Studies on synthesis and reactions of anionic *P*-NR_2/*P*-OR organophosphane complexes: Searching for the boundary between phosphanide and phosphinidenoid complexes

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Tagungsbeiträge

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- L. Duan, R. Streubel, 5th European Workshop on Phosphorus Chemistry, Regensburg/Germany, 10. March **2008**; (Participant).

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- V. Nesterov, L. Duan, T. Heurich, R. Streubel, 8th European Workshop on Phosphorus Chemistry, Muenster/Germany, March 28–29, **2011**; *"Acylphosphane complex-always stable?"*, (Poster)

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Life is like riding a bicycle. To keep your balance you must keep on moving.

--Albert Einstein

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Chapter 1. Introduction

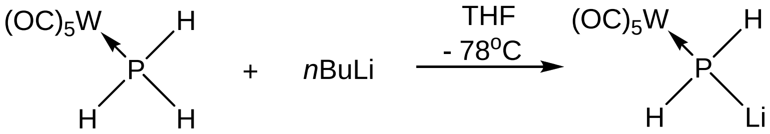
I. Introduction to phosphanides and complexes thereof

Metal phosphanides **I** and their complexes **II** (Figure 1) are classes of compounds in which, e.g., an alkali metal is formally bound to the phosphorus atom. They are considered as key transfer agents in both main group and transition metal chemistry [1] and valuable synthons for redox reactions as well as for the formation of multiple bonds between phosphorus and carbon or metal atoms. These species are generally represented by the formulae R_2PM or R(H)PM;[2] the structures of alkali metal phosphanides are mainly determined by the metal donor base interactions and/or to coordinating solvents.[3]

I **II**

Figure 1. Metal phosphanides **I** and complexes **II**. R, R' = organic substituents; M = alkali metals (**Li**, Na, K); ML_n = transition metal fragment.

For example, lithium phosphanides and their complexes can be generally prepared by lithiation of primary or secondary phosphanes (or their complexes) at low temperature.[4] In 1987, Mathey et al. devised a new synthetic route to the phosphanide tungsten complex **2**[5] (Scheme 1) by lithiation of (phosphane)pentacarbonyltungsten complex **1** using *n*-BuLi at –78 °C, which was different from the existing synthetic pathways established before.[6]

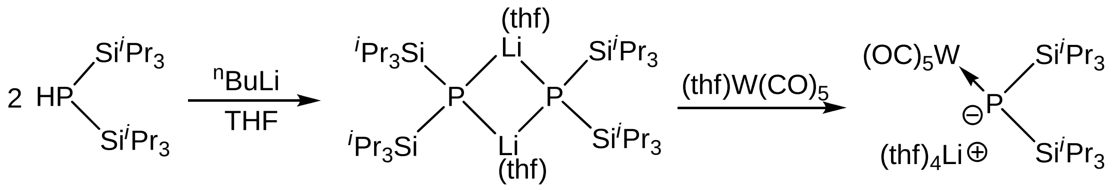


1 **2**

Scheme 1. Formation of the lithium phosphanide complex **2**.

The lithium *phosphanide* tungsten complex **2***, which was used in situ,* was identified by ^{31}P NMR spectroscopy as a triplet, indicating two protons bonded to the phosphorus atom. Furthermore, the δ value of complex **2** showed a chemical shift at high field (–273 ppm, $^{1}J_{(W,P)}$ = 68 Hz), with a $\Delta\delta$ of about 90 ppm *upfield* from the precursor complex **1** (δ = –183 ppm).

