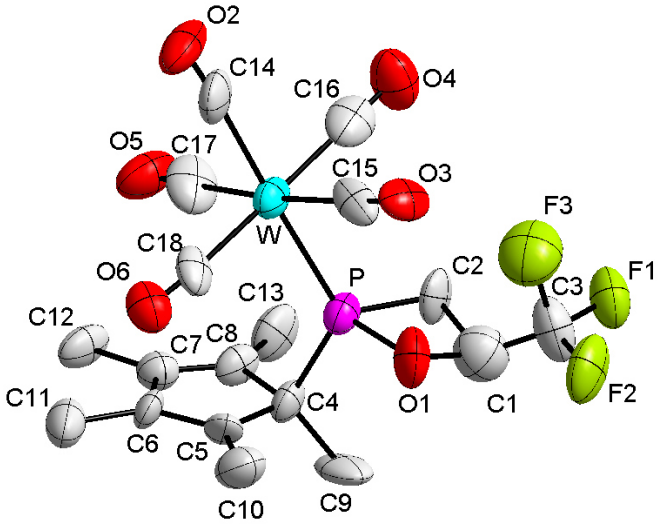


***Table 1:*** Crystal data and structure refinement for **21.2g**.

| | |
|---|---|
| Identification code | GSTR406, AKY-490 // GXray3961g |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{18}H_{18}O_6F_3PW$ |
| Moiety formula | C18 H18 F3 O6 P W |
| Formula weight | 602.14 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 9.86(2) |
| b/Å | 14.30(3) |
| c/Å | 16.92(3) |
| α/° | 90 |
| β/° | 94.00(11) |
| γ/° | 90 |
| Volume/Å$^3$ | 2381(8) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.680 |
| μ/mm$^{-1}$ | 4.969 |
| F(000) | 1160.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.06 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.3735; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.14 to 55.986° |
| Completeness to theta | 0.993 |
| Index ranges | -12 ≤ h ≤ 12, -13 ≤ k ≤ 18, -22 ≤ l ≤ 20 |
| Reflections collected | 29201 |
| Independent reflections | 5670 [$R_{int}$ = 0.3262, $R_{sigma}$ = 0.4193] |
| Data/restraints/parameters | 5670/19/267 |
| Goodness-of-fit on $F^2$ | 0.852 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1136, $wR_2$ = 0.2527 |
| Final R indexes [all data] | $R_1$ = 0.2554, $wR_2$ = 0.3744 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.79/-3.90 |

***Table 2:*** Bond lengths for **21.2g**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.554(7) | O4 | C16 | 1.20(4) |
| W | C14 | 2.17(3) | O5 | C17 | 1.15(3) |
| W | C15 | 2.11(3) | O6 | C18 | 1.24(3) |
| W | C16 | 2.17(4) | C1 | C2 | 1.62(4) |
| W | C17 | 2.13(3) | C1 | C3 | 1.43(4) |
| W | C18 | 2.16(3) | C4 | C5 | 1.59(3) |
| P | O1 | 1.761(17) | C4 | C8 | 1.61(3) |
| P | C2 | 1.95(2) | C4 | C9 | 1.57(3) |
| P | C4 | 1.96(2) | C5 | C6 | 1.42(3) |
| F1 | C3 | 1.42(3) | C5 | C10 | 1.52(3) |
| F2 | C3 | 1.35(3) | C6 | C7 | 1.53(3) |
| F3 | C3 | 1.57(3) | C6 | C11 | 1.59(3) |
| O1 | C1 | 1.60(3) | C7 | C8 | 1.42(3) |
| O2 | C14 | 1.14(3) | C7 | C12 | 1.60(3) |
| O3 | C15 | 1.23(3) | C8 | C13 | 1.56(4) |

***Table 3:*** Bond angles for **21.2g**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C14 | W | P | 177.8(8) | F2 | C3 | F1 | 111(2) |
| C14 | W | C16 | 89.1(11) | F2 | C3 | F3 | 100.1(19) |
| C15 | W | P | 86.7(6) | F2 | C3 | C1 | 121(3) |
| C15 | W | C14 | 92.9(9) | C1 | C3 | F3 | 102(2) |
| C15 | W | C16 | 86.8(10) | C5 | C4 | P | 107.0(14) |
| C15 | W | C17 | 174.8(11) | C5 | C4 | C8 | 102.6(17) |
| C15 | W | C18 | 91.6(9) | C8 | C4 | P | 105.7(14) |
| C16 | W | P | 88.7(7) | C9 | C4 | P | 112.7(15) |
| C17 | W | P | 94.9(8) | C9 | C4 | C5 | 111.3(18) |
| C17 | W | C14 | 85.2(10) | C9 | C4 | C8 | 116.7(19) |
| C17 | W | C16 | 88.4(12) | C6 | C5 | C4 | 110.3(19) |
| C17 | W | C18 | 93.2(11) | C6 | C5 | C10 | 125(2) |
| C18 | W | P | 93.0(6) | C10 | C5 | C4 | 124.8(19) |
| C18 | W | C14 | 89.2(10) | C5 | C6 | C7 | 108.0(19) |
| C18 | W | C16 | 177.5(8) | C5 | C6 | C11 | 131(2) |
| O1 | P | W | 115.1(7) | C7 | C6 | C11 | 121.2(18) |
| O1 | P | C2 | 79.1(8) | C6 | C7 | C12 | 121(2) |
| O1 | P | C4 | 103.9(9) | C8 | C7 | C6 | 111.4(18) |
| C2 | P | W | 119.6(8) | C8 | C7 | C12 | 128(2) |
| C2 | P | C4 | 106.6(10) | C7 | C8 | C4 | 108(2) |
| C4 | P | W | 123.2(6) | C7 | C8 | C13 | 130.4(19) |
| C1 | O1 | P | 96.0(15) | C13 | C8 | C4 | 122(2) |
| O1 | C1 | C2 | 95(2) | O2 | C14 | W | 175(3) |
| C3 | C1 | O1 | 114(2) | O3 | C15 | W | 176.5(19) |
| C3 | C1 | C2 | 119(3) | O4 | C16 | W | 179(3) |
| C1 | C2 | P | 88.4(17) | O5 | C17 | W | 177(3) |
| F1 | C3 | F3 | 99(2) | O6 | C18 | W | 174.1(18) |
| F1 | C3 | C1 | 118(2) | | | | |

***Table 4:*** Torsion angles for **21.2g**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | -127.4(14) | C5 | C4 | C8 | C7 | 1(2) |
| P | O1 | C1 | C2 | 11.5(17) | C5 | C4 | C8 | C13 | -176.7(19) |
| P | O1 | C1 | C3 | 136(2) | C5 | C6 | C7 | C8 | -2(2) |
| P | C4 | C5 | C6 | 108.7(17) | C5 | C6 | C7 | C12 | 176.4(18) |
| P | C4 | C5 | C10 | -68(2) | C6 | C7 | C8 | C4 | 0(2) |
| P | C4 | C8 | C7 | -110.8(17) | C6 | C7 | C8 | C13 | 178(2) |
| P | C4 | C8 | C13 | 71(2) | C8 | C4 | C5 | C6 | -2(2) |
| O1 | C1 | C2 | P | -10.3(15) | C8 | C4 | C5 | C10 | -179(2) |
| O1 | C1 | C3 | F1 | -158(2) | C9 | C4 | C5 | C6 | -128(2) |
| O1 | C1 | C3 | F2 | 59(4) | C9 | C4 | C5 | C10 | 55(3) |
| O1 | C1 | C3 | F3 | -51(3) | C9 | C4 | C8 | C7 | 123(2) |
| C2 | P | O1 | C1 | -9.6(15) | C9 | C4 | C8 | C13 | -55(3) |
| C2 | C1 | C3 | F1 | -47(4) | C10 | C5 | C6 | C7 | 179.5(19) |
| C2 | C1 | C3 | F2 | 169(2) | C10 | C5 | C6 | C11 | -3(4) |
| C2 | C1 | C3 | F3 | 60(3) | C11 | C6 | C7 | C8 | -179.7(18) |
| C3 | C1 | C2 | P | -132(3) | C11 | C6 | C7 | C12 | -2(3) |
| C4 | P | O1 | C1 | 95.0(16) | C12 | C7 | C8 | C4 | -177.7(19) |
| C4 | C5 | C6 | C7 | 2(2) | C12 | C7 | C8 | C13 | 0(4) |
| C4 | C5 | C6 | C11 | -179.9(19) | | | | | |

## 12.20 Pentacarbonyl[4,4-bis(trifluoromethyl)-2-(1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [25.2b]

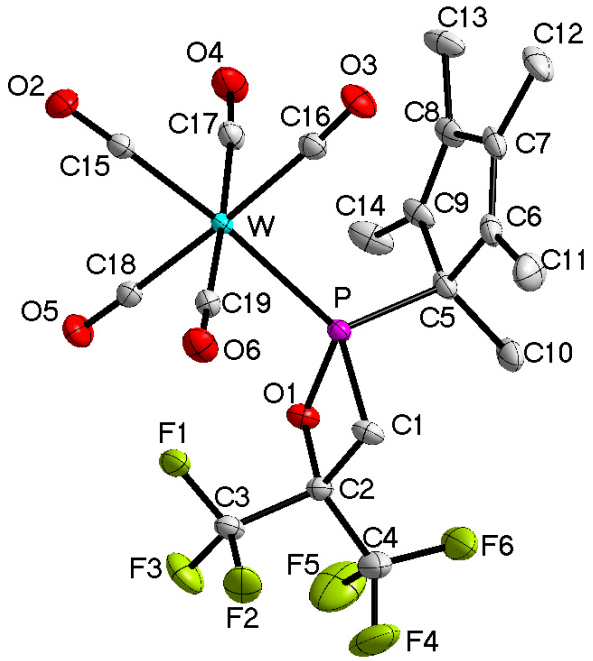


***Table 1:*** Crystal data and structure refinement for **25.2b**.

| | |
|---|---|
| Identification code | GSTR380, 3707f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{19}H_{17}F_6O_6PW$ |
| Formula weight | 670.15 |

| | |
|---|---|
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.3230(7) |
| b/Å | 14.0254(7) |
| c/Å | 16.2599(7) |
| α/° | 90.00 |
| β/° | 125.699(3) |
| γ/° | 90.00 |
| Volume/$Å^3$ | 2282.2(2) |
| Z | 4 |
| $\rho_{calc}g/cm^3$ | 1.950 |
| $\mu/mm^{-1}$ | 5.213 |
| F(000) | 1288.0 |
| Crystal size/$mm^3$ | 0.2 × 0.13 × 0.05 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4590; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.72 to 56° |
| Completeness to theta | 0.997 |
| Index ranges | -16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21 |
| Reflections collected | 48670 |
| Independent reflections | 5508 [$R_{int}$ = 0.0264, $R_{sigma}$ = 0.0144] |
| Data/restraints/parameters | 5508/2/298 |
| Goodness-of-fit on $F^2$ | 1.091 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0171, $wR_2$ = 0.0413 |
| Final R indexes [all data] | $R_1$ = 0.0191, $wR_2$ = 0.0422 |
| Largest diff. peak/hole / e $Å^{-3}$ | 1.59/-0.91 |

***Table 2:*** Bond lengths for **25.2b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4768(6) | O3 | C16 | 1.136(3) |
| W | C15 | 2.012(2) | O4 | C17 | 1.138(3) |
| W | C16 | 2.054(2) | O5 | C18 | 1.136(3) |
| W | C17 | 2.057(3) | O6 | C19 | 1.139(3) |
| W | C18 | 2.055(2) | C1 | C2 | 1.518(3) |
| W | C19 | 2.047(2) | C2 | C3 | 1.541(3) |
| P | O1 | 1.7272(17) | C2 | C4 | 1.545(4) |
| P | C1 | 1.835(2) | C5 | C6 | 1.524(3) |
| P | C2 | 2.349(2) | C5 | C9 | 1.513(4) |
| P | C5 | 1.849(2) | C5 | C10 | 1.538(3) |
| F1 | C3 | 1.326(3) | C6 | C7 | 1.346(4) |
| F2 | C3 | 1.332(3) | C6 | C11 | 1.502(4) |
| F3 | C3 | 1.335(3) | C7 | C8 | 1.473(4) |
| F4 | C4 | 1.299(4) | C7 | C12 | 1.509(3) |
| F5 | C4 | 1.355(4) | C8 | C9 | 1.351(3) |
| F6 | C4 | 1.310(3) | C8 | C13 | 1.499(4) |
| O1 | C2 | 1.446(3) | C9 | C14 | 1.497(3) |
| O2 | C15 | 1.150(3) | | | |

***Table 3:*** Bond angles for **25.2b**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C15 | W | P | 174.78(7) | C4 | C2 | P | 132.87(17) |
| C15 | W | C16 | 89.10(10) | F1 | C3 | F2 | 106.9(2) |
| C15 | W | C17 | 88.30(10) | F1 | C3 | F3 | 107.5(2) |
| C15 | W | C18 | 89.34(9) | F1 | C3 | C2 | 111.40(19) |
| C15 | W | C19 | 87.81(10) | F2 | C3 | F3 | 107.4(2) |
| C16 | W | P | 93.95(7) | F2 | C3 | C2 | 111.4(2) |
| C16 | W | C17 | 90.55(9) | F3 | C3 | C2 | 112.0(2) |
| C16 | W | C18 | 176.86(9) | F4 | C4 | F5 | 105.4(3) |
| C17 | W | P | 95.90(7) | F4 | C4 | F6 | 107.6(3) |
| C18 | W | P | 87.81(7) | F4 | C4 | C2 | 113.1(3) |
| C18 | W | C17 | 86.68(9) | F5 | C4 | C2 | 110.5(2) |
| C19 | W | P | 88.06(7) | F6 | C4 | F5 | 106.3(3) |
| C19 | W | C16 | 87.94(9) | F6 | C4 | C2 | 113.4(2) |
| C19 | W | C17 | 175.85(10) | C6 | C5 | P | 106.48(16) |
| C19 | W | C18 | 94.72(9) | C6 | C5 | C10 | 111.9(2) |
| O1 | P | W | 116.92(7) | C9 | C5 | P | 107.60(17) |
| O1 | P | C1 | 77.70(9) | C9 | C5 | C6 | 103.08(19) |
| O1 | P | C2 | 37.83(8) | C9 | C5 | C10 | 110.4(2) |
| O1 | P | C5 | 106.48(10) | C10 | C5 | P | 116.43(17) |
| C1 | P | W | 121.01(8) | C7 | C6 | C5 | 108.6(2) |
| C1 | P | C2 | 40.24(9) | C7 | C6 | C11 | 128.1(2) |
| C1 | P | C5 | 107.91(12) | C11 | C6 | C5 | 123.2(2) |
| C2 | P | W | 124.19(6) | C6 | C7 | C8 | 109.9(2) |
| C5 | P | W | 119.11(8) | C6 | C7 | C12 | 128.2(3) |
| C5 | P | C2 | 116.42(10) | C8 | C7 | C12 | 121.9(2) |
| C2 | O1 | P | 95.08(13) | C7 | C8 | C13 | 122.9(2) |
| C2 | C1 | P | 88.44(15) | C9 | C8 | C7 | 109.4(2) |
| O1 | C2 | P | 47.08(9) | C9 | C8 | C13 | 127.7(2) |
| O1 | C2 | C1 | 97.88(17) | C8 | C9 | C5 | 109.0(2) |
| O1 | C2 | C3 | 110.49(19) | C8 | C9 | C14 | 129.3(2) |
| O1 | C2 | C4 | 109.8(2) | C14 | C9 | C5 | 121.6(2) |
| C1 | C2 | P | 51.32(11) | O2 | C15 | W | 178.4(2) |
| C1 | C2 | C3 | 112.1(2) | O3 | C16 | W | 176.0(2) |
| C1 | C2 | C4 | 117.1(2) | O4 | C17 | W | 174.7(2) |
| C3 | C2 | P | 117.63(16) | O5 | C18 | W | 177.4(2) |
| C3 | C2 | C4 | 108.86(19) | O6 | C19 | W | 177.6(2) |

***Table 4:*** Torsion angles for **25.2b**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C2 | -111.96(12) | C5 | P | C1 | C2 | -110.00(15) |
| W | P | C1 | C2 | 107.74(13) | C5 | P | C2 | O1 | -82.91(16) |
| W | P | C2 | O1 | 90.99(13) | C5 | P | C2 | C1 | 86.82(17) |
| W | P | C2 | C1 | -99.28(15) | C5 | P | C2 | C3 | -175.94(17) |
| W | P | C2 | C3 | -2.0(2) | C5 | P | C2 | C4 | -6.3(3) |
| W | P | C2 | C4 | 167.6(2) | C5 | C6 | C7 | C8 | 1.9(3) |
| W | P | C5 | C6 | 61.37(18) | C5 | C6 | C7 | C12 | -176.3(2) |
| W | P | C5 | C9 | -48.60(17) | C6 | C5 | C9 | C8 | 3.2(3) |
| W | P | C5 | C10 | -173.07(17) | C6 | C5 | C9 | C14 | 179.8(2) |
| P | W | C15 | O2 | 10(8) | C6 | C7 | C8 | C9 | 0.2(3) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| P | W | C16 | O3 | -164(3) | C6 | C7 | C8 | C13 | -178.4(2) |
| P | W | C17 | O4 | 158(2) | C7 | C8 | C9 | C5 | -2.2(3) |
| P | W | C18 | O5 | -99(5) | C7 | C8 | C9 | C14 | -178.5(3) |
| P | W | C19 | O6 | 135(5) | C9 | C5 | C6 | C7 | -3.1(3) |
| P | O1 | C2 | C1 | -8.08(17) | C9 | C5 | C6 | C11 | -179.9(2) |
| P | O1 | C2 | C3 | 109.18(17) | C10 | C5 | C6 | C7 | 115.6(2) |
| P | O1 | C2 | C4 | -130.72(18) | C10 | C5 | C6 | C11 | -61.3(3) |
| P | C1 | C2 | O1 | 7.58(16) | C10 | C5 | C9 | C8 | -116.5(2) |
| P | C1 | C2 | C3 | -108.39(18) | C10 | C5 | C9 | C14 | 60.1(3) |
| P | C1 | C2 | C4 | 124.7(2) | C11 | C6 | C7 | C8 | 178.6(3) |
| P | C2 | C3 | F1 | -0.2(3) | C11 | C6 | C7 | C12 | 0.3(4) |
| P | C2 | C3 | F2 | -119.45(19) | C12 | C7 | C8 | C9 | 178.6(2) |
| P | C2 | C3 | F3 | 120.24(19) | C12 | C7 | C8 | C13 | 0.0(4) |
| P | C2 | C4 | F4 | 145.5(2) | C13 | C8 | C9 | C5 | 176.3(2) |
| P | C2 | C4 | F5 | -96.6(3) | C13 | C8 | C9 | C14 | 0.1(5) |
| P | C2 | C4 | F6 | 22.6(4) | C15 | W | P | O1 | 55.6(8) |
| P | C5 | C6 | C7 | -116.2(2) | C15 | W | P | C1 | -35.9(8) |
| P | C5 | C6 | C11 | 67.0(3) | C15 | W | P | C2 | 12.1(8) |
| P | C5 | C9 | C8 | 115.5(2) | C15 | W | P | C5 | -174.1(8) |
| P | C5 | C9 | C14 | -67.9(3) | C15 | W | C16 | O3 | 11(3) |
| O1 | P | C1 | C2 | -6.43(14) | C15 | W | C17 | O4 | -19(2) |
| O1 | P | C2 | C1 | 169.7(2) | C15 | W | C18 | O5 | 85(5) |
| O1 | P | C2 | C3 | -93.0(2) | C15 | W | C19 | O6 | -48(5) |
| O1 | P | C2 | C4 | 76.6(3) | C16 | W | P | O1 | -178.80(10) |
| O1 | P | C5 | C6 | -163.80(16) | C16 | W | P | C1 | 89.70(11) |
| O1 | P | C5 | C9 | 86.23(16) | C16 | W | P | C2 | 137.75(10) |
| O1 | P | C5 | C10 | -38.2(2) | C16 | W | P | C5 | -48.50(11) |
| O1 | C2 | C3 | F1 | -51.5(3) | C16 | W | C15 | O2 | -116(8) |
| O1 | C2 | C3 | F2 | -170.78(19) | C16 | W | C17 | O4 | -108(2) |
| O1 | C2 | C3 | F3 | 68.9(2) | C16 | W | C18 | O5 | 25(6) |
| O1 | C2 | C4 | F4 | -165.2(2) | C16 | W | C19 | O6 | 41(5) |
| O1 | C2 | C4 | F5 | -47.3(3) | C17 | W | P | O1 | -87.83(10) |
| O1 | C2 | C4 | F6 | 71.9(3) | C17 | W | P | C1 | -179.34(11) |
| C1 | P | O1 | C2 | 6.77(14) | C17 | W | P | C2 | -131.28(10) |
| C1 | P | C2 | O1 | -169.7(2) | C17 | W | P | C5 | 42.47(11) |
| C1 | P | C2 | C3 | 97.2(2) | C17 | W | C15 | O2 | 153(8) |
| C1 | P | C2 | C4 | -93.1(3) | C17 | W | C16 | O3 | 100(3) |
| C1 | P | C5 | C6 | -81.73(18) | C17 | W | C18 | O5 | -3(5) |
| C1 | P | C5 | C9 | 168.30(15) | C17 | W | C19 | O6 | -28(6) |
| C1 | P | C5 | C10 | 43.8(2) | C18 | W | P | O1 | -1.39(10) |
| C1 | C2 | C3 | F1 | 56.6(3) | C18 | W | P | C1 | -92.90(11) |
| C1 | C2 | C3 | F2 | -62.7(3) | C18 | W | P | C2 | -44.85(10) |
| C1 | C2 | C3 | F3 | 177.0(2) | C18 | W | P | C5 | 128.90(11) |
| C1 | C2 | C4 | F4 | 84.4(3) | C18 | W | C15 | O2 | 67(8) |
| C1 | C2 | C4 | F5 | -157.7(2) | C18 | W | C16 | O3 | 71(4) |
| C1 | C2 | C4 | F6 | -38.5(4) | C18 | W | C17 | O4 | 70(2) |
| C2 | P | C5 | C6 | -124.40(16) | C18 | W | C19 | O6 | -138(5) |
| C2 | P | C5 | C9 | 125.63(15) | C19 | W | P | O1 | 93.40(10) |
| C2 | P | C5 | C10 | 1.2(2) | C19 | W | P | C1 | 1.90(11) |
| C3 | C2 | C4 | F4 | -44.1(3) | C19 | W | P | C2 | 49.95(10) |
| C3 | C2 | C4 | F5 | 73.7(3) | C19 | W | P | C5 | -136.30(11) |
| C3 | C2 | C4 | F6 | -167.0(3) | C19 | W | C15 | O2 | -28(8) |
| C4 | C2 | C3 | F1 | -172.2(2) | C19 | W | C16 | O3 | -77(3) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C4 | C2 | C3 | F2 | 68.5(3) | C19 | W | C17 | O4 | -40(3) |
| C4 | C2 | C3 | F3 | -51.8(3) | C19 | W | C18 | O5 | 173(5) |
| C5 | P | O1 | C2 | 112.07(15) | | | | | |

## 12.21 Pentacarbonyl[4-methyl-2-(triphenylmethyl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.3a]

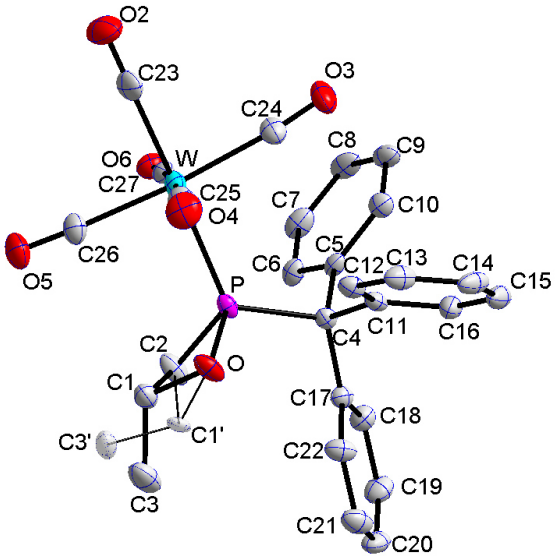


***Table 1:*** Crystal data and structure refinement for **21.3a**.

| | |
|---|---|
| Identification code | GSTR399, AKY-484 // GXray3939f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{27}H_{21}O_6PW$ |
| Moiety formula | C27 H21 O6 P W |
| Formula weight | 656.26 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.6166(9) |
| b/Å | 10.6720(12) |
| c/Å | 12.9879(12) |
| α/° | 75.820(6) |
| β/° | 83.265(5) |
| γ/° | 73.806(6) |
| Volume/Å$^3$ | 1239.3(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.759 |
| μ/mm$^{-1}$ | 4.765 |
| F(000) | 640.0 |
| Crystal size/mm$^3$ | 0.12 × 0.09 × 0.06 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4935; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.466 to 56° |
| Completeness to theta | 0.997 |
| Index ranges | -12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17 |
| Reflections collected | 24114 |
| Independent reflections | 5969 [$R_{int}$ = 0.0473, $R_{sigma}$ = 0.0441] |

| | |
|---|---|
| Data/restraints/parameters | 5969/0/337 |
| Goodness-of-fit on $F^2$ | 1.102 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0327, $wR_2$ = 0.0761 |
| Final R indexes [all data] | $R_1$ = 0.0424, $wR_2$ = 0.0810 |
| Largest diff. peak/hole / e $Å^{-3}$ | 2.09/-1.42 |

***Table 2:*** Bond lengths for **21.3a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4926(12) | C4 | C11 | 1.542(5) |
| W | C23 | 2.028(5) | C4 | C17 | 1.535(6) |
| W | C24 | 2.064(5) | C5 | C6 | 1.397(6) |
| W | C25 | 2.057(5) | C5 | C10 | 1.397(6) |
| W | C26 | 2.038(5) | C6 | C7 | 1.387(6) |
| W | C27 | 2.032(5) | C7 | C8 | 1.372(7) |
| P | O1 | 1.656(3) | C8 | C9 | 1.384(7) |
| P | C2 | 1.843(4) | C9 | C10 | 1.383(6) |
| P | C4 | 1.905(4) | C11 | C12 | 1.385(6) |
| O1 | C1 | 1.515(8) | C11 | C16 | 1.404(6) |
| O1 | C1' | 1.512(11) | C12 | C13 | 1.391(6) |
| O2 | C23 | 1.132(6) | C13 | C14 | 1.371(7) |
| O3 | C24 | 1.131(6) | C14 | C15 | 1.383(7) |
| O4 | C25 | 1.137(6) | C15 | C16 | 1.387(6) |
| O5 | C26 | 1.137(5) | C17 | C18 | 1.393(6) |
| O6 | C27 | 1.140(5) | C17 | C22 | 1.397(6) |
| C1 | C2 | 1.547(9) | C18 | C19 | 1.387(6) |
| C1 | C3 | 1.515(15) | C19 | C20 | 1.391(7) |
| C1' | C2 | 1.611(12) | C20 | C21 | 1.388(7) |
| C1' | C3' | 1.51(2) | C21 | C22 | 1.383(7) |
| C4 | C5 | 1.539(5) | | | |

***Table 3:*** Bond angles for **21.3a**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C23 | W | P | 176.50(14) | C11 | C4 | P | 110.5(3) |
| C23 | W | C24 | 86.04(19) | C17 | C4 | P | 111.3(3) |
| C23 | W | C25 | 92.3(2) | C17 | C4 | C5 | 114.0(3) |
| C23 | W | C26 | 89.01(19) | C17 | C4 | C11 | 105.7(3) |
| C23 | W | C27 | 88.79(19) | C6 | C5 | C4 | 120.1(4) |
| C24 | W | P | 95.65(14) | C6 | C5 | C10 | 117.4(4) |
| C25 | W | P | 90.80(14) | C10 | C5 | C4 | 122.4(4) |
| C25 | W | C24 | 89.65(18) | C7 | C6 | C5 | 121.0(4) |
| C26 | W | P | 89.41(14) | C8 | C7 | C6 | 120.5(4) |
| C26 | W | C24 | 174.59(19) | C7 | C8 | C9 | 119.8(4) |
| C26 | W | C25 | 88.37(18) | C10 | C9 | C8 | 120.0(4) |
| C27 | W | P | 88.02(12) | C9 | C10 | C5 | 121.4(4) |
| C27 | W | C24 | 94.50(18) | C12 | C11 | C4 | 124.3(4) |
| C27 | W | C25 | 175.78(17) | C12 | C11 | C16 | 118.1(4) |
| C27 | W | C26 | 87.57(18) | C16 | C11 | C4 | 117.4(4) |
| O1 | P | W | 115.21(13) | C11 | C12 | C13 | 120.9(4) |
| O1 | P | C2 | 80.49(18) | C14 | C13 | C12 | 120.5(5) |
| O1 | P | C4 | 106.90(18) | C13 | C14 | C15 | 119.7(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2 | P | W | 117.62(17) | C14 | C15 | C16 | 120.2(5) |
| C2 | P | C4 | 107.1(2) | C15 | C16 | C11 | 120.6(4) |
| C4 | P | W | 121.82(13) | C18 | C17 | C4 | 123.2(4) |
| C1 | O1 | P | 91.8(3) | C18 | C17 | C22 | 117.3(4) |
| C1' | O1 | P | 97.5(4) | C22 | C17 | C4 | 119.3(4) |
| O1 | C1 | C2 | 95.4(5) | C19 | C18 | C17 | 121.1(4) |
| O1 | C1 | C3 | 107.8(8) | C18 | C19 | C20 | 120.9(4) |
| C3 | C1 | C2 | 114.1(9) | C21 | C20 | C19 | 118.4(4) |
| O1 | C1' | C2 | 92.9(6) | C22 | C21 | C20 | 120.5(4) |
| C3' | C1' | O1 | 105.5(11) | C21 | C22 | C17 | 121.7(4) |
| C3' | C1' | C2 | 113.6(12) | O2 | C23 | W | 177.1(5) |
| C1 | C2 | P | 84.0(4) | O3 | C24 | W | 174.0(4) |
| C1' | C2 | P | 87.0(4) | O4 | C25 | W | 179.5(5) |
| C5 | C4 | P | 102.6(3) | O5 | C26 | W | 177.2(4) |
| C5 | C4 | C11 | 112.8(3) | O6 | C27 | W | 175.1(4) |

***Table 4:*** Torsion angles for **21.3a**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | 95.8(5) | C4 | C5 | C10 | C9 | -178.0(4) |
| W | P | O1 | C1' | 126.8(7) | C4 | C11 | C12 | C13 | 174.9(4) |
| W | P | C2 | C1 | -93.6(5) | C4 | C11 | C16 | C15 | -175.9(4) |
| W | P | C2 | C1' | -123.5(6) | C4 | C17 | C18 | C19 | 177.9(4) |
| P | O1 | C1 | C2 | 24.2(6) | C4 | C17 | C22 | C21 | -177.8(4) |
| P | O1 | C1 | C3 | 141.7(8) | C5 | C4 | C11 | C12 | 120.7(4) |
| P | O1 | C1' | C2 | -12.0(7) | C5 | C4 | C11 | C16 | -65.0(5) |
| P | O1 | C1' | C3' | -127.5(9) | C5 | C4 | C17 | C18 | 0.0(5) |
| P | C4 | C5 | C6 | -60.8(4) | C5 | C4 | C17 | C22 | 175.6(4) |
| P | C4 | C5 | C10 | 116.0(4) | C5 | C6 | C7 | C8 | -1.1(7) |
| P | C4 | C11 | C12 | 6.4(5) | C6 | C5 | C10 | C9 | -1.1(6) |
| P | C4 | C11 | C16 | -179.3(3) | C6 | C7 | C8 | C9 | 0.0(7) |
| P | C4 | C17 | C18 | 115.6(4) | C7 | C8 | C9 | C10 | 0.5(7) |
| P | C4 | C17 | C22 | -68.9(4) | C8 | C9 | C10 | C5 | 0.1(7) |
| O1 | P | C2 | C1 | 20.0(5) | C10 | C5 | C6 | C7 | 1.6(6) |
| O1 | P | C2 | C1' | -9.9(6) | C11 | C4 | C5 | C6 | -179.7(4) |
| O1 | C1 | C2 | P | -21.7(5) | C11 | C4 | C5 | C10 | -3.0(5) |
| O1 | C1 | C2 | C1' | 72.7(10) | C11 | C4 | C17 | C18 | -124.4(4) |
| O1 | C1' | C2 | P | 10.7(7) | C11 | C4 | C17 | C22 | 51.1(5) |
| O1 | C1' | C2 | C1 | -72.5(10) | C11 | C12 | C13 | C14 | -0.2(7) |
| C1 | O1 | C1' | C2 | 69.0(10) | C12 | C11 | C16 | C15 | -1.3(6) |
| C1 | O1 | C1' | C3' | -46.5(12) | C12 | C13 | C14 | C15 | 0.4(7) |
| C1' | O1 | C1 | C2 | -77.3(11) | C13 | C14 | C15 | C16 | -1.1(7) |
| C1' | O1 | C1 | C3 | 40.2(11) | C14 | C15 | C16 | C11 | 1.5(7) |
| C2 | P | O1 | C1 | -20.3(5) | C16 | C11 | C12 | C13 | 0.6(6) |
| C2 | P | O1 | C1' | 10.6(7) | C17 | C4 | C5 | C6 | 59.7(5) |
| C3 | C1 | C2 | P | -134.0(8) | C17 | C4 | C5 | C10 | -123.5(4) |
| C3 | C1 | C2 | C1' | -39.6(11) | C17 | C4 | C11 | C12 | -114.1(4) |
| C3' | C1' | C2 | P | 119.0(11) | C17 | C4 | C11 | C16 | 60.2(5) |
| C3' | C1' | C2 | C1 | 35.9(12) | C17 | C18 | C19 | C20 | -1.1(7) |
| C4 | P | O1 | C1 | -125.4(5) | C18 | C17 | C22 | C21 | -2.0(7) |
| C4 | P | O1 | C1' | -94.4(7) | C18 | C19 | C20 | C21 | -0.3(7) |
| C4 | P | C2 | C1 | 124.9(5) | C19 | C20 | C21 | C22 | 0.6(7) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C4 | P | C2 | C1' | 95.0(6) | C20 | C21 | C22 | C17 | 0.6(7) |
| C4 | C5 | C6 | C7 | 178.6(4) | C22 | C17 | C18 | C19 | 2.2(6) |

## 12.22 Pentacarbonyl[4-(trifluoromethyl)-2-(triphenylmethyl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [21.3g]

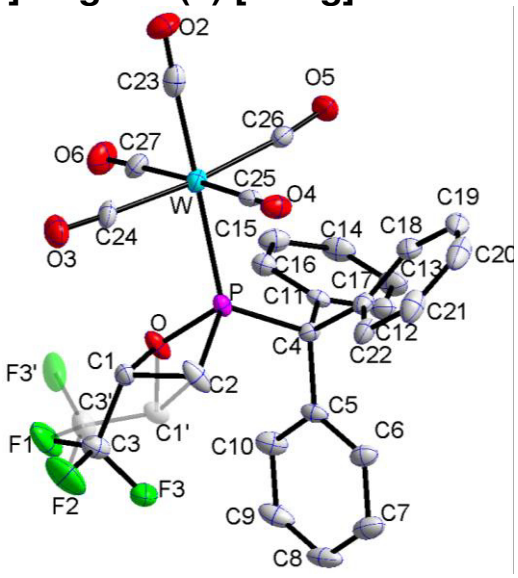


***Table 1:*** Crystal data and structure refinement for **21.3g**.

| | |
|---|---|
| Identification code | GSTR398, AKY-487 // GXray3940f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{27}H_{18}F_3O_6PW$ |
| Moiety formula | C27 H18 F3 O6 P W |
| Formula weight | 710.23 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.6002(10) |
| b/Å | 10.5444(11) |
| c/Å | 13.8429(14) |
| α/° | 71.032(3) |
| β/° | 76.087(3) |
| γ/° | 75.469(4) |
| Volume/Å$^3$ | 1263.3(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.867 |
| μ/mm$^{-1}$ | 4.699 |
| F(000) | 688.0 |
| Crystal size/mm$^3$ | 0.11 × 0.09 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5035; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.158 to 51.996° |
| Completeness to theta | 0.961 |
| Index ranges | -7 ≤ h ≤ 11, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17 |
| Reflections collected | 12605 |
| Independent reflections | 4756 [$R_{int}$ = 0.0286, $R_{sigma}$ = 0.0385] |
| Data/restraints/parameters | 4756/13/371 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.056 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0237, $wR_2$ = 0.0481 |
| Final R indexes [all data] | $R_1$ = 0.0298, $wR_2$ = 0.0511 |
| Largest diff. peak/hole / e $Å^{-3}$ | 1.17/-0.83 |

***Table 2:*** Bond lengths for **21.3g**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4695(9) | C3' | F3' | 1.369(9) |
| W | C23 | 2.035(4) | C4 | C5 | 1.542(4) |
| W | C24 | 2.018(4) | C4 | C11 | 1.532(4) |
| W | C25 | 2.037(4) | C4 | C17 | 1.547(5) |
| W | C26 | 2.063(4) | C5 | C6 | 1.383(5) |
| W | C27 | 2.045(4) | C5 | C10 | 1.396(5) |
| P | O1 | 1.681(2) | C6 | C7 | 1.395(5) |
| P | C2 | 1.841(4) | C7 | C8 | 1.374(6) |
| P | C4 | 1.885(4) | C8 | C9 | 1.370(6) |
| O1 | C1 | 1.457(6) | C9 | C10 | 1.386(5) |
| O1 | C1' | 1.538(9) | C11 | C12 | 1.388(5) |
| O2 | C23 | 1.116(4) | C11 | C16 | 1.388(5) |
| O3 | C24 | 1.145(4) | C12 | C13 | 1.373(5) |
| O4 | C25 | 1.137(4) | C13 | C14 | 1.384(6) |
| O5 | C26 | 1.121(4) | C14 | C15 | 1.371(6) |
| O6 | C27 | 1.137(4) | C15 | C16 | 1.383(5) |
| C1 | C3 | 1.503(10) | C17 | C18 | 1.379(5) |
| C1 | C2 | 1.603(7) | C17 | C22 | 1.394(5) |
| C3 | F1 | 1.305(9) | C18 | C19 | 1.392(5) |
| C3 | F2 | 1.325(9) | C19 | C20 | 1.372(6) |
| C3 | F3 | 1.316(10) | C20 | C21 | 1.359(6) |
| C1' | C3' | 1.429(18) | C21 | C22 | 1.381(5) |
| C1' | C2 | 1.556(9) | | | |

***Table 3:*** Bond angles for **21.3g**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C23 | W | P | 176.36(10) | C1' | C2 | P | 88.4(3) |
| C23 | W | C25 | 88.78(14) | C5 | C4 | P | 112.6(2) |
| C23 | W | C26 | 86.73(14) | C5 | C4 | C17 | 113.7(3) |
| C23 | W | C27 | 91.15(14) | C11 | C4 | P | 111.0(2) |
| C24 | W | P | 89.21(10) | C11 | C4 | C5 | 105.2(2) |
| C24 | W | C23 | 88.42(15) | C11 | C4 | C17 | 112.9(3) |
| C24 | W | C25 | 88.56(15) | C17 | C4 | P | 101.7(2) |
| C24 | W | C26 | 174.00(14) | C6 | C5 | C4 | 123.2(3) |
| C24 | W | C27 | 87.56(15) | C6 | C5 | C10 | 118.2(3) |
| C25 | W | P | 88.40(9) | C10 | C5 | C4 | 118.3(3) |
| C25 | W | C26 | 94.86(14) | C5 | C6 | C7 | 120.4(3) |
| C25 | W | C27 | 176.11(15) | C8 | C7 | C6 | 120.6(4) |
| C26 | W | P | 95.80(9) | C9 | C8 | C7 | 119.5(3) |
| C27 | W | P | 91.51(10) | C8 | C9 | C10 | 120.6(4) |
| C27 | W | C26 | 89.01(15) | C9 | C10 | C5 | 120.7(4) |
| O1 | P | W | 114.60(10) | C12 | C11 | C4 | 117.9(3) |
| O1 | P | C2 | 79.20(14) | C12 | C11 | C16 | 118.3(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 | P | C4 | 107.25(14) | C16 | C11 | C4 | 123.5(3) |
| C2 | P | W | 118.33(14) | C13 | C12 | C11 | 121.1(4) |
| C2 | P | C4 | 106.88(18) | C12 | C13 | C14 | 119.7(4) |
| C4 | P | W | 122.23(10) | C15 | C14 | C13 | 120.0(3) |
| C1 | O1 | P | 93.1(3) | C14 | C15 | C16 | 120.1(4) |
| C1' | O1 | P | 95.1(3) | C15 | C16 | C11 | 120.6(3) |
| O1 | C1 | C3 | 108.7(5) | C18 | C17 | C4 | 121.8(3) |
| O1 | C1 | C2 | 94.4(4) | C18 | C17 | C22 | 117.7(3) |
| C3 | C1 | C2 | 114.1(5) | C22 | C17 | C4 | 120.4(3) |
| F1 | C3 | C1 | 108.2(6) | C17 | C18 | C19 | 120.5(4) |
| F1 | C3 | F2 | 107.1(7) | C20 | C19 | C18 | 120.6(4) |
| F1 | C3 | F3 | 113.3(6) | C21 | C20 | C19 | 119.7(4) |
| F2 | C3 | C1 | 110.4(6) | C20 | C21 | C22 | 120.3(4) |
| F3 | C3 | C1 | 114.8(7) | C21 | C22 | C17 | 121.2(4) |
| F3 | C3 | F2 | 102.6(6) | O2 | C23 | W | 178.0(4) |
| O1 | C1' | C2 | 93.2(5) | O3 | C24 | W | 177.9(3) |
| C3' | C1' | O1 | 106.8(9) | O4 | C25 | W | 175.5(3) |
| C3' | C1' | C2 | 111.6(8) | O5 | C26 | W | 174.3(3) |
| F3' | C3' | C1' | 113.2(11) | O6 | C27 | W | 178.3(4) |
| C1 | C2 | P | 82.7(3) | | | | |

***Table 4:*** Torsion angles for **21.3g**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | -92.6(3) | C2 | C1 | C3 | F2 | 75.7(8) |
| W | P | O1 | C1' | -130.9(4) | C2 | C1 | C3 | F3 | -39.6(8) |
| W | P | C2 | C1 | 90.6(3) | C2 | C1' | C3' | F3' | 37.6(14) |
| W | P | C2 | C1' | 126.5(4) | C4 | P | O1 | C1 | 128.2(3) |
| W | P | C4 | C5 | 176.72(17) | C4 | P | O1 | C1' | 90.0(4) |
| W | P | C4 | C11 | -65.6(2) | C4 | P | C2 | C1 | -126.5(3) |
| W | P | C4 | C17 | 54.7(2) | C4 | P | C2 | C1' | -90.7(5) |
| P | O1 | C1 | C3 | -144.3(5) | C4 | C5 | C6 | C7 | -175.9(3) |
| P | O1 | C1 | C2 | -27.1(3) | C4 | C5 | C10 | C9 | 176.7(3) |
| P | O1 | C1' | C3' | 130.6(7) | C4 | C11 | C12 | C13 | 176.0(3) |
| P | O1 | C1' | C2 | 16.9(5) | C4 | C11 | C16 | C15 | -174.7(3) |
| P | C4 | C5 | C6 | -116.5(3) | C4 | C17 | C18 | C19 | 180.0(3) |
| P | C4 | C5 | C10 | 69.2(4) | C4 | C17 | C22 | C21 | 180.0(3) |
| P | C4 | C11 | C12 | 174.6(2) | C5 | C4 | C11 | C12 | -63.3(4) |
| P | C4 | C11 | C16 | -11.9(4) | C5 | C4 | C11 | C16 | 110.2(3) |
| P | C4 | C17 | C18 | -113.1(3) | C5 | C4 | C17 | C18 | 125.7(3) |
| P | C4 | C17 | C22 | 64.2(3) | C5 | C4 | C17 | C22 | -57.1(4) |
| O1 | P | C2 | C1 | -21.6(3) | C5 | C6 | C7 | C8 | -0.1(6) |
| O1 | P | C2 | C1' | 14.3(5) | C6 | C5 | C10 | C9 | 2.1(5) |
| O1 | P | C4 | C5 | -48.0(2) | C6 | C7 | C8 | C9 | 1.4(6) |
| O1 | P | C4 | C11 | 69.7(2) | C7 | C8 | C9 | C10 | -0.8(6) |
| O1 | P | C4 | C17 | -169.95(19) | C8 | C9 | C10 | C5 | -0.9(6) |
| O1 | C1 | C3 | F1 | -63.5(8) | C10 | C5 | C6 | C7 | -1.6(5) |
| O1 | C1 | C3 | F2 | 179.6(5) | C11 | C4 | C5 | C6 | 122.4(4) |
| O1 | C1 | C3 | F3 | 64.2(8) | C11 | C4 | C5 | C10 | -51.8(4) |
| O1 | C1 | C2 | P | 24.7(3) | C11 | C4 | C17 | C18 | 5.9(5) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | C2 | C1' | -72.5(6) | C11 | C4 | C17 | C22 | -176.8(3) |
| O1 | C1' | C3' | F3' | -62.9(12) | C11 | C12 | C13 | C14 | -1.6(5) |
| O1 | C1' | C2 | P | -15.4(5) | C12 | C11 | C16 | C15 | -1.3(5) |
| O1 | C1' | C2 | C1 | 64.5(6) | C12 | C13 | C14 | C15 | -0.1(6) |
| C1 | O1 | C1' | C3' | 42.1(8) | C13 | C14 | C15 | C16 | 1.0(5) |
| C1 | O1 | C1' | C2 | -71.6(6) | C14 | C15 | C16 | C11 | -0.3(5) |
| C3 | C1 | C2 | P | 137.5(5) | C16 | C11 | C12 | C13 | 2.2(5) |
| C3 | C1 | C2 | C1' | 40.2(7) | C17 | C4 | C5 | C6 | -1.6(5) |
| C1' | O1 | C1 | C3 | -50.0(7) | C17 | C4 | C5 | C10 | -175.8(3) |
| C1' | O1 | C1 | C2 | 67.2(7) | C17 | C4 | C11 | C12 | 61.2(4) |
| C3' | C1' | C2 | P | -124.9(8) | C17 | C4 | C11 | C16 | -125.3(3) |
| C3' | C1' | C2 | C1 | -45.0(9) | C17 | C18 | C19 | C20 | -1.1(6) |
| C2 | P | O1 | C1 | 23.7(3) | C18 | C17 | C22 | C21 | -2.7(5) |
| C2 | P | O1 | C1' | -14.5(5) | C18 | C19 | C20 | C21 | -0.6(6) |
| C2 | P | C4 | C5 | 35.7(3) | C19 | C20 | C21 | C22 | 0.6(6) |
| C2 | P | C4 | C11 | 153.4(2) | C20 | C21 | C22 | C17 | 1.1(6) |
| C2 | P | C4 | C17 | -86.3(2) | C22 | C17 | C18 | C19 | 2.7(5) |
| C2 | C1 | C3 | F1 | -167.3(5) | | | | | |