Another synthetic method for phosphanide complexes is the complexation of a non-ligated phosphanide as shown in scheme 2. Deprotonation of compound **3**[7] at low temperature gave the lithiated dimer **4** which was reacted with a pentacarbonyltungsten(thf)[8] solution, the phosphanide complex **5** was obtained and characterized[9] (Westerhausen, 2005). The ^{31}P NMR spectra showed a very high field shifted signal of phosphanide complex **5** (δ = –409.2 ppm), ca. 123 ppm *upfield* from the starting material **3** (δ = –286.2 ppm), and ca. 35 ppm *upfield* from the corresponding phosphanide **4** (δ = –374.7 ppm). Altogether these ^{31}P NMR data revealed that the increasing shielding (δ_3–>δ_4–>δ_5) correlates with the emergence of negative charge at the phosphorus atom. Or in other words, increasing negative charge at the phosphorus *usually* leads to an upfield shifted-resonance in the NMR spectrum.

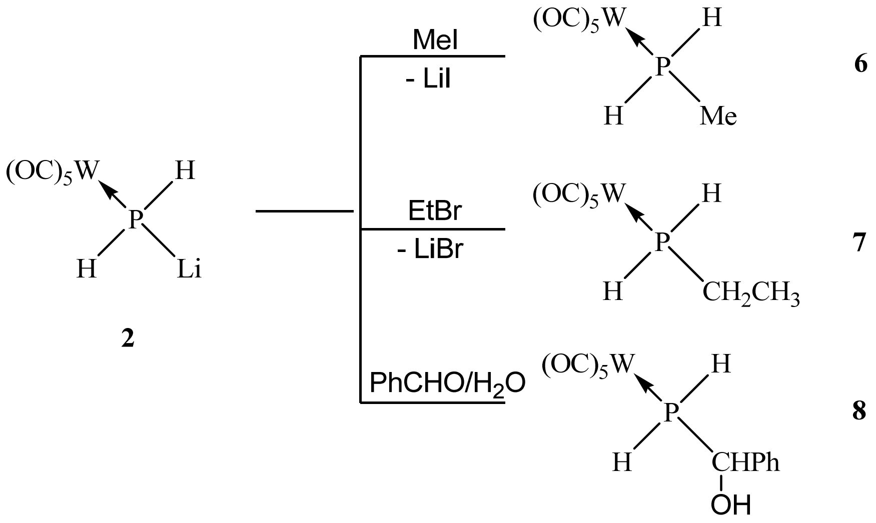


3 **4** **5**

Scheme 2. Formation of phosphanide complex **5** via complexation.[9]

The single-crystal X-ray structure of **4** revealed a P–Li distance (253.3(6) pm) that lies within the range usually observed for lithium phosphanides.[10] Because of the sterically demanding triisopropylsilyl group, a decreased coordination and a planar environment for lithium resulted. Whereas complexes **2** and **4** showed covalently bonded lithium, the structure of the phosphanide complex **5** was confirmed to be an ion pair complex. The P–W bond length (266.6 pm) in **5** is longer than those of other comparable phosphanide complexes[11] (ca. 250 pm), which probably is due to the steric repulsion between the two organometallic fragments.

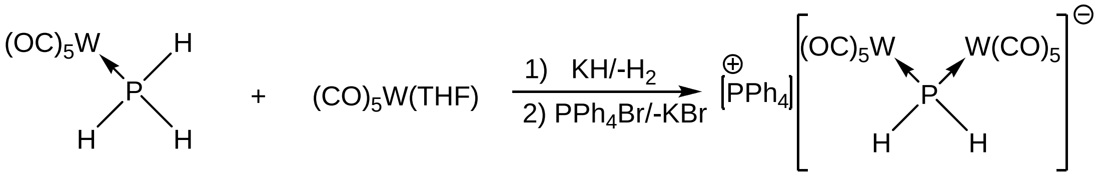
In general, phosphanides and their complexes are known for their nucleophilic reactivity (Scheme 3) and, for example, complex **2** reacts with electrophiles such as MeI, EtBr etc. to give phosphane complexes **6** and **7**.[5] Whereas it didn't react with benzophenone or acetone but with benzaldehyde to give the final product **8** (δ = –59.6 ppm, $^1J_{(W,P)}$ = 220 Hz, $^1J_{(P,H)}$ = 333.5 Hz). The latter nicely illustrates the relative low nucleophilicity of complex **2**.



Scheme 3. Reactions of complex **2** with MeI, EtBr and PhCHO.[4]

In 2004, Scheer reported a surprising phosphanide complex,[12] in which two hydrogen and two pentacarbonyltungsten moieties were attached to the same phosphorus centre, which was the parent compound of the class of complexes having the formular $[(LnM)_2PR_2]^-$ (R = H).[13] The complex was obtained by reacting (phosphane)pentacarbonyltungsten **1** and potassium hydride in the presence of $(CO)_5W(THF)$; the phosphanide complex **9** (Scheme 4) could be isolated after cation exchange using PPh_4Br using a mixture of methylenechloride and toluene as solvent.

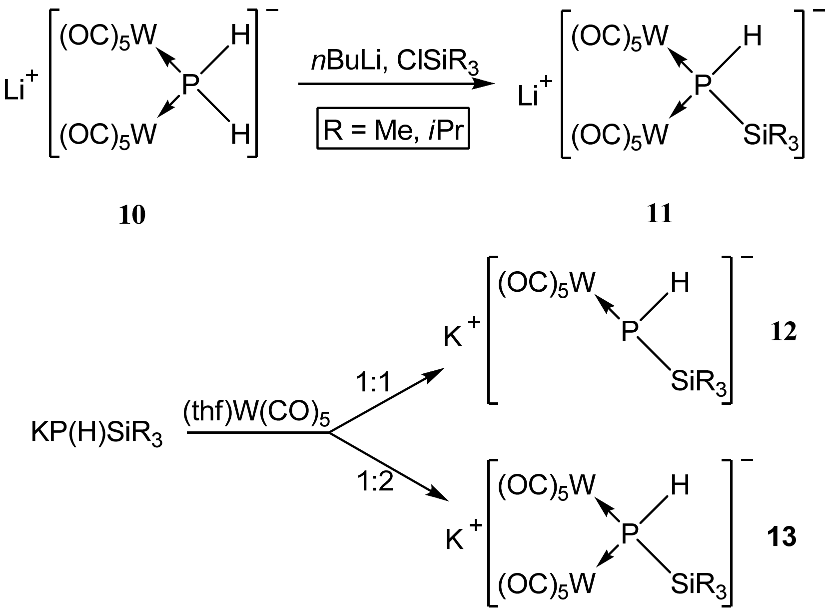
The ^{31}P NMR spectrum of phosphanide complex **9** showed a triplet at –267.7 ppm, accompanyed by a tungsten-phosphorus coupling constant $^{1}J_{(W,P)}$ = 146 Hz, which is larger than other coupling constants of phosphanide complexes such as **2** or **5**. This may result from the presence of the second pentacarbonyltungsten moiety acting as electron-withdrawing group that is attached to phosphorus thus leading to a higher coordination number of the phosphorus centre. Consequently this results in an upfield shift of the ^{31}P NMR resonance, a typical trend that is known for a wide range of different classes of compounds.[14] The single-crystal X-ray diffraction analysis confirmed this structure which showed a large W–P–W bond angle (126.79(7) °) that illustrates the low steric demand of the hydrogen atoms bonded to the phosphorus atom.



1 **9**

Scheme 4. Synthesis of the phosphanide complex **9** via subsequent cation exchange.[12]

In 2005, Westerhausen et al. described a series of mono/bis-pentacarbonyl tungsten phosphanide complexes with sterically demanding substituents at phosphorus atom[15] (Scheme 5) thus showing that derivatisation reaction of dinuclear complexes is possible, e.g. complex **11**.