## 12.23 Pentacarbonyl[4,4-bis(trifluoromethyl)-2-(triphenylmethyl)-1,2-oxaphosphetane-κ*P*]tungsten(0) [25.3b]

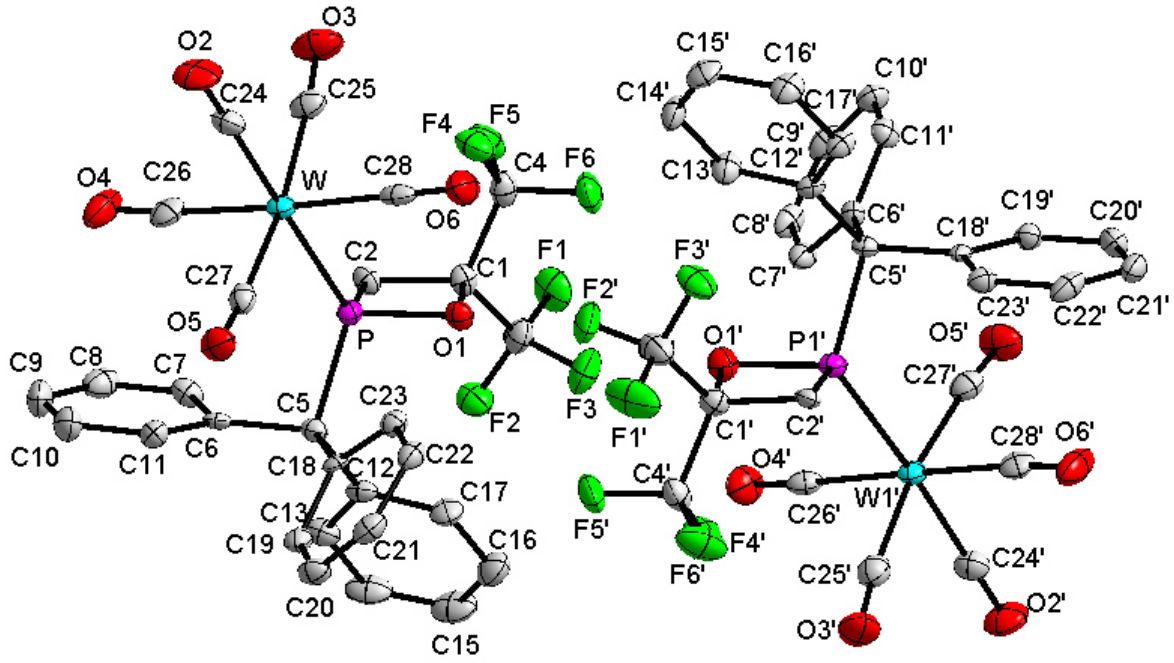


***Table 1:*** Crystal data and structure refinement for **25.3b**.

| | |
|---|---|
| Identification code | GSTR494, PB-13 // GXraymo_4641f |
| Crystal Habitus | clear colourless plate |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{28}H_{17}O_6F_6PW$ |
| Moiety formula | C28 H17 F6 O6 P W |
| Formula weight | 778.23 |
| Temperature/K | 150.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 14.5390(8) |

| | |
|---|---|
| b/Å | 11.5901(6) |
| c/Å | 32.8290(18) |
| α/° | 90 |
| β/° | 100.6203(19) |
| γ/° | 90 |
| Volume/Å$^3$ | 5437.2(5) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.901 |
| μ/mm$^{-1}$ | 4.391 |
| F(000) | 3008.0 |
| Crystal size/mm$^3$ | 0.14 × 0.12 × 0.05 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4359; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.3 to 55.996° |
| Completeness to theta | 1.000 |
| Index ranges | -19 ≤ h ≤ 19, -15 ≤ k ≤ 15, -43 ≤ l ≤ 43 |
| Reflections collected | 106615 |
| Independent reflections | 13119 [$R_{int}$ = 0.1371, $R_{sigma}$ = 0.0792] |
| Data/restraints/parameters | 13119/1/757 |
| Goodness-of-fit on F$^2$ | 1.008 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0384, $wR_2$ = 0.0603 |
| Final R indexes [all data] | $R_1$ = 0.0720, $wR_2$ = 0.0665 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.02/-1.08 |

***Table 2:*** Bond lengths for **25.3b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5017(11) | W1' | P1' | 2.4915(11) |
| W | C24 | 2.007(5) | W1' | C24' | 2.015(5) |
| W | C25 | 2.034(4) | W1' | C25' | 2.039(5) |
| W | C26 | 2.028(5) | W1' | C26' | 2.048(5) |
| W | C27 | 2.049(4) | W1' | C27' | 2.038(5) |
| W | C28 | 2.056(5) | W1' | C28' | 2.043(5) |
| P | O1 | 1.706(3) | P1' | O1' | 1.713(3) |
| P | C2 | 1.843(4) | P1' | C2' | 1.800(4) |
| P | C5 | 1.914(4) | P1' | C5' | 1.913(4) |
| F1 | C3 | 1.342(5) | F1' | C3' | 1.343(5) |
| F2 | C3 | 1.324(5) | F2' | C3' | 1.319(6) |
| F3 | C3 | 1.331(5) | F3' | C3' | 1.320(5) |
| F4 | C4 | 1.335(5) | F4' | C4' | 1.332(5) |
| F5 | C4 | 1.326(5) | F5' | C4' | 1.327(5) |
| F6 | C4 | 1.334(5) | F6' | C4' | 1.327(5) |
| O1 | C1 | 1.433(4) | O1' | C1' | 1.444(5) |
| O2 | C24 | 1.140(5) | O2' | C24' | 1.147(5) |
| O3 | C25 | 1.138(5) | O3' | C25' | 1.143(5) |
| O4 | C26 | 1.147(5) | O4' | C26' | 1.138(5) |
| O5 | C27 | 1.145(5) | O5' | C27' | 1.143(5) |
| O6 | C28 | 1.140(5) | O6' | C28' | 1.135(5) |
| C1 | C2 | 1.541(5) | C1' | C2' | 1.499(5) |
| C1 | C3 | 1.545(6) | C1' | C3' | 1.540(6) |
| C1 | C4 | 1.545(6) | C1' | C4' | 1.547(6) |
| C5 | C6 | 1.543(6) | C5' | C6' | 1.531(5) |

| | | | | | |
|---|---|---|---|---|---|
| C5 | C12 | 1.546(5) | C5' | C12' | 1.542(5) |
| C5 | C18 | 1.546(5) | C5' | C18' | 1.552(5) |
| C6 | C7 | 1.410(5) | C6' | C7' | 1.393(5) |
| C6 | C11 | 1.409(5) | C6' | C11' | 1.401(5) |
| C7 | C8 | 1.377(6) | C7' | C8' | 1.385(5) |
| C8 | C9 | 1.386(6) | C8' | C9' | 1.376(6) |
| C9 | C10 | 1.382(6) | C9' | C10' | 1.376(6) |
| C10 | C11 | 1.380(6) | C10' | C11' | 1.384(5) |
| C12 | C13 | 1.391(5) | C12' | C13' | 1.402(6) |
| C12 | C17 | 1.386(6) | C12' | C17' | 1.386(5) |
| C13 | C14 | 1.389(6) | C13' | C14' | 1.385(6) |
| C14 | C15 | 1.380(7) | C14' | C15' | 1.372(6) |
| C15 | C16 | 1.373(6) | C15' | C16' | 1.379(6) |
| C16 | C17 | 1.398(6) | C16' | C17' | 1.397(6) |
| C18 | C19 | 1.398(5) | C18' | C19' | 1.392(5) |
| C18 | C23 | 1.383(5) | C18' | C23' | 1.411(5) |
| C19 | C20 | 1.374(5) | C19' | C20' | 1.387(5) |
| C20 | C21 | 1.378(6) | C20' | C21' | 1.375(6) |
| C21 | C22 | 1.383(5) | C21' | C22' | 1.393(6) |
| C22 | C23 | 1.383(5) | C22' | C23' | 1.378(6) |

***Table 3:*** Bond angles for **25.3b**.

| **Atom** | **Atom** | **Atom** | **Angle/˚** | **Atom** | **Atom** | **Atom** | **Angle/˚** |
|---|---|---|---|---|---|---|---|
| C24 | W | P | 179.05(13) | C24' | W1' | P1' | 176.42(12) |
| C24 | W | C25 | 86.92(17) | C24' | W1' | C25' | 85.12(17) |
| C24 | W | C26 | 88.44(18) | C24' | W1' | C26' | 91.10(17) |
| C24 | W | C27 | 85.20(16) | C24' | W1' | C27' | 87.37(17) |
| C24 | W | C28 | 90.39(17) | C24' | W1' | C28' | 89.80(17) |
| C25 | W | P | 92.98(12) | C25' | W1' | P1' | 91.59(13) |
| C25 | W | C27 | 171.80(16) | C25' | W1' | C26' | 92.53(17) |
| C25 | W | C28 | 91.26(17) | C25' | W1' | C28' | 85.35(18) |
| C26 | W | P | 92.50(12) | C26' | W1' | P1' | 87.62(12) |
| C26 | W | C25 | 85.60(18) | C27' | W1' | P1' | 96.01(13) |
| C26 | W | C27 | 91.93(17) | C27' | W1' | C25' | 171.42(18) |
| C26 | W | C28 | 176.70(17) | C27' | W1' | C26' | 91.74(17) |
| C27 | W | P | 94.94(12) | C27' | W1' | C28' | 90.50(17) |
| C27 | W | C28 | 91.05(16) | C28' | W1' | P1' | 91.35(12) |
| C28 | W | P | 88.67(12) | C28' | W1' | C26' | 177.62(16) |
| O1 | P | W | 119.37(10) | O1' | P1' | W1' | 120.44(11) |
| O1 | P | C2 | 78.41(15) | O1' | P1' | C2' | 77.60(16) |
| O1 | P | C5 | 105.26(16) | O1' | P1' | C5' | 104.85(16) |
| C2 | P | W | 118.95(14) | C2' | P1' | W1' | 115.44(14) |
| C2 | P | C5 | 110.55(18) | C2' | P1' | C5' | 111.42(18) |
| C5 | P | W | 117.59(12) | C5' | P1' | W1' | 119.57(12) |
| C1 | O1 | P | 95.8(2) | C1' | O1' | P1' | 95.0(2) |
| O1 | C1 | C2 | 98.0(3) | O1' | C1' | C2' | 96.9(3) |
| O1 | C1 | C3 | 111.5(3) | O1' | C1' | C3' | 113.0(3) |
| O1 | C1 | C4 | 109.6(3) | O1' | C1' | C4' | 109.7(3) |
| C2 | C1 | C3 | 114.7(3) | C2' | C1' | C3' | 113.2(4) |
| C2 | C1 | C4 | 114.3(3) | C2' | C1' | C4' | 114.9(3) |
| C3 | C1 | C4 | 108.3(3) | C3' | C1' | C4' | 108.7(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C1 | C2 | P | 86.8(2) | C1' | C2' | P1' | 89.6(2) |
| F1 | C3 | C1 | 111.6(4) | F1' | C3' | C1' | 109.6(4) |
| F2 | C3 | F1 | 106.6(3) | F2' | C3' | F1' | 108.1(4) |
| F2 | C3 | F3 | 108.0(4) | F2' | C3' | F3' | 108.4(4) |
| F2 | C3 | C1 | 112.8(3) | F2' | C3' | C1' | 111.3(4) |
| F3 | C3 | F1 | 106.7(3) | F3' | C3' | F1' | 106.2(4) |
| F3 | C3 | C1 | 110.8(3) | F3' | C3' | C1' | 113.0(4) |
| F4 | C4 | C1 | 110.9(3) | F4' | C4' | C1' | 111.7(3) |
| F5 | C4 | F4 | 107.6(4) | F5' | C4' | F4' | 106.3(3) |
| F5 | C4 | F6 | 108.3(3) | F5' | C4' | C1' | 111.8(4) |
| F5 | C4 | C1 | 111.9(3) | F6' | C4' | F4' | 107.5(4) |
| F6 | C4 | F4 | 106.3(3) | F6' | C4' | F5' | 108.0(3) |
| F6 | C4 | C1 | 111.6(4) | F6' | C4' | C1' | 111.3(3) |
| C6 | C5 | P | 100.6(2) | C6' | C5' | P1' | 108.3(3) |
| C6 | C5 | C12 | 114.5(3) | C6' | C5' | C12' | 106.0(3) |
| C6 | C5 | C18 | 113.5(3) | C6' | C5' | C18' | 113.8(3) |
| C12 | C5 | P | 114.3(2) | C12' | C5' | P1' | 114.2(2) |
| C18 | C5 | P | 108.0(3) | C12' | C5' | C18' | 114.1(3) |
| C18 | C5 | C12 | 106.1(3) | C18' | C5' | P1' | 100.5(2) |
| C7 | C6 | C5 | 120.6(3) | C7' | C6' | C5' | 124.2(3) |
| C11 | C6 | C5 | 122.8(4) | C7' | C6' | C11' | 116.9(4) |
| C11 | C6 | C7 | 116.4(4) | C11' | C6' | C5' | 118.5(3) |
| C8 | C7 | C6 | 121.8(4) | C8' | C7' | C6' | 121.4(4) |
| C7 | C8 | C9 | 120.7(4) | C9' | C8' | C7' | 120.4(4) |
| C10 | C9 | C8 | 118.6(4) | C8' | C9' | C10' | 119.5(4) |
| C11 | C10 | C9 | 121.4(4) | C9' | C10' | C11' | 120.3(4) |
| C10 | C11 | C6 | 121.0(4) | C10' | C11' | C6' | 121.4(4) |
| C13 | C12 | C5 | 124.2(4) | C13' | C12' | C5' | 117.9(3) |
| C17 | C12 | C5 | 118.5(4) | C17' | C12' | C5' | 124.9(4) |
| C17 | C12 | C13 | 117.0(4) | C17' | C12' | C13' | 117.0(4) |
| C14 | C13 | C12 | 121.3(4) | C14' | C13' | C12' | 121.6(4) |
| C15 | C14 | C13 | 120.5(4) | C15' | C14' | C13' | 120.5(4) |
| C16 | C15 | C14 | 119.4(4) | C14' | C15' | C16' | 119.0(4) |
| C15 | C16 | C17 | 119.7(5) | C15' | C16' | C17' | 120.8(4) |
| C12 | C17 | C16 | 122.0(4) | C12' | C17' | C16' | 121.0(4) |
| C19 | C18 | C5 | 119.2(3) | C19' | C18' | C5' | 122.5(3) |
| C23 | C18 | C5 | 123.2(3) | C19' | C18' | C23' | 117.3(4) |
| C23 | C18 | C19 | 117.4(4) | C23' | C18' | C5' | 120.1(3) |
| C20 | C19 | C18 | 121.1(4) | C20' | C19' | C18' | 121.4(4) |
| C19 | C20 | C21 | 120.7(4) | C21' | C20' | C19' | 120.7(4) |
| C20 | C21 | C22 | 118.9(4) | C20' | C21' | C22' | 118.7(4) |
| C23 | C22 | C21 | 120.3(4) | C23' | C22' | C21' | 121.0(4) |
| C22 | C23 | C18 | 121.3(4) | C22' | C23' | C18' | 120.7(4) |
| O2 | C24 | W | 179.3(4) | O2' | C24' | W1' | 179.1(4) |
| O3 | C25 | W | 175.3(4) | O3' | C25' | W1' | 174.3(4) |
| O4 | C26 | W | 174.9(4) | O4' | C26' | W1' | 177.7(4) |
| O5 | C27 | W | 174.1(4) | O5' | C27' | W1' | 174.3(4) |
| O6 | C28 | W | 179.9(5) | O6' | C28' | W1' | 175.3(4) |

***Table 4:*** Torsion angles for **25.3b**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | -109.9(2) | W1' | P1' | O1' | C1' | 105.3(2) |
| W | P | C2 | C1 | 110.9(2) | W1' | P1' | C2' | C1' | -111.2(2) |
| P | O1 | C1 | C2 | -8.2(3) | P1' | O1' | C1' | C2' | 8.4(3) |
| P | O1 | C1 | C3 | -128.9(3) | P1' | O1' | C1' | C3' | 127.2(3) |
| P | O1 | C1 | C4 | 111.2(3) | P1' | O1' | C1' | C4' | -111.2(3) |
| P | C5 | C6 | C7 | 65.7(4) | P1' | C5' | C6' | C7' | 17.4(5) |
| P | C5 | C6 | C11 | -110.0(4) | P1' | C5' | C6' | C11' | -169.9(3) |
| P | C5 | C12 | C13 | -112.4(4) | P1' | C5' | C12' | C13' | -73.3(4) |
| P | C5 | C12 | C17 | 72.7(4) | P1' | C5' | C12' | C17' | 111.9(4) |
| P | C5 | C18 | C19 | 165.7(3) | P1' | C5' | C18' | C19' | 111.4(4) |
| P | C5 | C18 | C23 | -19.6(5) | P1' | C5' | C18' | C23' | -65.8(4) |
| O1 | P | C2 | C1 | -6.4(2) | O1' | P1' | C2' | C1' | 6.8(2) |
| O1 | C1 | C2 | P | 7.6(3) | O1' | C1' | C2' | P1' | -7.9(3) |
| O1 | C1 | C3 | F1 | -154.0(3) | O1' | C1' | C3' | F1' | 163.0(3) |
| O1 | C1 | C3 | F2 | 86.1(4) | O1' | C1' | C3' | F2' | 43.4(5) |
| O1 | C1 | C3 | F3 | -35.2(5) | O1' | C1' | C3' | F3' | -78.8(5) |
| O1 | C1 | C4 | F4 | -40.0(5) | O1' | C1' | C4' | F4' | 33.2(5) |
| O1 | C1 | C4 | F5 | -160.2(3) | O1' | C1' | C4' | F5' | -85.8(4) |
| O1 | C1 | C4 | F6 | 78.3(4) | O1' | C1' | C4' | F6' | 153.4(3) |
| C2 | P | O1 | C1 | 6.9(2) | C2' | P1' | O1' | C1' | -7.1(2) |
| C2 | C1 | C3 | F1 | 95.7(4) | C2' | C1' | C3' | F1' | -88.2(4) |
| C2 | C1 | C3 | F2 | -24.2(5) | C2' | C1' | C3' | F2' | 152.3(3) |
| C2 | C1 | C3 | F3 | -145.5(3) | C2' | C1' | C3' | F3' | 30.1(5) |
| C2 | C1 | C4 | F4 | 68.9(4) | C2' | C1' | C4' | F4' | -74.7(5) |
| C2 | C1 | C4 | F5 | -51.3(5) | C2' | C1' | C4' | F5' | 166.4(3) |
| C2 | C1 | C4 | F6 | -172.8(3) | C2' | C1' | C4' | F6' | 45.5(5) |
| C3 | C1 | C2 | P | 125.8(3) | C3' | C1' | C2' | P1' | -126.7(3) |
| C3 | C1 | C4 | F4 | -161.8(3) | C3' | C1' | C4' | F4' | 157.3(4) |
| C3 | C1 | C4 | F5 | 78.0(4) | C3' | C1' | C4' | F5' | 38.4(5) |
| C3 | C1 | C4 | F6 | -43.5(4) | C3' | C1' | C4' | F6' | -82.5(5) |
| C4 | C1 | C2 | P | -108.3(3) | C4' | C1' | C2' | P1' | 107.6(3) |
| C4 | C1 | C3 | F1 | -33.3(5) | C4' | C1' | C3' | F1' | 40.8(5) |
| C4 | C1 | C3 | F2 | -153.2(3) | C4' | C1' | C3' | F2' | -78.7(4) |
| C4 | C1 | C3 | F3 | 85.5(4) | C4' | C1' | C3' | F3' | 159.0(4) |
| C5 | P | O1 | C1 | 115.3(2) | C5' | P1' | O1' | C1' | -116.3(2) |
| C5 | P | C2 | C1 | -108.6(2) | C5' | P1' | C2' | C1' | 108.1(3) |
| C5 | C6 | C7 | C8 | -179.4(4) | C5' | C6' | C7' | C8' | 175.9(4) |
| C5 | C6 | C11 | C10 | 179.2(4) | C5' | C6' | C11' | C10' | -176.9(4) |
| C5 | C12 | C13 | C14 | -177.2(4) | C5' | C12' | C13' | C14' | -177.7(4) |
| C5 | C12 | C17 | C16 | 177.7(4) | C5' | C12' | C17' | C16' | 176.6(4) |
| C5 | C18 | C19 | C20 | -179.6(4) | C5' | C18' | C19' | C20' | 179.8(4) |
| C5 | C18 | C23 | C22 | -179.3(4) | C5' | C18' | C23' | C22' | 179.6(4) |
| C6 | C5 | C12 | C13 | 2.9(5) | C6' | C5' | C12' | C13' | 45.7(4) |
| C6 | C5 | C12 | C17 | -172.0(3) | C6' | C5' | C12' | C17' | -129.0(4) |
| C6 | C5 | C18 | C19 | 55.0(5) | C6' | C5' | C18' | C19' | -4.1(5) |
| C6 | C5 | C18 | C23 | -130.2(4) | C6' | C5' | C18' | C23' | 178.7(3) |
| C6 | C7 | C8 | C9 | 2.1(7) | C6' | C7' | C8' | C9' | -0.2(6) |
| C7 | C6 | C11 | C10 | 3.3(6) | C7' | C6' | C11' | C10' | -3.6(6) |
| C7 | C8 | C9 | C10 | -0.4(7) | C7' | C8' | C9' | C10' | -2.4(6) |
| C8 | C9 | C10 | C11 | 0.3(7) | C8' | C9' | C10' | C11' | 1.9(6) |
| C9 | C10 | C11 | C6 | -1.9(7) | C9' | C10' | C11' | C6' | 1.2(6) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C11 | C6 | C7 | C8 | -3.5(6) | C11' | C6' | C7' | C8' | 3.1(6) |
| C12 | C5 | C6 | C7 | -57.3(5) | C12' | C5' | C6' | C7' | -105.5(4) |
| C12 | C5 | C6 | C11 | 127.0(4) | C12' | C5' | C6' | C11' | 67.2(4) |
| C12 | C5 | C18 | C19 | -71.5(4) | C12' | C5' | C18' | C19' | -125.9(4) |
| C12 | C5 | C18 | C23 | 103.3(4) | C12' | C5' | C18' | C23' | 56.9(5) |
| C12 | C13 | C14 | C15 | 0.5(6) | C12' | C13' | C14' | C15' | 1.0(7) |
| C13 | C12 | C17 | C16 | 2.5(6) | C13' | C12' | C17' | C16' | 1.9(6) |
| C13 | C14 | C15 | C16 | 1.3(7) | C13' | C14' | C15' | C16' | 1.3(7) |
| C14 | C15 | C16 | C17 | -1.1(7) | C14' | C15' | C16' | C17' | -2.0(6) |
| C15 | C16 | C17 | C12 | -0.8(7) | C15' | C16' | C17' | C12' | 0.3(6) |
| C17 | C12 | C13 | C14 | -2.3(6) | C17' | C12' | C13' | C14' | -2.6(6) |
| C18 | C5 | C6 | C7 | -179.3(3) | C18' | C5' | C6' | C7' | 128.2(4) |
| C18 | C5 | C6 | C11 | 5.1(5) | C18' | C5' | C6' | C11' | -59.1(5) |
| C18 | C5 | C12 | C13 | 128.8(4) | C18' | C5' | C12' | C13' | 171.8(3) |
| C18 | C5 | C12 | C17 | -46.1(4) | C18' | C5' | C12' | C17' | -2.9(5) |
| C18 | C19 | C20 | C21 | -1.7(6) | C18' | C19' | C20' | C21' | 2.1(6) |
| C19 | C18 | C23 | C22 | -4.5(6) | C19' | C18' | C23' | C22' | 2.3(6) |
| C19 | C20 | C21 | C22 | -3.0(6) | C19' | C20' | C21' | C22' | -0.6(6) |
| C20 | C21 | C22 | C23 | 3.9(6) | C20' | C21' | C22' | C23' | -0.1(6) |
| C21 | C22 | C23 | C18 | -0.1(6) | C21' | C22' | C23' | C18' | -0.8(6) |
| C23 | C18 | C19 | C20 | 5.4(6) | C23' | C18' | C19' | C20' | -2.9(6) |

## 12.24 1,4-Bis[(pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-4-yl}-κ*P*)tungsten(0)]butane [29.1c]

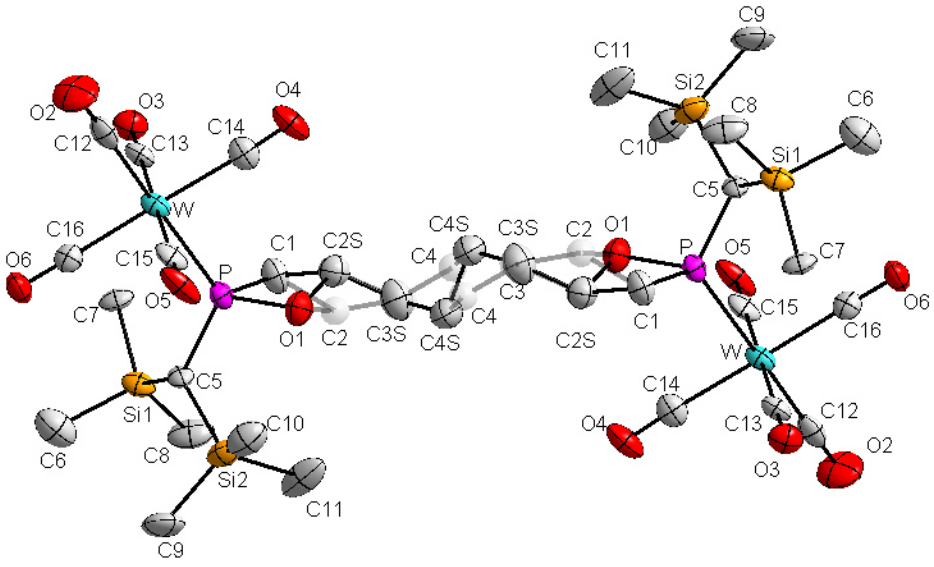


***Table 1:*** Crystal data and structure refinement for **29.1c**.

| | |
|---|---|
| Identification code | GSTR348, AKY-363 // GXray3322f |
| Crystal Habitus | colourless plate |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{32}H_{52}O_{12}P_2Si_4W_2$ |
| Moiety formula | C32 H52 O12 P2 Si4 W2 |
| Formula weight | 1170.74 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.416(3) |

| | |
|---|---|
| b/Å | 12.978(3) |
| c/Å | 18.692(4) |
| α/° | 90.00 |
| β/° | 129.782(11) |
| γ/° | 90.00 |
| Volume/Å$^3$ | 2314.6(10) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.680 |
| μ/mm$^{-1}$ | 5.189 |
| F(000) | 1148.0 |
| Crystal size/mm$^3$ | 0.12 × 0.05 × 0.03 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5748; 0.8599 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.48 to 50.5° |
| Completeness to theta | 0.975 |
| Index ranges | -12 ≤ h ≤ 14, -9 ≤ k ≤ 15, -22 ≤ l ≤ 15 |
| Reflections collected | 8151 |
| Independent reflections | 4088 [$R_{int}$ = 0.0483] |
| Data/restraints/parameters | 4088/67/264 |
| Goodness-of-fit on F$^2$ | 1.039 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0554, $wR_2$ = 0.1339 |
| Final R indexes [all data] | $R_1$ = 0.0843, $wR_2$ = 0.1500 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.38/-2.15 |

***Table 2:*** Bond lengths for **29.1c**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | C12 | 2.017(15) | Si2 | C11 | 1.890(15) |
| W | C15 | 2.025(14) | O1 | C2S | 1.47(2) |
| W | C13 | 2.034(12) | O1 | C2 | 1.58(7) |
| W | C16 | 2.036(13) | O3 | C13 | 1.155(14) |
| W | C14 | 2.046(13) | O4 | C14 | 1.120(15) |
| W | P | 2.480(3) | O5 | C15 | 1.151(15) |
| P | O1 | 1.689(9) | O6 | C16 | 1.160(14) |
| P | C5 | 1.809(12) | C1 | C2 | 1.53(7) |
| P | C1 | 1.824(14) | C1 | C2S | 1.55(2) |
| P | C2S | 2.312(18) | O2 | C12 | 1.138(16) |
| Si1 | C8 | 1.854(14) | C2 | C3 | 1.37(13) |
| Si1 | C6 | 1.857(17) | C3 | C4 | 1.61(8) |
| Si1 | C7 | 1.875(12) | C4 | C4$^1$ | 1.56(17) |
| Si1 | C5 | 1.948(12) | C2S | C3S | 1.40(3) |
| Si2 | C10 | 1.855(15) | C3S | C4S | 1.51(3) |
| Si2 | C9 | 1.861(16) | C4S | C4S$^1$ | 1.50(4) |
| Si2 | C5 | 1.870(13) | | | |

***Table 3:*** Bond angles for **29.1c**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C12 | W | C15 | 90.6(5) | C10 | Si2 | C5 | 109.7(6) |
| C12 | W | C13 | 90.2(5) | C9 | Si2 | C5 | 107.5(7) |
| C15 | W | C13 | 179.2(5) | C10 | Si2 | C11 | 108.7(8) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C12 | W | C16 | 91.2(5) | C9 | Si2 | C11 | 109.3(8) |
| C15 | W | C16 | 90.7(5) | C5 | Si2 | C11 | 113.7(6) |
| C13 | W | C16 | 89.3(5) | C2S | O1 | C2 | 33(3) |
| C12 | W | C14 | 90.4(5) | C2S | O1 | P | 93.8(8) |
| C15 | W | C14 | 89.9(5) | C2 | O1 | P | 94(3) |
| C13 | W | C14 | 90.1(5) | C2 | C1 | C2S | 33(3) |
| C16 | W | C14 | 178.3(5) | C2 | C1 | P | 90(3) |
| C12 | W | P | 177.3(4) | C2S | C1 | P | 86.0(9) |
| C15 | W | P | 87.1(4) | P | C5 | Si2 | 118.2(6) |
| C13 | W | P | 92.1(4) | P | C5 | Si1 | 110.6(6) |
| C16 | W | P | 90.1(3) | Si2 | C5 | Si1 | 117.7(6) |
| C14 | W | P | 88.3(4) | O3 | C13 | W | 178.3(11) |
| O1 | P | C5 | 108.0(5) | O4 | C14 | W | 177.0(12) |
| O1 | P | C1 | 79.1(5) | O5 | C15 | W | 179.3(13) |
| C5 | P | C1 | 111.7(6) | O6 | C16 | W | 178.4(11) |
| O1 | P | C2S | 39.4(5) | O2 | C12 | W | 177.1(13) |
| C5 | P | C2S | 126.8(7) | C3 | C2 | C1 | 126(7) |
| C1 | P | C2S | 42.1(6) | C3 | C2 | O1 | 128(6) |
| O1 | P | W | 114.0(3) | C1 | C2 | O1 | 92(4) |
| C5 | P | W | 116.7(4) | C2 | C3 | C4 | 121(8) |
| C1 | P | W | 120.9(5) | C4[1] | C4 | C3 | 124(8) |
| C2S | P | W | 115.8(5) | C3S | C2S | O1 | 112.0(18) |
| C8 | Si1 | C6 | 107.9(8) | C3S | C2S | C1 | 119.2(16) |
| C8 | Si1 | C7 | 110.4(6) | O1 | C2S | C1 | 95.5(12) |
| C6 | Si1 | C7 | 103.8(7) | C3S | C2S | P | 143.7(18) |
| C8 | Si1 | C5 | 112.4(7) | O1 | C2S | P | 46.8(6) |
| C6 | Si1 | C5 | 109.3(7) | C1 | C2S | P | 51.9(7) |
| C7 | Si1 | C5 | 112.4(5) | C2S | C3S | C4S | 119.2(18) |
| C10 | Si2 | C9 | 107.8(8) | C4S[1] | C4S | C3S | 113(2) |

***Table 4:*** Torsion angles for **29.1c**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| C12 | W | P | O1 | 25(8) | C14 | W | C13 | O3 | 84(36) |
| C15 | W | P | O1 | 54.1(5) | P | W | C13 | O3 | 172(36) |
| C13 | W | P | O1 | -126.0(5) | C12 | W | C14 | O4 | 7(21) |
| C16 | W | P | O1 | 144.7(5) | C15 | W | C14 | O4 | 98(21) |
| C14 | W | P | O1 | -36.0(5) | C13 | W | C14 | O4 | -83(21) |
| C12 | W | P | C5 | -102(8) | C16 | W | C14 | O4 | -151(19) |
| C15 | W | P | C5 | -73.0(6) | P | W | C14 | O4 | -175(21) |
| C13 | W | P | C5 | 107.0(5) | C12 | W | C15 | O5 | -82(100) |
| C16 | W | P | C5 | 17.7(6) | C13 | W | C15 | O5 | 98(100) |
| C14 | W | P | C5 | -163.0(6) | C16 | W | C15 | O5 | 9(100) |
| C12 | W | P | C1 | 117(8) | C14 | W | C15 | O5 | -173(100) |
| C15 | W | P | C1 | 145.5(6) | P | W | C15 | O5 | 99(100) |
| C13 | W | P | C1 | -34.5(6) | C12 | W | C16 | O6 | -95(41) |
| C16 | W | P | C1 | -123.8(6) | C15 | W | C16 | O6 | 174(100) |
| C14 | W | P | C1 | 55.5(6) | C13 | W | C16 | O6 | -5(41) |
| C12 | W | P | C2S | 69(8) | C14 | W | C16 | O6 | 63(50) |
| C15 | W | P | C2S | 97.7(6) | P | W | C16 | O6 | 87(41) |
| C13 | W | P | C2S | -82.3(6) | C15 | W | C12 | O2 | 6(25) |
| C16 | W | P | C2S | -171.7(6) | C13 | W | C12 | O2 | -174(25) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C14 | W | P | C2S | 7.7(6) | C16 | W | C12 | O2 | -85(25) |
| C5 | P | O1 | C2S | -126.6(10) | C14 | W | C12 | O2 | 96(25) |
| C1 | P | O1 | C2S | -17.1(10) | P | W | C12 | O2 | 35(31) |
| W | P | O1 | C2S | 102.0(9) | C2S | C1 | C2 | C3 | 77(9) |
| C5 | P | O1 | C2 | -94(3) | P | C1 | C2 | C3 | 159(8) |
| C1 | P | O1 | C2 | 16(3) | C2S | C1 | C2 | O1 | -65(4) |
| C2S | P | O1 | C2 | 33(3) | P | C1 | C2 | O1 | 17(3) |
| W | P | O1 | C2 | 135(3) | C2S | O1 | C2 | C3 | -67(9) |
| O1 | P | C1 | C2 | -16(3) | P | O1 | C2 | C3 | -159(9) |
| C5 | P | C1 | C2 | 89(3) | C2S | O1 | C2 | C1 | 73(5) |
| C2S | P | C1 | C2 | -32(3) | P | O1 | C2 | C1 | -18(4) |
| W | P | C1 | C2 | -128(3) | C1 | C2 | C3 | C4 | -115(10) |
| O1 | P | C1 | C2S | 16.2(10) | O1 | C2 | C3 | C4 | 14(15) |
| C5 | P | C1 | C2S | 121.4(10) | C2 | C3 | C4 | C4[1] | -55(16) |
| W | P | C1 | C2S | -95.3(10) | C2 | O1 | C2S | C3S | 54(5) |
| O1 | P | C5 | Si2 | -5.7(8) | P | O1 | C2S | C3S | 144.5(16) |
| C1 | P | C5 | Si2 | -90.9(8) | C2 | O1 | C2S | C1 | -71(5) |
| C2S | P | C5 | Si2 | -45.3(10) | P | O1 | C2S | C1 | 19.9(11) |
| W | P | C5 | Si2 | 124.2(6) | C2 | O1 | C2S | P | -91(5) |
| O1 | P | C5 | Si1 | 134.1(6) | C2 | C1 | C2S | C3S | -40(5) |
| C1 | P | C5 | Si1 | 48.9(8) | P | C1 | C2S | C3S | -137(2) |
| C2S | P | C5 | Si1 | 94.5(8) | C2 | C1 | C2S | O1 | 78(5) |
| W | P | C5 | Si1 | -96.0(6) | P | C1 | C2S | O1 | -18.4(10) |
| C10 | Si2 | C5 | P | -52.5(9) | C2 | C1 | C2S | P | 97(5) |
| C9 | Si2 | C5 | P | -169.5(8) | O1 | P | C2S | C3S | -66(2) |
| C11 | Si2 | C5 | P | 69.4(10) | C5 | P | C2S | C3S | 7(3) |
| C10 | Si2 | C5 | Si1 | 170.5(8) | C1 | P | C2S | C3S | 89(3) |
| C9 | Si2 | C5 | Si1 | 53.5(9) | W | P | C2S | C3S | -163(2) |
| C11 | Si2 | C5 | Si1 | -67.6(10) | C5 | P | C2S | O1 | 72.5(10) |
| C8 | Si1 | C5 | P | -99.9(8) | C1 | P | C2S | O1 | 154.5(15) |
| C6 | Si1 | C5 | P | 140.3(8) | W | P | C2S | O1 | -97.1(8) |
| C7 | Si1 | C5 | P | 25.5(8) | O1 | P | C2S | C1 | -154.5(15) |
| C8 | Si1 | C5 | Si2 | 40.1(10) | C5 | P | C2S | C1 | -82.0(11) |
| C6 | Si1 | C5 | Si2 | -79.7(9) | W | P | C2S | C1 | 108.5(9) |
| C7 | Si1 | C5 | Si2 | 165.5(7) | O1 | C2S | C3S | C4S | 52(3) |
| C12 | W | C13 | O3 | -7(36) | C1 | C2S | C3S | C4S | 162.3(19) |
| C15 | W | C13 | O3 | 173(32) | P | C2S | C3S | C4S | 98(3) |
| C16 | W | C13 | O3 | -98(36) | C2S | C3S | C4S | C4S[1] | 62(3) |

# 12.25 Pentacarbonyl{(2-iodoethoxy)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [33.1$_W$]

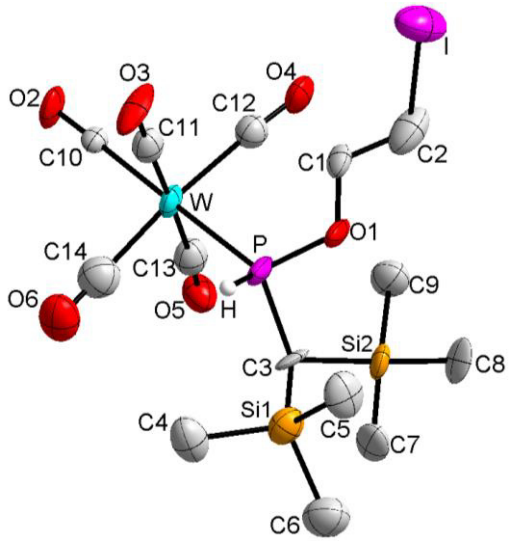


***Table 1:*** Crystal data and structure refinement for **33.1$_W$**.

| | |
|---|---|
| Identification code | GSTR383, AKY-424 // GXray3760f |
| Device Type | Bruker APEX-II CCD |
| Empirical formula | $C_{14}H_{24}IO_6PSi_2W$ |
| Formula weight | 686.23 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.179(3) |
| b/Å | 10.433(4) |
| c/Å | 14.066(5) |
| α/° | 86.293(10) |
| β/° | 81.810(10) |
| γ/° | 65.584(9) |
| Volume/Å$^3$ | 1214.0(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.877 |
| μ/mm$^{-1}$ | 6.216 |
| F(000) | 652.0 |
| Crystal size/mm$^3$ | 0.11 × 0.1 × 0.03 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.3610; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.92 to 50.5° |
| Completeness to theta | 0.852 |
| Index ranges | -10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16 |
| Reflections collected | 8231 |
| Independent reflections | 3734 [$R_{int}$ = 0.0751, $R_{sigma}$ = 0.1060] |
| Data/restraints/parameters | 3734/51/235 |
| Goodness-of-fit on F$^2$ | 1.231 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1405, $wR_2$ = 0.3049 |
| Final R indexes [all data] | $R_1$ = 0.1918, $wR_2$ = 0.3359 |
| Largest diff. peak/hole / e Å$^{-3}$ | 5.69/-4.76 |

***Table 2:*** Bond lengths for **33.1$_W$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.486(8) | Si2 | C7 | 1.88(5) |
| W | C14 | 1.98(6) | Si1 | C4 | 1.85(5) |
| W | C11 | 2.01(4) | Si1 | C6 | 1.88(5) |
| W | C10 | 2.07(3) | Si1 | C5 | 1.93(4) |
| W | C13 | 2.00(4) | Si1 | C3 | 1.87(4) |
| W | C12 | 2.02(5) | O4 | C12 | 1.20(5) |
| I | C2 | 2.16(5) | O2 | C10 | 1.09(3) |
| P | O1 | 1.63(2) | O1 | C1 | 1.46(4) |
| P | C3 | 1.79(3) | O5 | C13 | 1.21(5) |
| Si2 | C9 | 1.87(4) | O3 | C11 | 1.21(4) |
| Si2 | C8 | 1.81(4) | O6 | C14 | 1.10(6) |
| Si2 | C3 | 1.93(4) | C1 | C2 | 1.44(6) |

***Table 3:*** Bond angles for **33.1$_W$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C14 | W | P | 87.0(14) | C8 | Si2 | C3 | 110.6(16) |
| C14 | W | C11 | 90.8(19) | C8 | Si2 | C7 | 115.4(18) |
| C14 | W | C10 | 92.8(16) | C7 | Si2 | C3 | 106.8(17) |
| C14 | W | C13 | 88.3(19) | C4 | Si1 | C6 | 108(3) |
| C14 | W | C12 | 174.5(17) | C4 | Si1 | C5 | 112(2) |
| C11 | W | P | 86.6(10) | C4 | Si1 | C3 | 109.1(19) |
| C11 | W | C10 | 90.0(13) | C6 | Si1 | C5 | 103(2) |
| C11 | W | C12 | 92.6(16) | C3 | Si1 | C6 | 112(2) |
| C10 | W | P | 176.5(9) | C3 | Si1 | C5 | 112.0(19) |
| C13 | W | P | 94.8(11) | C1 | O1 | P | 120.8(18) |
| C13 | W | C11 | 178.3(16) | C2 | C1 | O1 | 105(3) |
| C13 | W | C10 | 88.6(13) | O6 | C14 | W | 174(5) |
| C13 | W | C12 | 88.3(17) | C1 | C2 | I | 109(3) |
| C12 | W | P | 88.9(10) | O3 | C11 | W | 177(4) |
| C12 | W | C10 | 91.5(14) | P | C3 | Si2 | 116(2) |
| O1 | P | W | 120.0(10) | P | C3 | Si1 | 111.8(19) |
| O1 | P | C3 | 99.5(14) | Si1 | C3 | Si2 | 116.6(15) |
| C3 | P | W | 122.5(12) | O2 | C10 | W | 175(3) |
| C9 | Si2 | C3 | 112.3(17) | O5 | C13 | W | 176(4) |
| C9 | Si2 | C7 | 107(2) | O4 | C12 | W | 171(3) |
| C8 | Si2 | C9 | 105(2) | | | | |

***Table 4:*** Torsion angles for **33.1$_W$**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | 51(3) | C11 | W | P | O1 | -75.4(17) |
| W | P | C3 | Si2 | 92.5(18) | C11 | W | P | C3 | 158(2) |
| W | P | C3 | Si1 | -130.9(13) | C11 | W | C14 | O6 | -23(42) |
| P | W | C14 | O6 | 64(42) | C11 | W | C10 | O2 | -29(33) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| P | W | C11 | O3 | 108(67) | C11 | W | C13 | O5 | -56(87) |
| P | W | C10 | O2 | -25(47) | C11 | W | C12 | O4 | -169(19) |
| P | W | C13 | O5 | 90(46) | C3 | P | O1 | C1 | -172(3) |
| P | W | C12 | O4 | 105(19) | C10 | W | P | O1 | -80(17) |
| P | O1 | C1 | C2 | -152(3) | C10 | W | P | C3 | 154(16) |
| O1 | P | C3 | Si2 | -43(2) | C10 | W | C14 | O6 | -113(42) |
| O1 | P | C3 | Si1 | 94(2) | C10 | W | C11 | O3 | -72(67) |
| O1 | C1 | C2 | I | -179(2) | C10 | W | C13 | O5 | -90(46) |
| C14 | W | P | O1 | -166.4(19) | C10 | W | C12 | O4 | -79(19) |
| C14 | W | P | C3 | 67(2) | C7 | Si2 | C3 | P | -147(2) |
| C14 | W | C11 | O3 | -165(67) | C7 | Si2 | C3 | Si1 | 78(2) |
| C14 | W | C10 | O2 | 62(33) | C13 | W | P | O1 | 105.5(18) |
| C14 | W | C13 | O5 | 3(46) | C13 | W | P | C3 | -21(2) |
| C14 | W | C12 | O4 | 63(30) | C13 | W | C14 | O6 | 159(42) |
| C9 | Si2 | C3 | P | -30(3) | C13 | W | C11 | O3 | -106(87) |
| C9 | Si2 | C3 | Si1 | -165(2) | C13 | W | C10 | O2 | 150(33) |
| C4 | Si1 | C3 | P | 64(3) | C13 | W | C12 | O4 | 10(19) |
| C4 | Si1 | C3 | Si2 | -159(2) | C12 | W | P | O1 | 17.3(16) |
| C6 | Si1 | C3 | P | -175(2) | C12 | W | P | C3 | -109(2) |
| C6 | Si1 | C3 | Si2 | -39(3) | C12 | W | C14 | O6 | 106(43) |
| C8 | Si2 | C3 | P | 86(2) | C12 | W | C11 | O3 | 19(67) |
| C8 | Si2 | C3 | Si1 | -48(3) | C12 | W | C10 | O2 | -122(33) |
| C5 | Si1 | C3 | P | -60(3) | C12 | W | C13 | O5 | 179(100) |
| C5 | Si1 | C3 | Si2 | 76(2) | | | | | |

## 12.26 Pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}tungsten(0) [34.1$_W$]

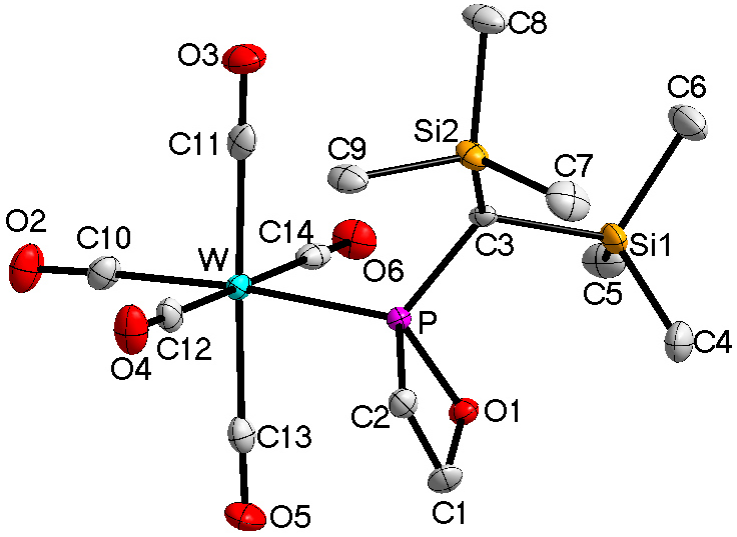


***Table 1:*** Crystal data and structure refinement for **34.1$_W$**.

| | |
|---|---|
| Identification code | GSTR389, AKY-466 // GXray3853f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{14}H_{23}O_6PSi_2W$ |
| Formula weight | 558.32 |
| Temperature/K | 100 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.7786(5) |

| | |
|---|---|
| b/Å | 9.9521(4) |
| c/Å | 21.9977(10) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2140.76(17) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.732 |
| μ/mm$^{-1}$ | 5.606 |
| F(000) | 1088.0 |
| Crystal size/mm$^3$ | 0.12 × 0.09 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5298; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.128 to 55.972° |
| Completeness to theta | 0.994 |
| Index ranges | -12 ≤ h ≤ 10, -11 ≤ k ≤ 13, -28 ≤ l ≤ 18 |
| Reflections collected | 15593 |
| Independent reflections | 5137 [$R_{int}$ = 0.0371, $R_{sigma}$ = 0.0490] |
| Data/restraints/parameters | 5137/0/217 |
| Goodness-of-fit on $F^2$ | 0.940 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0230, $wR_2$ = 0.0392 |
| Final R indexes [all data] | $R_1$ = 0.0252, $wR_2$ = 0.0398 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.44/-0.38 |
| Flack parameter | 0.126(5) |

***Table 2:*** Bond lengths for **34.1$_W$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4654(13) | Si1 | C6 | 1.876(5) |
| W | C10 | 2.022(6) | Si2 | C3 | 1.918(5) |
| W | C11 | 2.024(5) | Si2 | C7 | 1.862(6) |
| W | C12 | 2.028(6) | Si2 | C8 | 1.866(5) |
| W | C13 | 2.056(5) | Si2 | C9 | 1.867(5) |
| W | C14 | 2.056(5) | O1 | C1 | 1.462(6) |
| P | O1 | 1.672(3) | O2 | C10 | 1.142(7) |
| P | C2 | 1.830(5) | O3 | C11 | 1.150(5) |
| P | C3 | 1.810(4) | O4 | C12 | 1.152(6) |
| Si1 | C3 | 1.902(5) | O5 | C13 | 1.138(5) |
| Si1 | C4 | 1.857(6) | O6 | C14 | 1.141(6) |
| Si1 | C5 | 1.865(6) | C1 | C2 | 1.531(6) |

***Table 3:*** Bond angles for **34.1$_W$**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C10 | W | P | 174.96(14) | C4 | Si1 | C5 | 111.4(3) |
| C10 | W | C11 | 91.9(2) | C4 | Si1 | C6 | 107.8(3) |
| C10 | W | C12 | 88.6(2) | C5 | Si1 | C3 | 107.8(3) |
| C10 | W | C13 | 90.21(19) | C5 | Si1 | C6 | 107.7(3) |
| C10 | W | C14 | 93.2(2) | C6 | Si1 | C3 | 108.4(2) |
| C11 | W | P | 92.29(16) | C7 | Si2 | C3 | 112.6(3) |
| C11 | W | C12 | 88.72(19) | C7 | Si2 | C8 | 110.5(3) |
| C11 | W | C13 | 177.7(2) | C7 | Si2 | C9 | 107.6(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C11 | W | C14 | 90.22(18) | C8 | Si2 | C3 | 106.8(2) |
| C12 | W | P | 88.66(16) | C8 | Si2 | C9 | 107.9(2) |
| C12 | W | C13 | 92.2(2) | C9 | Si2 | C3 | 111.4(2) |
| C12 | W | C14 | 177.9(2) | C1 | O1 | P | 93.6(3) |
| C13 | W | P | 85.65(14) | O1 | C1 | C2 | 98.4(3) |
| C14 | W | P | 89.58(16) | C1 | C2 | P | 85.4(3) |
| C14 | W | C13 | 88.78(19) | P | C3 | Si1 | 114.2(2) |
| O1 | P | W | 113.90(15) | P | C3 | Si2 | 113.9(2) |
| O1 | P | C2 | 80.5(2) | Si1 | C3 | Si2 | 116.8(3) |
| O1 | P | C3 | 107.44(19) | O2 | C10 | W | 176.9(5) |
| C2 | P | W | 119.28(18) | O3 | C11 | W | 179.1(5) |
| C3 | P | W | 118.71(19) | O4 | C12 | W | 178.8(4) |
| C3 | P | C2 | 110.3(3) | O5 | C13 | W | 178.6(5) |
| C4 | Si1 | C3 | 113.5(2) | O6 | C14 | W | 179.8(5) |

***Table 4:*** Torsion angles for **34.1$_W$**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | -107.7(3) | O1 | P | C3 | Si2 | -133.9(3) |
| W | P | C2 | C1 | 102.4(3) | O1 | C1 | C2 | P | 11.2(3) |
| W | P | C3 | Si1 | -127.1(2) | C2 | P | O1 | C1 | 10.3(3) |
| W | P | C3 | Si2 | 95.1(3) | C2 | P | C3 | Si1 | 90.0(3) |
| P | O1 | C1 | C2 | -12.3(4) | C2 | P | C3 | Si2 | -47.8(4) |
| O1 | P | C2 | C1 | -9.8(3) | C3 | P | O1 | C1 | 118.7(3) |
| O1 | P | C3 | Si1 | 3.9(4) | C3 | P | C2 | C1 | -115.0(3) |

## 12.27 Pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}molybdenum(0) [34.1$_{Mo}$]

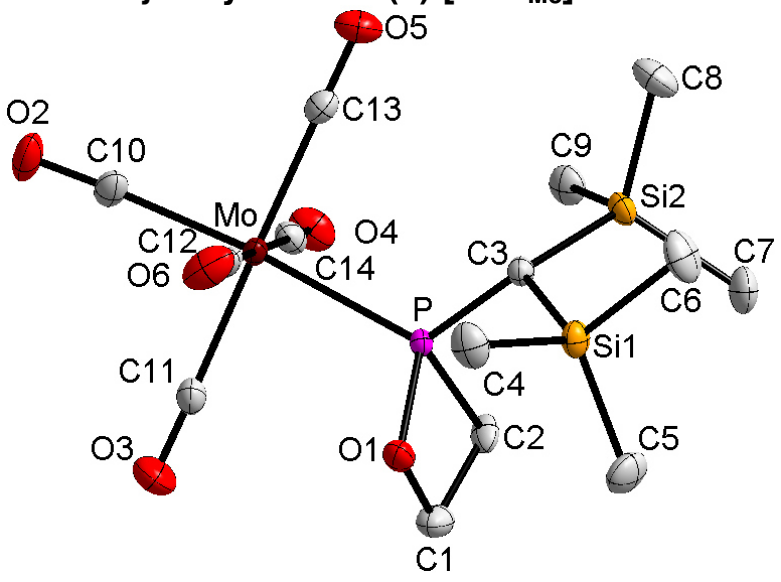


***Table 1:*** Crystal data and structure refinement for **34.1$_{Mo}$**.

| | |
|---|---|
| Identification code | GSTR493, FG-oxa // GXray4661f |
| Crystal Habitus | clear colourless block |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{14}H_{23}O_6Si_2PMo$ |
| Moiety formula | C14 H23 Mo O6 P Si2 |
| Formula weight | 470.41 |
| Temperature/K | 100 |

| | |
|---|---|
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 10.5481(4) |
| b/Å | 13.2373(4) |
| c/Å | 15.1957(5) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2121.75(12) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.473 |
| μ/mm$^{-1}$ | 0.830 |
| F(000) | 960.0 |
| Crystal size/mm$^3$ | 0.5 × 0.4 × 0.3 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.6030; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.08 to 55.998° |
| Completeness to theta | 0.991 |
| Index ranges | -8 ≤ h ≤ 13, -16 ≤ k ≤ 17, -10 ≤ l ≤ 20 |
| Reflections collected | 11052 |
| Independent reflections | 5081 [$R_{int}$ = 0.0204, $R_{sigma}$ = 0.0272] |
| Data/restraints/parameters | 5081/0/224 |
| Goodness-of-fit on F$^2$ | 1.019 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0184, $wR_2$ = 0.0416 |
| Final R indexes [all data] | $R_1$ = 0.0204, $wR_2$ = 0.0424 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.36/-0.57 |
| Flack parameter | 0.52(3) |

***Table 2:*** Bond lengths for **34.1$_{Mo}$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Mo | P | 2.4768(6) | Si1 | C6 | 1.873(3) |
| Mo | C10 | 2.023(2) | Si2 | C3 | 1.913(2) |
| Mo | C11 | 2.044(3) | Si2 | C7 | 1.874(3) |
| Mo | C12 | 2.038(3) | Si2 | C8 | 1.869(3) |
| Mo | C13 | 2.053(3) | Si2 | C9 | 1.866(3) |
| Mo | C14 | 2.065(3) | O1 | C1 | 1.462(3) |
| P | O1 | 1.6759(17) | O2 | C10 | 1.141(3) |
| P | C2 | 1.833(2) | O3 | C11 | 1.135(3) |
| P | C3 | 1.809(2) | O4 | C14 | 1.137(3) |
| Si1 | C3 | 1.908(2) | O5 | C13 | 1.136(3) |
| Si1 | C4 | 1.865(3) | O6 | C12 | 1.137(3) |
| Si1 | C5 | 1.858(3) | C1 | C2 | 1.543(4) |

***Table 3:*** Bond angles for **34.1$_{Mo}$**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C10 | Mo | P | 172.41(7) | C4 | Si1 | C6 | 106.35(14) |
| C10 | Mo | C11 | 88.69(10) | C5 | Si1 | C3 | 112.91(12) |
| C10 | Mo | C12 | 88.26(10) | C5 | Si1 | C4 | 110.29(14) |
| C10 | Mo | C13 | 92.01(10) | C5 | Si1 | C6 | 109.53(14) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C10 | Mo | C14 | 93.34(10) | C6 | Si1 | C3 | 109.07(12) |
| C11 | Mo | P | 87.22(7) | C7 | Si2 | C3 | 112.92(11) |
| C11 | Mo | C13 | 178.50(10) | C8 | Si2 | C3 | 106.80(11) |
| C11 | Mo | C14 | 90.34(10) | C8 | Si2 | C7 | 110.25(13) |
| C12 | Mo | P | 85.43(7) | C9 | Si2 | C3 | 111.62(11) |
| C12 | Mo | C11 | 91.16(10) | C9 | Si2 | C7 | 107.94(13) |
| C12 | Mo | C13 | 90.18(10) | C9 | Si2 | C8 | 107.17(13) |
| C12 | Mo | C14 | 177.83(10) | C1 | O1 | P | 94.28(14) |
| C13 | Mo | P | 92.23(7) | O1 | C1 | C2 | 97.95(19) |
| C13 | Mo | C14 | 88.30(9) | C1 | C2 | P | 85.64(15) |
| C14 | Mo | P | 93.08(7) | P | C3 | Si1 | 115.76(11) |
| O1 | P | Mo | 111.00(6) | P | C3 | Si2 | 112.51(12) |
| O1 | P | C2 | 80.40(11) | Si1 | C3 | Si2 | 115.84(11) |
| O1 | P | C3 | 108.33(10) | O2 | C10 | Mo | 175.6(2) |
| C2 | P | Mo | 123.09(8) | O3 | C11 | Mo | 178.7(2) |
| C3 | P | Mo | 118.17(7) | O6 | C12 | Mo | 178.8(2) |
| C3 | P | C2 | 108.86(11) | O5 | C13 | Mo | 179.5(2) |
| C4 | Si1 | C3 | 108.47(11) | O4 | C14 | Mo | 178.6(2) |

***Table 4:*** Torsion angles for **34.1$_{Mo}$**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Mo | P | O1 | C1 | 112.42(13) | O1 | P | C3 | Si2 | 137.28(11) |
| Mo | P | C2 | C1 | -99.91(15) | O1 | C1 | C2 | P | -10.24(16) |
| Mo | P | C3 | Si1 | 128.19(9) | C2 | P | O1 | C1 | -9.47(15) |
| Mo | P | C3 | Si2 | -95.45(11) | C2 | P | C3 | Si1 | -84.93(15) |
| P | O1 | C1 | C2 | 11.21(18) | C2 | P | C3 | Si2 | 51.44(15) |
| O1 | P | C2 | C1 | 8.96(14) | C3 | P | O1 | C1 | -116.29(15) |
| O1 | P | C3 | Si1 | 0.91(15) | C3 | P | C2 | C1 | 115.18(15) |

## 12.28 Pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphosphetane-κ*P*}chromium(0) [34.1$_{Cr}$]

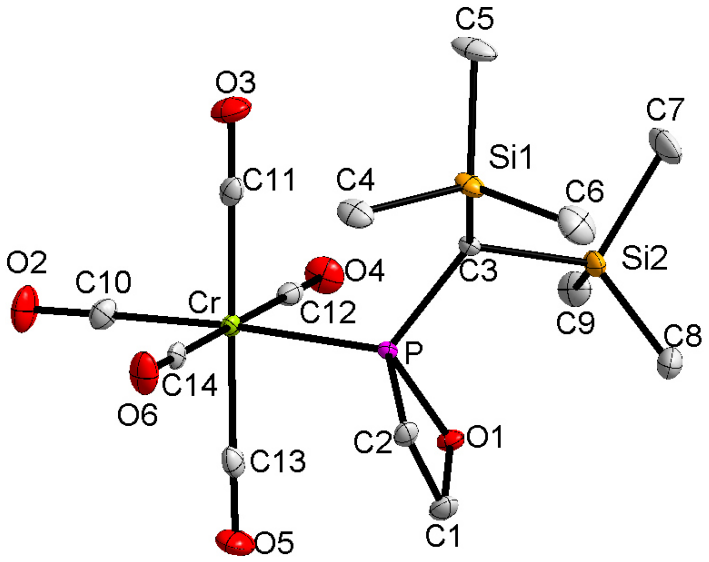

***Table 1:*** Crystal data and structure refinement for **34.1$_{Cr}$**.

| | |
|---|---|
| Identification code | GSTR461, AKY-526 // GXraymo_4477f |
| Crystal Habitus | clear colourless block |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{14}H_{23}O_6Si_2PCr$ |
| Moiety formula | C14 H23 Cr O6 P Si2 |
| Formula weight | 426.47 |
| Temperature/K | 100 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.5614(5) |
| b/Å | 9.8975(6) |
| c/Å | 21.8528(13) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2068.0(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.370 |
| μ/mm$^{-1}$ | 0.770 |
| F(000) | 888.0 |
| Crystal size/mm$^3$ | 0.26 × 0.24 × 0.24 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.6116; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.65 to 55.99° |
| Completeness to theta | 0.998 |
| Index ranges | -12 ≤ h ≤ 12, -13 ≤ k ≤ 12, -28 ≤ l ≤ 27 |
| Reflections collected | 19858 |
| Independent reflections | 4983 [$R_{int}$ = 0.0468, $R_{sigma}$ = 0.0481] |
| Data/restraints/parameters | 4983/0/229 |
| Goodness-of-fit on $F^2$ | 1.060 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0333, $wR_2$ = 0.0600 |
| Final R indexes [all data] | $R_1$ = 0.0405, $wR_2$ = 0.0618 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.31/-0.30 |
| Flack parameter | 0.005(10) |

***Table 2:*** Bond lengths for **34.1$_{Cr}$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cr | P | 2.3183(8) | Si1 | C6 | 1.869(3) |
| Cr | C10 | 1.875(3) | Si2 | C3 | 1.905(3) |
| Cr | C11 | 1.884(3) | Si2 | C7 | 1.867(4) |
| Cr | C12 | 1.905(3) | Si2 | C8 | 1.863(3) |
| Cr | C13 | 1.908(3) | Si2 | C9 | 1.865(3) |
| Cr | C14 | 1.890(3) | O1 | C1 | 1.470(4) |
| P | O1 | 1.669(2) | O2 | C10 | 1.142(4) |
| P | C1 | 2.304(3) | O3 | C11 | 1.144(4) |
| P | C2 | 1.838(3) | O4 | C12 | 1.144(4) |
| P | C3 | 1.808(3) | O5 | C13 | 1.138(4) |
| Si1 | C3 | 1.915(3) | O6 | C14 | 1.147(4) |
| Si1 | C4 | 1.868(3) | C1 | C2 | 1.529(4) |
| Si1 | C5 | 1.862(3) | | | |

***Table 3:*** Bond angles for **34.1$_{Cr}$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C10 | Cr | P | 176.34(10) | C4 | Si1 | C3 | 111.99(13) |
| C10 | Cr | C11 | 91.16(13) | C4 | Si1 | C6 | 106.94(16) |
| C10 | Cr | C12 | 92.30(13) | C5 | Si1 | C3 | 106.85(14) |
| C10 | Cr | C13 | 89.75(12) | C5 | Si1 | C4 | 107.97(15) |
| C10 | Cr | C14 | 89.42(12) | C5 | Si1 | C6 | 110.34(17) |
| C11 | Cr | P | 92.32(9) | C6 | Si1 | C3 | 112.68(14) |
| C11 | Cr | C12 | 90.32(13) | C7 | Si2 | C3 | 108.62(14) |
| C11 | Cr | C13 | 178.92(13) | C8 | Si2 | C3 | 113.30(14) |
| C11 | Cr | C14 | 88.97(13) | C8 | Si2 | C7 | 108.10(16) |
| C12 | Cr | P | 88.82(9) | C8 | Si2 | C9 | 110.97(16) |
| C12 | Cr | C13 | 89.06(13) | C9 | Si2 | C3 | 108.58(13) |
| C13 | Cr | P | 86.78(8) | C9 | Si2 | C7 | 107.06(16) |
| C14 | Cr | P | 89.51(8) | C1 | O1 | P | 94.21(16) |
| C14 | Cr | C12 | 178.15(13) | O1 | C1 | P | 46.27(11) |
| C14 | Cr | C13 | 91.63(13) | O1 | C1 | C2 | 97.8(2) |
| O1 | P | Cr | 114.00(8) | C2 | C1 | P | 52.71(14) |
| O1 | P | C1 | 39.52(10) | C1 | C2 | P | 85.86(18) |
| O1 | P | C2 | 80.11(11) | P | C3 | Si1 | 114.23(14) |
| O1 | P | C3 | 107.07(12) | P | C3 | Si2 | 114.33(14) |
| C1 | P | Cr | 120.07(9) | Si2 | C3 | Si1 | 116.52(14) |
| C2 | P | Cr | 120.29(10) | O2 | C10 | Cr | 178.3(3) |
| C2 | P | C1 | 41.44(12) | O3 | C11 | Cr | 179.0(3) |
| C3 | P | Cr | 118.66(9) | O4 | C12 | Cr | 179.4(3) |
| C3 | P | C1 | 120.74(12) | O5 | C13 | Cr | 178.9(3) |
| C3 | P | C2 | 109.79(13) | O6 | C14 | Cr | 179.2(3) |

***Table 4:*** Torsion angles for **34.1$_{Cr}$**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Cr | P | O1 | C1 | -108.79(15) | O1 | C1 | C2 | P | 10.95(19) |
| Cr | P | C2 | C1 | 102.42(16) | C1 | P | C3 | Si1 | -92.43(17) |
| Cr | P | C3 | Si1 | 95.96(13) | C1 | P | C3 | Si2 | 45.38(19) |
| Cr | P | C3 | Si2 | -126.23(11) | C2 | P | O1 | C1 | 10.08(17) |
| P | O1 | C1 | C2 | -12.1(2) | C2 | P | C3 | Si1 | -47.90(18) |
| O1 | P | C2 | C1 | -9.69(17) | C2 | P | C3 | Si2 | 89.91(17) |
| O1 | P | C3 | Si1 | -133.29(13) | C3 | P | O1 | C1 | 117.90(17) |
| O1 | P | C3 | Si2 | 4.52(17) | C3 | P | C2 | C1 | -114.40(18) |

# 12.29 Pentacarbonyl{2-[bis(trimethylsilyl)methyl]-1,2-oxaphospholane-κ*P*}tungsten(0) [19.1]

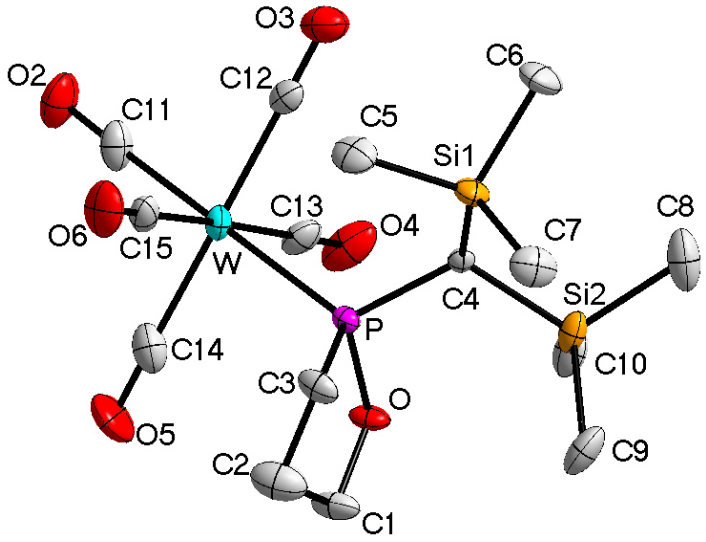


***Table 1:*** Crystal data and structure refinement for **19.1**.

| | |
|---|---|
| Identification code | GSTR485, AKY-554 // GXraymo_4626f |
| Crystal Habitus | clear light yellow plate |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{15}H_{25}O_6Si_2PW$ |
| Moiety formula | C15 H25 O6 P Si2 W |
| Formula weight | 572.35 |
| Temperature/K | 123 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.2343(4) |
| b/Å | 10.3502(4) |
| c/Å | 23.1652(11) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2214.06(17) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.717 |
| μ/mm$^{-1}$ | 5.422 |
| F(000) | 1120.0 |
| Crystal size/mm$^3$ | 0.26 × 0.14 × 0.05 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4738; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.278 to 55.994° |
| Completeness to theta | 0.998 |
| Index ranges | -9 ≤ h ≤ 12, -13 ≤ k ≤ 10, -30 ≤ l ≤ 24 |
| Reflections collected | 17907 |
| Independent reflections | 5344 [$R_{int}$ = 0.0633, $R_{sigma}$ = 0.0738] |
| Data/restraints/parameters | 5344/18/233 |
| Goodness-of-fit on F$^2$ | 0.999 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0367, $wR_2$ = 0.0549 |
| Final R indexes [all data] | $R_1$ = 0.0535, $wR_2$ = 0.0584 |

| | |
|---|---|
| Largest diff. peak/hole / e Å$^{-3}$ | 0.89/-1.02 |
| Flack parameter | 0.503(10) |

***Table 2:*** Bond lengths for **19.1**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4937(17) | Si2 | C4 | 1.912(6) |
| W | C11 | 2.018(8) | Si2 | C8 | 1.885(8) |
| W | C12 | 2.023(7) | Si2 | C9 | 1.861(9) |
| W | C13 | 2.031(8) | Si2 | C10 | 1.872(8) |
| W | C14 | 2.046(7) | O1 | C1 | 1.449(8) |
| W | C15 | 2.046(8) | O2 | C11 | 1.148(9) |
| P | O1 | 1.640(5) | O3 | C12 | 1.152(7) |
| P | C3 | 1.835(7) | O4 | C13 | 1.139(8) |
| P | C4 | 1.816(6) | O5 | C14 | 1.138(8) |
| Si1 | C4 | 1.910(7) | O6 | C15 | 1.146(8) |
| Si1 | C5 | 1.862(7) | C1 | C2 | 1.499(11) |
| Si1 | C6 | 1.872(7) | C2 | C3 | 1.520(9) |
| Si1 | C7 | 1.863(8) | | | |

***Table 3:*** Bond angles for **19.1**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C11 | W | P | 178.4(2) | C5 | Si1 | C7 | 106.4(5) |
| C11 | W | C12 | 88.1(3) | C6 | Si1 | C4 | 107.7(3) |
| C11 | W | C13 | 93.8(3) | C7 | Si1 | C4 | 111.4(3) |
| C11 | W | C14 | 90.3(4) | C7 | Si1 | C6 | 110.6(4) |
| C11 | W | C15 | 91.4(3) | C8 | Si2 | C4 | 109.5(3) |
| C12 | W | P | 92.4(2) | C9 | Si2 | C4 | 113.8(3) |
| C12 | W | C13 | 88.9(3) | C9 | Si2 | C8 | 107.4(4) |
| C12 | W | C14 | 177.3(3) | C9 | Si2 | C10 | 109.2(4) |
| C12 | W | C15 | 90.8(3) | C10 | Si2 | C4 | 109.4(3) |
| C13 | W | P | 84.7(2) | C10 | Si2 | C8 | 107.2(4) |
| C13 | W | C14 | 89.0(3) | C1 | O1 | P | 114.3(4) |
| C13 | W | C15 | 174.9(3) | O1 | C1 | C2 | 109.2(6) |
| C14 | W | P | 89.2(3) | C1 | C2 | C3 | 107.5(6) |
| C14 | W | C15 | 91.4(4) | C2 | C3 | P | 102.3(6) |
| C15 | W | P | 90.2(2) | P | C4 | Si1 | 114.1(3) |
| O1 | P | W | 110.7(2) | P | C4 | Si2 | 116.1(3) |
| O1 | P | C3 | 93.4(3) | Si1 | C4 | Si2 | 115.5(3) |
| O1 | P | C4 | 105.7(3) | O2 | C11 | W | 178.7(9) |
| C3 | P | W | 119.8(3) | O3 | C12 | W | 178.2(7) |
| C4 | P | W | 116.5(2) | O4 | C13 | W | 178.9(7) |
| C4 | P | C3 | 107.6(3) | O5 | C14 | W | 178.7(8) |
| C5 | Si1 | C4 | 114.2(3) | O6 | C15 | W | 178.8(7) |
| C5 | Si1 | C6 | 106.5(4) | | | | |

***Table 4:*** Torsion angles for **19.1**.

| A | B | C | D | Angle/˚ | A | B | C | D | Angle/˚ |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | C1 | -108.3(5) | O1 | C1 | C2 | C3 | -28.7(10) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C3 | C2 | 86.0(5) | C1 | C2 | C3 | P | 37.0(9) |
| W | P | C4 | Si1 | 89.9(3) | C3 | P | O1 | C1 | 15.4(6) |
| W | P | C4 | Si2 | -131.9(3) | C3 | P | C4 | Si1 | -47.9(4) |
| P | O1 | C1 | C2 | 5.3(9) | C3 | P | C4 | Si2 | 90.3(4) |
| O1 | P | C3 | C2 | -30.2(6) | C4 | P | O1 | C1 | 124.7(5) |
| O1 | P | C4 | Si1 | -146.8(3) | C4 | P | C3 | C2 | -137.9(5) |
| O1 | P | C4 | Si2 | -8.6(4) | | | | | |

# 12.30 Pentacarbonyl{catecholboranoxo[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [41.1]

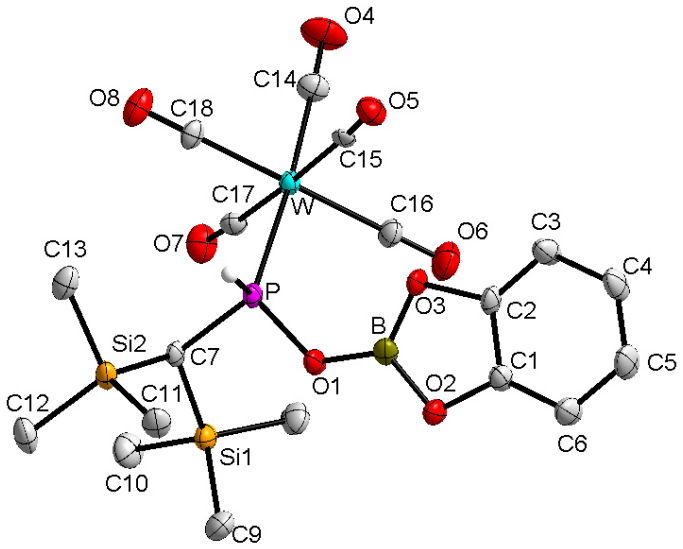


***Table 1:*** Crystal data and structure refinement for **41.1**.

| | |
|---|---|
| Identification code | GSTR385, AKY-458 // GXray3821 |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{18}H_{24}BO_8PSi_2W$ |
| Formula weight | 650.18 |
| Temperature/K | 123 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 8.7638(3) |
| b/Å | 11.0103(4) |
| c/Å | 14.5026(6) |
| α/° | 108.2413(19) |
| β/° | 105.4429(17) |
| γ/° | 91.170(2) |
| Volume/Å$^3$ | 1272.82(8) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.696 |
| μ/mm$^{-1}$ | 4.733 |
| F(000) | 636.0 |
| Crystal size/mm$^3$ | 0.34 × 0.16 × 0.1 |
| Absorption correction | multi-scan |
| Tmin; Tmax | 0.3464; 0.6657 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.86 to 56° |

| | |
|---|---|
| Completeness to theta | 0.999 |
| Index ranges | -11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19 |
| Reflections collected | 14299 |
| Independent reflections | 5900 [$R_{int}$ = 0.0610, $R_{sigma}$ = 0.0576] |
| Data/restraints/parameters | 5900/0/289 |
| Goodness-of-fit on $F^2$ | 1.013 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0329, $wR_2$ = 0.0763 |
| Final R indexes [all data] | $R_1$ = 0.0371, $wR_2$ = 0.0778 |
| Largest diff. peak/hole / e $Å^{-3}$ | 2.37/-2.35 |

***Table 2:*** Bond lengths for **41.1**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4695(9) | O1 | B | 1.353(5) |
| W | C14 | 2.024(4) | O2 | C1 | 1.386(5) |
| W | C15 | 2.051(4) | O2 | B | 1.387(5) |
| W | C16 | 2.064(4) | O3 | C2 | 1.400(4) |
| W | C17 | 2.045(4) | O3 | B | 1.376(6) |
| W | C18 | 2.037(4) | O4 | C14 | 1.135(5) |
| P | O1 | 1.656(3) | O5 | C15 | 1.135(5) |
| P | C7 | 1.798(4) | O6 | C16 | 1.126(5) |
| Si1 | C7 | 1.910(4) | O7 | C17 | 1.139(5) |
| Si1 | C8 | 1.865(4) | O8 | C18 | 1.136(5) |
| Si1 | C9 | 1.865(4) | C1 | C2 | 1.379(6) |
| Si1 | C10 | 1.875(4) | C1 | C6 | 1.368(6) |
| Si2 | C7 | 1.908(4) | C2 | C3 | 1.358(6) |
| Si2 | C11 | 1.872(4) | C3 | C4 | 1.394(6) |
| Si2 | C12 | 1.872(5) | C4 | C5 | 1.378(7) |
| Si2 | C13 | 1.867(4) | C5 | C6 | 1.403(6) |

***Table 3:*** Bond angles for **41.1**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C14 | W | P | 175.90(12) | C13 | Si2 | C7 | 107.62(17) |
| C14 | W | C15 | 90.30(16) | C13 | Si2 | C11 | 109.6(2) |
| C14 | W | C16 | 92.05(17) | C13 | Si2 | C12 | 107.3(2) |
| C14 | W | C17 | 88.42(16) | B | O1 | P | 127.2(3) |
| C14 | W | C18 | 89.85(17) | C1 | O2 | B | 104.1(3) |
| C15 | W | P | 90.15(9) | B | O3 | C2 | 104.1(3) |
| C15 | W | C16 | 89.73(17) | C2 | C1 | O2 | 109.7(3) |
| C16 | W | P | 92.03(11) | C6 | C1 | O2 | 128.7(4) |
| C17 | W | P | 90.99(10) | C6 | C1 | C2 | 121.6(4) |
| C17 | W | C15 | 177.69(13) | C1 | C2 | O3 | 109.1(3) |
| C17 | W | C16 | 92.23(17) | C3 | C2 | O3 | 127.8(4) |
| C18 | W | P | 86.09(11) | C3 | C2 | C1 | 123.1(4) |
| C18 | W | C15 | 87.83(16) | C2 | C3 | C4 | 116.2(4) |
| C18 | W | C16 | 176.92(14) | C5 | C4 | C3 | 121.4(4) |
| C18 | W | C17 | 90.25(16) | C4 | C5 | C6 | 121.5(4) |
| O1 | P | W | 121.76(10) | C1 | C6 | C5 | 116.2(4) |
| O1 | P | C7 | 100.11(16) | P | C7 | Si1 | 114.44(18) |
| C7 | P | W | 119.14(12) | P | C7 | Si2 | 111.2(2) |
| C8 | Si1 | C7 | 112.97(19) | Si2 | C7 | Si1 | 117.05(19) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C8 | Si1 | C10 | 107.8(2) | O4 | C14 | W | 178.2(4) |
| C9 | Si1 | C7 | 111.69(19) | O5 | C15 | W | 177.5(3) |
| C9 | Si1 | C8 | 107.4(2) | O6 | C16 | W | 177.6(4) |
| C9 | Si1 | C10 | 110.5(2) | O7 | C17 | W | 177.0(4) |
| C10 | Si1 | C7 | 106.42(19) | O8 | C18 | W | 179.8(4) |
| C11 | Si2 | C7 | 110.21(17) | O1 | B | O2 | 121.8(4) |
| C12 | Si2 | C7 | 110.8(2) | O1 | B | O3 | 125.2(4) |
| C12 | Si2 | C11 | 111.2(2) | O3 | B | O2 | 113.0(3) |

***Table 4:*** Torsion angles for **41.1**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | B | 45.0(4) | C12 | Si2 | C7 | Si1 | -46.6(3) |
| W | P | C7 | Si1 | 92.11(18) | C13 | Si2 | C7 | P | 62.3(2) |
| W | P | C7 | Si2 | -132.53(13) | C13 | Si2 | C7 | Si1 | -163.7(2) |
| P | W | C14 | O4 | -24(16) | C14 | W | P | O1 | -170.3(19) |
| P | W | C15 | O5 | -110(7) | C14 | W | P | C7 | 64.2(19) |
| P | W | C16 | O6 | -55(9) | C14 | W | C15 | O5 | 66(7) |
| P | W | C17 | O7 | 151(7) | C14 | W | C16 | O6 | 125(9) |
| P | W | C18 | O8 | 101(100) | C14 | W | C17 | O7 | -25(7) |
| P | O1 | B | O2 | -174.1(3) | C14 | W | C18 | O8 | -79(100) |
| P | O1 | B | O3 | 4.2(6) | C15 | W | P | O1 | -73.96(18) |
| O1 | P | C7 | Si1 | -43.3(2) | C15 | W | P | C7 | 160.49(18) |
| O1 | P | C7 | Si2 | 92.1(2) | C15 | W | C14 | O4 | -120(14) |
| O2 | C1 | C2 | O3 | 1.1(4) | C15 | W | C16 | O6 | 35(9) |
| O2 | C1 | C2 | C3 | -179.0(4) | C15 | W | C17 | O7 | 31(9) |
| O2 | C1 | C6 | C5 | 178.2(4) | C15 | W | C18 | O8 | 11(100) |
| O3 | C2 | C3 | C4 | -179.3(4) | C16 | W | P | O1 | 15.78(19) |
| C1 | O2 | B | O1 | 178.1(4) | C16 | W | P | C7 | -109.77(19) |
| C1 | O2 | B | O3 | -0.4(4) | C16 | W | C14 | O4 | 150(14) |
| C1 | C2 | C3 | C4 | 0.9(7) | C16 | W | C15 | O5 | 158(7) |
| C2 | O3 | B | O1 | -177.3(4) | C16 | W | C17 | O7 | -117(7) |
| C2 | O3 | B | O2 | 1.1(4) | C16 | W | C18 | O8 | 49(100) |
| C2 | C1 | C6 | C5 | 0.0(7) | C17 | W | P | O1 | 108.05(18) |
| C2 | C3 | C4 | C5 | -0.9(7) | C17 | W | P | C7 | -17.51(19) |
| C3 | C4 | C5 | C6 | 0.4(8) | C17 | W | C14 | O4 | 58(14) |
| C4 | C5 | C6 | C1 | 0.0(7) | C17 | W | C15 | O5 | 10(9) |
| C6 | C1 | C2 | O3 | 179.7(4) | C17 | W | C16 | O6 | -147(9) |
| C6 | C1 | C2 | C3 | -0.5(7) | C17 | W | C18 | O8 | -168(100) |
| C7 | P | O1 | B | 178.8(3) | C18 | W | P | O1 | -161.77(18) |
| C8 | Si1 | C7 | P | -27.6(3) | C18 | W | P | C7 | 72.68(19) |
| C8 | Si1 | C7 | Si2 | -160.2(2) | C18 | W | C14 | O4 | -32(14) |
| C9 | Si1 | C7 | P | 93.6(2) | C18 | W | C15 | O5 | -24(7) |
| C9 | Si1 | C7 | Si2 | -39.0(3) | C18 | W | C16 | O6 | -3(11) |
| C10 | Si1 | C7 | P | -145.7(2) | C18 | W | C17 | O7 | 65(7) |
| C10 | Si1 | C7 | Si2 | 81.7(2) | B | O2 | C1 | C2 | -0.4(4) |
| C11 | Si2 | C7 | P | -57.2(3) | B | O2 | C1 | C6 | -178.8(4) |
| C11 | Si2 | C7 | Si1 | 76.9(3) | B | O3 | C2 | C1 | -1.3(4) |
| C12 | Si2 | C7 | P | 179.3(2) | B | O3 | C2 | C3 | 178.8(4) |

## 12.31 Pentacarbonyl[4-methyl-2-(triphenylmethyl)-1,2-thiaphosphetane-κ*P*]tungsten(0) [46.3]

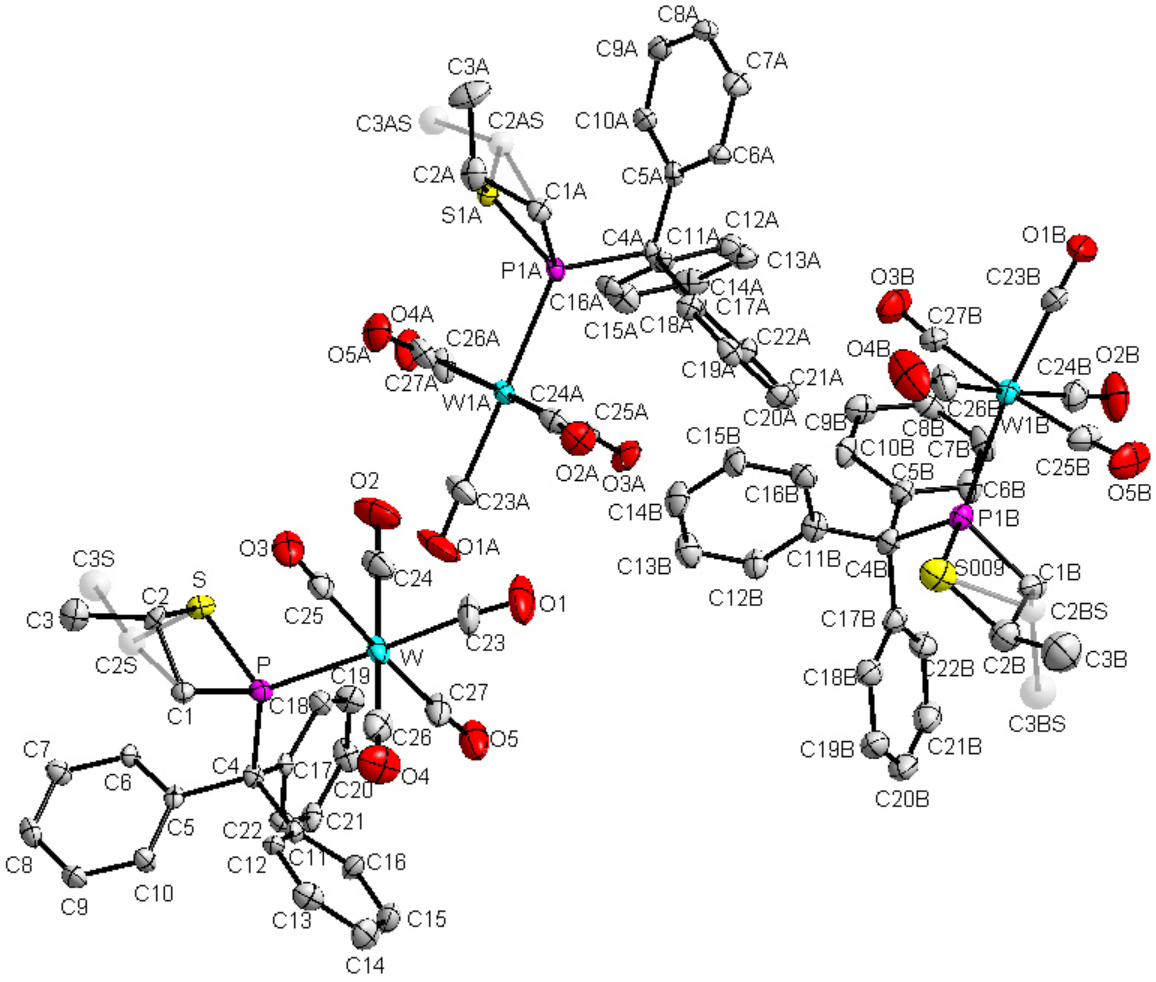


***Table 1:*** Crystal data and structure refinement for **46.3**.

| | |
|---|---|
| Identification code | GSTR523, AKY-583 // GXray4889af |
| Crystal Habitus | clear colourless plate |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{27}H_{21}O_5PSW$ |
| Moiety formula | C27 H21 O5 P S W |
| Formula weight | 672.32 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 10.8752(8) |
| b/Å | 44.889(3) |
| c/Å | 16.0622(12) |
| α/° | 90 |
| β/° | 90.964(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 7840.0(10) |
| Z | 12 |
| $\rho_{calc}$g/cm$^3$ | 1.709 |
| μ/mm$^{-1}$ | 4.596 |
| F(000) | 3936.0 |

| | |
|---|---|
| Crystal size/mm$^3$ | 0.08 × 0.04 × 0.01 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5126; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.854 to 56° |
| Completeness to theta | 0.998 |
| Index ranges | -14 ≤ h ≤ 14, -59 ≤ k ≤ 59, -21 ≤ l ≤ 14 |
| Reflections collected | 107550 |
| Independent reflections | 18901 [$R_{int}$ = 0.1095, $R_{sigma}$ = 0.0837] |
| Data/restraints/parameters | 18901/54/1009 |
| Goodness-of-fit on $F^2$ | 1.121 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0559, $wR_2$ = 0.0983 |
| Final R indexes [all data] | $R_1$ = 0.0922, $wR_2$ = 0.1168 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.39/-2.57 |

***Table 2:*** Bond lengths for **46.3**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5158(18) | C4A | C11A | 1.531(9) |
| W | C23 | 1.997(8) | C4A | C17A | 1.553(9) |
| W | C24 | 2.031(9) | C5A | C6A | 1.383(9) |
| W | C25 | 2.033(8) | C5A | C10A | 1.401(9) |
| W | C26 | 2.031(9) | C6A | C7A | 1.387(9) |
| W | C27 | 2.054(8) | C7A | C8A | 1.388(10) |
| S | P | 2.125(3) | C8A | C9A | 1.380(10) |
| S | C2 | 1.876(10) | C9A | C10A | 1.384(10) |
| S | C2S | 1.82(3) | C11A | C12A | 1.397(9) |
| P | C1 | 1.861(7) | C11A | C16A | 1.391(9) |
| P | C4 | 1.922(7) | C12A | C13A | 1.379(10) |
| O1 | C23 | 1.144(9) | C13A | C14A | 1.382(10) |
| O2 | C24 | 1.148(10) | C14A | C15A | 1.382(10) |
| O3 | C25 | 1.137(9) | C15A | C16A | 1.387(9) |
| O4 | C26 | 1.147(10) | C17A | C18A | 1.401(9) |
| O5 | C27 | 1.135(9) | C17A | C22A | 1.374(9) |
| C1 | C2 | 1.529(12) | C18A | C19A | 1.377(9) |
| C1 | C2S | 1.62(3) | C19A | C20A | 1.389(10) |
| C2 | C3 | 1.514(19) | C20A | C21A | 1.363(10) |
| C2S | C3S | 1.49(4) | C21A | C22A | 1.389(10) |
| C4 | C5 | 1.549(9) | W1B | P1B | 2.539(2) |
| C4 | C11 | 1.534(9) | W1B | C23B | 2.006(8) |
| C4 | C17 | 1.539(9) | W1B | C24B | 2.031(9) |
| C5 | C6 | 1.393(9) | W1B | C25B | 2.023(8) |
| C5 | C10 | 1.414(9) | W1B | C26B | 2.045(9) |
| C6 | C7 | 1.384(9) | W1B | C27B | 2.049(8) |
| C7 | C8 | 1.375(10) | S009 | P1B | 2.115(3) |
| C8 | C9 | 1.383(10) | S009 | C2B | 1.832(16) |
| C9 | C10 | 1.377(9) | S009 | C2BS | 1.92(2) |
| C11 | C12 | 1.404(9) | P1B | C1B | 1.872(8) |
| C11 | C16 | 1.382(9) | P1B | C4B | 1.936(7) |
| C12 | C13 | 1.383(9) | O1B | C23B | 1.136(9) |
| C13 | C14 | 1.391(11) | O2B | C24B | 1.148(9) |
| C14 | C15 | 1.391(11) | O3B | C27B | 1.143(9) |
| C15 | C16 | 1.380(10) | O4B | C26B | 1.136(10) |

| | | | | | |
|---|---|---|---|---|---|
| C17 | C18 | 1.390(9) | O5B | C25B | 1.124(9) |
| C17 | C22 | 1.402(9) | C1B | C2B | 1.612(17) |
| C18 | C19 | 1.386(9) | C1B | C2BS | 1.50(2) |
| C19 | C20 | 1.367(10) | C2B | C3B | 1.51(3) |
| C20 | C21 | 1.390(10) | C2BS | C3BS | 1.57(4) |
| C21 | C22 | 1.382(9) | C4B | C5B | 1.521(10) |
| W1A | P1A | 2.5060(18) | C4B | C11B | 1.550(10) |
| W1A | C23A | 2.006(8) | C4B | C17B | 1.537(10) |
| W1A | C24A | 2.056(8) | C5B | C6B | 1.392(10) |
| W1A | C25A | 2.044(8) | C5B | C10B | 1.414(9) |
| W1A | C26A | 2.049(8) | C6B | C7B | 1.372(10) |
| W1A | C27A | 2.037(8) | C7B | C8B | 1.390(11) |
| S1A | P1A | 2.132(2) | C8B | C9B | 1.381(11) |
| S1A | C2A | 1.901(11) | C9B | C10B | 1.386(10) |
| S1A | C2AS | 1.83(2) | C11B | C12B | 1.400(10) |
| P1A | C1A | 1.856(7) | C11B | C16B | 1.374(10) |
| P1A | C4A | 1.920(7) | C12B | C13B | 1.383(10) |
| O1A | C23A | 1.132(9) | C13B | C14B | 1.383(11) |
| O2A | C24A | 1.133(8) | C14B | C15B | 1.374(10) |
| O3A | C25A | 1.132(9) | C15B | C16B | 1.406(10) |
| O4A | C26A | 1.131(9) | C17B | C18B | 1.423(10) |
| O5A | C27A | 1.139(9) | C17B | C22B | 1.394(10) |
| C1A | C2A | 1.509(13) | C18B | C19B | 1.392(11) |
| C1A | C2AS | 1.66(3) | C19B | C20B | 1.371(12) |
| C2A | C3A | 1.52(2) | C20B | C21B | 1.385(12) |
| C2AS | C3AS | 1.50(4) | C21B | C22B | 1.381(11) |
| C4A | C5A | 1.544(9) | | | |