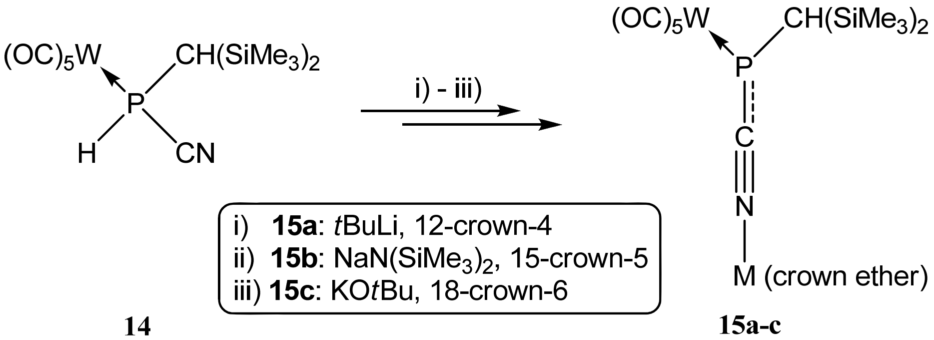


10 **11** **12** **13**

Scheme 5. Preparation of series of phosphanide complexes **11–13**. R = ^{i}Pr, ^{t}Bu.

All ^{31}P NMR signals of complexes **9–13** appeared at *high field* (**9** δ = –267.7 ppm, $^{1}J_{(W,P)}$ = 146.0 Hz; **10** δ = –266.7 ppm, $^{1}J_{(W,P)}$ = 146.5 Hz; **11** $^{1}J_{(W,P)}$ = 138.3 Hz (R = Me) and 140.9 Hz (R = *i*Pr); **12** $^{1}J_{(W,P)}$ = 77.0 Hz (R = *i*Pr) and 85.7 Hz (R = *t*Bu); **13** $^{1}J_{(W,P)}$ = 140.9 Hz (R = *i*Pr) and 141.9 Hz (R = *t*Bu) and accompanied by a ^{183}W satellites.[16,17] Comparison of ^{31}P NMR data of complexes **9** and **10** thus revealed that the cation does not affect the ^{31}P chemical shift and coupling constants if the situation is correctly described as solvent separated ion pair in solution. Bis(pentacarbonyltungsten) phosphanide complexes **11** and **13**, showed larger tungsten, phosphorus coupling constants than mono(tungstenpentacarbonyl) phosphanide complex **12**. It has been found that the coupling constant of $^{1}J_{(W,P)}$ is somehow dependent on the coordination numbers of phosphorus atom.[18]

In 2007, Streubel et al. reported the synthesis and reactions of an unusual phosphanide complex[19] that revealed an unexpected structural motif in the solid state, in which the metal cation is coordinated to the nitrogen atom but not to the phosphorus centre. Complexes **15a–c** were synthesized by addition of different bases to solutions of complex **14**[20] at –78 °C in the presence of stoichiometric amounts of crown ether as shown in scheme 6.