***Table 3:*** Bond angles for **46.3**.

| **Atom** | **Atom** | **Atom** | **Angle/˚** | **Atom** | **Atom** | **Atom** | **Angle/˚** |
|---|---|---|---|---|---|---|---|
| C23 | W | P | 177.6(3) | C11A | C4A | P1A | 112.1(4) |
| C23 | W | C24 | 89.1(4) | C11A | C4A | C5A | 107.1(5) |
| C23 | W | C25 | 90.9(3) | C11A | C4A | C17A | 111.5(5) |
| C23 | W | C26 | 86.9(4) | C17A | C4A | P1A | 103.9(4) |
| C23 | W | C27 | 88.0(3) | C6A | C5A | C4A | 124.5(6) |
| C24 | W | P | 90.4(3) | C6A | C5A | C10A | 117.3(6) |
| C24 | W | C25 | 84.4(3) | C10A | C5A | C4A | 118.2(6) |
| C24 | W | C26 | 172.1(3) | C5A | C6A | C7A | 121.9(7) |
| C24 | W | C27 | 92.2(4) | C6A | C7A | C8A | 119.8(7) |
| C25 | W | P | 86.7(2) | C9A | C8A | C7A | 119.5(7) |
| C25 | W | C27 | 176.5(3) | C8A | C9A | C10A | 120.2(7) |
| C26 | W | P | 93.3(2) | C9A | C10A | C5A | 121.3(7) |
| C26 | W | C25 | 88.9(3) | C12A | C11A | C4A | 118.6(6) |
| C26 | W | C27 | 94.4(4) | C16A | C11A | C4A | 124.4(6) |
| C27 | W | P | 94.4(2) | C16A | C11A | C12A | 116.9(6) |
| C2 | S | P | 78.7(3) | C13A | C12A | C11A | 122.2(7) |
| C2S | S | P | 82.2(8) | C12A | C13A | C14A | 119.4(7) |
| S | P | W | 113.59(9) | C13A | C14A | C15A | 120.1(7) |
| C1 | P | W | 117.4(2) | C14A | C15A | C16A | 119.8(7) |
| C1 | P | S | 80.8(2) | C15A | C16A | C11A | 121.6(7) |
| C1 | P | C4 | 105.7(3) | C18A | C17A | C4A | 119.2(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C4 | P | W | 121.6(2) | C22A | C17A | C4A | 123.8(6) |
| C4 | P | S | 110.5(2) | C22A | C17A | C18A | 117.0(6) |
| C2 | C1 | P | 96.8(5) | C19A | C18A | C17A | 121.4(7) |
| C2S | C1 | P | 96.6(10) | C18A | C19A | C20A | 120.2(7) |
| C1 | C2 | S | 98.5(6) | C21A | C20A | C19A | 119.0(7) |
| C3 | C2 | S | 112.8(9) | C20A | C21A | C22A | 120.6(7) |
| C3 | C2 | C1 | 113.8(10) | C17A | C22A | C21A | 121.7(7) |
| C1 | C2S | S | 97.5(14) | O1A | C23A | W1A | 177.8(8) |
| C3S | C2S | S | 114(2) | O2A | C24A | W1A | 175.2(7) |
| C3S | C2S | C1 | 114(2) | O3A | C25A | W1A | 176.5(7) |
| C5 | C4 | P | 110.7(4) | O4A | C26A | W1A | 177.6(7) |
| C11 | C4 | P | 103.1(4) | O5A | C27A | W1A | 179.0(7) |
| C11 | C4 | C5 | 112.5(5) | C23B | W1B | P1B | 172.3(2) |
| C11 | C4 | C17 | 112.5(5) | C23B | W1B | C24B | 86.9(3) |
| C17 | C4 | P | 110.4(4) | C23B | W1B | C25B | 85.8(3) |
| C17 | C4 | C5 | 107.7(5) | C23B | W1B | C26B | 89.7(3) |
| C6 | C5 | C4 | 120.0(6) | C23B | W1B | C27B | 90.5(3) |
| C6 | C5 | C10 | 117.4(6) | C24B | W1B | P1B | 93.2(2) |
| C10 | C5 | C4 | 122.6(6) | C24B | W1B | C26B | 176.5(3) |
| C7 | C6 | C5 | 121.2(6) | C24B | W1B | C27B | 90.2(3) |
| C8 | C7 | C6 | 120.6(7) | C25B | W1B | P1B | 86.5(2) |
| C7 | C8 | C9 | 119.3(7) | C25B | W1B | C24B | 89.2(3) |
| C10 | C9 | C8 | 120.8(7) | C25B | W1B | C26B | 89.8(4) |
| C9 | C10 | C5 | 120.6(6) | C25B | W1B | C27B | 176.4(3) |
| C12 | C11 | C4 | 119.2(6) | C26B | W1B | P1B | 90.1(3) |
| C16 | C11 | C4 | 122.9(6) | C26B | W1B | C27B | 90.5(3) |
| C16 | C11 | C12 | 117.9(6) | C27B | W1B | P1B | 97.1(2) |
| C13 | C12 | C11 | 121.2(7) | C2B | S009 | P1B | 82.1(5) |
| C12 | C13 | C14 | 120.0(7) | C2BS | S009 | P1B | 77.0(6) |
| C13 | C14 | C15 | 118.9(7) | S009 | P1B | W1B | 114.19(10) |
| C16 | C15 | C14 | 120.7(8) | C1B | P1B | W1B | 114.4(3) |
| C15 | C16 | C11 | 121.2(7) | C1B | P1B | S009 | 81.8(3) |
| C18 | C17 | C4 | 125.2(6) | C1B | P1B | C4B | 106.7(3) |
| C18 | C17 | C22 | 117.8(6) | C4B | P1B | W1B | 124.5(2) |
| C22 | C17 | C4 | 116.9(6) | C4B | P1B | S009 | 106.9(2) |
| C19 | C18 | C17 | 120.2(7) | C2B | C1B | P1B | 96.3(7) |
| C20 | C19 | C18 | 121.8(7) | C2BS | C1B | P1B | 95.9(9) |
| C19 | C20 | C21 | 119.0(7) | C1B | C2B | S009 | 98.7(9) |
| C22 | C21 | C20 | 119.9(7) | C3B | C2B | S009 | 110.6(13) |
| C21 | C22 | C17 | 121.4(7) | C3B | C2B | C1B | 114.9(14) |
| O1 | C23 | W | 175.2(9) | C1B | C2BS | S009 | 99.3(12) |
| O2 | C24 | W | 175.1(8) | C1B | C2BS | C3BS | 111.0(18) |
| O3 | C25 | W | 178.4(7) | C3BS | C2BS | S009 | 112.5(17) |
| O4 | C26 | W | 174.7(8) | C5B | C4B | P1B | 105.3(5) |
| O5 | C27 | W | 176.1(7) | C5B | C4B | C11B | 110.6(6) |
| C23A | W1A | P1A | 177.6(3) | C5B | C4B | C17B | 112.5(6) |
| C23A | W1A | C24A | 87.8(3) | C11B | C4B | P1B | 109.5(5) |
| C23A | W1A | C25A | 87.3(3) | C17B | C4B | P1B | 109.5(5) |
| C23A | W1A | C26A | 89.3(3) | C17B | C4B | C11B | 109.4(6) |
| C23A | W1A | C27A | 92.4(3) | C6B | C5B | C4B | 121.3(7) |
| C24A | W1A | P1A | 94.6(2) | C6B | C5B | C10B | 117.2(7) |
| C25A | W1A | P1A | 92.0(2) | C10B | C5B | C4B | 121.5(7) |
| C25A | W1A | C24A | 93.1(3) | C7B | C6B | C5B | 122.6(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C25A | W1A | C26A | 92.3(3) | C6B | C7B | C8B | 119.7(8) |
| C26A | W1A | P1A | 88.4(2) | C9B | C8B | C7B | 119.3(8) |
| C26A | W1A | C24A | 173.7(3) | C8B | C9B | C10B | 121.2(8) |
| C27A | W1A | P1A | 88.3(2) | C9B | C10B | C5B | 120.1(7) |
| C27A | W1A | C24A | 88.3(3) | C12B | C11B | C4B | 118.9(6) |
| C27A | W1A | C25A | 178.6(3) | C16B | C11B | C4B | 122.3(7) |
| C27A | W1A | C26A | 86.3(3) | C16B | C11B | C12B | 118.7(7) |
| C2A | S1A | P1A | 78.0(4) | C13B | C12B | C11B | 120.0(7) |
| C2AS | S1A | P1A | 83.7(8) | C12B | C13B | C14B | 121.1(7) |
| S1A | P1A | W1A | 113.52(9) | C15B | C14B | C13B | 119.2(7) |
| C1A | P1A | W1A | 118.0(2) | C14B | C15B | C16B | 120.1(7) |
| C1A | P1A | S1A | 80.6(2) | C11B | C16B | C15B | 120.8(7) |
| C1A | P1A | C4A | 106.0(3) | C18B | C17B | C4B | 118.8(7) |
| C4A | P1A | W1A | 122.1(2) | C22B | C17B | C4B | 123.5(7) |
| C4A | P1A | S1A | 108.9(2) | C22B | C17B | C18B | 117.7(7) |
| C2A | C1A | P1A | 97.7(6) | C19B | C18B | C17B | 119.4(8) |
| C2AS | C1A | P1A | 97.9(9) | C20B | C19B | C18B | 121.5(8) |
| C1A | C2A | S1A | 98.1(7) | C19B | C20B | C21B | 119.5(8) |
| C1A | C2A | C3A | 114.6(13) | C22B | C21B | C20B | 120.2(8) |
| C3A | C2A | S1A | 113.0(11) | C21B | C22B | C17B | 121.6(8) |
| C1A | C2AS | S1A | 95.7(12) | O1B | C23B | W1B | 176.8(7) |
| C3AS | C2AS | S1A | 115(2) | O2B | C24B | W1B | 177.2(7) |
| C3AS | C2AS | C1A | 111(2) | O5B | C25B | W1B | 175.5(8) |
| C5A | C4A | P1A | 110.7(4) | O4B | C26B | W1B | 176.7(8) |
| C5A | C4A | C17A | 111.6(5) | O3B | C27B | W1B | 175.2(7) |

***Table 4:*** Torsion angles for **46.3**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | 94.6(6) | C5A | C4A | C17A | C18A | 65.7(8) |
| W | P | C1 | C2S | 124.5(13) | C5A | C4A | C17A | C22A | -111.9(7) |
| S | P | C1 | C2 | -17.3(6) | C5A | C6A | C7A | C8A | 2.0(11) |
| S | P | C1 | C2S | 12.6(13) | C6A | C5A | C10A | C9A | -1.9(10) |
| P | S | C2 | C1 | -17.3(6) | C6A | C7A | C8A | C9A | -2.8(11) |
| P | S | C2 | C3 | -137.7(11) | C7A | C8A | C9A | C10A | 1.2(11) |
| P | S | C2S | C1 | 12.8(13) | C8A | C9A | C10A | C5A | 1.1(11) |
| P | S | C2S | C3S | 133(3) | C10A | C5A | C6A | C7A | 0.3(10) |
| P | C1 | C2 | S | 19.6(6) | C11A | C4A | C5A | C6A | -130.2(7) |
| P | C1 | C2 | C3 | 139.3(9) | C11A | C4A | C5A | C10A | 50.1(8) |
| P | C1 | C2S | S | -14.7(15) | C11A | C4A | C17A | C18A | -174.6(6) |
| P | C1 | C2S | C3S | -135(2) | C11A | C4A | C17A | C22A | 7.8(9) |
| P | C4 | C5 | C6 | 69.5(7) | C11A | C12A | C13A | C14A | 2.4(11) |
| P | C4 | C5 | C10 | -113.6(6) | C12A | C11A | C16A | C15A | 2.1(11) |
| P | C4 | C11 | C12 | 58.4(7) | C12A | C13A | C14A | C15A | -0.2(11) |
| P | C4 | C11 | C16 | -121.2(6) | C13A | C14A | C15A | C16A | -1.0(12) |
| P | C4 | C17 | C18 | 5.0(8) | C14A | C15A | C16A | C11A | 0.0(12) |
| P | C4 | C17 | C22 | -178.0(5) | C16A | C11A | C12A | C13A | -3.3(10) |
| C4 | P | C1 | C2 | -126.1(6) | C17A | C4A | C5A | C6A | -7.9(9) |
| C4 | P | C1 | C2S | -96.2(13) | C17A | C4A | C5A | C10A | 172.4(6) |
| C4 | C5 | C6 | C7 | -178.2(6) | C17A | C4A | C11A | C12A | -68.8(8) |
| C4 | C5 | C10 | C9 | 179.9(6) | C17A | C4A | C11A | C16A | 111.9(7) |
| C4 | C11 | C12 | C13 | 177.3(6) | C17A | C18A | C19A | C20A | -0.2(11) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C4 | C11 | C16 | C15 | -177.7(7) | C18A | C17A | C22A | C21A | -1.7(10) |
| C4 | C17 | C18 | C19 | 177.5(6) | C18A | C19A | C20A | C21A | -0.6(11) |
| C4 | C17 | C22 | C21 | -177.1(6) | C19A | C20A | C21A | C22A | 0.3(11) |
| C5 | C4 | C11 | C12 | -60.8(8) | C20A | C21A | C22A | C17A | 0.9(11) |
| C5 | C4 | C11 | C16 | 119.6(7) | C22A | C17A | C18A | C19A | 1.3(10) |
| C5 | C4 | C17 | C18 | 125.9(7) | W1B | P1B | C1B | C2B | 120.8(7) |
| C5 | C4 | C17 | C22 | -57.0(7) | W1B | P1B | C1B | C2BS | 93.8(11) |
| C5 | C6 | C7 | C8 | -2.7(11) | S009 | P1B | C1B | C2B | 7.9(7) |
| C6 | C5 | C10 | C9 | -3.2(10) | S009 | P1B | C1B | C2BS | -19.1(11) |
| C6 | C7 | C8 | C9 | -1.2(11) | P1B | S009 | C2B | C1B | 8.1(8) |
| C7 | C8 | C9 | C10 | 2.8(11) | P1B | S009 | C2B | C3B | 128.9(14) |
| C8 | C9 | C10 | C5 | -0.6(11) | P1B | C1B | C2B | S009 | -9.1(9) |
| C10 | C5 | C6 | C7 | 4.8(10) | P1B | C1B | C2B | C3B | -126.7(14) |
| C11 | C4 | C5 | C6 | -175.8(6) | P1B | C1B | C2BS | S009 | 21.2(11) |
| C11 | C4 | C5 | C10 | 1.1(9) | P1B | C1B | C2BS | C3BS | 139.8(17) |
| C11 | C4 | C17 | C18 | -109.6(7) | P1B | C4B | C5B | C6B | 49.9(8) |
| C11 | C4 | C17 | C22 | 67.5(7) | P1B | C4B | C5B | C10B | -130.3(6) |
| C11 | C12 | C13 | C14 | 0.6(11) | P1B | C4B | C11B | C12B | -155.7(6) |
| C12 | C11 | C16 | C15 | 2.7(11) | P1B | C4B | C11B | C16B | 28.1(8) |
| C12 | C13 | C14 | C15 | 2.2(12) | P1B | C4B | C17B | C18B | 76.4(7) |
| C13 | C14 | C15 | C16 | -2.6(12) | P1B | C4B | C17B | C22B | -104.8(7) |
| C14 | C15 | C16 | C11 | 0.1(12) | C4B | P1B | C1B | C2B | -97.4(8) |
| C16 | C11 | C12 | C13 | -3.0(10) | C4B | P1B | C1B | C2BS | -124.4(11) |
| C17 | C4 | C5 | C6 | -51.2(8) | C4B | C5B | C6B | C7B | 179.1(7) |
| C17 | C4 | C5 | C10 | 125.6(6) | C4B | C5B | C10B | C9B | -178.9(7) |
| C17 | C4 | C11 | C12 | 177.4(6) | C4B | C11B | C12B | C13B | -177.7(7) |
| C17 | C4 | C11 | C16 | -2.3(9) | C4B | C11B | C16B | C15B | 177.5(7) |
| C17 | C18 | C19 | C20 | -0.8(11) | C4B | C17B | C18B | C19B | -179.7(7) |
| C18 | C17 | C22 | C21 | 0.2(10) | C4B | C17B | C22B | C21B | -179.7(7) |
| C18 | C19 | C20 | C21 | 0.4(11) | C5B | C4B | C11B | C12B | 88.8(8) |
| C19 | C20 | C21 | C22 | 0.4(11) | C5B | C4B | C11B | C16B | -87.5(8) |
| C20 | C21 | C22 | C17 | -0.6(11) | C5B | C4B | C17B | C18B | -167.0(6) |
| C22 | C17 | C18 | C19 | 0.5(10) | C5B | C4B | C17B | C22B | 11.9(10) |
| W1A | P1A | C1A | C2A | -93.2(7) | C5B | C6B | C7B | C8B | 0.5(12) |
| W1A | P1A | C1A | C2AS | -122.5(12) | C6B | C5B | C10B | C9B | 0.9(11) |
| S1A | P1A | C1A | C2A | 18.5(7) | C6B | C7B | C8B | C9B | -0.5(12) |
| S1A | P1A | C1A | C2AS | -10.7(12) | C7B | C8B | C9B | C10B | 0.7(12) |
| P1A | S1A | C2AS | C1A | -10.8(12) | C8B | C9B | C10B | C5B | -1.0(12) |
| P1A | S1A | C2AS | C3AS | -128(3) | C10B | C5B | C6B | C7B | -0.7(11) |
| P1A | C1A | C2A | S1A | -20.8(8) | C11B | C4B | C5B | C6B | 168.1(7) |
| P1A | C1A | C2A | C3A | -140.7(12) | C11B | C4B | C5B | C10B | -12.1(9) |
| P1A | C1A | C2AS | S1A | 12.4(14) | C11B | C4B | C17B | C18B | -43.6(8) |
| P1A | C1A | C2AS | C3AS | 133(2) | C11B | C4B | C17B | C22B | 135.2(7) |
| P1A | C4A | C5A | C6A | 107.4(7) | C11B | C12B | C13B | C14B | 0.9(12) |
| P1A | C4A | C5A | C10A | -72.3(7) | C12B | C11B | C16B | C15B | 1.2(11) |
| P1A | C4A | C11A | C12A | 175.1(5) | C12B | C13B | C14B | C15B | -0.3(13) |
| P1A | C4A | C11A | C16A | -4.2(9) | C13B | C14B | C15B | C16B | 0.2(12) |
| P1A | C4A | C17A | C18A | -53.6(7) | C14B | C15B | C16B | C11B | -0.7(12) |
| P1A | C4A | C17A | C22A | 128.8(6) | C16B | C11B | C12B | C13B | -1.3(11) |
| C4A | P1A | C1A | C2A | 125.6(8) | C17B | C4B | C5B | C6B | -69.2(9) |
| C4A | P1A | C1A | C2AS | 96.3(12) | C17B | C4B | C5B | C10B | 110.6(8) |
| C4A | C5A | C6A | C7A | -179.4(7) | C17B | C4B | C11B | C12B | -35.7(8) |
| C4A | C5A | C10A | C9A | 177.8(6) | C17B | C4B | C11B | C16B | 148.0(7) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C4A | C11A | C12A | C13A | 177.3(6) | C17B | C18B | C19B | C20B | -1.0(12) |
| C4A | C11A | C16A | C15A | -178.6(7) | C18B | C17B | C22B | C21B | -0.8(11) |
| C4A | C17A | C18A | C19A | -176.4(6) | C18B | C19B | C20B | C21B | 0.0(13) |
| C4A | C17A | C22A | C21A | 175.9(6) | C19B | C20B | C21B | C22B | 0.6(13) |
| C5A | C4A | C11A | C12A | 53.5(8) | C20B | C21B | C22B | C17B | -0.2(12) |
| C5A | C4A | C11A | C16A | -125.8(7) | C22B | C17B | C18B | C19B | 1.4(11) |

## 12.32 Pentacarbonyl{chloro(2-hydroxyethyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [47.1a]

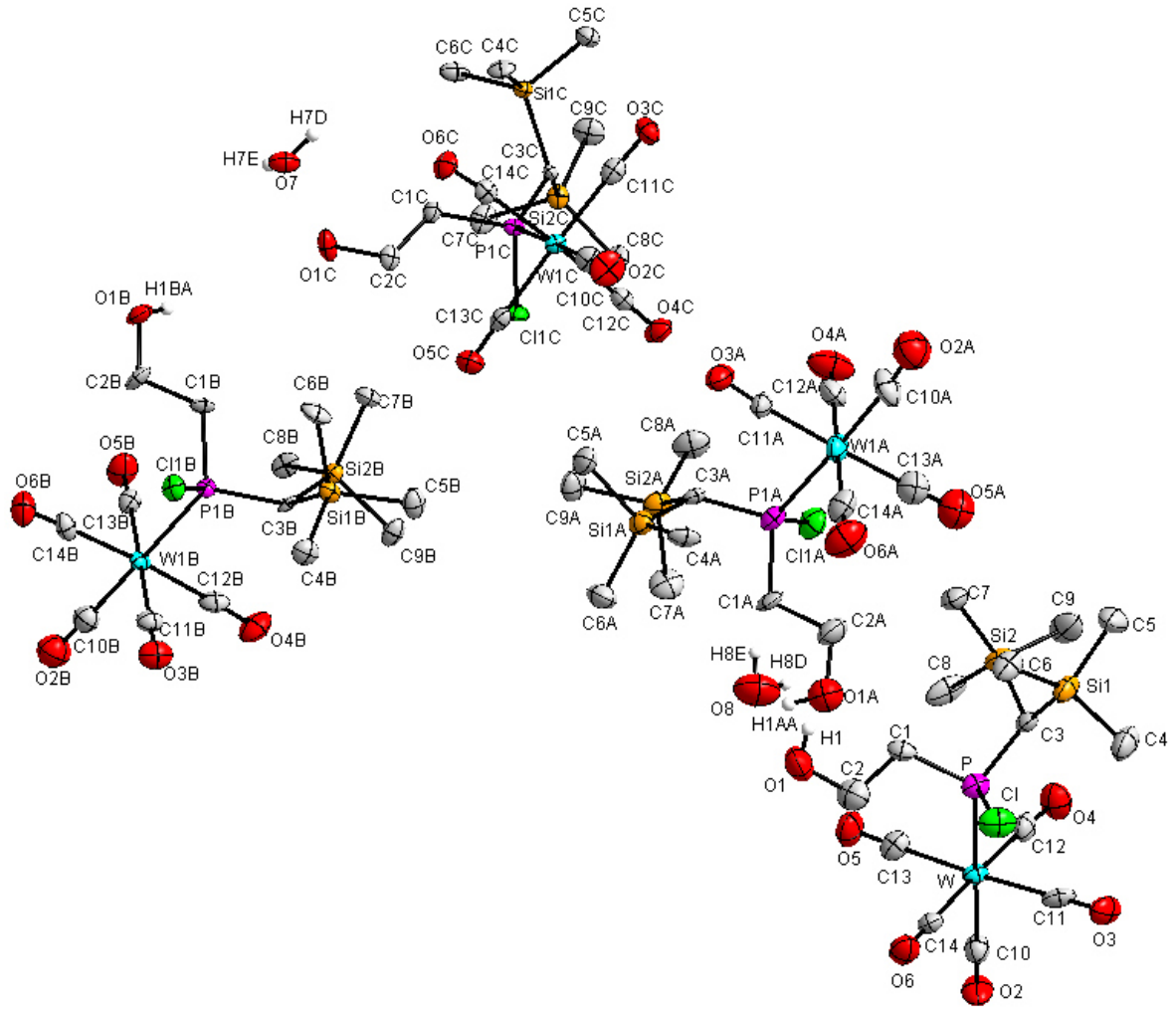


***Table 1:*** Crystal data and structure refinement for **47.1a**.

| | |
|---|---|
| Identification code | GSTR488, AKY-546 // GXraymo_4589f |
| Crystal Habitus | colourless plank |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{56}H_{98}Cl_4O_{25}P_4Si_8W_4$ |
| Moiety formula | 4(C14 H24 Cl O6 P Si2 W), H2 O |
| Formula weight | 2397.14 |
| Temperature/K | 123 |
| Crystal system | monoclinic |
| Space group | P2/c |
| a/Å | 30.4139(18) |
| b/Å | 9.3529(6) |

| | |
|---|---|
| c/Å | 33.347(2) |
| α/° | 90 |
| β/° | 103.110(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 9238.5(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.723 |
| μ/mm$^{-1}$ | 5.315 |
| F(000) | 4680.0 |
| Crystal size/mm$^3$ | 0.13 × 0.05 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.6755; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.314 to 56° |
| Completeness to theta | 0.999 |
| Index ranges | -40 ≤ h ≤ 40, -12 ≤ k ≤ 12, -42 ≤ l ≤ 44 |
| Reflections collected | 121518 |
| Independent reflections | 22312 [$R_{int}$ = 0.1186, $R_{sigma}$ = 0.0917] |
| Data/restraints/parameters | 22312/36/921 |
| Goodness-of-fit on F$^2$ | 1.052 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0701, $wR_2$ = 0.1317 |
| Final R indexes [all data] | $R_1$ = 0.1227, $wR_2$ = 0.1490 |
| Largest diff. peak/hole / e Å$^{-3}$ | 4.66/-3.18 |

***Table 2:*** Bond lengths for **47.1a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.491(3) | W1B | P1B | 2.501(2) |
| W | C10 | 2.020(12) | W1B | C10B | 1.980(12) |
| W | C11 | 2.046(12) | W1B | C11B | 2.057(11) |
| W | C12 | 2.019(13) | W1B | C12B | 2.041(12) |
| W | C13 | 2.035(12) | W1B | C13B | 2.025(11) |
| W | C14 | 2.021(12) | W1B | C14B | 2.039(11) |
| Cl | P | 2.082(4) | Cl1B | P1B | 2.085(3) |
| P | C1 | 1.842(11) | P1B | C1B | 1.816(9) |
| P | C3 | 1.803(11) | P1B | C3B | 1.807(9) |
| Si1 | C3 | 1.928(11) | Si1B | C3B | 1.938(9) |
| Si1 | C4 | 1.865(12) | Si1B | C4B | 1.844(10) |
| Si1 | C5 | 1.862(13) | Si1B | C5B | 1.869(10) |
| Si1 | C6 | 1.870(12) | Si1B | C6B | 1.874(10) |
| Si2 | C3 | 1.917(10) | Si2B | C3B | 1.925(9) |
| Si2 | C7 | 1.871(11) | Si2B | C7B | 1.863(9) |
| Si2 | C8 | 1.897(12) | Si2B | C8B | 1.890(10) |
| Si2 | C9 | 1.847(12) | Si2B | C9B | 1.869(10) |
| O1 | C2 | 1.427(15) | O1B | C2B | 1.429(11) |
| O2 | C10 | 1.132(13) | O2B | C10B | 1.177(13) |
| O3 | C11 | 1.130(13) | O3B | C11B | 1.137(12) |
| O4 | C12 | 1.156(14) | O4B | C12B | 1.134(13) |
| O5 | C13 | 1.139(13) | O5B | C13B | 1.143(12) |
| O6 | C14 | 1.164(13) | O6B | C14B | 1.141(13) |
| C1 | C2 | 1.484(16) | C1B | C2B | 1.525(13) |
| W1A | P1A | 2.494(3) | W1C | P1C | 2.490(2) |
| W1A | C10A | 1.995(13) | W1C | C10C | 2.020(11) |

| | | | | | |
|---|---|---|---|---|---|
| W1A | C11A | 2.024(11) | W1C | C11C | 2.032(11) |
| W1A | C12A | 2.050(15) | W1C | C12C | 2.033(11) |
| W1A | C13A | 2.030(14) | W1C | C13C | 2.042(11) |
| W1A | C14A | 2.007(14) | W1C | C14C | 2.057(10) |
| Cl1A | P1A | 2.101(4) | Cl1C | P1C | 2.090(3) |
| P1A | C1A | 1.823(10) | P1C | C1C | 1.836(9) |
| P1A | C3A | 1.801(10) | P1C | C3C | 1.811(9) |
| Si1A | C3A | 1.946(10) | Si1C | C3C | 1.933(9) |
| Si1A | C4A | 1.876(10) | Si1C | C4C | 1.865(10) |
| Si1A | C5A | 1.853(11) | Si1C | C5C | 1.850(10) |
| Si1A | C6A | 1.863(11) | Si1C | C6C | 1.871(10) |
| Si2A | C3A | 1.906(10) | Si2C | C3C | 1.927(10) |
| Si2A | C7A | 1.868(12) | Si2C | C7C | 1.853(10) |
| Si2A | C8A | 1.895(12) | Si2C | C8C | 1.880(10) |
| Si2A | C9A | 1.885(11) | Si2C | C9C | 1.868(10) |
| O1A | C2A | 1.425(14) | O1C | C2C | 1.411(11) |
| O2A | C10A | 1.161(15) | O2C | C10C | 1.131(12) |
| O3A | C11A | 1.147(12) | O3C | C11C | 1.154(12) |
| O4A | C12A | 1.118(15) | O4C | C12C | 1.138(12) |
| O5A | C13A | 1.160(15) | O5C | C13C | 1.143(12) |
| O6A | C14A | 1.159(15) | O6C | C14C | 1.134(11) |
| C1A | C2A | 1.524(14) | C1C | C2C | 1.521(13) |

***Table 3:*** Bond angles for **47.1a**.

| **Atom** | **Atom** | **Atom** | **Angle/˚** | **Atom** | **Atom** | **Atom** | **Angle/˚** |
|---|---|---|---|---|---|---|---|
| C10 | W | P | 176.6(4) | C10B | W1B | P1B | 178.2(3) |
| C10 | W | C11 | 91.1(4) | C10B | W1B | C11B | 91.7(4) |
| C10 | W | C13 | 91.3(5) | C10B | W1B | C12B | 89.1(4) |
| C10 | W | C14 | 89.8(5) | C10B | W1B | C13B | 88.1(4) |
| C11 | W | P | 86.7(3) | C10B | W1B | C14B | 90.0(4) |
| C12 | W | P | 92.5(3) | C11B | W1B | P1B | 87.2(3) |
| C12 | W | C10 | 89.9(5) | C12B | W1B | P1B | 92.2(3) |
| C12 | W | C11 | 85.7(4) | C12B | W1B | C11B | 87.8(4) |
| C12 | W | C13 | 92.2(4) | C13B | W1B | P1B | 93.0(3) |
| C12 | W | C14 | 177.0(4) | C13B | W1B | C11B | 179.4(4) |
| C13 | W | P | 91.1(3) | C13B | W1B | C12B | 92.8(4) |
| C13 | W | C11 | 176.8(4) | C13B | W1B | C14B | 92.4(4) |
| C14 | W | P | 87.7(3) | C14B | W1B | P1B | 88.6(3) |
| C14 | W | C11 | 91.3(4) | C14B | W1B | C11B | 87.0(4) |
| C14 | W | C13 | 90.8(4) | C14B | W1B | C12B | 174.7(4) |
| Cl | P | W | 105.90(14) | Cl1B | P1B | W1B | 106.99(12) |
| C1 | P | W | 118.8(4) | C1B | P1B | W1B | 121.1(3) |
| C1 | P | Cl | 97.7(4) | C1B | P1B | Cl1B | 97.6(3) |
| C3 | P | W | 120.8(4) | C3B | P1B | W1B | 117.5(3) |
| C3 | P | Cl | 105.9(4) | C3B | P1B | Cl1B | 107.4(3) |
| C3 | P | C1 | 104.5(5) | C3B | P1B | C1B | 103.9(4) |
| C4 | Si1 | C3 | 111.3(5) | C4B | Si1B | C3B | 109.2(4) |
| C4 | Si1 | C6 | 113.3(6) | C4B | Si1B | C5B | 105.6(5) |
| C5 | Si1 | C3 | 110.6(6) | C4B | Si1B | C6B | 111.5(5) |
| C5 | Si1 | C4 | 102.5(6) | C5B | Si1B | C3B | 109.7(4) |
| C5 | Si1 | C6 | 108.4(6) | C5B | Si1B | C6B | 108.8(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C6 | Si1 | C3 | 110.4(5) | C6B | Si1B | C3B | 111.9(4) |
| C7 | Si2 | C3 | 111.3(5) | C7B | Si2B | C3B | 111.8(4) |
| C7 | Si2 | C8 | 105.7(5) | C7B | Si2B | C8B | 106.6(5) |
| C8 | Si2 | C3 | 112.7(5) | C7B | Si2B | C9B | 111.1(5) |
| C9 | Si2 | C3 | 108.7(5) | C8B | Si2B | C3B | 114.1(4) |
| C9 | Si2 | C7 | 112.3(6) | C9B | Si2B | C3B | 107.0(4) |
| C9 | Si2 | C8 | 106.0(7) | C9B | Si2B | C8B | 106.1(5) |
| C2 | C1 | P | 114.6(8) | C2B | C1B | P1B | 115.6(7) |
| O1 | C2 | C1 | 111.4(10) | O1B | C2B | C1B | 111.4(8) |
| P | C3 | Si1 | 117.2(6) | P1B | C3B | Si1B | 117.9(4) |
| P | C3 | Si2 | 115.8(6) | P1B | C3B | Si2B | 114.1(4) |
| Si2 | C3 | Si1 | 113.1(5) | Si2B | C3B | Si1B | 113.4(5) |
| O2 | C10 | W | 179.0(12) | O2B | C10B | W1B | 176.3(10) |
| O3 | C11 | W | 178.6(11) | O3B | C11B | W1B | 179.6(11) |
| O4 | C12 | W | 176.6(10) | O4B | C12B | W1B | 177.1(10) |
| O5 | C13 | W | 179.2(12) | O5B | C13B | W1B | 177.3(9) |
| O6 | C14 | W | 178.4(10) | O6B | C14B | W1B | 177.9(10) |
| C10A | W1A | P1A | 176.5(4) | C10C | W1C | P1C | 178.5(3) |
| C10A | W1A | C11A | 87.9(5) | C10C | W1C | C11C | 90.1(4) |
| C10A | W1A | C12A | 93.4(5) | C10C | W1C | C12C | 89.8(4) |
| C10A | W1A | C13A | 92.4(6) | C10C | W1C | C13C | 90.9(4) |
| C10A | W1A | C14A | 89.2(6) | C10C | W1C | C14C | 90.3(4) |
| C11A | W1A | P1A | 91.1(3) | C11C | W1C | P1C | 91.3(3) |
| C11A | W1A | C12A | 88.9(5) | C11C | W1C | C12C | 89.2(4) |
| C11A | W1A | C13A | 177.0(5) | C11C | W1C | C13C | 177.1(4) |
| C12A | W1A | P1A | 83.2(4) | C11C | W1C | C14C | 93.7(4) |
| C13A | W1A | P1A | 88.5(4) | C12C | W1C | P1C | 89.5(3) |
| C13A | W1A | C12A | 88.1(5) | C12C | W1C | C13C | 88.1(4) |
| C14A | W1A | P1A | 94.2(4) | C12C | W1C | C14C | 177.1(4) |
| C14A | W1A | C11A | 93.3(5) | C13C | W1C | P1C | 87.7(3) |
| C14A | W1A | C12A | 176.6(5) | C13C | W1C | C14C | 89.0(4) |
| C14A | W1A | C13A | 89.7(5) | C14C | W1C | P1C | 90.2(3) |
| Cl1A | P1A | W1A | 107.82(15) | Cl1C | P1C | W1C | 106.11(11) |
| C1A | P1A | W1A | 122.2(4) | C1C | P1C | W1C | 118.9(3) |
| C1A | P1A | Cl1A | 96.8(4) | C1C | P1C | Cl1C | 97.6(3) |
| C3A | P1A | W1A | 116.8(3) | C3C | P1C | W1C | 120.5(3) |
| C3A | P1A | Cl1A | 106.2(3) | C3C | P1C | Cl1C | 106.6(3) |
| C3A | P1A | C1A | 104.2(5) | C3C | P1C | C1C | 104.0(4) |
| C4A | Si1A | C3A | 113.4(5) | C4C | Si1C | C3C | 114.5(4) |
| C5A | Si1A | C3A | 107.3(5) | C4C | Si1C | C6C | 106.8(5) |
| C5A | Si1A | C4A | 107.9(5) | C5C | Si1C | C3C | 108.8(4) |
| C5A | Si1A | C6A | 110.8(6) | C5C | Si1C | C4C | 103.9(5) |
| C6A | Si1A | C3A | 110.8(5) | C5C | Si1C | C6C | 111.4(5) |
| C6A | Si1A | C4A | 106.7(5) | C6C | Si1C | C3C | 111.2(4) |
| C7A | Si2A | C3A | 111.7(5) | C7C | Si2C | C3C | 112.0(4) |
| C7A | Si2A | C8A | 112.0(6) | C7C | Si2C | C8C | 111.2(5) |
| C7A | Si2A | C9A | 109.0(6) | C7C | Si2C | C9C | 107.3(5) |
| C8A | Si2A | C3A | 108.8(5) | C8C | Si2C | C3C | 110.4(4) |
| C9A | Si2A | C3A | 109.9(5) | C9C | Si2C | C3C | 110.8(4) |
| C9A | Si2A | C8A | 105.1(6) | C9C | Si2C | C8C | 104.9(5) |
| C2A | C1A | P1A | 114.4(8) | C2C | C1C | P1C | 115.0(6) |
| O1A | C2A | C1A | 110.9(10) | O1C | C2C | C1C | 110.8(8) |
| P1A | C3A | Si1A | 112.4(5) | P1C | C3C | Si1C | 113.6(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P1A | C3A | Si2A | 119.9(5) | P1C | C3C | Si2C | 117.5(5) |
| Si2A | C3A | Si1A | 113.9(5) | Si2C | C3C | Si1C | 113.5(4) |
| O2A | C10A | W1A | 174.2(13) | O2C | C10C | W1C | 179.9(14) |
| O3A | C11A | W1A | 175.3(10) | O3C | C11C | W1C | 177.2(9) |
| O4A | C12A | W1A | 176.3(12) | O4C | C12C | W1C | 178.7(9) |
| O5A | C13A | W1A | 177.5(13) | O5C | C13C | W1C | 178.2(9) |
| O6A | C14A | W1A | 178.6(13) | O6C | C14C | W1C | 176.8(9) |

***Table 4:*** Torsion angles for **47.1a**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | 47.9(10) | W1B | P1B | C1B | C2B | 48.9(8) |
| W | P | C3 | Si1 | -138.3(4) | W1B | P1B | C3B | Si1B | -139.1(4) |
| W | P | C3 | Si2 | 84.0(6) | W1B | P1B | C3B | Si2B | 84.2(5) |
| Cl | P | C1 | C2 | -65.1(9) | Cl1B | P1B | C1B | C2B | -66.2(7) |
| Cl | P | C3 | Si1 | -18.2(6) | Cl1B | P1B | C3B | Si1B | -18.5(5) |
| Cl | P | C3 | Si2 | -155.9(5) | Cl1B | P1B | C3B | Si2B | -155.3(3) |
| P | C1 | C2 | O1 | 176.2(9) | P1B | C1B | C2B | O1B | -174.9(7) |
| C1 | P | C3 | Si1 | 84.4(6) | C1B | P1B | C3B | Si1B | 84.2(6) |
| C1 | P | C3 | Si2 | -53.3(7) | C1B | P1B | C3B | Si2B | -52.6(6) |
| C3 | P | C1 | C2 | -173.8(9) | C3B | P1B | C1B | C2B | -176.2(7) |
| W1A | P1A | C1A | C2A | -49.5(10) | W1C | P1C | C1C | C2C | -50.0(8) |
| W1A | P1A | C3A | Si1A | -84.8(5) | W1C | P1C | C3C | Si1C | -84.9(5) |
| W1A | P1A | C3A | Si2A | 137.3(4) | W1C | P1C | C3C | Si2C | 139.1(3) |
| Cl1A | P1A | C1A | C2A | 66.6(9) | Cl1C | P1C | C1C | C2C | 63.3(7) |
| Cl1A | P1A | C3A | Si1A | 154.9(4) | Cl1C | P1C | C3C | Si1C | 154.3(4) |
| Cl1A | P1A | C3A | Si2A | 17.0(6) | Cl1C | P1C | C3C | Si2C | 18.3(5) |
| P1A | C1A | C2A | O1A | 176.6(9) | P1C | C1C | C2C | O1C | -175.4(6) |
| C1A | P1A | C3A | Si1A | 53.3(6) | C1C | P1C | C3C | Si1C | 51.7(6) |
| C1A | P1A | C3A | Si2A | -84.6(7) | C1C | P1C | C3C | Si2C | -84.3(6) |
| C3A | P1A | C1A | C2A | 175.3(9) | C3C | P1C | C1C | C2C | 172.6(7) |

## 12.33 Pentacarbonyl{chloro(2-hydroxypropyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [47.1b]

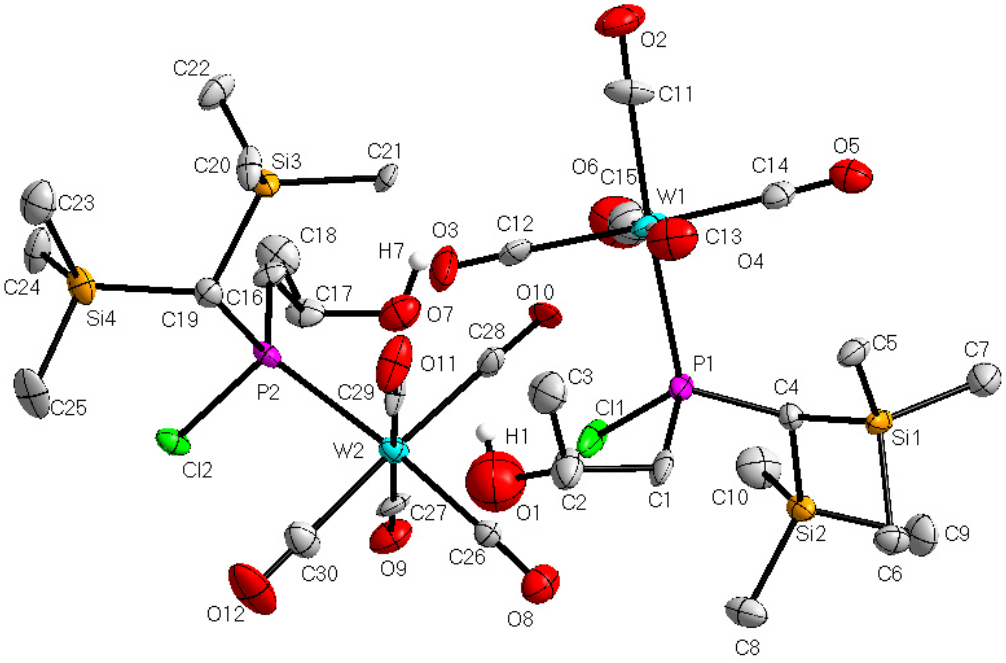


***Table 1:*** Crystal data and structure refinement for **47.1b**.

| | |
|---|---|
| Identification code | GSTR337, AKY-326 // GXray3181 |
| Crystal Habitus | colourless block |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{15}H_{26}ClO_6PSi_2W$ |
| Moiety formula | C15 H26 Cl O6 P Si2 W |
| Formula weight | 608.81 |
| Temperature/K | 123(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 22.215(2) |
| b/Å | 9.2037(8) |
| c/Å | 23.011(2) |
| α/° | 90.00 |
| β/° | 97.555(4) |
| γ/° | 90.00 |
| Volume/Å$^3$ | 4664.0(7) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.734 |
| μ/mm$^{-1}$ | 5.264 |
| F(000) | 2384.0 |
| Crystal size/mm$^3$ | 0.32 × 0.26 × 0.22 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.2836; 0.3905 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.4 to 50.5° |
| Completeness to theta | 0.941 |
| Index ranges | -26 ≤ h ≤ 26, 0 ≤ k ≤ 10, 0 ≤ l ≤ 27 |
| Reflections collected | 8532 |
| Independent reflections | 8538 [$R_{int}$ = 0.0000] |

| | |
|---|---|
| Data/restraints/parameters | 8538/126/486 |
| Goodness-of-fit on $F^2$ | 1.177 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0850, $wR_2$ = 0.1843 |
| Final R indexes [all data] | $R_1$ = 0.1039, $wR_2$ = 0.1930 |
| Largest diff. peak/hole / e $Å^{-3}$ | 3.07/-1.35 |

***Table 2:*** Bond lengths for **47.1b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | C2 | 1.58(3) | C17 | O7 | 1.44(2) |
| C1 | P1 | 1.84(2) | C17 | C18 | 1.52(3) |
| C2 | C3 | 1.30(3) | C19 | P2 | 1.796(19) |
| C2 | O1 | 1.50(3) | C19 | Si3 | 1.917(19) |
| C4 | P1 | 1.818(18) | C19 | Si4 | 1.930(19) |
| C4 | Si2 | 1.919(18) | C20 | Si3 | 1.868(19) |
| C4 | Si1 | 1.924(18) | C21 | Si3 | 1.863(18) |
| C5 | Si1 | 1.89(2) | C22 | Si3 | 1.88(2) |
| C6 | Si1 | 1.895(19) | C23 | Si4 | 1.88(2) |
| C7 | Si1 | 1.87(2) | C24 | Si4 | 1.87(2) |
| C8 | Si2 | 1.84(2) | C25 | Si4 | 1.86(2) |
| C9 | Si2 | 1.89(2) | C26 | O8 | 1.14(2) |
| C10 | Si2 | 1.85(2) | C26 | W2 | 2.002(19) |
| C11 | O2 | 1.09(2) | C27 | O9 | 1.16(2) |
| C11 | W1 | 2.04(2) | C27 | W2 | 2.02(2) |
| C12 | O3 | 1.12(3) | C28 | O10 | 1.12(2) |
| C12 | W1 | 2.07(2) | C28 | W2 | 2.07(2) |
| C13 | O4 | 1.13(3) | C29 | O11 | 1.14(2) |
| C13 | W1 | 2.05(3) | C29 | W2 | 2.018(19) |
| C14 | O5 | 1.15(2) | C30 | O12 | 1.14(3) |
| C14 | W1 | 2.02(2) | C30 | W2 | 2.03(2) |
| C15 | O6 | 1.13(3) | P1 | Cl1 | 2.098(7) |
| C15 | W1 | 2.03(3) | P1 | W1 | 2.503(5) |
| C16 | C17 | 1.52(2) | P2 | Cl2 | 2.117(6) |
| C16 | P2 | 1.849(18) | P2 | W2 | 2.504(5) |

***Table 3:*** Bond angles for **47.1b**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C2 | C1 | P1 | 117.7(16) | C25 | Si4 | C19 | 110.2(10) |
| C3 | C2 | O1 | 103(2) | C24 | Si4 | C19 | 113.0(9) |
| C3 | C2 | C1 | 112(2) | C23 | Si4 | C19 | 111.5(9) |
| O1 | C2 | C1 | 111(2) | C4 | P1 | C1 | 103.5(9) |
| P1 | C4 | Si2 | 118.9(9) | C4 | P1 | Cl1 | 105.5(6) |
| P1 | C4 | Si1 | 113.4(10) | C1 | P1 | Cl1 | 98.3(7) |
| Si2 | C4 | Si1 | 114.2(9) | C4 | P1 | W1 | 116.8(6) |
| O2 | C11 | W1 | 178(2) | C1 | P1 | W1 | 122.2(6) |
| O3 | C12 | W1 | 178(2) | Cl1 | P1 | W1 | 108.0(2) |
| O4 | C13 | W1 | 178(2) | C19 | P2 | C16 | 102.0(8) |
| O5 | C14 | W1 | 178.1(18) | C19 | P2 | Cl2 | 105.9(6) |
| O6 | C15 | W1 | 178(3) | C16 | P2 | Cl2 | 96.5(6) |
| C17 | C16 | P2 | 114.5(13) | C19 | P2 | W2 | 117.8(6) |
| O7 | C17 | C18 | 108.8(17) | C16 | P2 | W2 | 125.5(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O7 | C17 | C16 | 107.0(16) | Cl2 | P2 | W2 | 105.9(2) |
| C18 | C17 | C16 | 111.4(16) | C14 | W1 | C15 | 89.2(10) |
| P2 | C19 | Si3 | 113.8(10) | C14 | W1 | C11 | 86.3(9) |
| P2 | C19 | Si4 | 120.2(10) | C15 | W1 | C11 | 93.6(10) |
| Si3 | C19 | Si4 | 113.6(10) | C14 | W1 | C13 | 93.0(8) |
| O8 | C26 | W2 | 177.2(17) | C15 | W1 | C13 | 177.2(9) |
| O9 | C27 | W2 | 178.1(18) | C11 | W1 | C13 | 88.2(8) |
| O10 | C28 | W2 | 177.3(18) | C14 | W1 | C12 | 177.6(8) |
| O11 | C29 | W2 | 177.8(19) | C15 | W1 | C12 | 89.0(11) |
| O12 | C30 | W2 | 177(2) | C11 | W1 | C12 | 92.2(9) |
| C7 | Si1 | C5 | 107.1(10) | C13 | W1 | C12 | 88.8(9) |
| C7 | Si1 | C6 | 111.4(10) | C14 | W1 | P1 | 90.9(6) |
| C5 | Si1 | C6 | 106.0(10) | C15 | W1 | P1 | 86.3(8) |
| C7 | Si1 | C4 | 107.0(10) | C11 | W1 | P1 | 177.2(7) |
| C5 | Si1 | C4 | 114.7(8) | C13 | W1 | P1 | 92.0(6) |
| C6 | Si1 | C4 | 110.6(8) | C12 | W1 | P1 | 90.6(6) |
| C8 | Si2 | C10 | 110.8(11) | C26 | W2 | C29 | 88.6(7) |
| C8 | Si2 | C9 | 107.2(10) | C26 | W2 | C27 | 91.6(8) |
| C10 | Si2 | C9 | 104.5(11) | C29 | W2 | C27 | 179.2(8) |
| C8 | Si2 | C4 | 113.1(9) | C26 | W2 | C30 | 87.9(8) |
| C10 | Si2 | C4 | 110.0(10) | C29 | W2 | C30 | 90.1(8) |
| C9 | Si2 | C4 | 110.8(9) | C27 | W2 | C30 | 90.6(9) |
| C21 | Si3 | C20 | 107.2(9) | C26 | W2 | C28 | 89.6(7) |
| C21 | Si3 | C22 | 104.5(10) | C29 | W2 | C28 | 89.4(8) |
| C20 | Si3 | C22 | 114.1(10) | C27 | W2 | C28 | 89.8(8) |
| C21 | Si3 | C19 | 115.4(9) | C30 | W2 | C28 | 177.4(8) |
| C20 | Si3 | C19 | 107.3(9) | C26 | W2 | P2 | 175.4(5) |
| C22 | Si3 | C19 | 108.5(9) | C29 | W2 | P2 | 91.9(5) |
| C25 | Si4 | C24 | 110.7(10) | C27 | W2 | P2 | 87.9(5) |
| C25 | Si4 | C23 | 104.9(11) | C30 | W2 | P2 | 87.6(6) |
| C24 | Si4 | C23 | 106.2(11) | C28 | W2 | P2 | 95.0(5) |

***Table 4:*** Torsion angles for **47.1b**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| P1 | C1 | C2 | C3 | -59(3) | O4 | C13 | W1 | C11 | -143(53) |
| P1 | C1 | C2 | O1 | 55(2) | O4 | C13 | W1 | C12 | 125(53) |
| P2 | C16 | C17 | O7 | -80.0(17) | O4 | C13 | W1 | P1 | 35(53) |
| P2 | C16 | C17 | C18 | 161.2(15) | O3 | C12 | W1 | C14 | 99(72) |
| P1 | C4 | Si1 | C7 | -143.7(11) | O3 | C12 | W1 | C15 | 55(76) |
| Si2 | C4 | Si1 | C7 | 75.9(12) | O3 | C12 | W1 | C11 | 149(76) |
| P1 | C4 | Si1 | C5 | -25.0(14) | O3 | C12 | W1 | C13 | -123(76) |
| Si2 | C4 | Si1 | C5 | -165.5(10) | O3 | C12 | W1 | P1 | -31(76) |
| P1 | C4 | Si1 | C6 | 94.8(12) | C4 | P1 | W1 | C14 | -10.9(9) |
| Si2 | C4 | Si1 | C6 | -45.6(13) | C1 | P1 | W1 | C14 | 118.1(9) |
| P1 | C4 | Si2 | C8 | -53.4(14) | Cl1 | P1 | W1 | C14 | -129.5(6) |
| Si1 | C4 | Si2 | C8 | 84.7(12) | C4 | P1 | W1 | C15 | 78.3(10) |
| P1 | C4 | Si2 | C10 | 71.1(14) | C1 | P1 | W1 | C15 | -152.8(11) |
| Si1 | C4 | Si2 | C10 | -150.8(11) | Cl1 | P1 | W1 | C15 | -40.3(8) |
| P1 | C4 | Si2 | C9 | -173.8(11) | C4 | P1 | W1 | C11 | -10(13) |
| Si1 | C4 | Si2 | C9 | -35.7(14) | C1 | P1 | W1 | C11 | 119(13) |
| P2 | C19 | Si3 | C21 | -23.3(14) | Cl1 | P1 | W1 | C11 | -128(13) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Si4 | C19 | Si3 | C21 | -165.7(10) | C4 | P1 | W1 | C13 | -103.9(9) |
| P2 | C19 | Si3 | C20 | -142.7(11) | C1 | P1 | W1 | C13 | 25.0(10) |
| Si4 | C19 | Si3 | C20 | 74.9(12) | Cl1 | P1 | W1 | C13 | 137.5(6) |
| P2 | C19 | Si3 | C22 | 93.5(12) | C4 | P1 | W1 | C12 | 167.3(10) |
| Si4 | C19 | Si3 | C22 | -48.9(13) | C1 | P1 | W1 | C12 | -63.8(11) |
| P2 | C19 | Si4 | C25 | 73.2(14) | Cl1 | P1 | W1 | C12 | 48.7(8) |
| Si3 | C19 | Si4 | C25 | -146.9(11) | O8 | C26 | W2 | C29 | 156(36) |
| P2 | C19 | Si4 | C24 | -51.2(15) | O8 | C26 | W2 | C27 | -25(36) |
| Si3 | C19 | Si4 | C24 | 88.7(13) | O8 | C26 | W2 | C30 | 66(36) |
| P2 | C19 | Si4 | C23 | -170.7(11) | O8 | C26 | W2 | C28 | -114(36) |
| Si3 | C19 | Si4 | C23 | -30.9(14) | O8 | C26 | W2 | P2 | 60(40) |
| Si2 | C4 | P1 | C1 | 85.4(12) | O11 | C29 | W2 | C26 | -83(46) |
| Si1 | C4 | P1 | C1 | -53.0(12) | O11 | C29 | W2 | C27 | 171(68) |
| Si2 | C4 | P1 | Cl1 | -17.3(12) | O11 | C29 | W2 | C30 | 4(46) |
| Si1 | C4 | P1 | Cl1 | -155.7(7) | O11 | C29 | W2 | C28 | -173(46) |
| Si2 | C4 | P1 | W1 | -137.2(8) | O11 | C29 | W2 | P2 | 92(46) |
| Si1 | C4 | P1 | W1 | 84.4(10) | O9 | C27 | W2 | C26 | 137(56) |
| C2 | C1 | P1 | C4 | -173.6(15) | O9 | C27 | W2 | C29 | -117(73) |
| C2 | C1 | P1 | Cl1 | -65.4(15) | O9 | C27 | W2 | C30 | 49(56) |
| C2 | C1 | P1 | W1 | 51.9(17) | O9 | C27 | W2 | C28 | -133(56) |
| Si3 | C19 | P2 | C16 | -59.1(12) | O9 | C27 | W2 | P2 | -38(56) |
| Si4 | C19 | P2 | C16 | 80.7(12) | O12 | C30 | W2 | C26 | 71(42) |
| Si3 | C19 | P2 | Cl2 | -159.4(8) | O12 | C30 | W2 | C29 | -18(42) |
| Si4 | C19 | P2 | Cl2 | -19.7(12) | O12 | C30 | W2 | C27 | 163(42) |
| Si3 | C19 | P2 | W2 | 82.4(10) | O12 | C30 | W2 | C28 | 63(52) |
| Si4 | C19 | P2 | W2 | -137.9(8) | O12 | C30 | W2 | P2 | -109(42) |
| C17 | C16 | P2 | C19 | -172.1(14) | O10 | C28 | W2 | C26 | -36(40) |
| C17 | C16 | P2 | Cl2 | -64.3(14) | O10 | C28 | W2 | C29 | 52(40) |
| C17 | C16 | P2 | W2 | 50.5(16) | O10 | C28 | W2 | C27 | -128(40) |
| O5 | C14 | W1 | C15 | 43(51) | O10 | C28 | W2 | C30 | -28(53) |
| O5 | C14 | W1 | C11 | -51(51) | O10 | C28 | W2 | P2 | 144(40) |
| O5 | C14 | W1 | C13 | -139(51) | C19 | P2 | W2 | C26 | 84(7) |
| O5 | C14 | W1 | C12 | -1(65) | C16 | P2 | W2 | C26 | -144(7) |
| O5 | C14 | W1 | P1 | 129(51) | Cl2 | P2 | W2 | C26 | -34(7) |
| O6 | C15 | W1 | C14 | -178(100) | C19 | P2 | W2 | C29 | -12.4(9) |
| O6 | C15 | W1 | C11 | -91(73) | C16 | P2 | W2 | C29 | 119.2(9) |
| O6 | C15 | W1 | C13 | 40(86) | Cl2 | P2 | W2 | C29 | -130.5(6) |
| O6 | C15 | W1 | C12 | 1(73) | C19 | P2 | W2 | C27 | 168.4(9) |
| O6 | C15 | W1 | P1 | 92(73) | C16 | P2 | W2 | C27 | -60.0(9) |
| O2 | C11 | W1 | C14 | 12(80) | Cl2 | P2 | W2 | C27 | 50.3(6) |
| O2 | C11 | W1 | C15 | -77(80) | C19 | P2 | W2 | C30 | 77.7(9) |
| O2 | C11 | W1 | C13 | 105(80) | C16 | P2 | W2 | C30 | -150.8(10) |
| O2 | C11 | W1 | C12 | -166(100) | Cl2 | P2 | W2 | C30 | -40.5(7) |
| O2 | C11 | W1 | P1 | 11(90) | C19 | P2 | W2 | C28 | -101.9(9) |
| O4 | C13 | W1 | C14 | -56(53) | C16 | P2 | W2 | C28 | 29.6(9) |
| O4 | C13 | W1 | C15 | 86(59) | Cl2 | P2 | W2 | C28 | 139.9(6) |

## 12.34 Pentacarbonyl{chloro(3,3,3-trifluoro-2-hydroxypropyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [47.1c]

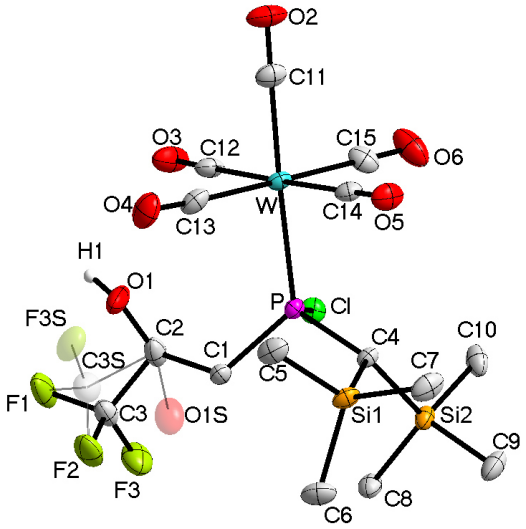


***Table 1:*** Crystal data and structure refinement for **47.1c**.

| | |
|---|---|
| Identification code | GSTR419, AKY-505 // GXray4067f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{15}H_{23}O_6F_3Si_2PClW$ |
| Moiety formula | C15 H23 Cl F3 O6 P Si2 W |
| Formula weight | 662.78 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.3179(3) |
| b/Å | 11.0538(4) |
| c/Å | 12.1332(4) |
| α/° | 101.7900(15) |
| β/° | 92.3518(16) |
| γ/° | 96.5430(15) |
| Volume/Å$^3$ | 1212.70(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.815 |
| μ/mm$^{-1}$ | 5.087 |
| F(000) | 644.0 |
| Crystal size/mm$^3$ | 0.14 × 0.11 × 0.03 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5045; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.706 to 55.998° |
| Completeness to theta | 0.995 |
| Index ranges | -12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -15 ≤ l ≤ 16 |
| Reflections collected | 34093 |
| Independent reflections | 5823 [$R_{int}$ = 0.0248, $R_{sigma}$ = 0.0178] |
| Data/restraints/parameters | 5823/0/298 |
| Goodness-of-fit on F$^2$ | 1.053 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0132, $wR_2$ = 0.0309 |
| Final R indexes [all data] | $R_1$ = 0.0142, $wR_2$ = 0.0312 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.81/-0.42 |

***Table 2:*** Bond lengths for **47.1c**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4872(4) | F1 | C3 | 1.344(2) |
| W | C11 | 2.0220(17) | F1 | C3S | 1.523(14) |
| W | C12 | 2.0444(18) | F2 | C3 | 1.356(2) |
| W | C13 | 2.0304(19) | F2 | C3S | 1.231(14) |
| W | C14 | 2.0449(17) | F3 | C3 | 1.340(3) |
| W | C15 | 2.0475(19) | F3S | C3S | 1.312(17) |
| Cl | P | 2.0969(5) | O1 | C2 | 1.441(2) |
| P | C1 | 1.8463(16) | O1S | C2 | 1.717(9) |
| P | C4 | 1.8131(16) | O2 | C11 | 1.137(2) |
| Si1 | C4 | 1.9306(16) | O3 | C12 | 1.138(2) |
| Si1 | C5 | 1.8714(18) | O4 | C13 | 1.145(2) |
| Si1 | C6 | 1.8693(19) | O5 | C14 | 1.140(2) |
| Si1 | C7 | 1.8618(19) | O6 | C15 | 1.140(2) |
| Si2 | C4 | 1.9224(15) | C1 | C2 | 1.517(2) |
| Si2 | C8 | 1.8686(17) | C2 | C3 | 1.490(3) |
| Si2 | C9 | 1.8706(19) | C2 | C3S | 1.527(14) |
| Si2 | C10 | 1.8710(19) | | | |

***Table 3:*** Bond angles for **47.1c**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C11 | W | P | 176.88(5) | C9 | Si2 | C4 | 110.10(8) |
| C11 | W | C12 | 89.82(7) | C9 | Si2 | C10 | 104.97(9) |
| C11 | W | C13 | 89.74(7) | C10 | Si2 | C4 | 109.00(8) |
| C11 | W | C14 | 88.95(7) | C2 | C1 | P | 114.88(11) |
| C11 | W | C15 | 90.08(8) | O1 | C2 | C1 | 106.57(14) |
| C12 | W | P | 89.65(5) | O1 | C2 | C3 | 108.41(16) |
| C12 | W | C14 | 178.75(6) | C1 | C2 | O1S | 93.0(3) |
| C12 | W | C15 | 90.42(7) | C1 | C2 | C3S | 112.5(6) |
| C13 | W | P | 93.32(5) | C3 | C2 | C1 | 112.61(15) |
| C13 | W | C12 | 88.89(7) | C3S | C2 | O1S | 93.2(7) |
| C13 | W | C14 | 90.86(7) | F1 | C3 | F2 | 105.64(17) |
| C13 | W | C15 | 179.29(7) | F1 | C3 | C2 | 111.74(17) |
| C14 | W | P | 91.59(4) | F2 | C3 | C2 | 113.39(18) |
| C14 | W | C15 | 89.82(7) | F3 | C3 | F1 | 109.27(18) |
| C15 | W | P | 86.85(5) | F3 | C3 | F2 | 106.55(18) |
| Cl | P | W | 106.553(19) | F3 | C3 | C2 | 110.00(18) |
| C1 | P | W | 123.67(5) | F1 | C3S | C2 | 100.6(9) |
| C1 | P | Cl | 96.28(5) | F2 | C3S | F1 | 102.2(9) |
| C4 | P | W | 117.76(5) | F2 | C3S | F3S | 113.5(12) |
| C4 | P | Cl | 105.85(5) | F2 | C3S | C2 | 118.8(11) |
| C4 | P | C1 | 103.48(7) | F3S | C3S | F1 | 122.7(11) |
| C5 | Si1 | C4 | 114.29(7) | F3S | C3S | C2 | 99.5(9) |
| C6 | Si1 | C4 | 111.22(8) | P | C4 | Si1 | 114.17(8) |
| C6 | Si1 | C5 | 106.76(9) | P | C4 | Si2 | 118.29(8) |
| C7 | Si1 | C4 | 106.90(8) | Si2 | C4 | Si1 | 114.43(8) |
| C7 | Si1 | C5 | 105.51(9) | O2 | C11 | W | 179.30(19) |
| C7 | Si1 | C6 | 112.11(9) | O3 | C12 | W | 178.75(16) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C8 | Si2 | C4 | 112.50(7) | O4 | C13 | W | 177.53(16) |
| C8 | Si2 | C9 | 108.50(8) | O5 | C14 | W | 179.11(14) |
| C8 | Si2 | C10 | 111.50(8) | O6 | C15 | W | 179.35(16) |

***Table 4:*** Torsion angles for **47.1c**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | 53.00(14) | C1 | C2 | C3 | F2 | 50.8(2) |
| W | P | C4 | Si1 | 85.42(8) | C1 | C2 | C3 | F3 | -68.4(2) |
| W | P | C4 | Si2 | -135.44(7) | C1 | C2 | C3S | F1 | -150.8(5) |
| Cl | P | C1 | C2 | -61.69(12) | C1 | C2 | C3S | F2 | -40.4(13) |
| Cl | P | C4 | Si1 | -155.62(6) | C1 | C2 | C3S | F3S | 83.1(9) |
| Cl | P | C4 | Si2 | -16.49(10) | C3 | F1 | C3S | F2 | -64.5(8) |
| P | C1 | C2 | O1 | -76.26(16) | C3 | F1 | C3S | F3S | 167.0(18) |
| P | C1 | C2 | O1S | 111.3(4) | C3 | F1 | C3S | C2 | 58.4(7) |
| P | C1 | C2 | C3 | 165.01(15) | C3 | F2 | C3S | F1 | 54.4(7) |
| P | C1 | C2 | C3S | -154.0(6) | C3 | F2 | C3S | F3S | -171.4(16) |
| O1 | C2 | C3 | F1 | 52.4(2) | C3 | F2 | C3S | C2 | -55.1(9) |
| O1 | C2 | C3 | F2 | -66.9(2) | C3 | C2 | C3S | F1 | -52.5(6) |
| O1 | C2 | C3 | F3 | 173.95(16) | C3 | C2 | C3S | F2 | 57.9(10) |
| O1 | C2 | C3S | F1 | 108.0(7) | C3 | C2 | C3S | F3S | -178.6(15) |
| O1 | C2 | C3S | F2 | -141.6(12) | C3S | F1 | C3 | F2 | 56.2(8) |
| O1 | C2 | C3S | F3S | -18.1(7) | C3S | F1 | C3 | F3 | 170.5(9) |
| O1S | C2 | C3 | F1 | -112.5(5) | C3S | F1 | C3 | C2 | -67.5(9) |
| O1S | C2 | C3 | F2 | 128.3(5) | C3S | F2 | C3 | F1 | -69.3(9) |
| O1S | C2 | C3 | F3 | 9.1(4) | C3S | F2 | C3 | F3 | 174.5(9) |
| O1S | C2 | C3S | F1 | -56.2(8) | C3S | F2 | C3 | C2 | 53.4(9) |
| O1S | C2 | C3S | F2 | 54.2(12) | C3S | C2 | C3 | F1 | 72.0(9) |
| O1S | C2 | C3S | F3S | 177.7(9) | C3S | C2 | C3 | F2 | -47.2(9) |
| C1 | P | C4 | Si1 | -54.96(10) | C3S | C2 | C3 | F3 | -166.4(9) |
| C1 | P | C4 | Si2 | 84.17(10) | C4 | P | C1 | C2 | -169.68(12) |
| C1 | C2 | C3 | F1 | 170.06(16) | | | | | |

## 12.35 Pentacarbonyl{fluoro(3,3,3-trifluoro-2-hydroxypropyl)[bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [48.1a]

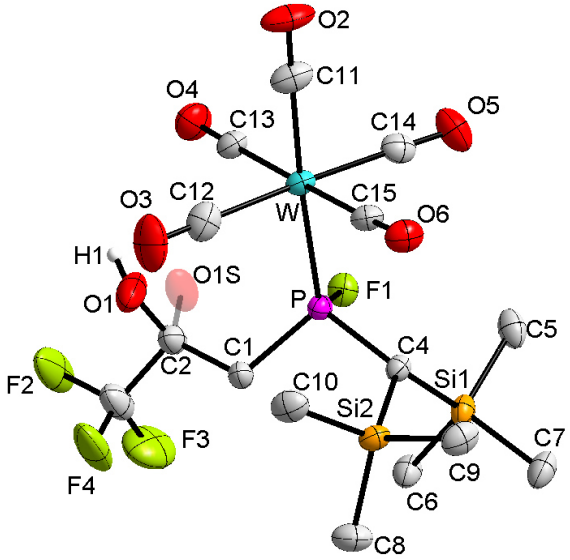

***Table 1:*** Crystal data and structure refinement for **48.1a**.

| | |
|---|---|
| Identification code | GSTR418, AKY-506 // GXray4066 |
| Device Type | STOE IPDS 2T |
| Empirical formula | $C_{15}H_{23}F_4O_6PSi_2W$ |
| Moiety formula | C15 H23 F4 O6 P Si2 W |
| Formula weight | 646.33 |
| Temperature/K | 123(2) |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.2501(4) |
| b/Å | 11.1432(4) |
| c/Å | 11.8158(5) |
| α/° | 100.802(3) |
| β/° | 92.088(3) |
| γ/° | 98.468(3) |
| Volume/Å$^3$ | 1180.73(8) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.818 |
| μ/mm$^{-1}$ | 5.119 |
| F(000) | 628.0 |
| Crystal size/mm$^3$ | 0.24 × 0.15 × 0.03 |
| Absorption correction | integration |
| Tmin; Tmax | 0.4061; 0.8325 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.37 to 50.5° |
| Completeness to theta | 0.900 |
| Index ranges | -10 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 11 |
| Reflections collected | 8394 |
| Independent reflections | 4182 [$R_{int}$ = 0.0367, $R_{sigma}$ = 0.0355] |
| Data/restraints/parameters | 4182/1/274 |
| Goodness-of-fit on F$^2$ | 0.979 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0229, w$R_2$ = 0.0533 |
| Final R indexes [all data] | $R_1$ = 0.0265, w$R_2$ = 0.0539 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.98/-1.00 |

***Table 2:*** Bond lengths for **48.1a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4682(9) | Si2 | C9 | 1.867(4) |
| W | C11 | 2.029(4) | Si2 | C10 | 1.873(4) |
| W | C12 | 2.041(5) | F2 | C3 | 1.338(6) |
| W | C13 | 2.048(4) | F3 | C3 | 1.325(7) |
| W | C14 | 2.045(4) | F4 | C3 | 1.307(6) |
| W | C15 | 2.044(4) | O1 | C2 | 1.343(6) |
| P | F1 | 1.614(2) | O1S | C2 | 1.319(7) |
| P | C1 | 1.835(4) | O2 | C11 | 1.133(5) |
| P | C4 | 1.803(4) | O3 | C12 | 1.125(6) |
| Si1 | C4 | 1.919(4) | O4 | C13 | 1.128(5) |
| Si1 | C5 | 1.871(4) | O5 | C14 | 1.140(5) |
| Si1 | C6 | 1.866(4) | O6 | C15 | 1.136(5) |
| Si1 | C7 | 1.872(4) | C1 | C2 | 1.502(5) |
| Si2 | C4 | 1.923(4) | C2 | C3 | 1.521(6) |
| Si2 | C8 | 1.871(4) | | | |

***Table 3:*** Bond angles for **48.1a**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C11 | W | P | 175.80(14) | C8 | Si2 | C4 | 111.48(19) |
| C11 | W | C12 | 91.57(19) | C8 | Si2 | C10 | 107.3(2) |
| C11 | W | C13 | 89.72(16) | C9 | Si2 | C4 | 106.97(18) |
| C11 | W | C14 | 90.74(18) | C9 | Si2 | C8 | 111.5(2) |
| C11 | W | C15 | 88.34(16) | C9 | Si2 | C10 | 106.0(2) |
| C12 | W | P | 92.63(13) | C10 | Si2 | C4 | 113.51(17) |
| C12 | W | C13 | 89.13(17) | C2 | C1 | P | 114.7(2) |
| C12 | W | C14 | 177.66(17) | O1 | C2 | C1 | 113.0(4) |
| C12 | W | C15 | 89.90(16) | O1 | C2 | C3 | 107.1(4) |
| C13 | W | P | 90.36(11) | O1S | C2 | C1 | 121.0(6) |
| C14 | W | P | 85.05(11) | O1S | C2 | C3 | 106.8(6) |
| C14 | W | C13 | 91.19(16) | C1 | C2 | C3 | 111.0(3) |
| C15 | W | P | 91.64(10) | F2 | C3 | C2 | 110.8(4) |
| C15 | W | C13 | 177.81(15) | F3 | C3 | F2 | 107.3(5) |
| C15 | W | C14 | 89.86(16) | F3 | C3 | C2 | 112.7(4) |
| F1 | P | W | 108.53(9) | F4 | C3 | F2 | 106.6(4) |
| F1 | P | C1 | 96.38(16) | F4 | C3 | F3 | 106.7(4) |
| F1 | P | C4 | 102.92(15) | F4 | C3 | C2 | 112.3(4) |
| C1 | P | W | 123.32(13) | P | C4 | Si1 | 115.5(2) |
| C4 | P | W | 117.44(12) | P | C4 | Si2 | 116.04(19) |
| C4 | P | C1 | 104.51(16) | Si1 | C4 | Si2 | 115.20(18) |
| C5 | Si1 | C4 | 108.81(17) | O2 | C11 | W | 178.3(4) |
| C5 | Si1 | C7 | 106.3(2) | O3 | C12 | W | 179.6(4) |
| C6 | Si1 | C4 | 112.41(17) | O4 | C13 | W | 177.7(4) |
| C6 | Si1 | C5 | 110.3(2) | O5 | C14 | W | 178.3(4) |
| C6 | Si1 | C7 | 109.14(19) | O6 | C15 | W | 178.7(3) |
| C7 | Si1 | C4 | 109.70(19) | | | | |

***Table 4:*** Torsion angles for **48.1a**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | 51.3(4) | O1 | C2 | C3 | F4 | -66.5(6) |
| W | P | C4 | Si1 | -133.33(14) | O1S | C2 | C3 | F2 | -49.7(8) |
| W | P | C4 | Si2 | 87.39(19) | O1S | C2 | C3 | F3 | 70.5(7) |
| P | C1 | C2 | O1 | -70.6(4) | O1S | C2 | C3 | F4 | -168.9(7) |
| P | C1 | C2 | O1S | 42.8(8) | C1 | P | C4 | Si1 | 86.0(2) |
| P | C1 | C2 | C3 | 169.1(3) | C1 | P | C4 | Si2 | -53.3(2) |
| F1 | P | C1 | C2 | -65.8(3) | C1 | C2 | C3 | F2 | 176.5(4) |
| F1 | P | C4 | Si1 | -14.2(2) | C1 | C2 | C3 | F3 | -63.3(5) |
| F1 | P | C4 | Si2 | -153.50(18) | C1 | C2 | C3 | F4 | 57.3(6) |
| O1 | C2 | C3 | F2 | 52.7(6) | C4 | P | C1 | C2 | -171.0(3) |
| O1 | C2 | C3 | F3 | 172.9(4) | | | | | |

# 12.36 Pentacarbonyl{[3,3,3-trifluoro-2-(trifluoromethyl)-2-hydroxypropyl][bis(trimethylsilyl)methyl]phosphane-κ*P*}tungsten(0) [48.1b]

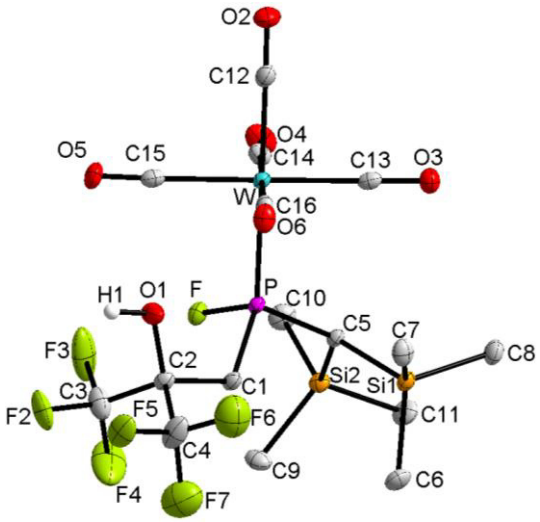


***Table 1:*** Crystal data and structure refinement for **48.1b**.

| | |
|---|---|
| Identification code | GSTR413, AKY-499A // GXray4033f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{16}H_{22}O_6F_7Si_2PW$ |
| Moiety formula | C16 H22 F7 O6 P Si2 W |
| Formula weight | 714.33 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.8833(5) |
| b/Å | 11.1477(7) |
| c/Å | 11.5906(6) |
| α/° | 78.723(3) |
| β/° | 87.936(3) |
| γ/° | 87.386(3) |
| Volume/Å$^3$ | 1250.57(12) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.897 |
| μ/mm$^{-1}$ | 4.859 |
| F(000) | 692.0 |
| Crystal size/mm$^3$ | 0.12 × 0.1 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5721; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.128 to 55.996° |
| Completeness to theta | 0.992 |
| Index ranges | -12 ≤ h ≤ 13, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15 |
| Reflections collected | 11761 |
| Independent reflections | 5964 [$R_{int}$ = 0.0226, $R_{sigma}$ = 0.0346] |
| Data/restraints/parameters | 5964/61/305 |
| Goodness-of-fit on F$^2$ | 1.056 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0280, $wR_2$ = 0.0664 |
| Final R indexes [all data] | $R_1$ = 0.0315, $wR_2$ = 0.0681 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.66/-1.85 |

***Table 2:*** Bond lengths for **48.1b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.4767(9) | Si2 | C11 | 1.871(4) |
| W | C12 | 2.030(4) | F2 | C3 | 1.334(5) |
| W | C13 | 2.045(4) | F3 | C3 | 1.323(6) |
| W | C14 | 2.051(4) | F4 | C3 | 1.310(6) |
| W | C15 | 2.068(4) | F5 | C4 | 1.332(5) |
| W | C16 | 2.031(4) | F6 | C4 | 1.311(6) |
| P | F1 | 1.600(2) | F7 | C4 | 1.339(6) |
| P | C1 | 1.844(4) | O1 | C2 | 1.391(5) |
| P | C5 | 1.812(4) | O2 | C12 | 1.137(5) |
| Si1 | C5 | 1.922(4) | O3 | C13 | 1.136(5) |
| Si1 | C6 | 1.870(4) | O4 | C14 | 1.131(5) |
| Si1 | C7 | 1.881(4) | O5 | C15 | 1.132(5) |
| Si1 | C8 | 1.864(4) | O6 | C16 | 1.140(5) |
| Si2 | C5 | 1.919(4) | C1 | C2 | 1.536(5) |
| Si2 | C9 | 1.869(4) | C2 | C3 | 1.536(6) |
| Si2 | C10 | 1.860(4) | C2 | C4 | 1.550(5) |

***Table 3:*** Bond angles for **48.1b**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C12 | W | P | 176.38(11) | C10 | Si2 | C9 | 109.5(2) |
| C12 | W | C13 | 88.70(15) | C10 | Si2 | C11 | 105.9(2) |
| C12 | W | C14 | 90.19(16) | C11 | Si2 | C5 | 110.16(18) |
| C12 | W | C15 | 90.23(15) | C2 | C1 | P | 121.3(3) |
| C12 | W | C16 | 89.74(15) | O1 | C2 | C1 | 110.2(3) |
| C13 | W | P | 91.36(10) | O1 | C2 | C3 | 109.3(3) |
| C13 | W | C14 | 89.51(15) | O1 | C2 | C4 | 107.9(3) |
| C13 | W | C15 | 177.64(14) | C1 | C2 | C4 | 107.7(3) |
| C14 | W | P | 86.19(11) | C3 | C2 | C1 | 111.9(3) |
| C14 | W | C15 | 92.60(16) | C3 | C2 | C4 | 109.8(3) |
| C15 | W | P | 89.84(11) | F2 | C3 | C2 | 111.7(3) |
| C16 | W | P | 93.88(10) | F3 | C3 | F2 | 106.0(4) |
| C16 | W | C13 | 90.04(14) | F3 | C3 | C2 | 110.0(4) |
| C16 | W | C14 | 179.54(16) | F4 | C3 | F2 | 108.4(4) |
| C16 | W | C15 | 87.85(15) | F4 | C3 | F3 | 106.9(4) |
| F1 | P | W | 109.63(9) | F4 | C3 | C2 | 113.5(4) |
| F1 | P | C1 | 98.49(15) | F5 | C4 | F7 | 107.3(4) |
| F1 | P | C5 | 103.01(14) | F5 | C4 | C2 | 112.4(4) |
| C1 | P | W | 125.75(12) | F6 | C4 | F5 | 106.9(4) |
| C5 | P | W | 115.50(12) | F6 | C4 | F7 | 107.7(4) |
| C5 | P | C1 | 101.20(16) | F6 | C4 | C2 | 111.0(4) |
| C6 | Si1 | C5 | 111.25(18) | F7 | C4 | C2 | 111.4(4) |
| C6 | Si1 | C7 | 106.92(19) | P | C5 | Si1 | 117.30(18) |
| C7 | Si1 | C5 | 114.27(17) | P | C5 | Si2 | 114.54(19) |
| C8 | Si1 | C5 | 106.99(17) | Si2 | C5 | Si1 | 115.90(18) |
| C8 | Si1 | C6 | 111.47(19) | O2 | C12 | W | 179.2(4) |
| C8 | Si1 | C7 | 105.89(19) | O3 | C13 | W | 179.0(3) |
| C9 | Si2 | C5 | 112.41(17) | O4 | C14 | W | 177.7(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C9 | Si2 | C11 | 109.22(19) | O5 | C15 | W | 176.8(3) |
| C10 | Si2 | C5 | 109.41(17) | O6 | C16 | W | 178.3(3) |

***Table 4:*** Torsion angles for **48.1b**.

| A | B | C | D | Angle/˚ | A | B | C | D | Angle/˚ |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | 50.4(4) | C1 | P | C5 | Si1 | -48.5(2) |
| W | P | C5 | Si1 | 90.51(19) | C1 | P | C5 | Si2 | 92.4(2) |
| W | P | C5 | Si2 | -128.61(14) | C1 | C2 | C3 | F2 | 173.3(3) |
| P | C1 | C2 | O1 | -37.4(4) | C1 | C2 | C3 | F3 | -69.4(4) |
| P | C1 | C2 | C3 | 84.4(4) | C1 | C2 | C3 | F4 | 50.4(5) |
| P | C1 | C2 | C4 | -154.8(3) | C1 | C2 | C4 | F5 | 174.1(4) |
| F1 | P | C1 | C2 | -71.3(3) | C1 | C2 | C4 | F6 | 54.5(5) |
| F1 | P | C5 | Si1 | -150.01(18) | C1 | C2 | C4 | F7 | -65.4(5) |
| F1 | P | C5 | Si2 | -9.1(2) | C3 | C2 | C4 | F5 | -63.7(5) |
| O1 | C2 | C3 | F2 | -64.4(5) | C3 | C2 | C4 | F6 | 176.7(4) |
| O1 | C2 | C3 | F3 | 52.9(4) | C3 | C2 | C4 | F7 | 56.7(5) |
| O1 | C2 | C3 | F4 | 172.7(4) | C4 | C2 | C3 | F2 | 53.7(5) |
| O1 | C2 | C4 | F5 | 55.2(5) | C4 | C2 | C3 | F3 | 171.0(4) |
| O1 | C2 | C4 | F6 | -64.4(5) | C4 | C2 | C3 | F4 | -69.2(5) |
| O1 | C2 | C4 | F7 | 175.7(4) | C5 | P | C1 | C2 | -176.5(3) |

## 12.37 Pentacarbonyl{fluoro[3,3,3-trifluoro-2-(trifluoromethyl)-2-hydroxypropyl](1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)phosphane-κ*P*}tungsten(0) [48.2b]

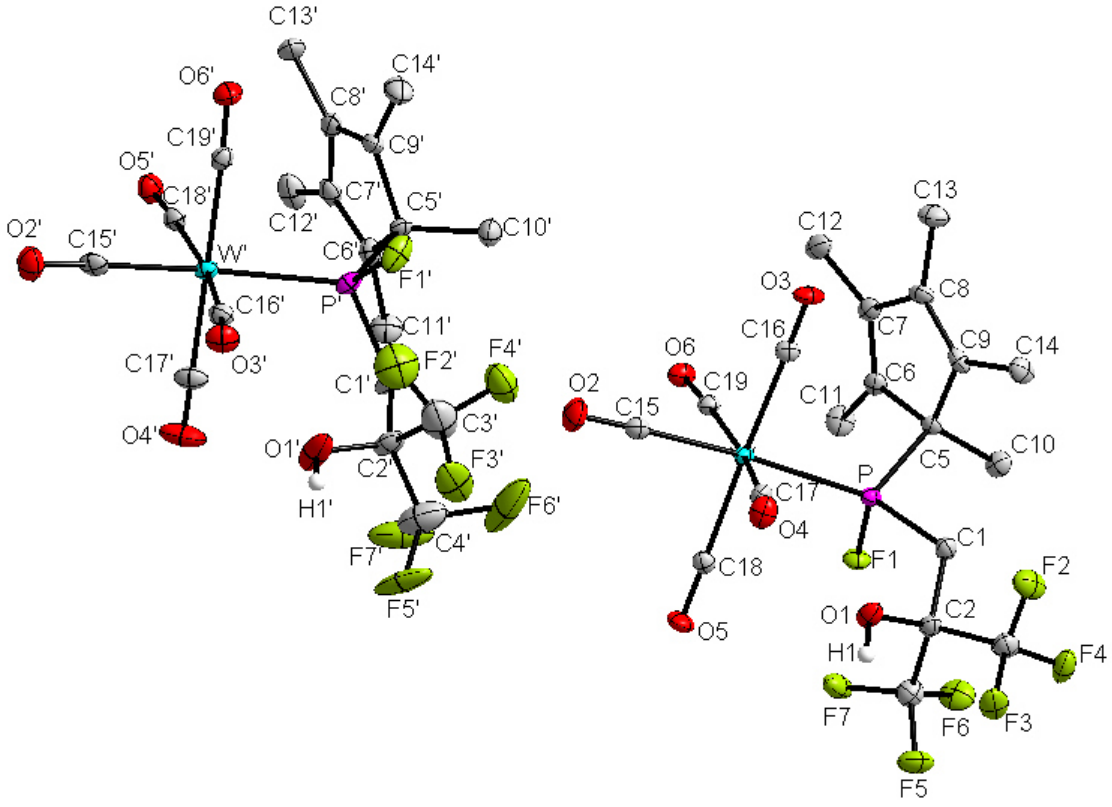

***Table 1:*** Crystal data and structure refinement for **48.2b**.

| | |
|---|---|
| Identification code | GSTR392, AKY-476 // GXray3908f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{19}H_{18}O_6F_7PW$ |
| Moiety formula | C19 H18 F7 O6 P W |
| Formula weight | 690.15 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 9.2003(6) |
| b/Å | 40.630(3) |
| c/Å | 12.4604(8) |
| α/° | 90 |
| β/° | 103.517(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 4528.8(5) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 2.024 |
| μ/mm$^{-1}$ | 5.263 |
| F(000) | 2656.0 |
| Crystal size/mm$^3$ | 0.12 × 0.11 × 0.05 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.5182; 0.7460 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.004 to 55.996° |
| Completeness to theta | 0.992 |
| Index ranges | -12 ≤ h ≤ 12, -53 ≤ k ≤ 53, -15 ≤ l ≤ 16 |
| Reflections collected | 83151 |
| Independent reflections | 10828 [$R_{int}$ = 0.0401, $R_{sigma}$ = 0.0293] |
| Data/restraints/parameters | 10828/37/625 |
| Goodness-of-fit on F$^2$ | 1.068 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0452, $wR_2$ = 0.1007 |
| Final R indexes [all data] | $R_1$ = 0.0495, $wR_2$ = 0.1027 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.42/-5.62 |

***Table 2:*** Bond lengths for **48.2b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5014(15) | W' | P' | 2.4793(16) |
| W | C15 | 1.998(6) | W' | C15' | 2.007(6) |
| W | C16 | 2.063(6) | W' | C16' | 2.051(6) |
| W | C17 | 2.051(6) | W' | C17' | 2.068(7) |
| W | C18 | 2.039(6) | W' | C18' | 2.059(6) |
| W | C19 | 2.052(6) | W' | C19' | 2.027(6) |
| P | F1 | 1.600(4) | P' | F1' | 1.598(4) |
| P | C1 | 1.849(6) | P' | C1' | 1.840(7) |
| P | C5 | 1.872(6) | P' | C5' | 1.862(6) |
| F2 | C3 | 1.335(8) | F2' | C3' | 1.389(12) |
| F3 | C3 | 1.338(7) | F3' | C3' | 1.324(10) |
| F4 | C3 | 1.328(8) | F4' | C3' | 1.266(10) |
| F5 | C4 | 1.337(8) | F5' | C4' | 1.359(10) |
| F6 | C4 | 1.340(8) | F6' | C4' | 1.477(13) |
| F7 | C4 | 1.332(7) | F7' | C4' | 1.294(12) |

| | | | | | |
|---|---|---|---|---|---|
| O1 | C2 | 1.394(7) | O1' | C2' | 1.356(8) |
| O2 | C15 | 1.153(8) | O2' | C15' | 1.149(8) |
| O3 | C16 | 1.128(7) | O3' | C16' | 1.139(8) |
| O4 | C17 | 1.140(8) | O4' | C17' | 1.121(8) |
| O5 | C18 | 1.134(7) | O5' | C18' | 1.139(8) |
| O6 | C19 | 1.140(7) | O6' | C19' | 1.146(8) |
| C1 | C2 | 1.543(8) | C1' | C2' | 1.535(9) |
| C2 | C3 | 1.557(8) | C2' | C3' | 1.591(12) |
| C2 | C4 | 1.538(9) | C2' | C4' | 1.517(11) |
| C5 | C6 | 1.528(8) | C5' | C6' | 1.506(8) |
| C5 | C9 | 1.526(8) | C5' | C9' | 1.526(8) |
| C5 | C10 | 1.537(8) | C5' | C10' | 1.539(8) |
| C6 | C7 | 1.340(8) | C6' | C7' | 1.347(9) |
| C6 | C11 | 1.502(8) | C6' | C11' | 1.500(9) |
| C7 | C8 | 1.474(8) | C7' | C8' | 1.469(9) |
| C7 | C12 | 1.500(9) | C7' | C12' | 1.512(9) |
| C8 | C9 | 1.343(9) | C8' | C9' | 1.346(9) |
| C8 | C13 | 1.489(8) | C8' | C13' | 1.497(9) |
| C9 | C14 | 1.504(8) | C9' | C14' | 1.496(9) |

***Table 3:*** Bond angles for **48.2b**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| C15 | W | P | 173.57(17) | C15' | W' | P' | 172.13(18) |
| C15 | W | C16 | 91.2(2) | C15' | W' | C16' | 83.7(2) |
| C15 | W | C17 | 85.0(2) | C15' | W' | C17' | 91.8(3) |
| C15 | W | C18 | 89.1(2) | C15' | W' | C18' | 87.4(2) |
| C15 | W | C19 | 84.4(2) | C15' | W' | C19' | 90.2(2) |
| C16 | W | P | 94.17(17) | C16' | W' | P' | 88.39(18) |
| C17 | W | P | 99.01(17) | C16' | W' | C17' | 93.7(3) |
| C17 | W | C16 | 85.2(2) | C16' | W' | C18' | 170.9(2) |
| C17 | W | C19 | 169.0(2) | C17' | W' | P' | 89.0(2) |
| C18 | W | P | 85.85(17) | C18' | W' | P' | 100.46(16) |
| C18 | W | C16 | 175.4(2) | C18' | W' | C17' | 88.7(3) |
| C18 | W | C17 | 90.3(2) | C19' | W' | P' | 89.99(17) |
| C18 | W | C19 | 92.5(2) | C19' | W' | C16' | 93.3(2) |
| C19 | W | P | 91.79(16) | C19' | W' | C17' | 172.8(2) |
| C19 | W | C16 | 92.2(2) | C19' | W' | C18' | 84.5(2) |
| F1 | P | W | 110.67(15) | F1' | P' | W' | 111.65(16) |
| F1 | P | C1 | 99.8(2) | F1' | P' | C1' | 100.5(3) |
| F1 | P | C5 | 98.5(2) | F1' | P' | C5' | 99.0(3) |
| C1 | P | W | 122.1(2) | C1' | P' | W' | 119.5(2) |
| C1 | P | C5 | 101.0(3) | C1' | P' | C5' | 100.8(3) |
| C5 | P | W | 120.52(19) | C5' | P' | W' | 121.70(19) |
| C2 | C1 | P | 123.1(4) | C2' | C1' | P' | 122.7(5) |
| O1 | C2 | C1 | 109.1(5) | O1' | C2' | C1' | 110.6(6) |
| O1 | C2 | C3 | 108.8(5) | O1' | C2' | C3' | 104.0(6) |
| O1 | C2 | C4 | 109.5(5) | O1' | C2' | C4' | 113.2(7) |
| C1 | C2 | C3 | 106.7(5) | C1' | C2' | C3' | 112.1(6) |
| C4 | C2 | C1 | 112.8(5) | C4' | C2' | C1' | 108.7(6) |
| C4 | C2 | C3 | 109.9(5) | C4' | C2' | C3' | 108.2(7) |
| F2 | C3 | F3 | 106.8(5) | F2' | C3' | C2' | 108.8(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| F2 | C3 | C2 | 110.5(5) | F3' | C3' | F2' | 109.5(8) |
| F3 | C3 | C2 | 111.0(5) | F3' | C3' | C2' | 109.4(8) |
| F4 | C3 | F2 | 108.3(5) | F4' | C3' | F2' | 104.8(8) |
| F4 | C3 | F3 | 108.0(5) | F4' | C3' | F3' | 111.0(8) |
| F4 | C3 | C2 | 112.1(5) | F4' | C3' | C2' | 113.3(8) |
| F5 | C4 | F6 | 107.6(5) | F5' | C4' | F6' | 111.1(8) |
| F5 | C4 | C2 | 111.2(5) | F5' | C4' | C2' | 112.5(7) |
| F6 | C4 | C2 | 112.4(5) | F6' | C4' | C2' | 104.4(8) |
| F7 | C4 | F5 | 107.2(5) | F7' | C4' | F5' | 105.8(9) |
| F7 | C4 | F6 | 107.6(5) | F7' | C4' | F6' | 108.3(8) |
| F7 | C4 | C2 | 110.6(5) | F7' | C4' | C2' | 114.8(8) |
| C6 | C5 | P | 105.7(4) | C6' | C5' | P' | 109.0(4) |
| C6 | C5 | C10 | 111.2(5) | C6' | C5' | C9' | 103.3(5) |
| C9 | C5 | P | 109.7(4) | C6' | C5' | C10' | 113.8(5) |
| C9 | C5 | C6 | 102.8(5) | C9' | C5' | P' | 105.9(4) |
| C9 | C5 | C10 | 113.1(5) | C9' | C5' | C10' | 110.8(5) |
| C10 | C5 | P | 113.5(4) | C10' | C5' | P' | 113.3(4) |
| C7 | C6 | C5 | 108.6(5) | C7' | C6' | C5' | 108.5(5) |
| C7 | C6 | C11 | 127.9(6) | C7' | C6' | C11' | 126.0(6) |
| C11 | C6 | C5 | 123.3(5) | C11' | C6' | C5' | 125.4(5) |
| C6 | C7 | C8 | 109.9(5) | C6' | C7' | C8' | 110.3(6) |
| C6 | C7 | C12 | 127.7(6) | C6' | C7' | C12' | 125.7(6) |
| C8 | C7 | C12 | 122.4(6) | C8' | C7' | C12' | 124.0(6) |
| C7 | C8 | C13 | 123.0(6) | C7' | C8' | C13' | 123.2(6) |
| C9 | C8 | C7 | 109.9(5) | C9' | C8' | C7' | 109.1(5) |
| C9 | C8 | C13 | 127.0(6) | C9' | C8' | C13' | 127.7(6) |
| C8 | C9 | C5 | 108.7(5) | C8' | C9' | C5' | 108.7(5) |
| C8 | C9 | C14 | 127.3(6) | C8' | C9' | C14' | 127.6(6) |
| C14 | C9 | C5 | 123.9(5) | C14' | C9' | C5' | 123.3(6) |
| O2 | C15 | W | 177.7(5) | O2' | C15' | W' | 176.7(5) |
| O3 | C16 | W | 175.5(5) | O3' | C16' | W' | 173.9(6) |
| O4 | C17 | W | 171.9(5) | O4' | C17' | W' | 177.3(6) |
| O5 | C18 | W | 177.9(5) | O5' | C18' | W' | 173.0(5) |
| O6 | C19 | W | 172.3(5) | O6' | C19' | W' | 174.9(5) |