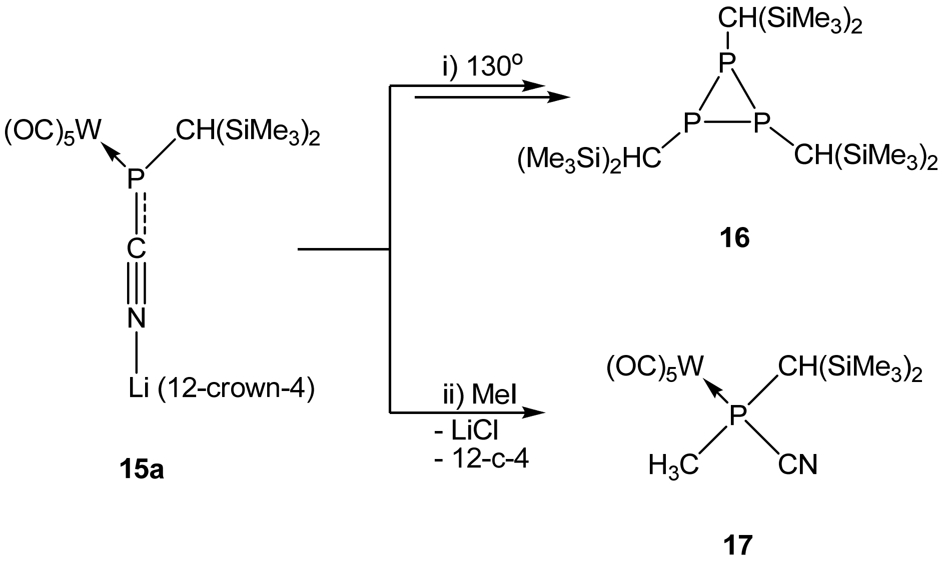
14 **15a-c**

Scheme 6. Synthesis of complexes **15a–c** via metalation with different bases using corresponding crown ethers as co-ligands.[19]

The $^{31}P\{^1H\}$ NMR spectra of complexes **15a–c** displayed resonance signals in the high field range at about –150 to –153 ppm, thus revealing comparatively strongly shielded phosphorus nuclei. Furthermore the relatively small tungsten-phosphorus coupling constants ($^1J_{(W,P)}$ = 100.4 Hz (**15a**), 99.2 Hz (**15b**, **15c**) somehow provide indirect evidence that the electron densities at the phosphorus centre of complexes **15a–c** were largely enhanced, therefore leading to a decrease in the coupling constants (see examples and discussion beforehand).[cf.12] This was further supported by structural arguments obtained from the single-crystal X-ray structure of **15a** that showed a strongly pyramidalized phosphorus (see also below). DFT calculations showed that the removal of 12-crown-4 from complex **15a** resulted in a *downfield* shift of the ^{31}P NMR signal.

The single-crystal X-ray diffraction analysis established the monomeric structure of complex **15a**, which features a trigonal pyramidal geometry at the phosphorus atom (sum of bond angles at P: 311.5°) and a quasi-linear C–N–Li unit (160.4(2)°). Here, the authors suggested that complex **15a** represents a phosphinidenoid-like phosphanide complex rather than a 1-aza-3-phospha-3-allenide complex.[21] The description was also supported by the elongated P–C (C from CN moiety) bond distance and the short C–N distance.

The reactivity of complex **15a** was also investigated (Scheme 7), whereby reactions in the molten state of complex **15a** yielded the cyclotriphosphane derivative **16**[22] as the major phosphorus-containing product; here, a terminal phosphinidene complex might have been transiently formed that trimerized to give the compound **16**. Treatment of complex **15a** with electrophiles, such as MeI and CF_3SO_3Me, led to the *P*-methyl-substituted phosphane complex **17**, which indicated that the nucleophilicity of the phosphanide complex resides mainly at phosphorus.



Scheme 7. Reaction of phosphanide complex **15a**: thermal reaction (i) and with MeI as electrophile (ii).[19]

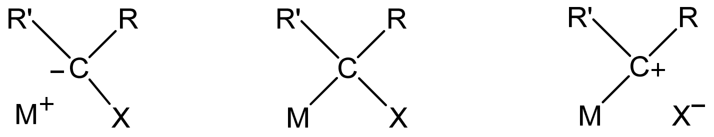
II. Introduction to carbenoids and silylenoids

In order to provide a larger background picture a short introduction into the chemistry of carbenoids and silylenoids will be given hereafter. Carbenoids[23] (Figure 2) are a class of carbon compounds, most often formally tetravalent, in which an electronegative atom or group such as an halide, alkoxide, etc. and an electropositive atom such as an alkali metal, i.e. **Li**, Na, K, are bound to the same carbon center (**III**).

III **IV**

Figure 2. Carbenoids **III** and silylenoids **IV** (R, R' = organic substituents, X = halogen, alkoxy, M = Li, Na, K).