***Table 4:*** Torsion angles for **48.2b**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | 56.7(6) | W' | P' | C1' | C2' | -63.9(7) |
| W | P | C5 | C6 | -46.4(4) | W' | P' | C5' | C6' | -62.9(4) |
| W | P | C5 | C9 | 63.8(4) | W' | P' | C5' | C9' | 47.7(4) |
| W | P | C5 | C10 | -168.6(3) | W' | P' | C5' | C10' | 169.2(3) |
| P | C1 | C2 | O1 | -57.8(7) | P' | C1' | C2' | O1' | 50.3(9) |
| P | C1 | C2 | C3 | -175.1(4) | P' | C1' | C2' | C3' | -65.3(8) |
| P | C1 | C2 | C4 | 64.1(7) | P' | C1' | C2' | C4' | 175.1(7) |
| P | C5 | C6 | C7 | 111.9(5) | P' | C5' | C6' | C7' | 111.2(5) |
| P | C5 | C6 | C11 | -72.7(6) | P' | C5' | C6' | C11' | -72.6(7) |
| P | C5 | C9 | C8 | -110.0(5) | P' | C5' | C9' | C8' | -112.8(5) |
| P | C5 | C9 | C14 | 73.9(6) | P' | C5' | C9' | C14' | 73.9(6) |
| F1 | P | C1 | C2 | -65.4(5) | F1' | P' | C1' | C2' | 58.5(7) |
| F1 | P | C5 | C6 | 73.7(4) | F1' | P' | C5' | C6' | 174.6(4) |
| F1 | P | C5 | C9 | -176.1(4) | F1' | P' | C5' | C9' | -74.8(4) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| F1 | P | C5 | C10 | -48.4(4) | F1' | P' | C5' | C10' | 46.8(5) |
| O1 | C2 | C3 | F2 | -66.8(6) | O1' | C2' | C3' | F2' | -41.0(8) |
| O1 | C2 | C3 | F3 | 51.4(7) | O1' | C2' | C3' | F3' | 78.5(8) |
| O1 | C2 | C3 | F4 | 172.3(5) | O1' | C2' | C3' | F4' | -157.2(8) |
| O1 | C2 | C4 | F5 | -73.3(6) | O1' | C2' | C4' | F5' | -39.3(11) |
| O1 | C2 | C4 | F6 | 166.0(5) | O1' | C2' | C4' | F6' | -159.8(6) |
| O1 | C2 | C4 | F7 | 45.7(7) | O1' | C2' | C4' | F7' | 81.8(10) |
| C1 | P | C5 | C6 | 175.5(4) | C1' | P' | C5' | C6' | 72.0(5) |
| C1 | P | C5 | C9 | -74.3(4) | C1' | P' | C5' | C9' | -177.4(4) |
| C1 | P | C5 | C10 | 53.4(5) | C1' | P' | C5' | C10' | -55.8(5) |
| C1 | C2 | C3 | F2 | 50.7(7) | C1' | C2' | C3' | F2' | 78.5(8) |
| C1 | C2 | C3 | F3 | 168.9(5) | C1' | C2' | C3' | F3' | -162.0(7) |
| C1 | C2 | C3 | F4 | -70.2(6) | C1' | C2' | C3' | F4' | -37.7(10) |
| C1 | C2 | C4 | F5 | 165.1(5) | C1' | C2' | C4' | F5' | -162.6(8) |
| C1 | C2 | C4 | F6 | 44.4(7) | C1' | C2' | C4' | F6' | 76.9(8) |
| C1 | C2 | C4 | F7 | -75.9(6) | C1' | C2' | C4' | F7' | -41.5(11) |
| C3 | C2 | C4 | F5 | 46.2(7) | C3' | C2' | C4' | F5' | 75.4(10) |
| C3 | C2 | C4 | F6 | -74.5(7) | C3' | C2' | C4' | F6' | -45.1(8) |
| C3 | C2 | C4 | F7 | 165.2(5) | C3' | C2' | C4' | F7' | -163.5(8) |
| C4 | C2 | C3 | F2 | 173.3(5) | C4' | C2' | C3' | F2' | -161.7(7) |
| C4 | C2 | C3 | F3 | -68.5(7) | C4' | C2' | C3' | F3' | -42.1(10) |
| C4 | C2 | C3 | F4 | 52.4(7) | C4' | C2' | C3' | F4' | 82.2(9) |
| C5 | P | C1 | C2 | -166.1(5) | C5' | P' | C1' | C2' | 159.9(6) |
| C5 | C6 | C7 | C8 | 3.0(7) | C5' | C6' | C7' | C8' | 0.0(7) |
| C5 | C6 | C7 | C12 | -177.3(6) | C5' | C6' | C7' | C12' | 178.2(6) |
| C6 | C5 | C9 | C8 | 2.1(6) | C6' | C5' | C9' | C8' | 1.8(6) |
| C6 | C5 | C9 | C14 | -174.1(5) | C6' | C5' | C9' | C14' | -171.5(6) |
| C6 | C7 | C8 | C9 | -1.6(7) | C6' | C7' | C8' | C9' | 1.2(7) |
| C6 | C7 | C8 | C13 | 174.2(6) | C6' | C7' | C8' | C13' | -179.7(6) |
| C7 | C8 | C9 | C5 | -0.5(7) | C7' | C8' | C9' | C5' | -1.8(7) |
| C7 | C8 | C9 | C14 | 175.5(6) | C7' | C8' | C9' | C14' | 171.1(6) |
| C9 | C5 | C6 | C7 | -3.1(6) | C9' | C5' | C6' | C7' | -1.1(6) |
| C9 | C5 | C6 | C11 | 172.2(5) | C9' | C5' | C6' | C11' | 175.1(6) |
| C10 | C5 | C6 | C7 | -124.5(5) | C10' | C5' | C6' | C7' | -121.3(6) |
| C10 | C5 | C6 | C11 | 50.9(7) | C10' | C5' | C6' | C11' | 54.9(8) |
| C10 | C5 | C9 | C8 | 122.2(5) | C10' | C5' | C9' | C8' | 124.1(6) |
| C10 | C5 | C9 | C14 | -54.0(7) | C10' | C5' | C9' | C14' | -49.2(8) |
| C11 | C6 | C7 | C8 | -172.1(6) | C11' | C6' | C7' | C8' | -176.1(6) |
| C11 | C6 | C7 | C12 | 7.7(10) | C11' | C6' | C7' | C12' | 2.0(10) |
| C12 | C7 | C8 | C9 | 178.6(5) | C12' | C7' | C8' | C9' | -177.0(6) |
| C12 | C7 | C8 | C13 | -5.6(9) | C12' | C7' | C8' | C13' | 2.1(10) |
| C13 | C8 | C9 | C5 | -176.1(6) | C13' | C8' | C9' | C5' | 179.1(6) |
| C13 | C8 | C9 | C14 | -0.1(10) | C13' | C8' | C9' | C14' | -8.0(11) |

## 12.38 Pentacarbonyl{6-methyl-4-[bis(trimethylsilyl)methyl]-2-phenyl-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [54.1]

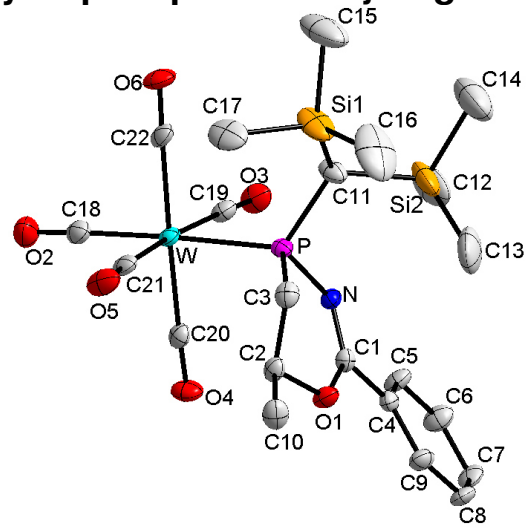


***Table 1:*** Crystal data and structure refinement for **54.1**.

| | |
|---|---|
| Identification code | GSTR345,AKY-343 // GXray3334 |
| Crystal Habitus | colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{22}H_{30}NO_6PSi_2W$ |
| Moiety formula | C22 H30 N O6 P Si2 W |
| Formula weight | 675.47 |
| Temperature/K | 123(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 9.1834(2) |
| b/Å | 22.5886(6) |
| c/Å | 15.4583(4) |
| α/° | 90.00 |
| β/° | 117.6820(10) |
| γ/° | 90.00 |
| Volume/Å$^3$ | 2839.64(12) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.580 |
| μ/mm$^{-1}$ | 4.242 |
| F(000) | 1336.0 |
| Crystal size/mm$^3$ | 0.42 × 0.36 × 0.12 |
| Absorption correction | Multi-Scan |
| Tmin; Tmax | 0.2688; 0.6300 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.84 to 52° |
| Completeness to theta | 0.997 |
| Index ranges | -11 ≤ h ≤ 11, -25 ≤ k ≤ 27, -12 ≤ l ≤ 19 |
| Reflections collected | 14906 |
| Independent reflections | 5564 [$R_{int}$ = 0.0584] |
| Data/restraints/parameters | 5564/17/305 |
| Goodness-of-fit on F$^2$ | 1.037 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0295, $wR_2$ = 0.0743 |
| Final R indexes [all data] | $R_1$ = 0.0354, $wR_2$ = 0.0762 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.81/-1.89 |

***Table 2:*** Bond lengths for **54.1**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | C18 | 2.014(4) | O1 | C1 | 1.357(4) |
| W | C20 | 2.039(4) | O1 | C2 | 1.458(4) |
| W | C21 | 2.041(4) | O2 | C18 | 1.147(5) |
| W | C19 | 2.052(4) | O3 | C19 | 1.137(5) |
| W | C22 | 2.052(4) | O4 | C20 | 1.135(4) |
| W | P | 2.4989(10) | O5 | C21 | 1.134(5) |
| P | N | 1.703(3) | O6 | C22 | 1.139(5) |
| P | C11 | 1.821(4) | N | C1 | 1.271(4) |
| P | C3 | 1.828(4) | C1 | C4 | 1.481(5) |
| Si1 | C13 | 1.845(6) | C2 | C3 | 1.517(5) |
| Si1 | C12 | 1.858(6) | C2 | C10 | 1.519(5) |
| Si1 | C14 | 1.882(6) | C4 | C9 | 1.394(5) |
| Si1 | C11 | 1.906(4) | C4 | C5 | 1.402(5) |
| Si2 | C17 | 1.871(5) | C5 | C6 | 1.390(5) |
| Si2 | C16 | 1.873(7) | C6 | C7 | 1.387(5) |
| Si2 | C15 | 1.882(6) | C7 | C8 | 1.364(6) |
| Si2 | C11 | 1.915(4) | C8 | C9 | 1.387(5) |

***Table 3:*** Bond angles for **54.1**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C18 | W | C20 | 90.12(15) | C16 | Si2 | C15 | 112.2(3) |
| C18 | W | C21 | 91.56(16) | C17 | Si2 | C11 | 114.9(2) |
| C20 | W | C21 | 90.94(15) | C16 | Si2 | C11 | 111.5(3) |
| C18 | W | C19 | 94.59(16) | C15 | Si2 | C11 | 106.8(2) |
| C20 | W | C19 | 87.65(15) | C1 | O1 | C2 | 118.9(3) |
| C21 | W | C19 | 173.69(15) | C1 | N | P | 123.7(3) |
| C18 | W | C22 | 90.09(16) | N | C1 | O1 | 128.6(3) |
| C20 | W | C22 | 176.94(14) | N | C1 | C4 | 120.4(3) |
| C21 | W | C22 | 92.10(15) | O1 | C1 | C4 | 111.0(3) |
| C19 | W | C22 | 89.30(15) | O1 | C2 | C3 | 111.6(3) |
| C18 | W | P | 177.45(11) | O1 | C2 | C10 | 105.7(3) |
| C20 | W | P | 87.35(11) | C3 | C2 | C10 | 113.5(3) |
| C21 | W | P | 88.15(12) | C2 | C3 | P | 108.0(2) |
| C19 | W | P | 85.64(11) | C9 | C4 | C5 | 118.9(4) |
| C22 | W | P | 92.45(11) | C9 | C4 | C1 | 121.7(3) |
| N | P | C11 | 104.83(17) | C5 | C4 | C1 | 119.4(3) |
| N | P | C3 | 99.80(16) | C6 | C5 | C4 | 120.2(3) |
| C11 | P | C3 | 105.63(18) | C7 | C6 | C5 | 119.9(4) |
| N | P | W | 107.06(11) | C8 | C7 | C6 | 120.1(4) |
| C11 | P | W | 118.40(15) | C7 | C8 | C9 | 121.0(3) |
| C3 | P | W | 118.70(13) | C8 | C9 | C4 | 119.9(4) |
| C13 | Si1 | C12 | 111.5(3) | P | C11 | Si1 | 115.2(2) |
| C13 | Si1 | C14 | 106.8(3) | P | C11 | Si2 | 115.0(2) |
| C12 | Si1 | C14 | 105.7(3) | Si1 | C11 | Si2 | 115.7(2) |
| C13 | Si1 | C11 | 112.8(2) | O2 | C18 | W | 177.3(3) |
| C12 | Si1 | C11 | 109.3(2) | O3 | C19 | W | 177.6(3) |
| C14 | Si1 | C11 | 110.5(2) | O4 | C20 | W | 177.9(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C17 | Si2 | C16 | 106.3(3) | O5 | C21 | W | 176.6(4) |
| C17 | Si2 | C15 | 105.2(3) | O6 | C22 | W | 178.1(3) |

***Table 4:*** Torsion angles for **54.1**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| C18 | W | P | N | 44(2) | C3 | P | C11 | Si1 | 91.7(2) |
| C20 | W | P | N | 36.85(14) | W | P | C11 | Si1 | -132.41(18) |
| C21 | W | P | N | 127.88(15) | N | P | C11 | Si2 | -151.6(2) |
| C19 | W | P | N | -50.99(15) | C3 | P | C11 | Si2 | -46.7(3) |
| C22 | W | P | N | -140.10(15) | W | P | C11 | Si2 | 89.2(2) |
| C18 | W | P | C11 | 162(2) | C13 | Si1 | C11 | P | -55.3(3) |
| C20 | W | P | C11 | 154.90(17) | C12 | Si1 | C11 | P | 69.4(3) |
| C21 | W | P | C11 | -114.07(18) | C14 | Si1 | C11 | P | -174.7(3) |
| C19 | W | P | C11 | 67.06(18) | C13 | Si1 | C11 | Si2 | 82.8(3) |
| C22 | W | P | C11 | -22.04(18) | C12 | Si1 | C11 | Si2 | -152.5(3) |
| C18 | W | P | C3 | -67(2) | C14 | Si1 | C11 | Si2 | -36.6(4) |
| C20 | W | P | C3 | -74.92(17) | C17 | Si2 | C11 | P | -28.2(3) |
| C21 | W | P | C3 | 16.10(18) | C16 | Si2 | C11 | P | 92.8(3) |
| C19 | W | P | C3 | -162.76(18) | C15 | Si2 | C11 | P | -144.3(3) |
| C22 | W | P | C3 | 108.13(17) | C17 | Si2 | C11 | Si1 | -166.4(2) |
| C11 | P | N | C1 | 127.5(3) | C16 | Si2 | C11 | Si1 | -45.4(3) |
| C3 | P | N | C1 | 18.3(3) | C15 | Si2 | C11 | Si1 | 77.5(3) |
| W | P | N | C1 | -106.0(3) | C20 | W | C18 | O2 | 47(8) |
| P | N | C1 | O1 | 0.4(6) | C21 | W | C18 | O2 | -44(8) |
| P | N | C1 | C4 | -178.9(3) | C19 | W | C18 | O2 | 135(8) |
| C2 | O1 | C1 | N | 9.7(5) | C22 | W | C18 | O2 | -136(8) |
| C2 | O1 | C1 | C4 | -170.9(3) | P | W | C18 | O2 | 40(10) |
| C1 | O1 | C2 | C3 | -44.1(4) | C18 | W | C19 | O3 | -150(9) |
| C1 | O1 | C2 | C10 | -167.9(3) | C20 | W | C19 | O3 | -60(9) |
| O1 | C2 | C3 | P | 62.0(3) | C21 | W | C19 | O3 | 17(10) |
| C10 | C2 | C3 | P | -178.7(3) | C22 | W | C19 | O3 | 120(9) |
| N | P | C3 | C2 | -46.7(3) | P | W | C19 | O3 | 27(9) |
| C11 | P | C3 | C2 | -155.3(3) | C18 | W | C20 | O4 | 143(9) |
| W | P | C3 | C2 | 69.0(3) | C21 | W | C20 | O4 | -125(9) |
| N | C1 | C4 | C9 | 161.2(4) | C19 | W | C20 | O4 | 48(9) |
| O1 | C1 | C4 | C9 | -18.3(5) | C22 | W | C20 | O4 | 49(11) |
| N | C1 | C4 | C5 | -19.7(5) | P | W | C20 | O4 | -37(9) |
| O1 | C1 | C4 | C5 | 160.9(3) | C18 | W | C21 | O5 | 160(7) |
| C9 | C4 | C5 | C6 | -0.6(6) | C20 | W | C21 | O5 | 70(7) |
| C1 | C4 | C5 | C6 | -179.7(4) | C19 | W | C21 | O5 | -7(7) |
| C4 | C5 | C6 | C7 | 0.1(6) | C22 | W | C21 | O5 | -110(7) |
| C5 | C6 | C7 | C8 | -0.5(6) | P | W | C21 | O5 | -17(7) |
| C6 | C7 | C8 | C9 | 1.4(6) | C18 | W | C22 | O6 | -107(11) |
| C7 | C8 | C9 | C4 | -1.9(6) | C20 | W | C22 | O6 | -13(13) |
| C5 | C4 | C9 | C8 | 1.4(6) | C21 | W | C22 | O6 | 161(11) |
| C1 | C4 | C9 | C8 | -179.4(3) | C19 | W | C22 | O6 | -13(11) |
| N | P | C11 | Si1 | -13.2(3) | P | W | C22 | O6 | 73(11) |

## 12.39 Pentacarbonyl{2-methyl-4-[bis(trimethylsilyl)methyl]-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [55.1a]

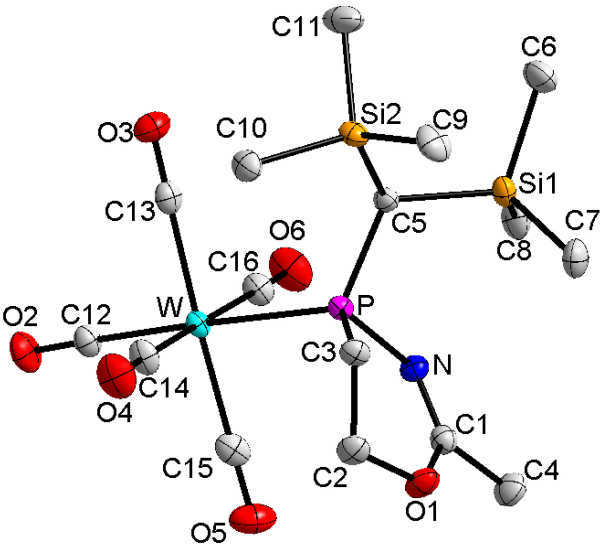


***Table 1:*** Crystal data and structure refinement for **55.1a**.

| | |
|---|---|
| Identification code | GSTR510, AKY-569 // GXray4796 |
| Crystal Habitus | clear colourless plank |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{16}H_{26}NO_6PSi_2W$ |
| Moiety formula | C16 H26 N O6 P Si2 W |
| Formula weight | 599.38 |
| Temperature/K | 123 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.52110(10) |
| b/Å | 10.1536(2) |
| c/Å | 24.1643(5) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2336.05(7) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.704 |
| μ/mm$^{-1}$ | 5.145 |
| F(000) | 1176.0 |
| Crystal size/mm$^3$ | 0.14 × 0.07 × 0.06 |
| Absorption correction | multi-scan |
| Tmin; Tmax | 0.6259; 0.7323 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.866 to 55.996° |
| Completeness to theta | 0.998 |
| Index ranges | -11 ≤ h ≤ 12, -13 ≤ k ≤ 9, -29 ≤ l ≤ 31 |
| Reflections collected | 13893 |
| Independent reflections | 5546 [$R_{int}$ = 0.0338, $R_{sigma}$ = 0.0386] |
| Data/restraints/parameters | 5546/0/252 |
| Goodness-of-fit on F$^2$ | 1.030 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0225, $wR_2$ = 0.0456 |
| Final R indexes [all data] | $R_1$ = 0.0241, $wR_2$ = 0.0462 |

| | |
|---|---|
| Largest diff. peak/hole / e Å$^{-3}$ | 0.85/-0.56 |
| Flack parameter | 0.469(7) |

***Table 2:*** Bond lengths for **55.1a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5089(12) | Si2 | C9 | 1.859(6) |
| W | C12 | 2.018(5) | Si2 | C10 | 1.887(5) |
| W | C13 | 2.042(5) | Si2 | C11 | 1.861(6) |
| W | C14 | 2.030(5) | O1 | C1 | 1.355(6) |
| W | C15 | 2.056(6) | O1 | C2 | 1.449(6) |
| W | C16 | 2.066(5) | O2 | C12 | 1.139(6) |
| P | N | 1.700(4) | O3 | C13 | 1.137(6) |
| P | C3 | 1.835(5) | O4 | C14 | 1.137(6) |
| P | C5 | 1.820(5) | O5 | C15 | 1.131(6) |
| Si1 | C5 | 1.920(5) | O6 | C16 | 1.121(6) |
| Si1 | C6 | 1.872(5) | N | C1 | 1.268(6) |
| Si1 | C7 | 1.866(5) | C1 | C4 | 1.497(7) |
| Si1 | C8 | 1.868(5) | C2 | C3 | 1.520(7) |
| Si2 | C5 | 1.907(5) | | | |

***Table 3:*** Bond angles for **55.1a**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C12 | W | P | 176.44(15) | C7 | Si1 | C8 | 111.7(3) |
| C12 | W | C13 | 90.2(2) | C8 | Si1 | C5 | 110.4(2) |
| C12 | W | C14 | 92.8(2) | C8 | Si1 | C6 | 105.3(3) |
| C12 | W | C15 | 90.6(2) | C9 | Si2 | C5 | 112.2(3) |
| C12 | W | C16 | 89.7(2) | C9 | Si2 | C10 | 106.7(3) |
| C13 | W | P | 92.27(13) | C9 | Si2 | C11 | 109.9(3) |
| C13 | W | C15 | 177.2(2) | C10 | Si2 | C5 | 113.6(2) |
| C13 | W | C16 | 88.6(2) | C11 | Si2 | C5 | 107.9(2) |
| C14 | W | P | 89.69(15) | C11 | Si2 | C10 | 106.3(3) |
| C14 | W | C13 | 91.3(2) | C1 | O1 | C2 | 119.0(4) |
| C14 | W | C15 | 91.3(2) | C1 | N | P | 124.5(3) |
| C14 | W | C16 | 177.5(2) | O1 | C1 | C4 | 109.6(4) |
| C15 | W | P | 86.83(14) | N | C1 | O1 | 128.3(4) |
| C15 | W | C16 | 88.7(2) | N | C1 | C4 | 122.2(5) |
| C16 | W | P | 87.76(15) | O1 | C2 | C3 | 112.8(4) |
| N | P | W | 108.69(14) | C2 | C3 | P | 107.3(4) |
| N | P | C3 | 98.8(2) | P | C5 | Si1 | 115.2(3) |
| N | P | C5 | 105.3(2) | P | C5 | Si2 | 114.7(2) |
| C3 | P | W | 119.12(17) | Si2 | C5 | Si1 | 115.9(3) |
| C5 | P | W | 116.73(16) | O2 | C12 | W | 178.7(5) |
| C5 | P | C3 | 105.9(2) | O3 | C13 | W | 179.5(5) |
| C6 | Si1 | C5 | 109.5(2) | O4 | C14 | W | 177.8(4) |
| C7 | Si1 | C5 | 112.0(2) | O5 | C15 | W | 179.0(5) |
| C7 | Si1 | C6 | 107.8(3) | O6 | C16 | W | 179.1(5) |

***Table 4:*** Torsion angles for **55.1a**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| W | P | N | C1 | -104.8(4) | N | P | C5 | Si2 | -149.3(2) |
| W | P | C3 | C2 | 69.1(4) | C1 | O1 | C2 | C3 | -40.8(6) |
| W | P | C5 | Si1 | -131.6(2) | C2 | O1 | C1 | N | 5.3(8) |
| W | P | C5 | Si2 | 90.0(3) | C2 | O1 | C1 | C4 | -174.7(4) |
| P | N | C1 | O1 | 1.7(7) | C3 | P | N | C1 | 20.2(5) |
| P | N | C1 | C4 | -178.4(4) | C3 | P | C5 | Si1 | 93.2(3) |
| O1 | C2 | C3 | P | 61.8(5) | C3 | P | C5 | Si2 | -45.2(3) |
| N | P | C3 | C2 | -48.2(4) | C5 | P | N | C1 | 129.4(4) |
| N | P | C5 | Si1 | -10.9(3) | C5 | P | C3 | C2 | -157.0(4) |

## 12.40 Pentacarbonyl{4-[bis(trimethylsilyl)methyl]-2-phenyl-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [55.1b]

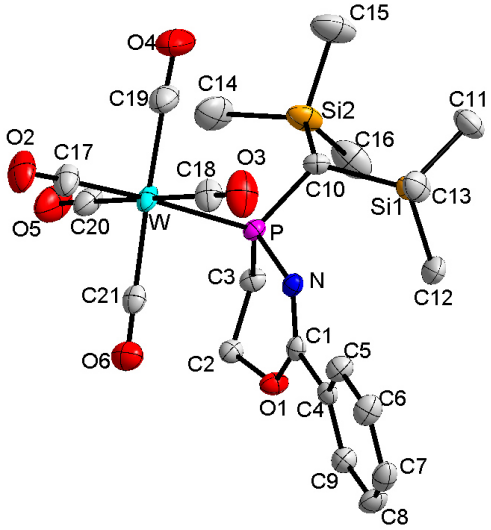


***Table 1:*** Crystal data and structure refinement for **55.1b**.

| | |
|---|---|
| Identification code | GSTR509, AKY-570 // GXray4797 |
| Crystal Habitus | clear colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{21}H_{28}NO_6PSi_2W$ |
| Moiety formula | C21 H28 N O6 P Si2 W |
| Formula weight | 661.44 |
| Temperature/K | 123 |
| Crystal system | monoclinic |
| Space group | $P2_1/a$ |
| a/Å | 10.1827(3) |
| b/Å | 15.4432(3) |
| c/Å | 17.7407(4) |
| α/° | 90 |
| β/° | 104.4804(11) |
| γ/° | 90 |
| Volume/Å$^3$ | 2701.16(11) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.626 |
| μ/mm$^{-1}$ | 4.458 |
| F(000) | 1304.0 |
| Crystal size/mm$^3$ | 0.15 × 0.14 × 0.05 |

| | |
|---|---|
| Absorption correction | multi-scan |
| Tmin; Tmax | 0.7175; 1.2457 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.976 to 56° |
| Completeness to theta | 0.999 |
| Index ranges | -13 ≤ h ≤ 12, -20 ≤ k ≤ 16, -23 ≤ l ≤ 23 |
| Reflections collected | 28202 |
| Independent reflections | 6519 [$R_{int}$ = 0.0678, $R_{sigma}$ = 0.0398] |
| Data/restraints/parameters | 6519/54/295 |
| Goodness-of-fit on $F^2$ | 1.023 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0307, $wR_2$ = 0.0714 |
| Final R indexes [all data] | $R_1$ = 0.0385, $wR_2$ = 0.0754 |
| Largest diff. peak/hole / e $Å^{-3}$ | 1.92/-1.74 |

***Table 2:*** Bond lengths for **55.1b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5171(8) | O1 | C1 | 1.358(4) |
| W | C17 | 2.017(4) | O1 | C2 | 1.443(4) |
| W | C18 | 2.058(4) | O2 | C17 | 1.143(5) |
| W | C19 | 2.023(4) | O3 | C18 | 1.131(5) |
| W | C20 | 2.036(4) | O4 | C19 | 1.158(5) |
| W | C21 | 2.032(4) | O5 | C20 | 1.138(5) |
| P | N | 1.696(3) | O6 | C21 | 1.145(4) |
| P | C3 | 1.833(3) | N | C1 | 1.272(4) |
| P | C10 | 1.827(3) | C1 | C4 | 1.485(4) |
| Si1 | C10 | 1.914(4) | C2 | C3 | 1.520(5) |
| Si1 | C11 | 1.872(4) | C4 | C5 | 1.392(5) |
| Si1 | C12 | 1.868(4) | C4 | C9 | 1.394(5) |
| Si1 | C13 | 1.860(4) | C5 | C6 | 1.383(5) |
| Si2 | C10 | 1.910(3) | C6 | C7 | 1.392(5) |
| Si2 | C14 | 1.880(5) | C7 | C8 | 1.376(6) |
| Si2 | C15 | 1.876(5) | C8 | C9 | 1.393(5) |
| Si2 | C16 | 1.864(5) | | | |

***Table 3:*** Bond angles for **55.1b**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C17 | W | P | 172.64(13) | C15 | Si2 | C10 | 107.5(2) |
| C17 | W | C18 | 89.85(16) | C15 | Si2 | C14 | 106.2(2) |
| C17 | W | C19 | 92.35(18) | C16 | Si2 | C10 | 112.09(19) |
| C17 | W | C20 | 90.85(17) | C16 | Si2 | C14 | 106.6(2) |
| C17 | W | C21 | 89.69(16) | C16 | Si2 | C15 | 110.9(2) |
| C18 | W | P | 84.04(11) | C1 | O1 | C2 | 119.7(3) |
| C19 | W | P | 91.69(13) | C1 | N | P | 124.8(2) |
| C19 | W | C18 | 89.52(18) | O1 | C1 | C4 | 111.3(3) |
| C19 | W | C20 | 90.34(17) | N | C1 | O1 | 127.6(3) |
| C19 | W | C21 | 177.81(16) | N | C1 | C4 | 121.1(3) |
| C20 | W | P | 95.27(12) | O1 | C2 | C3 | 113.7(3) |
| C20 | W | C18 | 179.29(17) | C2 | C3 | P | 108.6(2) |
| C21 | W | P | 86.20(10) | C5 | C4 | C1 | 119.1(3) |
| C21 | W | C18 | 89.69(16) | C5 | C4 | C9 | 119.2(3) |
| C21 | W | C20 | 90.43(15) | C9 | C4 | C1 | 121.7(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N | P | W | 103.91(10) | C6 | C5 | C4 | 120.3(3) |
| N | P | C3 | 100.12(15) | C5 | C6 | C7 | 120.2(3) |
| N | P | C10 | 105.42(14) | C8 | C7 | C6 | 119.8(3) |
| C3 | P | W | 121.37(12) | C7 | C8 | C9 | 120.3(3) |
| C10 | P | W | 118.54(11) | C8 | C9 | C4 | 120.1(3) |
| C10 | P | C3 | 104.79(16) | P | C10 | Si1 | 114.97(17) |
| C11 | Si1 | C10 | 111.70(18) | P | C10 | Si2 | 113.84(18) |
| C12 | Si1 | C10 | 113.08(17) | Si2 | C10 | Si1 | 115.48(18) |
| C12 | Si1 | C11 | 106.3(2) | O2 | C17 | W | 177.2(4) |
| C13 | Si1 | C10 | 107.81(17) | O3 | C18 | W | 179.6(4) |
| C13 | Si1 | C11 | 105.5(2) | O4 | C19 | W | 178.3(4) |
| C13 | Si1 | C12 | 112.2(2) | O5 | C20 | W | 178.2(4) |
| C14 | Si2 | C10 | 113.46(19) | O6 | C21 | W | 179.6(4) |

***Table 4:*** Torsion angles for **55.1b**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | N | C1 | 106.2(3) | C1 | C4 | C5 | C6 | 179.1(3) |
| W | P | C3 | C2 | -69.4(3) | C1 | C4 | C9 | C8 | -179.7(3) |
| W | P | C10 | Si1 | 133.57(14) | C2 | O1 | C1 | N | -11.9(5) |
| W | P | C10 | Si2 | -90.00(18) | C2 | O1 | C1 | C4 | 168.4(3) |
| P | N | C1 | O1 | 3.7(5) | C3 | P | N | C1 | -19.9(3) |
| P | N | C1 | C4 | -176.6(2) | C3 | P | C10 | Si1 | -87.3(2) |
| O1 | C1 | C4 | C5 | -166.1(3) | C3 | P | C10 | Si2 | 49.2(2) |
| O1 | C1 | C4 | C9 | 13.0(4) | C4 | C5 | C6 | C7 | 0.2(6) |
| O1 | C2 | C3 | P | -57.8(3) | C5 | C4 | C9 | C8 | -0.5(5) |
| N | P | C3 | C2 | 43.9(3) | C5 | C6 | C7 | C8 | 0.4(6) |
| N | P | C10 | Si1 | 17.9(2) | C6 | C7 | C8 | C9 | -1.1(6) |
| N | P | C10 | Si2 | 154.30(17) | C7 | C8 | C9 | C4 | 1.1(5) |
| N | C1 | C4 | C5 | 14.1(5) | C9 | C4 | C5 | C6 | -0.1(5) |
| N | C1 | C4 | C9 | -166.7(3) | C10 | P | N | C1 | -128.4(3) |
| C1 | O1 | C2 | C3 | 42.1(4) | C10 | P | C3 | C2 | 152.9(2) |

# 12.41 Pentacarbonyl{2-(1,1-dimethylethyl)-4-[bis(trimethylsilyl)methyl]-1-oxa-3-aza-5,6-dihydrophosphinine-κ*P*}tungsten(0) [55.1c]

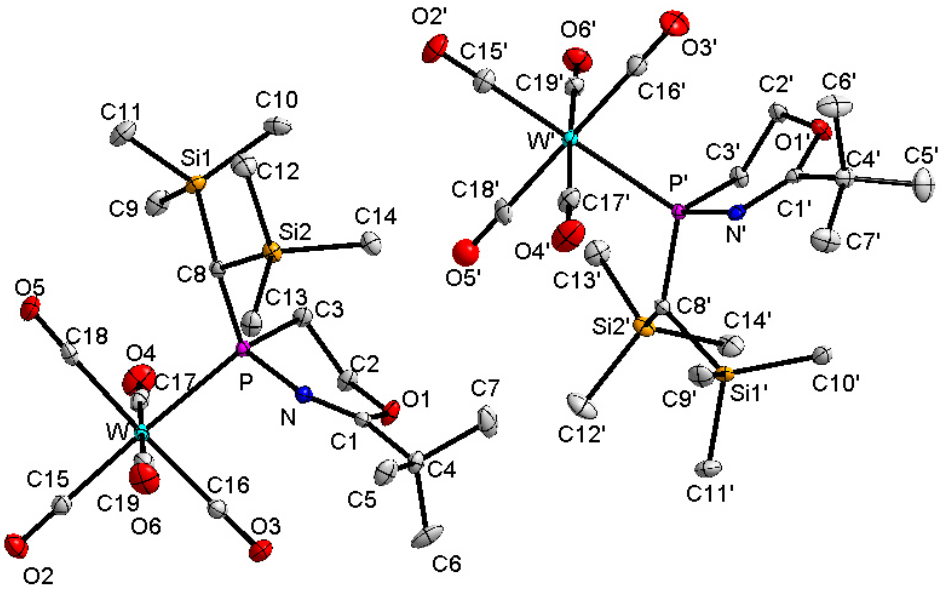


***Table 1:*** Crystal data and structure refinement for **55.1c**.

| | |
|---|---|
| Identification code | GSTR529, AKY-599 // GXraymo_4925f |
| Crystal Habitus | clear colourless plate |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{19}H_{32}NO_6Si_2PW$ |
| Moiety formula | C19 H32 N O6 P Si2 W |
| Formula weight | 641.45 |
| Temperature/K | 100.0 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 12.6617(9) |
| b/Å | 13.6989(10) |
| c/Å | 16.0934(13) |
| α/° | 72.085(3) |
| β/° | 88.886(3) |
| γ/° | 77.237(3) |
| Volume/Å$^3$ | 2586.9(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.647 |
| μ/mm$^{-1}$ | 4.652 |
| F(000) | 1272.0 |
| Crystal size/mm$^3$ | 0.18 × 0.15 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.4504; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.35 to 55.998° |
| Completeness to theta | 0.999 |
| Index ranges | -16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21 |
| Reflections collected | 114135 |
| Independent reflections | 12480 [$R_{int}$ = 0.0815, $R_{sigma}$ = 0.0395] |
| Data/restraints/parameters | 12480/0/559 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.023 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0250, $wR_2$ = 0.0565 |
| Final R indexes [all data] | $R_1$ = 0.0385, $wR_2$ = 0.0624 |
| Largest diff. peak/hole / e $Å^{-3}$ | 1.40/-1.64 |

***Table 2:*** Bond lengths for **55.1c**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5084(8) | W' | P' | 2.5030(8) |
| W | C15 | 2.017(3) | W' | C15' | 2.012(3) |
| W | C16 | 2.041(3) | W' | C16' | 2.047(4) |
| W | C17 | 2.039(3) | W' | C17' | 2.062(3) |
| W | C18 | 2.030(3) | W' | C18' | 2.028(4) |
| W | C19 | 2.067(4) | W' | C19' | 2.038(3) |
| P | N | 1.702(3) | P' | N' | 1.705(3) |
| P | C3 | 1.830(3) | P' | C3' | 1.826(3) |
| P | C8 | 1.833(3) | P' | C8' | 1.832(3) |
| Si1 | C8 | 1.913(3) | Si1' | C8' | 1.912(3) |
| Si1 | C9 | 1.885(4) | Si1' | C9' | 1.863(4) |
| Si1 | C10 | 1.868(4) | Si1' | C10' | 1.878(3) |
| Si1 | C11 | 1.874(4) | Si1' | C11' | 1.870(3) |
| Si2 | C8 | 1.908(3) | Si2' | C8' | 1.910(3) |
| Si2 | C12 | 1.877(3) | Si2' | C12' | 1.869(4) |
| Si2 | C13 | 1.865(3) | Si2' | C13' | 1.874(4) |
| Si2 | C14 | 1.873(3) | Si2' | C14' | 1.877(4) |
| O1 | C1 | 1.358(4) | O1' | C1' | 1.358(4) |
| O1 | C2 | 1.443(4) | O1' | C2' | 1.443(4) |
| O2 | C15 | 1.141(4) | O2' | C15' | 1.149(4) |
| O3 | C16 | 1.145(4) | O3' | C16' | 1.142(4) |
| O4 | C17 | 1.146(4) | O4' | C17' | 1.129(4) |
| O5 | C18 | 1.145(4) | O5' | C18' | 1.142(4) |
| O6 | C19 | 1.131(4) | O6' | C19' | 1.139(4) |
| N | C1 | 1.270(4) | N' | C1' | 1.265(4) |
| C1 | C4 | 1.526(4) | C1' | C4' | 1.532(4) |
| C2 | C3 | 1.518(4) | C2' | C3' | 1.512(4) |
| C4 | C5 | 1.521(5) | C4' | C5' | 1.534(5) |
| C4 | C6 | 1.530(5) | C4' | C6' | 1.540(5) |
| C4 | C7 | 1.535(5) | C4' | C7' | 1.522(5) |

***Table 3:*** Bond angles for **55.1c**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C15 | W | P | 174.14(10) | C15' | W' | P' | 176.16(10) |
| C15 | W | C16 | 91.33(13) | C15' | W' | C16' | 89.88(14) |
| C15 | W | C17 | 93.17(14) | C15' | W' | C17' | 91.91(14) |
| C15 | W | C18 | 91.02(13) | C15' | W' | C18' | 90.14(14) |
| C15 | W | C19 | 88.15(13) | C15' | W' | C19' | 92.88(13) |
| C16 | W | P | 87.91(9) | C16' | W' | P' | 88.37(10) |
| C16 | W | C19 | 91.12(14) | C16' | W' | C17' | 90.69(15) |
| C17 | W | P | 92.65(10) | C17' | W' | P' | 84.69(10) |
| C17 | W | C16 | 90.16(13) | C18' | W' | P' | 91.60(10) |
| C17 | W | C19 | 178.14(13) | C18' | W' | C16' | 179.95(16) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C18 | W | P | 89.84(9) | C18' | W' | C17' | 89.26(14) |
| C18 | W | C16 | 177.52(12) | C18' | W' | C19' | 87.75(14) |
| C18 | W | C17 | 88.92(13) | C19' | W' | P' | 90.61(9) |
| C18 | W | C19 | 89.75(13) | C19' | W' | C16' | 92.30(14) |
| C19 | W | P | 86.05(10) | C19' | W' | C17' | 174.36(13) |
| N | P | W | 108.06(9) | N' | P' | W' | 109.37(9) |
| N | P | C3 | 99.46(14) | N' | P' | C3' | 99.04(14) |
| N | P | C8 | 106.04(14) | N' | P' | C8' | 105.42(13) |
| C3 | P | W | 119.05(11) | C3' | P' | W' | 118.47(11) |
| C3 | P | C8 | 106.92(14) | C3' | P' | C8' | 106.43(14) |
| C8 | P | W | 115.43(10) | C8' | P' | W' | 116.08(10) |
| C9 | Si1 | C8 | 114.34(15) | C9' | Si1' | C8' | 108.77(15) |
| C10 | Si1 | C8 | 111.21(15) | C9' | Si1' | C10' | 113.87(16) |
| C10 | Si1 | C9 | 107.58(17) | C9' | Si1' | C11' | 104.54(17) |
| C10 | Si1 | C11 | 110.76(17) | C10' | Si1' | C8' | 112.17(14) |
| C11 | Si1 | C8 | 108.13(15) | C11' | Si1' | C8' | 111.52(16) |
| C11 | Si1 | C9 | 104.65(17) | C11' | Si1' | C10' | 105.71(16) |
| C12 | Si2 | C8 | 111.23(15) | C12' | Si2' | C8' | 107.92(15) |
| C13 | Si2 | C8 | 108.94(15) | C12' | Si2' | C13' | 105.09(17) |
| C13 | Si2 | C12 | 104.71(16) | C12' | Si2' | C14' | 110.85(17) |
| C13 | Si2 | C14 | 112.64(16) | C13' | Si2' | C8' | 115.13(15) |
| C14 | Si2 | C8 | 112.45(15) | C13' | Si2' | C14' | 107.04(17) |
| C14 | Si2 | C12 | 106.59(16) | C14' | Si2' | C8' | 110.69(15) |
| C1 | O1 | C2 | 120.3(2) | C1' | O1' | C2' | 119.0(2) |
| C1 | N | P | 124.2(2) | C1' | N' | P' | 124.4(2) |
| O1 | C1 | C4 | 109.3(3) | O1' | C1' | C4' | 109.3(3) |
| N | C1 | O1 | 127.7(3) | N' | C1' | O1' | 128.2(3) |
| N | C1 | C4 | 123.0(3) | N' | C1' | C4' | 122.5(3) |
| O1 | C2 | C3 | 113.7(3) | O1' | C2' | C3' | 113.5(2) |
| C2 | C3 | P | 108.0(2) | C2' | C3' | P' | 107.8(2) |
| C1 | C4 | C6 | 108.5(3) | C1' | C4' | C5' | 110.2(3) |
| C1 | C4 | C7 | 108.7(3) | C1' | C4' | C6' | 107.3(3) |
| C5 | C4 | C1 | 110.5(3) | C5' | C4' | C6' | 110.0(3) |
| C5 | C4 | C6 | 109.4(3) | C7' | C4' | C1' | 110.8(3) |
| C5 | C4 | C7 | 110.1(3) | C7' | C4' | C5' | 109.8(3) |
| C6 | C4 | C7 | 109.6(3) | C7' | C4' | C6' | 108.7(3) |
| P | C8 | Si1 | 115.14(16) | P' | C8' | Si1' | 115.16(16) |
| P | C8 | Si2 | 116.31(16) | P' | C8' | Si2' | 115.20(16) |
| Si2 | C8 | Si1 | 114.71(15) | Si2' | C8' | Si1' | 115.37(16) |
| O2 | C15 | W | 178.6(3) | O2' | C15' | W' | 178.9(3) |
| O3 | C16 | W | 178.5(3) | O3' | C16' | W' | 179.4(3) |
| O4 | C17 | W | 178.7(3) | O4' | C17' | W' | 177.5(3) |
| O5 | C18 | W | 178.5(3) | O5' | C18' | W' | 179.8(4) |
| O6 | C19 | W | 179.2(3) | O6' | C19' | W' | 177.1(3) |

***Table 4:*** Torsion angles for **55.1c**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | N | C1 | 102.5(3) | W' | P' | N' | C1' | -104.6(3) |
| W | P | C3 | C2 | -69.5(2) | W' | P' | C3' | C2' | 70.8(2) |
| W | P | C8 | Si1 | -93.43(16) | W' | P' | C8' | Si1' | -131.57(13) |
| W | P | C8 | Si2 | 128.22(13) | W' | P' | C8' | Si2' | 90.34(16) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| P | N | C1 | O1 | 1.8(5) | P' | N' | C1' | O1' | 0.8(5) |
| P | N | C1 | C4 | -178.4(2) | P' | N' | C1' | C4' | 179.3(2) |
| O1 | C1 | C4 | C5 | -178.4(3) | O1' | C1' | C4' | C5' | -46.3(3) |
| O1 | C1 | C4 | C6 | -58.5(3) | O1' | C1' | C4' | C6' | 73.4(3) |
| O1 | C1 | C4 | C7 | 60.7(4) | O1' | C1' | C4' | C7' | -168.1(3) |
| O1 | C2 | C3 | P | -58.4(3) | O1' | C2' | C3' | P' | 60.8(3) |
| N | P | C3 | C2 | 47.3(2) | N' | P' | C3' | C2' | -47.1(2) |
| N | P | C8 | Si1 | 146.97(16) | N' | P' | C8' | Si1' | -10.4(2) |
| N | P | C8 | Si2 | 8.6(2) | N' | P' | C8' | Si2' | -148.46(16) |
| N | C1 | C4 | C5 | 1.7(4) | N' | C1' | C4' | C5' | 135.0(3) |
| N | C1 | C4 | C6 | 121.7(3) | N' | C1' | C4' | C6' | -105.3(4) |
| N | C1 | C4 | C7 | -119.2(4) | N' | C1' | C4' | C7' | 13.2(4) |
| C1 | O1 | C2 | C3 | 37.9(4) | C1' | O1' | C2' | C3' | -40.4(4) |
| C2 | O1 | C1 | N | -6.0(5) | C2' | O1' | C1' | N' | 6.0(5) |
| C2 | O1 | C1 | C4 | 174.1(3) | C2' | O1' | C1' | C4' | -172.6(3) |
| C3 | P | N | C1 | -22.4(3) | C3' | P' | N' | C1' | 20.0(3) |
| C3 | P | C8 | Si1 | 41.5(2) | C3' | P' | C8' | Si1' | 94.18(19) |
| C3 | P | C8 | Si2 | -96.82(19) | C3' | P' | C8' | Si2' | -43.9(2) |
| C8 | P | N | C1 | -133.2(3) | C8' | P' | N' | C1' | 129.9(3) |
| C8 | P | C3 | C2 | 157.4(2) | C8' | P' | C3' | C2' | -156.3(2) |

## 12.42 Lithium(1,4,7,10-tetraoxacyclododecane) pentacarbonyl{[3,3,3-trifluoro-2-hydroxypropyl](triphenylmethyl)phosphanoxido-κ*P*}tungsten(0) [57.3a]

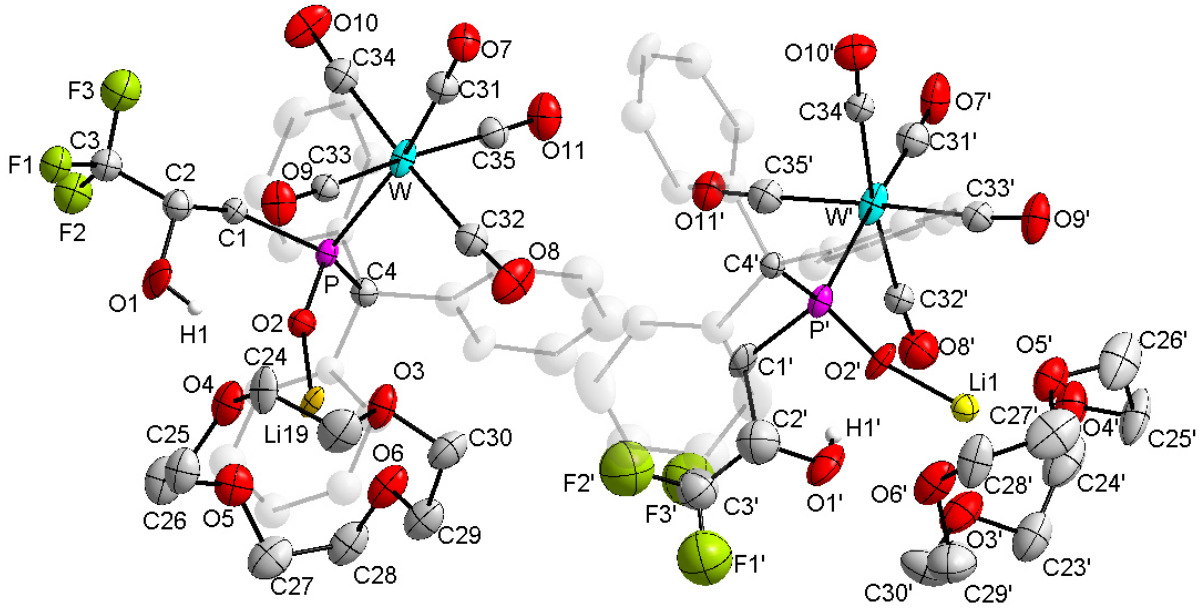


***Table 1:*** Crystal data and structure refinement for **57.3a**.

| | |
|---|---|
| Identification code | GSTR505, PB-12 // GXraycu_4642g |
| Crystal Habitus | clear colourless plank |
| Device Type | Bruker D8-Venture |
| Empirical formula | $C_{35}H_{35}LiO_{11}F_3PW$ |
| Moiety formula | C35 H35 F3 Li O11 P W |
| Formula weight | 910.39 |
| Temperature/K | 100 |

| | |
|---|---|
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 11.7656(6) |
| b/Å | 17.3287(8) |
| c/Å | 18.3627(8) |
| α/° | 100.314(2) |
| β/° | 96.610(2) |
| γ/° | 92.386(3) |
| Volume/Å$^3$ | 3651.4(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.656 |
| μ/mm$^{-1}$ | 6.923 |
| F(000) | 1808.0 |
| Crystal size/mm$^3$ | 0.16 × 0.04 × 0.03 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.2779; 0.7542 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.93 to 135.496° |
| Completeness to theta | 0.985 |
| Index ranges | -14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -22 ≤ l ≤ 22 |
| Reflections collected | 62711 |
| Independent reflections | 13041 [$R_{int}$ = 0.1191, $R_{sigma}$ = 0.0826] |
| Data/restraints/parameters | 13041/382/939 |
| Goodness-of-fit on F$^2$ | 1.878 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1909, $wR_2$ = 0.4301 |
| Final R indexes [all data] | $R_1$ = 0.2084, $wR_2$ = 0.4480 |
| Largest diff. peak/hole / e Å$^{-3}$ | 11.26/-12.98 |

***Table 2***: Bond lengths for **57.3a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.553(4) | W' | P' | 2.569(4) |
| W | C31 | 1.94(2) | W' | C31' | 1.92(2) |
| W | C32 | 2.01(2) | W' | C32' | 2.051(17) |
| W | C33 | 1.993(17) | W' | C33' | 2.04(2) |
| W | C34 | 2.00(2) | W' | C34' | 2.037(17) |
| W | C35 | 2.051(19) | W' | C35' | 2.07(2) |
| P | O2 | 1.547(13) | P' | O2' | 1.556(12) |
| P | C1 | 1.856(16) | P' | C1' | 1.88(2) |
| P | C4 | 1.965(18) | P' | C4' | 1.943(17) |
| F1 | C3 | 1.32(2) | F1' | C3' | 1.26(3) |
| F2 | C3 | 1.33(2) | F2' | C3' | 1.40(4) |
| F3 | C3 | 1.37(2) | F3' | C3' | 1.29(3) |
| O1 | C2 | 1.41(2) | O1' | C2' | 1.43(3) |
| O2 | Li19 | 1.84(3) | O2' | Li1 | 1.77(3) |
| O3 | C23 | 1.40(3) | O3' | C23' | 1.47(3) |
| O3 | C30 | 1.42(3) | O3' | C30' | 1.395(10) |
| O3 | Li19 | 2.11(3) | O3' | Li1 | 2.06(3) |
| O4 | C24 | 1.44(3) | O4' | C24' | 1.394(10) |
| O4 | C25 | 1.42(3) | O4' | C25' | 1.41(3) |
| O4 | Li19 | 2.13(3) | O4' | Li1 | 2.23(3) |
| O5 | C26 | 1.43(3) | O5' | C26' | 1.389(10) |
| O5 | C27 | 1.43(3) | O5' | C27' | 1.42(3) |

| | | | | | |
|---|---|---|---|---|---|
| O5 | Li19 | 2.14(3) | O5' | Li1 | 2.15(3) |
| O6 | C28 | 1.45(3) | O6' | C28' | 1.43(3) |
| O6 | C29 | 1.391(10) | O6' | C29' | 1.46(3) |
| O6 | Li19 | 2.08(3) | O6' | Li1 | 2.16(3) |
| O7 | C31 | 1.23(2) | O7' | C31' | 1.18(3) |
| O8 | C32 | 1.14(3) | O8' | C32' | 1.15(2) |
| O9 | C33 | 1.17(2) | O9' | C33' | 1.14(2) |
| O10 | C34 | 1.19(3) | O10' | C34' | 1.12(2) |
| O11 | C35 | 1.14(2) | O11' | C35' | 1.12(3) |
| C1 | C2 | 1.50(2) | C1' | C2' | 1.45(3) |
| C2 | C3 | 1.48(3) | C2' | C3' | 1.51(4) |
| C4 | C5 | 1.53(2) | C4' | C5' | 1.53(2) |
| C4 | C11 | 1.54(3) | C4' | C11' | 1.57(2) |
| C4 | C17 | 1.55(3) | C4' | C17' | 1.54(2) |
| C5 | C6 | 1.33(3) | C5' | C6' | 1.39(3) |
| C5 | C10 | 1.40(3) | C5' | C10' | 1.41(3) |
| C6 | C7 | 1.42(3) | C6' | C7' | 1.37(3) |
| C7 | C8 | 1.44(3) | C7' | C8' | 1.36(3) |
| C8 | C9 | 1.37(3) | C8' | C9' | 1.35(3) |
| C9 | C10 | 1.44(3) | C9' | C10' | 1.42(3) |
| C11 | C12 | 1.39(3) | C11' | C12' | 1.34(3) |
| C11 | C16 | 1.39(3) | C11' | C16' | 1.43(3) |
| C12 | C13 | 1.33(3) | C12' | C13' | 1.39(3) |
| C13 | C14 | 1.41(3) | C13' | C14' | 1.42(3) |
| C14 | C15 | 1.39(3) | C14' | C15' | 1.37(3) |
| C15 | C16 | 1.38(3) | C15' | C16' | 1.45(3) |
| C17 | C18 | 1.40(3) | C17' | C18' | 1.36(3) |
| C17 | C22 | 1.42(3) | C17' | C22' | 1.41(4) |
| C18 | C19 | 1.42(4) | C18' | C19' | 1.39(4) |
| C19 | C20 | 1.29(4) | C19' | C20' | 1.32(5) |
| C20 | C21 | 1.38(4) | C20' | C21' | 1.37(4) |
| C21 | C22 | 1.35(4) | C21' | C22' | 1.40(4) |
| C23 | C24 | 1.51(3) | C23' | C24' | 1.55(4) |
| C25 | C26 | 1.54(3) | C25' | C26' | 1.58(3) |
| C27 | C28 | 1.50(4) | C27' | C28' | 1.48(4) |
| C29 | C30 | 1.57(3) | C29' | C30' | 1.50(4) |

***Table 3:*** Bond angles for **57.3a**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| C31 | W | P | 167.9(6) | C31' | W' | P' | 174.1(6) |
| C31 | W | C32 | 89.0(8) | C31' | W' | C32' | 89.9(8) |
| C31 | W | C33 | 87.0(8) | C31' | W' | C33' | 92.4(9) |
| C31 | W | C34 | 91.5(9) | C31' | W' | C34' | 87.2(8) |
| C31 | W | C35 | 89.8(8) | C31' | W' | C35' | 89.8(9) |
| C32 | W | P | 93.4(6) | C32' | W' | P' | 84.3(5) |
| C32 | W | C35 | 85.4(8) | C32' | W' | C35' | 91.9(8) |
| C33 | W | P | 81.3(5) | C33' | W' | P' | 88.6(5) |
| C33 | W | C32 | 88.2(8) | C33' | W' | C32' | 86.4(7) |
| C33 | W | C34 | 96.1(8) | C33' | W' | C35' | 177.3(8) |
| C33 | W | C35 | 172.9(8) | C34' | W' | P' | 98.7(5) |
| C34 | W | P | 87.0(6) | C34' | W' | C32' | 173.6(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C34 | W | C32 | 175.6(8) | C34' | W' | C33' | 88.0(7) |
| C34 | W | C35 | 90.3(8) | C34' | W' | C35' | 93.7(8) |
| C35 | W | P | 102.2(5) | C35' | W' | P' | 89.1(6) |
| O2 | P | W | 111.3(5) | O2' | P' | W' | 113.1(5) |
| O2 | P | C1 | 102.3(7) | O2' | P' | C1' | 103.6(8) |
| O2 | P | C4 | 107.1(7) | O2' | P' | C4' | 106.0(7) |
| C1 | P | W | 110.6(5) | C1' | P' | W' | 110.5(7) |
| C1 | P | C4 | 100.9(8) | C1' | P' | C4' | 102.5(8) |
| C4 | P | W | 122.4(5) | C4' | P' | W' | 119.5(5) |
| P | O2 | Li19 | 156.7(12) | P' | O2' | Li1 | 164.6(13) |
| C23 | O3 | C30 | 115.3(19) | C23' | O3' | Li1 | 116.3(17) |
| C23 | O3 | Li19 | 110.5(16) | C30' | O3' | C23' | 115(2) |
| C30 | O3 | Li19 | 108.8(16) | C30' | O3' | Li1 | 111.7(16) |
| C24 | O4 | Li19 | 108.9(13) | C24' | O4' | C25' | 113.3(19) |
| C25 | O4 | C24 | 113.5(17) | C24' | O4' | Li1 | 107.0(17) |
| C25 | O4 | Li19 | 112.9(15) | C25' | O4' | Li1 | 109.9(16) |
| C26 | O5 | Li19 | 109.4(15) | C26' | O5' | C27' | 117(2) |
| C27 | O5 | C26 | 117.8(18) | C26' | O5' | Li1 | 112.0(15) |
| C27 | O5 | Li19 | 110.0(16) | C27' | O5' | Li1 | 111.2(17) |
| C28 | O6 | Li19 | 110.0(15) | C28' | O6' | C29' | 111(2) |
| C29 | O6 | C28 | 112.1(17) | C28' | O6' | Li1 | 109.9(16) |
| C29 | O6 | Li19 | 110.9(14) | C29' | O6' | Li1 | 110.2(19) |
| C2 | C1 | P | 113.8(13) | C2' | C1' | P' | 112.7(16) |
| O1 | C2 | C1 | 110.2(14) | O1' | C2' | C1' | 114(2) |
| O1 | C2 | C3 | 106.5(15) | O1' | C2' | C3' | 102(2) |
| C3 | C2 | C1 | 115.8(17) | C1' | C2' | C3' | 113(2) |
| F1 | C3 | F2 | 108.7(15) | F1' | C3' | F2' | 103(2) |
| F1 | C3 | F3 | 106.6(15) | F1' | C3' | F3' | 115(3) |
| F1 | C3 | C2 | 114.1(17) | F1' | C3' | C2' | 109(3) |
| F2 | C3 | F3 | 104.6(16) | F2' | C3' | C2' | 109(2) |
| F2 | C3 | C2 | 112.3(16) | F3' | C3' | F2' | 103(2) |
| F3 | C3 | C2 | 110.0(15) | F3' | C3' | C2' | 117(2) |
| C5 | C4 | P | 112.6(12) | C5' | C4' | P' | 109.5(11) |
| C5 | C4 | C11 | 110.2(14) | C5' | C4' | C11' | 107.0(13) |
| C5 | C4 | C17 | 110.4(14) | C5' | C4' | C17' | 109.4(14) |
| C11 | C4 | P | 104.4(11) | C11' | C4' | P' | 110.1(12) |
| C11 | C4 | C17 | 113.0(14) | C17' | C4' | P' | 108.5(11) |
| C17 | C4 | P | 106.1(13) | C17' | C4' | C11' | 112.3(14) |
| C6 | C5 | C4 | 124.4(16) | C6' | C5' | C4' | 124.2(17) |
| C6 | C5 | C10 | 119.8(17) | C6' | C5' | C10' | 117.4(17) |
| C10 | C5 | C4 | 115.5(15) | C10' | C5' | C4' | 118.5(15) |
| C5 | C6 | C7 | 123.3(18) | C7' | C6' | C5' | 122.7(19) |
| C6 | C7 | C8 | 117.8(19) | C8' | C7' | C6' | 119.9(19) |
| C9 | C8 | C7 | 119(2) | C9' | C8' | C7' | 120(2) |
| C8 | C9 | C10 | 121(2) | C8' | C9' | C10' | 121(2) |
| C5 | C10 | C9 | 119.0(18) | C5' | C10' | C9' | 118.2(18) |
| C12 | C11 | C4 | 123.2(16) | C12' | C11' | C4' | 123.0(18) |
| C12 | C11 | C16 | 115.5(18) | C12' | C11' | C16' | 121.5(19) |
| C16 | C11 | C4 | 121.3(16) | C16' | C11' | C4' | 115.1(16) |
| C13 | C12 | C11 | 124(2) | C11' | C12' | C13' | 121(2) |
| C12 | C13 | C14 | 121(2) | C12' | C13' | C14' | 121(2) |
| C15 | C14 | C13 | 117(2) | C15' | C14' | C13' | 116.8(19) |
| C16 | C15 | C14 | 120(2) | C14' | C15' | C16' | 124(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C15 | C16 | C11 | 122(2) | C11' | C16' | C15' | 115.0(18) |
| C18 | C17 | C4 | 124(2) | C18' | C17' | C4' | 126.9(18) |
| C18 | C17 | C22 | 120(2) | C18' | C17' | C22' | 118.2(19) |
| C22 | C17 | C4 | 116.8(17) | C22' | C17' | C4' | 114.9(18) |
| C17 | C18 | C19 | 119(2) | C17' | C18' | C19' | 123(2) |
| C20 | C19 | C18 | 120(3) | C20' | C19' | C18' | 118(3) |
| C19 | C20 | C21 | 123(3) | C19' | C20' | C21' | 122(3) |
| C22 | C21 | C20 | 121(3) | C20' | C21' | C22' | 120(3) |
| C21 | C22 | C17 | 118(2) | C21' | C22' | C17' | 118(2) |
| O3 | C23 | C24 | 107.8(19) | O3' | C23' | C24' | 103(2) |
| O4 | C24 | C23 | 109.3(18) | O4' | C24' | C23' | 112(2) |
| O4 | C25 | C26 | 103.0(19) | O4' | C25' | C26' | 103.6(18) |
| O5 | C26 | C25 | 109.7(18) | O5' | C26' | C25' | 110.0(19) |
| O5 | C27 | C28 | 106(2) | O5' | C27' | C28' | 110(2) |
| O6 | C28 | C27 | 109.9(18) | O6' | C28' | C27' | 111.6(18) |
| O6 | C29 | C30 | 105.5(17) | O6' | C29' | C30' | 103(2) |
| O3 | C30 | C29 | 108.9(19) | O3' | C30' | C29' | 111(2) |
| O7 | C31 | W | 176.9(16) | O7' | C31' | W' | 177.9(19) |
| O8 | C32 | W | 173.9(18) | O8' | C32' | W' | 175.3(16) |
| O9 | C33 | W | 178.2(16) | O9' | C33' | W' | 174.9(17) |
| O10 | C34 | W | 176.3(18) | O10' | C34' | W' | 176.5(16) |
| O11 | C35 | W | 176.0(17) | O11' | C35' | W' | 178(2) |
| O2 | Li19 | O3 | 128.2(16) | O2' | Li1 | O3' | 104.3(15) |
| O2 | Li19 | O4 | 114.2(13) | O2' | Li1 | O4' | 122.0(16) |
| O2 | Li19 | O5 | 102.8(14) | O2' | Li1 | O5' | 132.9(16) |
| O2 | Li19 | O6 | 114.5(13) | O2' | Li1 | O6' | 107.6(14) |
| O3 | Li19 | O4 | 79.6(11) | O3' | Li1 | O4' | 78.1(11) |
| O3 | Li19 | O5 | 129.0(14) | O3' | Li1 | O5' | 122.4(15) |
| O4 | Li19 | O5 | 77.9(10) | O3' | Li1 | O6' | 78.4(11) |
| O6 | Li19 | O3 | 80.5(11) | O5' | Li1 | O4' | 76.8(11) |
| O6 | Li19 | O4 | 129.7(14) | O5' | Li1 | O6' | 78.7(12) |
| O6 | Li19 | O5 | 79.9(12) | O6' | Li1 | O4' | 128.8(15) |

***Table 4:*** Torsion angles for **57.3a**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O2 | Li19 | -45(3) | W' | P' | O2' | Li1 | 44(5) |
| W | P | C1 | C2 | -73.1(12) | W' | P' | C1' | C2' | 123.9(17) |
| P | O2 | Li19 | O3 | 32(4) | P' | O2' | Li1 | O3' | -146(4) |
| P | O2 | Li19 | O4 | 128(2) | P' | O2' | Li1 | O4' | -61(5) |
| P | O2 | Li19 | O5 | -150(2) | P' | O2' | Li1 | O5' | 41(6) |
| P | O2 | Li19 | O6 | -65(4) | P' | O2' | Li1 | O6' | 132(4) |
| P | C1 | C2 | O1 | -64.9(17) | P' | C1' | C2' | O1' | -63(3) |
| P | C1 | C2 | C3 | 174.2(12) | P' | C1' | C2' | C3' | -178.1(19) |
| P | C4 | C5 | C6 | 33(2) | P' | C4' | C5' | C6' | 33(2) |
| P | C4 | C5 | C10 | -153.9(15) | P' | C4' | C5' | C10' | -146.6(14) |
| P | C4 | C11 | C12 | -112.7(17) | P' | C4' | C11' | C12' | -133.8(17) |
| P | C4 | C11 | C16 | 65.3(18) | P' | C4' | C11' | C16' | 53.3(18) |
| P | C4 | C17 | C18 | -128.1(19) | P' | C4' | C17' | C18' | -113(2) |
| P | C4 | C17 | C22 | 55.8(19) | P' | C4' | C17' | C22' | 65(2) |
| O1 | C2 | C3 | F1 | 54(2) | O1' | C2' | C3' | F1' | 73(3) |
| O1 | C2 | C3 | F2 | -70(2) | O1' | C2' | C3' | F2' | -176(2) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C2 | C3 | F3 | 173.5(16) | O1' | C2' | C3' | F3' | -60(3) |
| O2 | P | C1 | C2 | 45.6(13) | O2' | P' | C1' | C2' | 3(2) |
| O3 | C23 | C24 | O4 | 55(3) | O3' | C23' | C24' | O4' | 54(3) |
| O4 | C25 | C26 | O5 | 57(2) | O4' | C25' | C26' | O5' | 58(3) |
| O5 | C27 | C28 | O6 | 54(2) | O5' | C27' | C28' | O6' | 49(3) |
| O6 | C29 | C30 | O3 | 56(2) | O6' | C29' | C30' | O3' | 55(3) |
| C1 | P | O2 | Li19 | -163(3) | C1' | P' | O2' | Li1 | 164(5) |
| C1 | C2 | C3 | F1 | 176.7(14) | C1' | C2' | C3' | F1' | -165(2) |
| C1 | C2 | C3 | F2 | 52(2) | C1' | C2' | C3' | F2' | -53(3) |
| C1 | C2 | C3 | F3 | -64(2) | C1' | C2' | C3' | F3' | 62(3) |
| C4 | P | O2 | Li19 | 91(3) | C4' | P' | O2' | Li1 | -89(5) |
| C4 | P | C1 | C2 | 156.0(12) | C4' | P' | C1' | C2' | -107.6(19) |
| C4 | C5 | C6 | C7 | 176(2) | C4' | C5' | C6' | C7' | 177.6(17) |
| C4 | C5 | C10 | C9 | -176.5(19) | C4' | C5' | C10' | C9' | -175.3(16) |
| C4 | C11 | C12 | C13 | 177.6(19) | C4' | C11' | C12' | C13' | -172.9(18) |
| C4 | C11 | C16 | C15 | -177.8(18) | C4' | C11' | C16' | C15' | 178.0(16) |
| C4 | C17 | C18 | C19 | -180(2) | C4' | C17' | C18' | C19' | 179(2) |
| C4 | C17 | C22 | C21 | 176(2) | C4' | C17' | C22' | C21' | -178(2) |
| C5 | C4 | C11 | C12 | 8(2) | C5' | C4' | C11' | C12' | -15(2) |
| C5 | C4 | C11 | C16 | -173.5(16) | C5' | C4' | C11' | C16' | 172.3(15) |
| C5 | C4 | C17 | C18 | 110(2) | C5' | C4' | C17' | C18' | 127(2) |
| C5 | C4 | C17 | C22 | -67(2) | C5' | C4' | C17' | C22' | -55(2) |
| C5 | C6 | C7 | C8 | -3(3) | C5' | C6' | C7' | C8' | -1(3) |
| C6 | C5 | C10 | C9 | -3(3) | C6' | C5' | C10' | C9' | 5(3) |
| C6 | C7 | C8 | C9 | 2(3) | C6' | C7' | C8' | C9' | 2(3) |
| C7 | C8 | C9 | C10 | -2(3) | C7' | C8' | C9' | C10' | 0(3) |
| C8 | C9 | C10 | C5 | 2(3) | C8' | C9' | C10' | C5' | -4(3) |
| C10 | C5 | C6 | C7 | 3(3) | C10' | C5' | C6' | C7' | -2(3) |
| C11 | C4 | C5 | C6 | -84(2) | C11' | C4' | C5' | C6' | -86(2) |
| C11 | C4 | C5 | C10 | 90(2) | C11' | C4' | C5' | C10' | 94.1(18) |
| C11 | C4 | C17 | C18 | -14(3) | C11' | C4' | C17' | C18' | 9(3) |
| C11 | C4 | C17 | C22 | 169.6(16) | C11' | C4' | C17' | C22' | -173.5(18) |
| C11 | C12 | C13 | C14 | 1(3) | C11' | C12' | C13' | C14' | -4(3) |
| C12 | C11 | C16 | C15 | 0(3) | C12' | C11' | C16' | C15' | 5(3) |
| C12 | C13 | C14 | C15 | -2(3) | C12' | C13' | C14' | C15' | 4(3) |
| C13 | C14 | C15 | C16 | 1(3) | C13' | C14' | C15' | C16' | 1(3) |
| C14 | C15 | C16 | C11 | -1(3) | C14' | C15' | C16' | C11' | -5(3) |
| C16 | C11 | C12 | C13 | -1(3) | C16' | C11' | C12' | C13' | 0(3) |
| C17 | C4 | C5 | C6 | 151(2) | C17' | C4' | C5' | C6' | 152.1(17) |
| C17 | C4 | C5 | C10 | -36(2) | C17' | C4' | C5' | C10' | -28(2) |
| C17 | C4 | C11 | C12 | 132.5(19) | C17' | C4' | C11' | C12' | 105(2) |
| C17 | C4 | C11 | C16 | -50(2) | C17' | C4' | C11' | C16' | -68(2) |
| C17 | C18 | C19 | C20 | 4(4) | C17' | C18' | C19' | C20' | 0(4) |
| C18 | C17 | C22 | C21 | 0(3) | C18' | C17' | C22' | C21' | 0(4) |
| C18 | C19 | C20 | C21 | 0(5) | C18' | C19' | C20' | C21' | -3(4) |
| C19 | C20 | C21 | C22 | -4(5) | C19' | C20' | C21' | C22' | 4(5) |
| C20 | C21 | C22 | C17 | 4(4) | C20' | C21' | C22' | C17' | -2(4) |
| C22 | C17 | C18 | C19 | -4(3) | C22' | C17' | C18' | C19' | 1(3) |
| C23 | O3 | C30 | C29 | 86(2) | C23' | O3' | C30' | C29' | 93(3) |
| C24 | O4 | C25 | C26 | -168.9(16) | C24' | O4' | C25' | C26' | -166(2) |
| C25 | O4 | C24 | C23 | 88(2) | C25' | O4' | C24' | C23' | 76(3) |
| C26 | O5 | C27 | C28 | -168.5(18) | C26' | O5' | C27' | C28' | -166(2) |
| C27 | O5 | C26 | C25 | 84(2) | C27' | O5' | C26' | C25' | 90(3) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C28 | O6 | C29 | C30 | -167.8(17) | C28' | O6' | C29' | C30' | -163(2) |
| C29 | O6 | C28 | C27 | 85(2) | C29' | O6' | C28' | C27' | 86(3) |
| C30 | O3 | C23 | C24 | -167(2) | C30' | O3' | C23' | C24' | -170.7(19) |
| Li19 | O3 | C23 | C24 | -43(2) | Li1 | O3' | C23' | C24' | -37(3) |
| Li19 | O3 | C30 | C29 | -38(2) | Li1 | O3' | C30' | C29' | -43(3) |
| Li19 | O4 | C24 | C23 | -38(2) | Li1 | O4' | C24' | C23' | -45(2) |
| Li19 | O4 | C25 | C26 | -44(2) | Li1 | O4' | C25' | C26' | -47(2) |
| Li19 | O5 | C26 | C25 | -43(2) | Li1 | O5' | C26' | C25' | -40(3) |
| Li19 | O5 | C27 | C28 | -42(2) | Li1 | O5' | C27' | C28' | -36(2) |
| Li19 | O6 | C28 | C27 | -39(2) | Li1 | O6' | C28' | C27' | -36(3) |
| Li19 | O6 | C29 | C30 | -45(2) | Li1 | O6' | C29' | C30' | -41(3) |

## 12.43 Lithium(1,4,7,10-tetraoxacyclododecane) pentacarbonyl{[3,3,3-trifluoro-2-(trifluoromethyl)-2-hydroxypropyl](triphenylmethyl)phosphanoxido-κ*P*}tungsten(0) [57.3b]

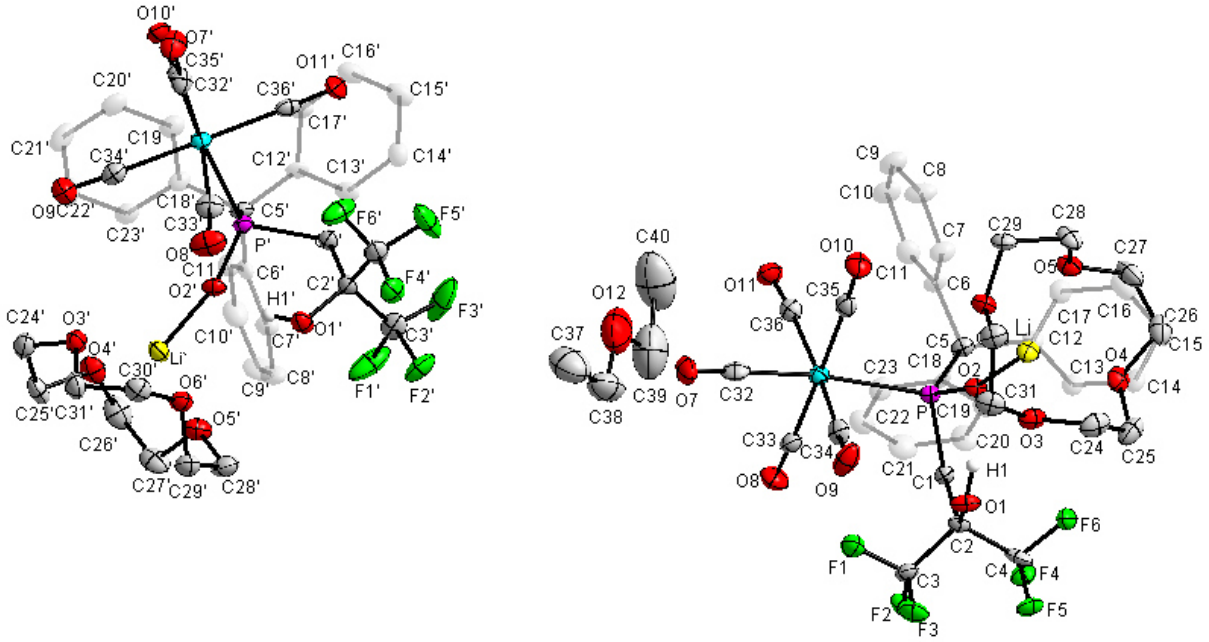


***Table 1:*** Crystal data and structure refinement for **57.3b**.

| | |
|---|---|
| Identification code | GSTR410, AKY-488-2 // GXray4012f |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{76}H_{78}F_{12}Li_2O_{23}P_2W_2$ |
| Moiety formula | 2(C36 H34 F6 Li O11 P W), C4 H10 O |
| Formula weight | 2030.90 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 11.7408(5) |
| b/Å | 18.5934(8) |
| c/Å | 20.0735(8) |
| α/° | 86.722(3) |
| β/° | 74.872(2) |
| γ/° | 73.209(3) |
| Volume/Å$^3$ | 4049.1(3) |

| | |
|---|---|
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.666 |
| μ/mm$^{-1}$ | 2.979 |
| F(000) | 2020.0 |
| Crystal size/mm$^3$ | 0.1 × 0.08 × 0.04 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.6293; 0.7459 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.936 to 56° |
| Completeness to theta | 0.997 |
| Index ranges | -15 ≤ h ≤ 15, -24 ≤ k ≤ 24, -26 ≤ l ≤ 26 |
| Reflections collected | 97310 |
| Independent reflections | 19472 [$R_{int}$ = 0.0787, $R_{sigma}$ = 0.0923] |
| Data/restraints/parameters | 19472/27/1058 |
| Goodness-of-fit on $F^2$ | 1.010 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0516, $wR_2$ = 0.1223 |
| Final R indexes [all data] | $R_1$ = 0.1086, $wR_2$ = 0.1496 |
| Largest diff. peak/hole / e Å$^{-3}$ | 4.51/-2.56 |

***Table 2:*** Bond lengths for **57.3b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5759(16) | C14 | C13 | 1.390(9) |
| W | C36 | 2.051(7) | C6 | C11 | 1.390(8) |
| W | C33 | 2.042(7) | C6 | C5 | 1.529(8) |
| W | C34 | 2.030(7) | C11 | C10 | 1.387(9) |
| W | C32 | 1.982(7) | F5' | C4' | 1.340(8) |
| W | C35 | 2.042(7) | C23 | C22 | 1.373(9) |
| W' | P' | 2.5633(15) | C11' | C10' | 1.378(9) |
| W' | C35' | 2.041(6) | C12 | C5 | 1.538(9) |
| W' | C32' | 1.992(7) | C12 | C17 | 1.396(8) |
| W' | C33' | 2.034(7) | C12 | C13 | 1.392(9) |
| W' | C36' | 2.034(7) | C17 | C16 | 1.388(9) |
| W' | C34' | 2.046(7) | C16' | C17' | 1.375(9) |
| P' | O2' | 1.542(4) | C16' | C15' | 1.377(9) |
| P' | C1' | 1.903(6) | C23' | C22' | 1.382(9) |
| P' | C5' | 1.948(6) | C20' | C19' | 1.388(9) |
| P | C1 | 1.892(5) | C20' | C21' | 1.390(10) |
| P | O2 | 1.542(4) | C7' | C8' | 1.392(9) |
| P | C5 | 1.952(6) | C15 | C16 | 1.364(10) |
| O10' | C35' | 1.142(7) | C10 | C9 | 1.373(10) |
| F5 | C4 | 1.353(7) | C9' | C8' | 1.362(10) |
| F2 | C3 | 1.345(7) | C9' | C10' | 1.384(10) |
| F4 | C4 | 1.325(7) | C17' | C12' | 1.415(8) |
| F2' | C3' | 1.394(7) | C22 | C21 | 1.375(9) |
| O11 | C36 | 1.140(8) | C14' | C15' | 1.393(9) |
| F1 | C3 | 1.327(7) | C14' | C13' | 1.393(8) |
| O1 | C2 | 1.392(7) | C8 | C9 | 1.385(10) |
| C1 | C2 | 1.555(8) | C22' | C21' | 1.380(9) |
| C18 | C23 | 1.374(9) | O5 | C28 | 1.436(7) |
| C18 | C5 | 1.534(8) | O5 | C27 | 1.443(8) |
| C18 | C19 | 1.414(8) | O5 | Li | 2.087(11) |
| F3 | C3 | 1.334(7) | O4 | C26 | 1.432(8) |

| | | | | | |
|---|---|---|---|---|---|
| O1' | C2' | 1.388(7) | O4 | C25 | 1.436(8) |
| O2' | Li' | 1.847(11) | O4 | Li | 2.076(12) |
| O8 | C33 | 1.134(7) | O6 | C29 | 1.436(7) |
| F6 | C4 | 1.359(7) | O6 | C30 | 1.433(7) |
| O2 | Li | 1.848(11) | O6 | Li | 2.164(11) |
| O10 | C35 | 1.146(7) | O3 | C31 | 1.452(7) |
| C1' | C2' | 1.545(8) | O3 | C24 | 1.432(8) |
| F4' | C4' | 1.331(7) | O3 | Li | 2.078(11) |
| C2 | C4 | 1.535(9) | C29 | C28 | 1.507(9) |
| C2 | C3 | 1.550(8) | C31 | C30 | 1.496(8) |
| O7' | C32' | 1.157(7) | C26 | C27 | 1.498(10) |
| F6' | C4' | 1.322(8) | C24 | C25 | 1.511(9) |
| C2' | C3' | 1.481(9) | C12' | C13' | 1.385(8) |
| C2' | C4' | 1.541(9) | O12 | C38 | 1.478(11) |
| C5' | C6' | 1.552(8) | O12 | C39 | 1.422(8) |
| C5' | C18' | 1.537(9) | C38 | C37 | 1.541(13) |
| C5' | C12' | 1.538(8) | Li' | O3' | 2.125(12) |
| O9' | C34' | 1.154(8) | Li' | O5' | 2.115(11) |
| O11' | C36' | 1.140(8) | Li' | O6' | 2.082(11) |
| C6' | C11' | 1.392(9) | Li' | O4' | 2.130(12) |
| C6' | C7' | 1.379(8) | C39 | C40 | 1.710(17) |
| C33' | O8' | 1.151(7) | O3' | C24' | 1.437(8) |
| C18' | C23' | 1.392(9) | O3' | C31' | 1.442(8) |
| C18' | C19' | 1.400(8) | O5' | C27' | 1.420(8) |
| C20 | C21 | 1.381(10) | O5' | C28' | 1.425(8) |
| C20 | C19 | 1.385(9) | O6' | C30' | 1.428(8) |
| C3' | F1' | 1.350(8) | O6' | C29' | 1.441(7) |
| C3' | F3' | 1.342(8) | O4' | C25' | 1.429(8) |
| O9 | C34 | 1.142(8) | O4' | C26' | 1.423(8) |
| O7 | C32 | 1.161(8) | C24' | C25' | 1.499(9) |
| C7 | C6 | 1.390(8) | C30' | C31' | 1.481(9) |
| C7 | C8 | 1.380(8) | C29' | C28' | 1.497(9) |
| C14 | C15 | 1.371(9) | C26' | C27' | 1.512(10) |

***Table 3:*** Bond angles for **57.3b**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C36 | W | P | 101.78(18) | C17 | C12 | C5 | 119.8(6) |
| C33 | W | P | 88.98(19) | C13 | C12 | C5 | 124.0(5) |
| C33 | W | C36 | 89.9(2) | C13 | C12 | C17 | 115.9(6) |
| C34 | W | P | 86.04(18) | C18 | C5 | P | 106.7(4) |
| C34 | W | C36 | 170.3(2) | C18 | C5 | C12 | 111.0(5) |
| C34 | W | C33 | 96.0(2) | C6 | C5 | P | 105.8(4) |
| C34 | W | C35 | 86.3(3) | C6 | C5 | C18 | 112.2(5) |
| C32 | W | P | 171.59(19) | C6 | C5 | C12 | 107.8(5) |
| C32 | W | C36 | 86.5(3) | C12 | C5 | P | 113.3(4) |
| C32 | W | C33 | 89.7(3) | C16 | C17 | C12 | 121.8(6) |
| C32 | W | C34 | 85.8(3) | C17' | C16' | C15' | 120.7(6) |
| C32 | W | C35 | 90.2(2) | C22' | C23' | C18' | 121.6(6) |
| C35 | W | P | 91.45(18) | C19' | C20' | C21' | 120.7(6) |
| C35 | W | C36 | 87.8(2) | C6' | C7' | C8' | 121.0(6) |
| C35 | W | C33 | 177.7(2) | O9' | C34' | W' | 178.3(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C35' | W' | P' | 102.96(16) | C16 | C15 | C14 | 119.4(7) |
| C35' | W' | C34' | 86.6(2) | C9 | C10 | C11 | 120.1(6) |
| C32' | W' | P' | 168.8(2) | C8' | C9' | C10' | 119.4(6) |
| C32' | W' | C35' | 86.3(2) | C9' | C8' | C7' | 120.7(7) |
| C32' | W' | C33' | 88.0(3) | O10 | C35 | W | 176.8(6) |
| C32' | W' | C36' | 86.3(3) | C16' | C17' | C12' | 121.5(6) |
| C32' | W' | C34' | 95.0(3) | C23 | C22 | C21 | 121.2(7) |
| C33' | W' | P' | 83.80(18) | C14 | C13 | C12 | 122.3(6) |
| C33' | W' | C35' | 168.9(3) | C15' | C14' | C13' | 120.6(6) |
| C33' | W' | C36' | 97.5(3) | C22 | C21 | C20 | 117.9(6) |
| C33' | W' | C34' | 84.4(3) | C20 | C19 | C18 | 120.1(6) |
| C36' | W' | P' | 87.15(17) | C15 | C16 | C17 | 120.6(6) |
| C36' | W' | C35' | 91.6(2) | C7 | C8 | C9 | 119.8(6) |
| C36' | W' | C34' | 177.7(2) | C16' | C15' | C14' | 118.9(6) |
| C34' | W' | P' | 91.80(17) | C21' | C22' | C23' | 120.6(7) |
| O2' | P' | W' | 111.64(16) | C10 | C9 | C8 | 119.8(6) |
| O2' | P' | C1' | 103.0(2) | C20' | C19' | C18' | 120.7(6) |
| O2' | P' | C5' | 108.6(2) | C22' | C21' | C20' | 118.9(7) |
| C1' | P' | W' | 114.14(19) | C11' | C10' | C9' | 119.7(7) |
| C1' | P' | C5' | 98.9(3) | F4' | C4' | C2' | 113.2(5) |
| C5' | P' | W' | 118.77(18) | F4' | C4' | F5' | 106.8(5) |
| C1 | P | W | 113.44(19) | F6' | C4' | F4' | 106.7(5) |
| C1 | P | C5 | 100.3(2) | F6' | C4' | C2' | 111.1(5) |
| O2 | P | W | 111.52(16) | F6' | C4' | F5' | 106.2(5) |
| O2 | P | C1 | 103.3(2) | F5' | C4' | C2' | 112.5(5) |
| O2 | P | C5 | 107.6(2) | C28 | O5 | C27 | 114.2(5) |
| C5 | P | W | 119.06(19) | C28 | O5 | Li | 109.0(4) |
| O10' | C35' | W' | 173.3(5) | C27 | O5 | Li | 107.9(5) |
| C2 | C1 | P | 116.7(4) | C26 | O4 | C25 | 114.6(5) |
| O11 | C36 | W | 173.3(6) | C26 | O4 | Li | 112.1(5) |
| C23 | C18 | C5 | 121.8(5) | C25 | O4 | Li | 110.0(5) |
| C23 | C18 | C19 | 117.0(6) | C29 | O6 | Li | 109.3(4) |
| C19 | C18 | C5 | 121.2(6) | C30 | O6 | C29 | 114.0(5) |
| P' | O2' | Li' | 160.6(4) | C30 | O6 | Li | 110.5(5) |
| P | O2 | Li | 160.4(4) | C31 | O3 | Li | 109.9(4) |
| C2' | C1' | P' | 117.4(4) | C24 | O3 | C31 | 114.7(5) |
| O1 | C2 | C1 | 116.8(4) | C24 | O3 | Li | 107.8(5) |
| O1 | C2 | C4 | 107.1(5) | O6 | C29 | C28 | 109.6(5) |
| O1 | C2 | C3 | 105.3(5) | O5 | C28 | C29 | 105.5(5) |
| C4 | C2 | C1 | 109.1(5) | O3 | C31 | C30 | 110.4(5) |
| C4 | C2 | C3 | 108.2(5) | O4 | C26 | C27 | 106.8(6) |
| C3 | C2 | C1 | 110.0(5) | O6 | C30 | C31 | 106.8(5) |
| O1' | C2' | C1' | 117.1(5) | O3 | C24 | C25 | 105.8(5) |
| O1' | C2' | C3' | 106.6(5) | O4 | C25 | C24 | 108.9(5) |
| O1' | C2' | C4' | 105.9(5) | O5 | C27 | C26 | 110.7(6) |
| C3' | C2' | C1' | 106.2(5) | C17' | C12' | C5' | 120.2(5) |
| C3' | C2' | C4' | 108.5(5) | C13' | C12' | C5' | 122.6(5) |
| C4' | C2' | C1' | 112.1(5) | C13' | C12' | C17' | 117.1(6) |
| O7' | C32' | W' | 175.5(6) | C12' | C13' | C14' | 121.1(6) |
| O8 | C33 | W | 177.1(6) | C39 | O12 | C38 | 104.1(9) |
| C6' | C5' | P' | 114.5(4) | O12 | C38 | C37 | 104.5(8) |
| C18' | C5' | P' | 106.4(4) | O2' | Li' | O3' | 118.7(6) |
| C18' | C5' | C6' | 106.1(5) | O2' | Li' | O5' | 110.4(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C18' | C5' | C12' | 115.0(5) | O2' | Li' | O6' | 104.0(5) |
| C12' | C5' | P' | 106.4(4) | O2' | Li' | O4' | 126.0(6) |
| C12' | C5' | C6' | 108.7(5) | O3' | Li' | O4' | 79.4(4) |
| F5 | C4 | F6 | 104.6(5) | O5' | Li' | O3' | 130.1(5) |
| F5 | C4 | C2 | 113.1(5) | O5' | Li' | O4' | 79.1(4) |
| F4 | C4 | F5 | 106.9(5) | O6' | Li' | O3' | 80.2(4) |
| F4 | C4 | F6 | 106.4(5) | O6' | Li' | O5' | 80.1(4) |
| F4 | C4 | C2 | 115.8(6) | O6' | Li' | O4' | 129.8(5) |
| F6 | C4 | C2 | 109.2(5) | O2 | Li | O5 | 127.5(6) |
| C11' | C6' | C5' | 117.1(5) | O2 | Li | O4 | 112.9(5) |
| C7' | C6' | C5' | 125.3(6) | O2 | Li | O6 | 115.1(6) |
| C7' | C6' | C11' | 117.4(6) | O2 | Li | O3 | 101.7(5) |
| O8' | C33' | W' | 172.9(6) | O5 | Li | O6 | 78.9(4) |
| C23' | C18' | C5' | 118.2(5) | O4 | Li | O5 | 80.8(4) |
| C23' | C18' | C19' | 117.6(6) | O4 | Li | O6 | 130.7(5) |
| C19' | C18' | C5' | 124.0(6) | O4 | Li | O3 | 80.8(4) |
| C21 | C20 | C19 | 121.6(6) | O3 | Li | O5 | 130.7(6) |
| F2' | C3' | C2' | 114.6(5) | O3 | Li | O6 | 79.5(4) |
| F1' | C3' | F2' | 102.4(5) | O12 | C39 | C40 | 94.7(9) |
| F1' | C3' | C2' | 112.1(6) | C24' | O3' | Li' | 110.0(5) |
| F3' | C3' | F2' | 103.2(5) | C24' | O3' | C31' | 113.8(5) |
| F3' | C3' | C2' | 117.0(6) | C31' | O3' | Li' | 109.5(5) |
| F3' | C3' | F1' | 106.0(5) | C27' | O5' | Li' | 111.8(5) |
| O9 | C34 | W | 172.9(6) | C27' | O5' | C28' | 114.8(5) |
| C8 | C7 | C6 | 121.5(6) | C28' | O5' | Li' | 108.7(5) |
| C15 | C14 | C13 | 120.0(7) | C30' | O6' | Li' | 109.6(5) |
| O7 | C32 | W | 178.4(5) | C30' | O6' | C29' | 114.6(5) |
| O11' | C36' | W' | 178.6(5) | C29' | O6' | Li' | 109.6(5) |
| F2 | C3 | C2 | 111.3(5) | C25' | O4' | Li' | 107.9(5) |
| F1 | C3 | F2 | 107.1(5) | C26' | O4' | Li' | 109.4(5) |
| F1 | C3 | F3 | 107.2(5) | C26' | O4' | C25' | 114.0(5) |
| F1 | C3 | C2 | 111.4(5) | O3' | C24' | C25' | 109.5(5) |
| F3 | C3 | F2 | 107.0(5) | O6' | C30' | C31' | 110.7(5) |
| F3 | C3 | C2 | 112.6(5) | O6' | C29' | C28' | 105.6(5) |
| C7 | C6 | C5 | 118.3(5) | O4' | C25' | C24' | 106.8(5) |
| C11 | C6 | C7 | 117.6(5) | O3' | C31' | C30' | 107.4(5) |
| C11 | C6 | C5 | 123.8(5) | O4' | C26' | C27' | 110.5(6) |
| C10 | C11 | C6 | 121.2(6) | O5' | C27' | C26' | 107.0(5) |
| C22 | C23 | C18 | 122.2(6) | O5' | C28' | C29' | 110.5(6) |
| C10' | C11' | C6' | 121.8(6) | | | | |