Because elimination of MX from carbenoids can occur – but not necessarily must – and thus leading to the intermediate formation of so-called *carbenes*, carbenoids show a "*carbene-like*" reactivity. According to the work of Köbrich[24,23b] lithium carbenoids display 1) thermal lability, 2) an ambiphilic reactivity behavior due to the co-existence of electron-donating and electron-withdrawing substituents at the same carbon center (Figure 3); as a consequence, lithium carbenoids show nucleophilic as well as electrophilic reactivity as illustrated by the *bond non-bond*[25] formalism.

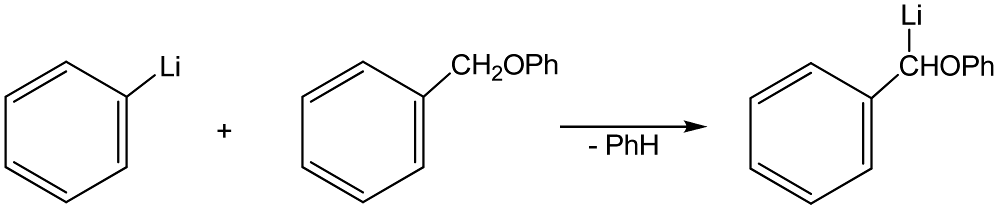


A' **A** **A''**

Figure 3. *Bond non-bond* resonance structures of carbenoids.

As Figure 3 shows the electrophilic reactivity could be anticipated from formula **A''**, while the nucleophilic character is somehow expressed by the bond non-bond[25] resonance formula **A'**, so that the ambiphilic reactivity of carbenoid **A** becomes apparent. With respect to the α-heteroatom X, the carbenoid character is most pronounced in the *C*-halogen substituted derivatives, but it has also been observed in *C*-alkoxy substituted carbenoids.

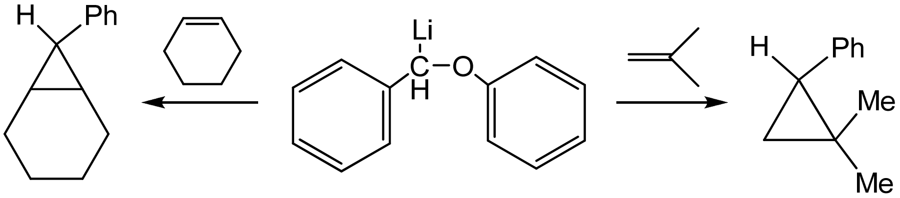
To generate Li/OR carbenoids, a strong base is generally required in order to achieve the deprotonation of alkyl ethers and there are two common synthetic routes that yield Li/OR carbenoids: 1) deprotonation using organolithium derivatives or 2) via tin-lithium exchange. The first example of an Li/OR carbenoid derivative[26] was described by Lüttringhaus and Sääf in 1938 (Scheme 8). They treated an excess amount of phenyl lithium **18** with benzyl phenyl ether **19** which gave the α-lithiated benzyl phenyl ether **20**.



18 **19** **20**

Scheme 8. Formation of the Li/OR carbenoid **20**.

Later in 1963, Schöllkopf and Eisert made further investigations on the reactivity of this carbenoid[27] and found that substituted cyclopropanes **21** and **22** were generated by treating olefins with the α-lithiated benzyl phenyl ether **20** (Scheme 9). However, the yields were very low as side-reactions occurred. Nevertheless, the outcome proved strongly the carbenoid nature of compound **20**. Afterwards, other Li/alkoxy carbenoids such as $H_2CLi(OMe)$[28], $H_2CLi(O^nBu)$[29] were reported by Gellert and Hoberg, respectively, moreover, their reactivity was discussed in great detail.[30]