***Table 4:*** Torsion angles for **57.3b**.

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | C1 | C2 | -84.3(4) | C23 | C22 | C21 | C20 | 1.1(10) |
| W | P | O2 | Li | -86.0(13) | C11' | C6' | C7' | C8' | 0.7(9) |
| W' | P' | O2' | Li' | 81.9(13) | C12 | C17 | C16 | C15 | 1.5(10) |
| P' | O2' | Li' | O3' | -72.1(15) | C5 | P | C1 | C2 | 147.7(4) |
| P' | O2' | Li' | O5' | 117.0(12) | C5 | P | O2 | Li | 46.4(13) |
| P' | O2' | Li' | O6' | -158.4(10) | C5 | C18 | C23 | C22 | -175.2(6) |
| P' | O2' | Li' | O4' | 25.9(18) | C5 | C18 | C19 | C20 | 176.3(6) |
| P' | C1' | C2' | O1' | 16.0(7) | C5 | C6 | C11 | C10 | -176.3(6) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| P' | C1' | C2' | C3' | 134.9(5) | C5 | C12 | C17 | C16 | -173.3(6) |
| P' | C1' | C2' | C4' | -106.7(5) | C5 | C12 | C13 | C14 | 172.2(5) |
| P' | C5' | C6' | C11' | 164.6(5) | C17 | C12 | C5 | P | -155.3(4) |
| P' | C5' | C6' | C7' | -20.1(8) | C17 | C12 | C5 | C18 | 84.7(6) |
| P' | C5' | C18' | C23' | -58.2(6) | C17 | C12 | C5 | C6 | -38.7(7) |
| P' | C5' | C18' | C19' | 126.6(5) | C17 | C12 | C13 | C14 | -0.3(8) |
| P' | C5' | C12' | C17' | -64.9(6) | C16' | C17' | C12' | C5' | 178.1(6) |
| P' | C5' | C12' | C13' | 111.3(6) | C16' | C17' | C12' | C13' | 1.7(9) |
| P | C1 | C2 | O1 | -5.4(7) | C23' | C18' | C19' | C20' | 1.4(9) |
| P | C1 | C2 | C4 | -127.0(4) | C23' | C22' | C21' | C20' | 0.0(10) |
| P | C1 | C2 | C3 | 114.5(5) | C7' | C6' | C11' | C10' | -0.4(10) |
| P | O2 | Li | O5 | -17.9(18) | C15 | C14 | C13 | C12 | 0.1(9) |
| P | O2 | Li | O4 | -114.0(12) | C8' | C9' | C10' | C11' | 2.7(11) |
| P | O2 | Li | O6 | 77.4(14) | C17' | C16' | C15' | C14' | -1.1(10) |
| P | O2 | Li | O3 | 161.1(10) | C17' | C12' | C13' | C14' | -1.4(9) |
| O1 | C2 | C4 | F5 | 62.4(6) | C13 | C14 | C15 | C16 | 1.0(10) |
| O1 | C2 | C4 | F4 | -173.7(4) | C13 | C12 | C5 | P | 32.4(7) |
| O1 | C2 | C4 | F6 | -53.7(6) | C13 | C12 | C5 | C18 | -87.6(7) |
| O1 | C2 | C3 | F2 | -167.4(5) | C13 | C12 | C5 | C6 | 149.1(5) |
| O1 | C2 | C3 | F1 | 73.2(6) | C13 | C12 | C17 | C16 | -0.5(9) |
| O1 | C2 | C3 | F3 | -47.2(6) | C21 | C20 | C19 | C18 | 0.1(10) |
| C1 | P | O2 | Li | 151.9(13) | C19 | C18 | C23 | C22 | 2.2(9) |
| C1 | C2 | C4 | F5 | -170.3(5) | C19 | C18 | C5 | P | -117.9(5) |
| C1 | C2 | C4 | F4 | -46.5(6) | C19 | C18 | C5 | C6 | 126.7(6) |
| C1 | C2 | C4 | F6 | 73.6(6) | C19 | C18 | C5 | C12 | 6.0(7) |
| C1 | C2 | C3 | F2 | 66.0(6) | C19 | C20 | C21 | C22 | -0.1(10) |
| C1 | C2 | C3 | F1 | -53.5(6) | C8 | C7 | C6 | C11 | 3.3(10) |
| C1 | C2 | C3 | F3 | -173.9(5) | C8 | C7 | C6 | C5 | 177.5(6) |
| C18 | C23 | C22 | C21 | -2.3(10) | C15' | C16' | C17' | C12' | -0.4(10) |
| O1' | C2' | C3' | F2' | -59.0(7) | C15' | C14' | C13' | C12' | 0.0(10) |
| O1' | C2' | C3' | F1' | 57.2(7) | C19' | C18' | C23' | C22' | -1.3(9) |
| O1' | C2' | C3' | F3' | 179.9(5) | C19' | C20' | C21' | C22' | 0.0(10) |
| O1' | C2' | C4' | F4' | 49.9(7) | C21' | C20' | C19' | C18' | -0.8(10) |
| O1' | C2' | C4' | F6' | -70.1(6) | C10' | C9' | C8' | C7' | -2.4(11) |
| O1' | C2' | C4' | F5' | 171.0(5) | C4' | C2' | C3' | F2' | 54.7(7) |
| O2 | P | C1 | C2 | 36.6(5) | C4' | C2' | C3' | F1' | 170.9(5) |
| C1' | P' | O2' | Li' | -155.2(13) | C4' | C2' | C3' | F3' | -66.4(7) |
| C1' | C2' | C3' | F2' | 175.4(5) | O4 | C26 | C27 | O5 | 51.9(7) |
| C1' | C2' | C3' | F1' | -68.4(6) | O6 | C29 | C28 | O5 | 56.4(7) |
| C1' | C2' | C3' | F3' | 54.3(7) | O3 | C31 | C30 | O6 | 53.4(7) |
| C1' | C2' | C4' | F4' | 178.8(5) | O3 | C24 | C25 | O4 | 56.0(7) |
| C1' | C2' | C4' | F6' | 58.7(7) | C29 | O6 | C30 | C31 | -161.6(5) |
| C1' | C2' | C4' | F5' | -60.1(7) | C28 | O5 | C27 | C26 | 79.5(6) |
| C5' | P' | O2' | Li' | -51.0(13) | C31 | O3 | C24 | C25 | -171.8(5) |
| C5' | C6' | C11' | C10' | 175.2(6) | C26 | O4 | C25 | C24 | 92.9(7) |
| C5' | C6' | C7' | C8' | -174.5(6) | C30 | O6 | C29 | C28 | 91.2(6) |
| C5' | C18' | C23' | C22' | -176.8(6) | C24 | O3 | C31 | C30 | 79.4(7) |
| C5' | C18' | C19' | C20' | 176.6(6) | C25 | O4 | C26 | C27 | -162.2(5) |
| C5' | C12' | C13' | C14' | -177.8(6) | C27 | O5 | C28 | C29 | -172.5(5) |
| C4 | C2 | C3 | F2 | -53.2(7) | C12' | C5' | C6' | C11' | -76.6(7) |
| C4 | C2 | C3 | F1 | -172.6(5) | C12' | C5' | C6' | C7' | 98.7(7) |
| C4 | C2 | C3 | F3 | 67.0(6) | C12' | C5' | C18' | C23' | -175.7(5) |
| C6' | C5' | C18' | C23' | 64.1(7) | C12' | C5' | C18' | C19' | 9.1(8) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C6' | C5' | C18' | C19' | -111.0(6) | C13' | C14' | C15' | C16' | 1.3(10) |
| C6' | C5' | C12' | C17' | 171.3(5) | C38 | O12 | C39 | C40 | 179.2(8) |
| C6' | C5' | C12' | C13' | -12.5(8) | Li' | O3' | C24' | C25' | 34.9(6) |
| C6' | C11' | C10' | C9' | -1.3(11) | Li' | O3' | C31' | C30' | 39.4(7) |
| C6' | C7' | C8' | C9' | 0.7(10) | Li' | O5' | C27' | C26' | 39.5(7) |
| C18' | C5' | C6' | C11' | 47.6(7) | Li' | O5' | C28' | C29' | 37.5(7) |
| C18' | C5' | C6' | C7' | -137.1(6) | Li' | O6' | C30' | C31' | 40.3(7) |
| C18' | C5' | C12' | C17' | 52.6(8) | Li' | O6' | C29' | C28' | 45.9(7) |
| C18' | C5' | C12' | C13' | -131.2(6) | Li' | O4' | C25' | C24' | 48.8(7) |
| C18' | C23' | C22' | C21' | 0.6(10) | Li' | O4' | C26' | C27' | 39.3(7) |
| C3' | C2' | C4' | F4' | -64.2(7) | Li | O5 | C28 | C29 | -51.8(6) |
| C3' | C2' | C4' | F6' | 175.7(5) | Li | O5 | C27 | C26 | -41.9(7) |
| C3' | C2' | C4' | F5' | 56.9(7) | Li | O4 | C26 | C27 | -35.9(7) |
| C7 | C6 | C11 | C10 | -2.4(10) | Li | O4 | C25 | C24 | -34.5(7) |
| C7 | C6 | C5 | P | 54.2(6) | Li | O6 | C29 | C28 | -33.0(7) |
| C7 | C6 | C5 | C18 | 170.1(5) | Li | O6 | C30 | C31 | -38.1(7) |
| C7 | C6 | C5 | C12 | -67.3(7) | Li | O3 | C31 | C30 | -42.1(7) |
| C7 | C8 | C9 | C10 | 1.0(11) | Li | O3 | C24 | C25 | -49.1(6) |
| C14 | C15 | C16 | C17 | -1.8(10) | C39 | O12 | C38 | C37 | -179.9(9) |
| C3 | C2 | C4 | F5 | -50.7(7) | O3' | C24' | C25' | O4' | -56.5(7) |
| C3 | C2 | C4 | F4 | 73.2(6) | O6' | C30' | C31' | O3' | -53.6(7) |
| C3 | C2 | C4 | F6 | -166.8(5) | O6' | C29' | C28' | O5' | -55.9(7) |
| C6 | C7 | C8 | C9 | -2.6(11) | O4' | C26' | C27' | O5' | -52.7(7) |
| C6 | C11 | C10 | C9 | 0.9(10) | C24' | O3' | C31' | C30' | 163.0(5) |
| C11 | C6 | C5 | P | -132.0(5) | C30' | O6' | C29' | C28' | 169.5(5) |
| C11 | C6 | C5 | C18 | -16.0(8) | C29' | O6' | C30' | C31' | -83.3(7) |
| C11 | C6 | C5 | C12 | 106.5(7) | C25' | O4' | C26' | C27' | -81.6(7) |
| C11 | C10 | C9 | C8 | -0.1(11) | C31' | O3' | C24' | C25' | -88.4(6) |
| C23 | C18 | C5 | P | 59.3(6) | C26' | O4' | C25' | C24' | 170.6(5) |
| C23 | C18 | C5 | C6 | -56.0(7) | C27' | O5' | C28' | C29' | -88.6(7) |
| C23 | C18 | C5 | C12 | -176.8(5) | C28' | O5' | C27' | C26' | 164.0(5) |
| C23 | C18 | C19 | C20 | -1.1(9) | | | | | |

## 12.44 Pentacarbonyl[6,6-bis(trifluoromethyl)-2,2-dimethyl-4-triphenylmethyl-1,3,4,2-dioxaphosphasilinan-κ*P*]tungsten(0) [60.3a]

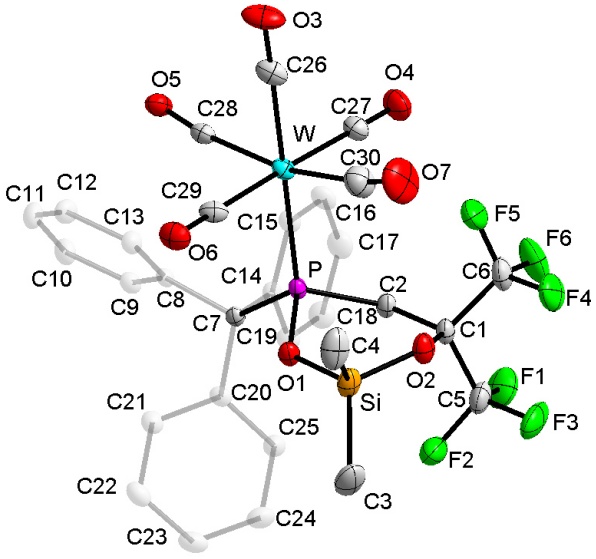

***Table 1:*** Crystal data and structure refinement for **60.3a**.

| | |
|---|---|
| Identification code | GSTR504, PB-35 // GXray4737 |
| Crystal Habitus | clear colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{30}H_{23}F_6O_7PSiW$ |
| Moiety formula | C30 H23 F6 O7 P Si W |
| Formula weight | 852.39 |
| Temperature/K | 123 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 8.9870(3) |
| b/Å | 13.1455(3) |
| c/Å | 13.3173(2) |
| α/° | 87.0836(15) |
| β/° | 82.7857(15) |
| γ/° | 89.8868(13) |
| Volume/Å$^3$ | 1558.80(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.816 |
| μ/mm$^{-1}$ | 3.877 |
| F(000) | 832.0 |
| Crystal size/mm$^3$ | 0.22 × 0.14 × 0.1 |
| Absorption correction | multi-scan |
| Tmin; Tmax | 0.5781; 1.071 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.182 to 55.998° |
| Completeness to theta | 0.998 |
| Index ranges | -11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17 |
| Reflections collected | 20755 |
| Independent reflections | 7500 [$R_{int}$ = 0.0446, $R_{sigma}$ = 0.0371] |
| Data/restraints/parameters | 7500/0/417 |
| Goodness-of-fit on $F^2$ | 1.025 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0249, $wR_2$ = 0.0582 |
| Final R indexes [all data] | $R_1$ = 0.0277, $wR_2$ = 0.0598 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.14/-1.74 |

***Table 2:*** Bond lengths for **60.3a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5376(7) | C1 | C2 | 1.563(4) |
| W | C26 | 2.007(3) | C1 | C5 | 1.545(4) |
| W | C27 | 2.040(3) | C1 | C6 | 1.544(4) |
| W | C28 | 2.044(3) | C7 | C8 | 1.538(3) |
| W | C29 | 2.044(3) | C7 | C14 | 1.535(3) |
| W | C30 | 2.030(3) | C7 | C20 | 1.549(3) |
| P | O1 | 1.623(2) | C8 | C9 | 1.397(4) |
| P | C2 | 1.869(3) | C8 | C13 | 1.392(4) |
| P | C7 | 1.957(3) | C9 | C10 | 1.391(4) |
| Si | O1 | 1.662(2) | C10 | C11 | 1.391(4) |
| Si | O2 | 1.665(2) | C11 | C12 | 1.381(4) |
| Si | C3 | 1.844(4) | C12 | C13 | 1.397(4) |
| Si | C4 | 1.834(4) | C14 | C15 | 1.403(4) |
| F1 | C5 | 1.327(4) | C14 | C19 | 1.397(4) |

| | | | | | |
|---|---|---|---|---|---|
| F2 | C5 | 1.347(4) | C15 | C16 | 1.387(4) |
| F3 | C5 | 1.326(4) | C16 | C17 | 1.392(4) |
| F4 | C6 | 1.326(4) | C17 | C18 | 1.390(4) |
| F5 | C6 | 1.318(4) | C18 | C19 | 1.392(4) |
| F6 | C6 | 1.339(4) | C20 | C21 | 1.398(4) |
| O2 | C1 | 1.410(3) | C20 | C25 | 1.391(4) |
| O3 | C26 | 1.139(4) | C21 | C22 | 1.393(4) |
| O4 | C27 | 1.144(4) | C22 | C23 | 1.387(4) |
| O5 | C28 | 1.144(3) | C23 | C24 | 1.374(4) |
| O6 | C29 | 1.143(4) | C24 | C25 | 1.391(4) |
| O7 | C30 | 1.145(4) | | | |

***Table 3:*** Bond angles for **60.3a**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C26 | W | P | 177.30(8) | F4 | C6 | F6 | 107.2(3) |
| C26 | W | C27 | 88.72(12) | F4 | C6 | C1 | 112.7(3) |
| C26 | W | C28 | 80.73(11) | F5 | C6 | F4 | 107.6(3) |
| C26 | W | C29 | 92.21(11) | F5 | C6 | F6 | 107.3(3) |
| C26 | W | C30 | 85.42(13) | F5 | C6 | C1 | 111.2(2) |
| C27 | W | P | 89.56(8) | F6 | C6 | C1 | 110.6(3) |
| C27 | W | C28 | 91.29(11) | C8 | C7 | P | 107.55(16) |
| C27 | W | C29 | 177.99(11) | C8 | C7 | C20 | 108.3(2) |
| C28 | W | P | 97.23(7) | C14 | C7 | P | 105.68(16) |
| C29 | W | P | 89.58(7) | C14 | C7 | C8 | 111.0(2) |
| C29 | W | C28 | 90.62(11) | C14 | C7 | C20 | 112.1(2) |
| C30 | W | P | 96.66(10) | C20 | C7 | P | 112.17(16) |
| C30 | W | C27 | 89.89(14) | C9 | C8 | C7 | 119.2(2) |
| C30 | W | C28 | 166.07(12) | C13 | C8 | C7 | 122.3(2) |
| C30 | W | C29 | 88.41(13) | C13 | C8 | C9 | 118.3(2) |
| O1 | P | W | 113.69(7) | C10 | C9 | C8 | 121.2(3) |
| O1 | P | C2 | 101.81(11) | C9 | C10 | C11 | 119.8(3) |
| O1 | P | C7 | 101.67(10) | C12 | C11 | C10 | 119.6(3) |
| C2 | P | W | 114.98(9) | C11 | C12 | C13 | 120.6(3) |
| C2 | P | C7 | 101.91(11) | C8 | C13 | C12 | 120.5(3) |
| C7 | P | W | 120.28(7) | C15 | C14 | C7 | 119.7(2) |
| O1 | Si | O2 | 103.66(11) | C19 | C14 | C7 | 122.8(2) |
| O1 | Si | C3 | 109.34(15) | C19 | C14 | C15 | 117.5(2) |
| O1 | Si | C4 | 112.58(13) | C16 | C15 | C14 | 121.4(2) |
| O2 | Si | C3 | 112.45(15) | C15 | C16 | C17 | 120.5(3) |
| O2 | Si | C4 | 107.57(15) | C18 | C17 | C16 | 118.7(3) |
| C4 | Si | C3 | 111.05(19) | C17 | C18 | C19 | 120.8(3) |
| P | O1 | Si | 126.51(12) | C18 | C19 | C14 | 121.0(2) |
| C1 | O2 | Si | 131.04(18) | C21 | C20 | C7 | 120.9(2) |
| O2 | C1 | C2 | 115.7(2) | C25 | C20 | C7 | 122.0(2) |
| O2 | C1 | C5 | 107.1(2) | C25 | C20 | C21 | 117.0(2) |
| O2 | C1 | C6 | 105.0(2) | C22 | C21 | C20 | 121.5(2) |
| C5 | C1 | C2 | 109.3(2) | C23 | C22 | C21 | 120.2(3) |
| C6 | C1 | C2 | 110.8(2) | C24 | C23 | C22 | 119.1(3) |
| C6 | C1 | C5 | 108.8(2) | C23 | C24 | C25 | 120.6(3) |
| C1 | C2 | P | 117.63(19) | C24 | C25 | C20 | 121.7(3) |
| F1 | C5 | F2 | 106.6(3) | O3 | C26 | W | 177.0(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| F1 | C5 | C1 | 112.2(3) | O4 | C27 | W | 178.6(3) |
| F2 | C5 | C1 | 110.1(2) | O5 | C28 | W | 170.2(2) |
| F3 | C5 | F1 | 108.0(3) | O6 | C29 | W | 179.3(3) |
| F3 | C5 | F2 | 106.4(3) | O7 | C30 | W | 171.6(3) |
| F3 | C5 | C1 | 113.2(3) | | | | |

***Table 4:*** Torsion angles for **60.3a**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | Si | -77.94(15) | C6 | C1 | C5 | F3 | 54.7(4) |
| W | P | C2 | C1 | 82.4(2) | C7 | P | O1 | Si | 151.31(14) |
| P | C7 | C8 | C9 | -53.4(3) | C7 | P | C2 | C1 | -145.8(2) |
| P | C7 | C8 | C13 | 132.6(2) | C7 | C8 | C9 | C10 | -176.4(2) |
| P | C7 | C14 | C15 | -57.2(3) | C7 | C8 | C13 | C12 | 176.0(2) |
| P | C7 | C14 | C19 | 123.5(2) | C7 | C14 | C15 | C16 | 179.3(2) |
| P | C7 | C20 | C21 | 133.9(2) | C7 | C14 | C19 | C18 | -179.8(2) |
| P | C7 | C20 | C25 | -50.2(3) | C7 | C20 | C21 | C22 | 177.7(2) |
| Si | O2 | C1 | C2 | 33.4(3) | C7 | C20 | C25 | C24 | -177.8(3) |
| Si | O2 | C1 | C5 | -88.7(3) | C8 | C7 | C14 | C15 | 59.1(3) |
| Si | O2 | C1 | C6 | 155.8(2) | C8 | C7 | C14 | C19 | -120.1(3) |
| O1 | P | C2 | C1 | -41.0(2) | C8 | C7 | C20 | C21 | 15.3(3) |
| O1 | Si | O2 | C1 | -30.4(3) | C8 | C7 | C20 | C25 | -168.7(2) |
| O2 | Si | O1 | P | -18.16(18) | C8 | C9 | C10 | C11 | 0.6(4) |
| O2 | C1 | C2 | P | 8.2(3) | C9 | C8 | C13 | C12 | 1.9(4) |
| O2 | C1 | C5 | F1 | 179.3(2) | C9 | C10 | C11 | C12 | 1.2(4) |
| O2 | C1 | C5 | F2 | 60.7(3) | C10 | C11 | C12 | C13 | -1.4(4) |
| O2 | C1 | C5 | F3 | -58.2(3) | C11 | C12 | C13 | C8 | -0.2(4) |
| O2 | C1 | C6 | F4 | 51.4(3) | C13 | C8 | C9 | C10 | -2.1(4) |
| O2 | C1 | C6 | F5 | -69.6(3) | C14 | C7 | C8 | C9 | -168.6(2) |
| O2 | C1 | C6 | F6 | 171.4(2) | C14 | C7 | C8 | C13 | 17.4(3) |
| C2 | P | O1 | Si | 46.32(17) | C14 | C7 | C20 | C21 | -107.4(3) |
| C2 | C1 | C5 | F1 | 53.3(3) | C14 | C7 | C20 | C25 | 68.5(3) |
| C2 | C1 | C5 | F2 | -65.2(3) | C14 | C15 | C16 | C17 | 1.0(4) |
| C2 | C1 | C5 | F3 | 175.8(3) | C15 | C14 | C19 | C18 | 1.0(4) |
| C2 | C1 | C6 | F4 | 176.9(2) | C15 | C16 | C17 | C18 | -0.1(4) |
| C2 | C1 | C6 | F5 | 56.0(3) | C16 | C17 | C18 | C19 | -0.4(4) |
| C2 | C1 | C6 | F6 | -63.1(3) | C17 | C18 | C19 | C14 | -0.1(4) |
| C3 | Si | O1 | P | -138.28(18) | C19 | C14 | C15 | C16 | -1.4(4) |
| C3 | Si | O2 | C1 | 87.6(3) | C20 | C7 | C8 | C9 | 68.0(3) |
| C4 | Si | O1 | P | 97.8(2) | C20 | C7 | C8 | C13 | -106.0(3) |
| C4 | Si | O2 | C1 | -149.9(2) | C20 | C7 | C14 | C15 | -179.7(2) |
| C5 | C1 | C2 | P | 129.1(2) | C20 | C7 | C14 | C19 | 1.1(3) |
| C5 | C1 | C6 | F4 | -62.9(3) | C20 | C21 | C22 | C23 | -0.1(4) |
| C5 | C1 | C6 | F5 | 176.1(3) | C21 | C20 | C25 | C24 | -1.7(4) |
| C5 | C1 | C6 | F6 | 57.0(3) | C21 | C22 | C23 | C24 | -1.2(5) |
| C6 | C1 | C2 | P | -111.1(2) | C22 | C23 | C24 | C25 | 1.0(5) |
| C6 | C1 | C5 | F1 | -67.8(3) | C23 | C24 | C25 | C20 | 0.5(5) |
| C6 | C1 | C5 | F2 | 173.7(3) | C25 | C20 | C21 | C22 | 1.6(4) |

# 12.45 Pentacarbonyl[6,6-bis(trifluoromethyl)-2,2-dimethyl-4-triphenylmethyl-1,3,4,2-dioxaphosphagerminan-κ*P*]tungsten(0) [60.3b]

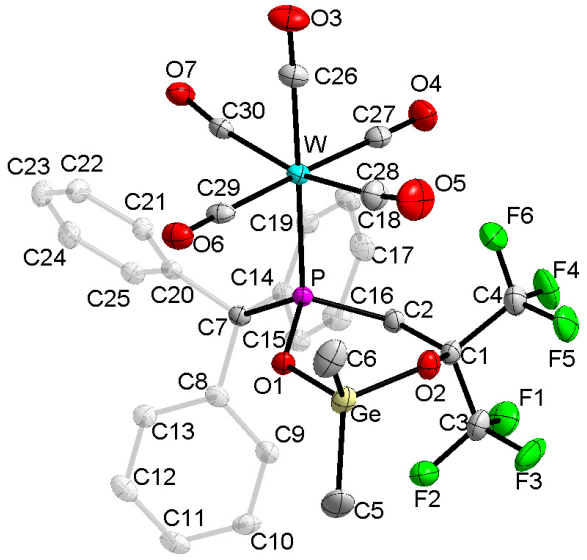


***Table 1:*** Crystal data and structure refinement for **60.3b**.

| | |
|---|---|
| Identification code | GSTR507, PB-47 // GXray4813 |
| Crystal Habitus | clear colourless plate |
| Device Type | Nonius KappaCCD |
| Empirical formula | $C_{30}H_{23}F_6GeO_7PW$ |
| Moiety formula | C30 H23 F6 Ge O7 P W |
| Formula weight | 896.89 |
| Temperature/K | 123(2) |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a/Å | 9.0079(2) |
| b/Å | 13.1369(3) |
| c/Å | 13.2698(2) |
| α/° | 92.8970(10) |
| β/° | 97.6730(10) |
| γ/° | 90.1710(10) |
| Volume/Å$^3$ | 1554.17(5) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.917 |
| μ/mm$^{-1}$ | 4.798 |
| F(000) | 868.0 |
| Crystal size/mm$^3$ | 0.3 × 0.22 × 0.04 |
| Absorption correction | multi-scan |
| Tmin; Tmax | 0.3452; 0.7795 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.852 to 55.996° |
| Completeness to theta | 0.999 |
| Index ranges | -11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17 |
| Reflections collected | 36507 |
| Independent reflections | 7498 [$R_{int}$ = 0.0689, $R_{sigma}$ = 0.0401] |
| Data/restraints/parameters | 7498/0/417 |
| Goodness-of-fit on F$^2$ | 1.059 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0263, $wR_2$ = 0.0611 |

| | |
|---|---|
| Final R indexes [all data] | $R_1$ = 0.0304, $wR_2$ = 0.0628 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.24/-1.62 |

***Table 2:*** Bond lengths for **60.3b**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.5439(7) | C1 | C2 | 1.561(4) |
| W | C26 | 1.998(3) | C1 | C3 | 1.549(4) |
| W | C27 | 2.040(3) | C1 | C4 | 1.541(4) |
| W | C28 | 2.032(3) | C7 | C8 | 1.547(4) |
| W | C29 | 2.037(3) | C7 | C14 | 1.542(4) |
| W | C30 | 2.048(3) | C7 | C20 | 1.532(4) |
| Ge | O1 | 1.803(2) | C8 | C9 | 1.394(4) |
| Ge | O2 | 1.804(2) | C8 | C13 | 1.401(4) |
| Ge | C5 | 1.926(4) | C9 | C10 | 1.387(4) |
| Ge | C6 | 1.911(4) | C10 | C11 | 1.377(5) |
| P | O1 | 1.613(2) | C11 | C12 | 1.379(5) |
| P | C2 | 1.875(3) | C12 | C13 | 1.397(4) |
| P | C7 | 1.959(3) | C14 | C15 | 1.398(4) |
| F1 | C3 | 1.333(4) | C14 | C19 | 1.398(4) |
| F2 | C3 | 1.346(4) | C15 | C16 | 1.392(4) |
| F3 | C3 | 1.326(4) | C16 | C17 | 1.379(4) |
| F4 | C4 | 1.342(4) | C17 | C18 | 1.386(4) |
| F5 | C4 | 1.323(4) | C18 | C19 | 1.386(4) |
| F6 | C4 | 1.327(4) | C20 | C21 | 1.393(4) |
| O2 | C1 | 1.401(4) | C20 | C25 | 1.403(4) |
| O3 | C26 | 1.146(4) | C21 | C22 | 1.396(4) |
| O4 | C27 | 1.140(4) | C22 | C23 | 1.384(5) |
| O5 | C28 | 1.141(4) | C23 | C24 | 1.387(5) |
| O6 | C29 | 1.148(4) | C24 | C25 | 1.386(4) |
| O7 | C30 | 1.139(4) | | | |

***Table 3:*** Bond angles for **60.3b**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C26 | W | P | 177.27(9) | F4 | C4 | C1 | 111.1(3) |
| C26 | W | C27 | 88.69(12) | F5 | C4 | F4 | 107.2(3) |
| C26 | W | C28 | 85.72(14) | F5 | C4 | F6 | 107.6(3) |
| C26 | W | C29 | 92.35(12) | F5 | C4 | C1 | 113.1(3) |
| C26 | W | C30 | 80.43(12) | F6 | C4 | F4 | 107.0(3) |
| C27 | W | P | 90.12(8) | F6 | C4 | C1 | 110.6(3) |
| C27 | W | C30 | 91.00(12) | C8 | C7 | P | 111.48(19) |
| C28 | W | P | 96.72(10) | C14 | C7 | P | 105.75(18) |
| C28 | W | C27 | 88.84(14) | C14 | C7 | C8 | 112.2(2) |
| C28 | W | C29 | 90.00(14) | C20 | C7 | P | 107.91(18) |
| C28 | W | C30 | 166.15(13) | C20 | C7 | C8 | 108.4(2) |
| C29 | W | P | 88.89(8) | C20 | C7 | C14 | 111.0(2) |
| C29 | W | C27 | 178.38(12) | C9 | C8 | C7 | 122.3(3) |
| C29 | W | C30 | 90.40(12) | C9 | C8 | C13 | 116.7(3) |
| C30 | W | P | 97.13(8) | C13 | C8 | C7 | 120.9(3) |
| O1 | Ge | O2 | 100.62(9) | C10 | C9 | C8 | 121.9(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 | Ge | C5 | 107.66(15) | C11 | C10 | C9 | 120.5(3) |
| O1 | Ge | C6 | 112.88(13) | C10 | C11 | C12 | 119.2(3) |
| O2 | Ge | C5 | 113.23(14) | C11 | C12 | C13 | 120.5(3) |
| O2 | Ge | C6 | 105.46(14) | C12 | C13 | C8 | 121.3(3) |
| C6 | Ge | C5 | 116.01(18) | C15 | C14 | C7 | 122.7(2) |
| O1 | P | W | 113.93(8) | C19 | C14 | C7 | 119.7(2) |
| O1 | P | C2 | 103.45(12) | C19 | C14 | C15 | 117.6(3) |
| O1 | P | C7 | 101.05(11) | C16 | C15 | C14 | 120.8(3) |
| C2 | P | W | 114.23(9) | C17 | C16 | C15 | 120.5(3) |
| C2 | P | C7 | 102.04(12) | C16 | C17 | C18 | 119.6(3) |
| C7 | P | W | 119.96(9) | C17 | C18 | C19 | 119.9(3) |
| P | O1 | Ge | 124.16(12) | C18 | C19 | C14 | 121.6(3) |
| C1 | O2 | Ge | 128.42(18) | C21 | C20 | C7 | 122.5(2) |
| O2 | C1 | C2 | 116.8(2) | C21 | C20 | C25 | 118.2(3) |
| O2 | C1 | C3 | 107.9(2) | C25 | C20 | C7 | 119.1(2) |
| O2 | C1 | C4 | 104.6(2) | C20 | C21 | C22 | 120.7(3) |
| C3 | C1 | C2 | 108.6(3) | C23 | C22 | C21 | 120.2(3) |
| C4 | C1 | C2 | 110.0(2) | C22 | C23 | C24 | 119.7(3) |
| C4 | C1 | C3 | 108.7(3) | C25 | C24 | C23 | 120.1(3) |
| C1 | C2 | P | 118.4(2) | C24 | C25 | C20 | 121.0(3) |
| F1 | C3 | F2 | 106.4(3) | O3 | C26 | W | 177.0(3) |
| F1 | C3 | C1 | 112.9(3) | O4 | C27 | W | 179.1(3) |
| F2 | C3 | C1 | 110.0(3) | O5 | C28 | W | 171.9(3) |
| F3 | C3 | F1 | 107.9(3) | O6 | C29 | W | 178.9(3) |
| F3 | C3 | F2 | 106.4(3) | O7 | C30 | W | 170.0(2) |
| F3 | C3 | C1 | 112.9(3) | | | | |

***Table 4:*** Torsion angles for **60.3b**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| W | P | O1 | Ge | 75.92(14) | C6 | Ge | O2 | C1 | 151.5(2) |
| W | P | C2 | C1 | -81.2(2) | C7 | P | O1 | Ge | -154.05(14) |
| Ge | O2 | C1 | C2 | -40.0(3) | C7 | P | C2 | C1 | 147.8(2) |
| Ge | O2 | C1 | C3 | 82.6(3) | C7 | C8 | C9 | C10 | 178.4(3) |
| Ge | O2 | C1 | C4 | -161.8(2) | C7 | C8 | C13 | C12 | -178.4(3) |
| P | C7 | C8 | C9 | 51.1(3) | C7 | C14 | C15 | C16 | 179.8(3) |
| P | C7 | C8 | C13 | -132.0(2) | C7 | C14 | C19 | C18 | -178.8(3) |
| P | C7 | C14 | C15 | -122.6(3) | C7 | C20 | C21 | C22 | -176.5(2) |
| P | C7 | C14 | C19 | 57.8(3) | C7 | C20 | C25 | C24 | 177.2(2) |
| P | C7 | C20 | C21 | -132.8(2) | C8 | C7 | C14 | C15 | -0.9(4) |
| P | C7 | C20 | C25 | 52.4(3) | C8 | C7 | C14 | C19 | 179.5(3) |
| O1 | Ge | O2 | C1 | 34.0(3) | C8 | C7 | C20 | C21 | 106.3(3) |
| O1 | P | C2 | C1 | 43.2(2) | C8 | C7 | C20 | C25 | -68.5(3) |
| O2 | Ge | O1 | P | 18.41(16) | C8 | C9 | C10 | C11 | -0.2(5) |
| O2 | C1 | C2 | P | -3.8(3) | C9 | C8 | C13 | C12 | -1.3(4) |
| O2 | C1 | C3 | F1 | 178.3(2) | C9 | C10 | C11 | C12 | -1.2(5) |
| O2 | C1 | C3 | F2 | -63.1(3) | C10 | C11 | C12 | C13 | 1.3(5) |
| O2 | C1 | C3 | F3 | 55.6(3) | C11 | C12 | C13 | C8 | 0.0(5) |
| O2 | C1 | C4 | F4 | -174.2(3) | C13 | C8 | C9 | C10 | 1.4(4) |
| O2 | C1 | C4 | F5 | -53.6(4) | C14 | C7 | C8 | C9 | -67.3(3) |
| O2 | C1 | C4 | F6 | 67.2(3) | C14 | C7 | C8 | C13 | 109.6(3) |
| C2 | P | O1 | Ge | -48.67(17) | C14 | C7 | C20 | C21 | -17.3(3) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C2 | C1 | C3 | F1 | -54.2(3) | C14 | C7 | C20 | C25 | 167.8(2) |
| C2 | C1 | C3 | F2 | 64.4(3) | C14 | C15 | C16 | C17 | -0.5(5) |
| C2 | C1 | C3 | F3 | -176.9(3) | C15 | C14 | C19 | C18 | 1.5(4) |
| C2 | C1 | C4 | F4 | 59.7(3) | C15 | C16 | C17 | C18 | 0.7(5) |
| C2 | C1 | C4 | F5 | -179.7(3) | C16 | C17 | C18 | C19 | 0.2(5) |
| C2 | C1 | C4 | F6 | -59.0(3) | C17 | C18 | C19 | C14 | -1.3(5) |
| C3 | C1 | C2 | P | -126.0(2) | C19 | C14 | C15 | C16 | -0.6(5) |
| C3 | C1 | C4 | F4 | -59.1(4) | C20 | C7 | C8 | C9 | 169.7(3) |
| C3 | C1 | C4 | F5 | 61.5(4) | C20 | C7 | C8 | C13 | -13.3(3) |
| C3 | C1 | C4 | F6 | -177.8(3) | C20 | C7 | C14 | C15 | 120.6(3) |
| C4 | C1 | C2 | P | 115.1(2) | C20 | C7 | C14 | C19 | -59.0(3) |
| C4 | C1 | C3 | F1 | 65.4(4) | C20 | C21 | C22 | C23 | 0.1(4) |
| C4 | C1 | C3 | F2 | -176.0(3) | C21 | C20 | C25 | C24 | 2.1(4) |
| C4 | C1 | C3 | F3 | -57.3(4) | C21 | C22 | C23 | C24 | 0.9(4) |
| C5 | Ge | O1 | P | 137.15(18) | C22 | C23 | C24 | C25 | -0.4(4) |
| C5 | Ge | O2 | C1 | -80.6(3) | C23 | C24 | C25 | C20 | -1.1(4) |
| C6 | Ge | O1 | P | -93.51(19) | C25 | C20 | C21 | C22 | -1.6(4) |

## 12.46 Tetrabutylammonium pentacarbonyl[(2-hydroxyethyl)methylphosphanoxido-κ*P*]tungsten(0) [61]

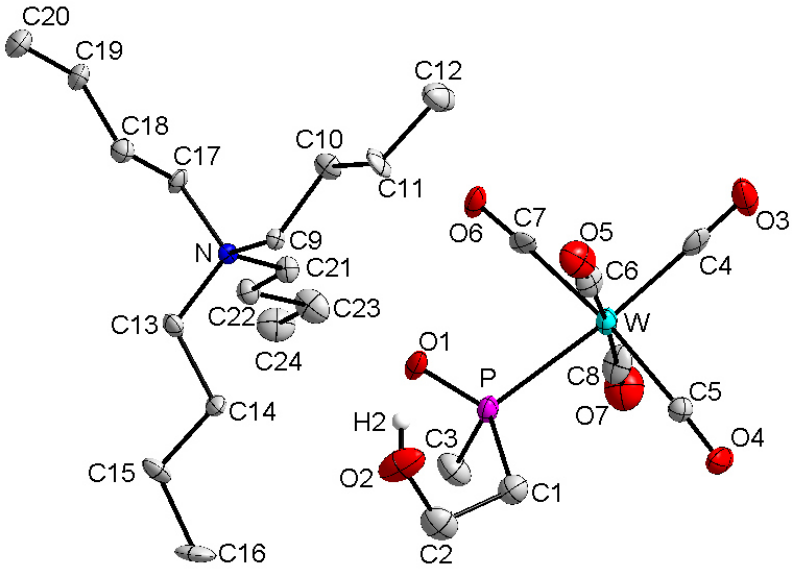


***Table 1:*** Crystal data and structure refinement for **63**.

| | |
|---|---|
| Identification code | GSTR545, AKY-610 // GXrayneu |
| Crystal Habitus | clear colourless block |
| Device Type | Bruker X8-KappaApexII |
| Empirical formula | $C_{24}H_{44}NO_7PW$ |
| Moiety formula | C8 H8 O7 P W, C16 H36 N |
| Formula weight | 673.42 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 11.2279(8) |
| b/Å | 13.5773(8) |
| c/Å | 20.1880(14) |

| | |
|---|---|
| α/° | 90 |
| β/° | 105.457(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 2966.2(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.508 |
| μ/mm$^{-1}$ | 3.986 |
| F(000) | 1360.0 |
| Crystal size/mm$^3$ | 0.2 × 0.14 × 0.1 |
| Absorption correction | empirical |
| Tmin; Tmax | 0.227682; 0.746070 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.788 to 50.052° |
| Completeness to theta | 0.982 |
| Index ranges | -14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26 |
| Reflections collected | 5140 |
| Independent reflections | 5140 [$R_{int}$ = 0.0929, $R_{sigma}$ = 0.0564] |
| Data/restraints/parameters | 5140/30/313 |
| Goodness-of-fit on F$^2$ | 1.070 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0730, $wR_2$ = 0.1635 |
| Final R indexes [all data] | $R_1$ = 0.0944, $wR_2$ = 0.1720 |
| Largest diff. peak/hole / e Å$^{-3}$ | 10.14/-1.50 |

***Table 2:*** Bond lengths for **61**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| W | P | 2.529(3) | N | C9 | 1.533(12) |
| W | C4 | 2.025(13) | N | C13 | 1.523(13) |
| W | C5 | 2.030(12) | N | C17 | 1.521(13) |
| W | C6 | 2.058(14) | N | C21 | 1.528(13) |
| W | C7 | 2.047(12) | C9 | C10 | 1.501(15) |
| W | C8 | 2.027(12) | C10 | C11 | 1.551(15) |
| P | O1 | 1.526(8) | C11 | C12 | 1.489(16) |
| P | C1 | 1.858(13) | C13 | C14 | 1.520(15) |
| P | C3 | 1.843(13) | C14 | C15 | 1.518(15) |
| O2 | C2 | 1.399(16) | C15 | C16 | 1.538(17) |
| O3 | C4 | 1.121(15) | C17 | C18 | 1.507(15) |
| O4 | C5 | 1.144(14) | C18 | C19 | 1.547(16) |
| O5 | C6 | 1.136(15) | C19 | C20 | 1.516(17) |
| O6 | C7 | 1.137(14) | C21 | C22 | 1.520(15) |
| O7 | C8 | 1.135(15) | C22 | C23 | 1.502(16) |
| C1 | C2 | 1.532(18) | C23 | C24 | 1.528(17) |

***Table 3:*** Bond angles for **61**.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C4 | W | P | 173.3(4) | O3 | C4 | W | 178.5(12) |
| C4 | W | C5 | 93.8(4) | O4 | C5 | W | 177.5(10) |
| C4 | W | C6 | 90.9(5) | O5 | C6 | W | 178.4(11) |
| C4 | W | C7 | 92.3(4) | O6 | C7 | W | 176.8(11) |
| C4 | W | C8 | 92.5(5) | O7 | C8 | W | 178.6(12) |
| C5 | W | P | 89.4(3) | C13 | N | C9 | 108.2(7) |
| C5 | W | C6 | 91.6(5) | C13 | N | C21 | 111.3(8) |
| C5 | W | C7 | 173.5(5) | C17 | N | C9 | 111.1(8) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C6 | W | P | 83.1(4) | C17 | N | C13 | 109.6(8) |
| C7 | W | P | 84.8(3) | C17 | N | C21 | 108.8(8) |
| C7 | W | C6 | 90.8(5) | C21 | N | C9 | 107.9(7) |
| C8 | W | P | 93.4(4) | C10 | C9 | N | 115.4(8) |
| C8 | W | C5 | 89.0(5) | C9 | C10 | C11 | 110.2(9) |
| C8 | W | C6 | 176.5(5) | C12 | C11 | C10 | 111.1(10) |
| C8 | W | C7 | 88.3(5) | C14 | C13 | N | 115.1(8) |
| O1 | P | W | 114.9(3) | C15 | C14 | C13 | 110.0(9) |
| O1 | P | C1 | 106.2(5) | C14 | C15 | C16 | 110.8(10) |
| O1 | P | C3 | 108.4(6) | C18 | C17 | N | 116.2(9) |
| C1 | P | W | 112.4(4) | C17 | C18 | C19 | 107.0(9) |
| C3 | P | W | 113.1(4) | C20 | C19 | C18 | 111.2(10) |
| C3 | P | C1 | 100.6(6) | C22 | C21 | N | 114.0(9) |
| C2 | C1 | P | 112.5(9) | C23 | C22 | C21 | 109.4(9) |
| O2 | C2 | C1 | 111.0(11) | C22 | C23 | C24 | 111.4(11) |