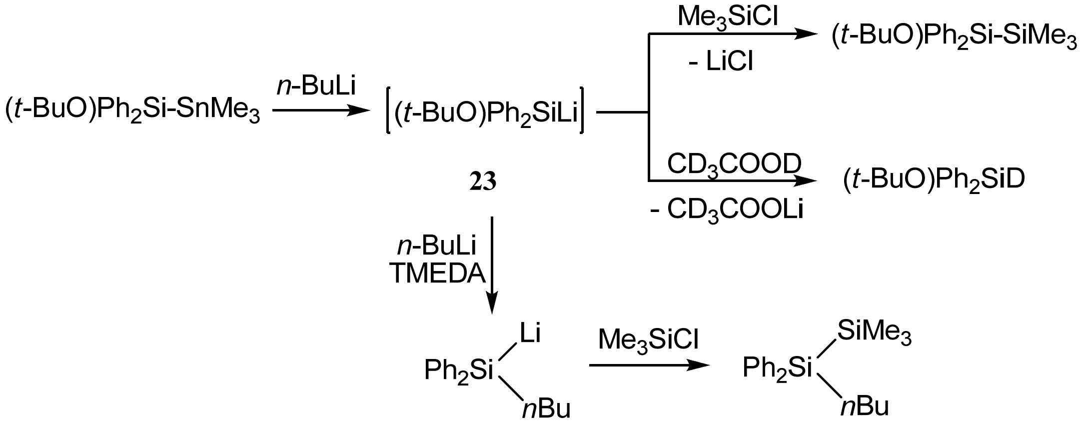
21 **20** **22**

Scheme 9. Reactions of Li/OR carbenoid **20** with olefins to yield **21, 22**.

Besides these reactivity aspects, there are also NMR characteristics (= NMR signature) for the carbenoid nature of these compounds. In 1979, Seebach was the first to perform NMR investigations[31] on Li/halogen carbenoids and found that carbon resonances were markedly shifted *downfield* compared to the non-litiated precursors. Later, in 1993, Boche confirmed the NMR signature[32] for Li/alkoxy carbenoids. The most interesting result was that the δ values of $H_2CLi(OPh)$ (74.5 ppm) and $H_2CLi(OC_6F_5)$ (92.2 ppm) implied that $H_2CLi(OC_6F_5)$ possessed a "better" leaving group $LiOC_6F_5$ because of this *downfield* chemical shift.

Usual and because of "thermal lability", it has been proven difficult to obtain structural information of carbenoids for the solid state. Until now there are just few examples of tetra-coordinated derivatives[33–35] reported by Boche and some tri-coordinated derivatives[36] by Niecke. All tetra-coordinated examples exhibited a markedly *elongated* C–O bond (ca. 7–10 pm) as compared to those of the corresponding non–lithiated precursors.

In contrast to carbenoids, the silicon analogues, named silylenoids[37] (Figure 2, **IV**), have been much less explored. To date, theoretical studies were first performed by Clark and von Schleyer in 1980 and their results[38] showed that the structures of H_2SiFLi and its carbenoid counterpart H_2CFLi are closely related, and they suggested that the Si–F bond was weakened if lithium was attached to the silicon atom, thus leading to the "appearance" of positive charge on the silicon center. Recently, Marschner also reported a theoretical study about the effect of α substituent (X) on the configuration stability of silyl anions $X(H_3Si)MeSiLi$ (X = F, OH, NH2, Cl and PH_2) and their tendency to form silylenoid or to dissociate to silylenes.[39] In 1995, Tamao was the first to report on experimental aspects of silylenoid chemistry obtained from studies on $Ph_2SiLi(OtBu)$ (**23**),[37a] which was generated by tin-lithium exchange reaction (Scheme 10) at low temperature and trapped with Me_3SiCl and CD_3COOD to give the corresponding silanes in good yields. Here, a pronounced nucleophilic reactivity of **23** was observed. The electrophilic character of compound **23** was also demonstrated by the reaction with *n*-BuLi/TMEDA, which, after quenching with trimethylsilane, yielded diphenyl-trimethylsilyl-*n*-butylsilane **24**.



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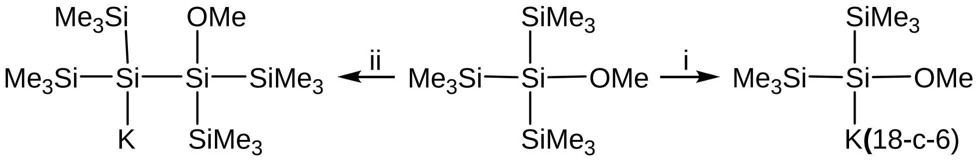
Scheme 10. Synthesis of compound **23** and its ambiphilic reactivities.[37a]

Here, one further aspect should be commented: although the ambiphilicity of silylenoids allowed the successive introduction of an electrophile and a nucleophile into the silylene moiety, a nucleophile can be introduced predominantly because of very high electrophilicity of the silylenoids.

The ^{29}Si NMR signal of silylenoid **23** was observed at 11.3 ppm (–80 °C, THF), which was largely *downfield* shifted compared to the related organosilylstannane compounds such as δ(Cl(Me)$_2$SiSnMe$_3$) = –38.4 ppm and δ((Me)$_2$HSiSnMe$_3$) = –37.0 ppm.[40] So this large downfield shift of compound **23** was in good agreement with the trends observed earlier for carbenoids and thus with the ^{13}C NMR signature of carbenoids.[31]

As silylenoids have a similar thermal lability as carbenoids, it was difficult to get informations on the solid state, e.g. through crystal structures. In 2004, Marschner reported the first structurally characterized silylenoid[41] derivative, the methoxylbis(trimethylsilyl)silyl potassium **26**, which was synthesized by reacting potassium *tert*-butoxide with methoxybis(trimethylsilyl)silane **25** in the presence of 18-crown-6 (Scheme 11). The ^{29}Si NMR spectra of **26** displayed a pronounced *downfield* shifted signal (δ = 32.3 ppm) as compared to the starting material **25** (δ = 3.9 ppm), thus being in strong contrast to common silanides.[42,43] So again, the marked downfield shift upon metalation has to be regarded as one charactaristic properties of the silylenoid character.[37a] The silylenoid character of compound **26** was also “confirmed” by a condensation reaction (route ii, Scheme 11) that took place in the absence of 18-crown-6 to yiled **27**, in which one entity acted as an electrophile towards the other.



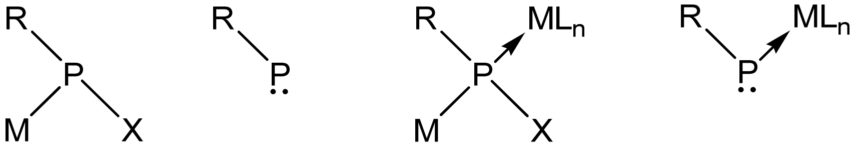
27 **25** **26**

Scheme 11. Formation and reaction of potassium methoxybis(trimethylsilyl) silylenoid **26**. i) *t*BuOK, 18-crown-6, toluene, r.t.; ii) *t*BuOK, THF, r.t.

The single-crystal X-ray structure of **26** showed a covalent bonding between the silicon atom to the oxygen of the methoxy group and to potassium. A further (weak) interaction between the potassium and the carbon of a trimethylsilyl group of the neighboring molecule was observed,[44] too. Important was that the crystallographic data revealed a markedly *elongated* Si–O bond (1.754(3) Å), compared to the normal range for Si–O single bonds (1.63–1.66 Å).[45] In total, both the NMR signature and the crystallographic parameters are necessary to confirm the silylenoid nature of a given compound – to which reactivity studies have to be added pointing in the same direction to justify this specific name coinage.

III. Introduction to Li/X phosphinidenoid complexes and terminal phosphinidene complexes

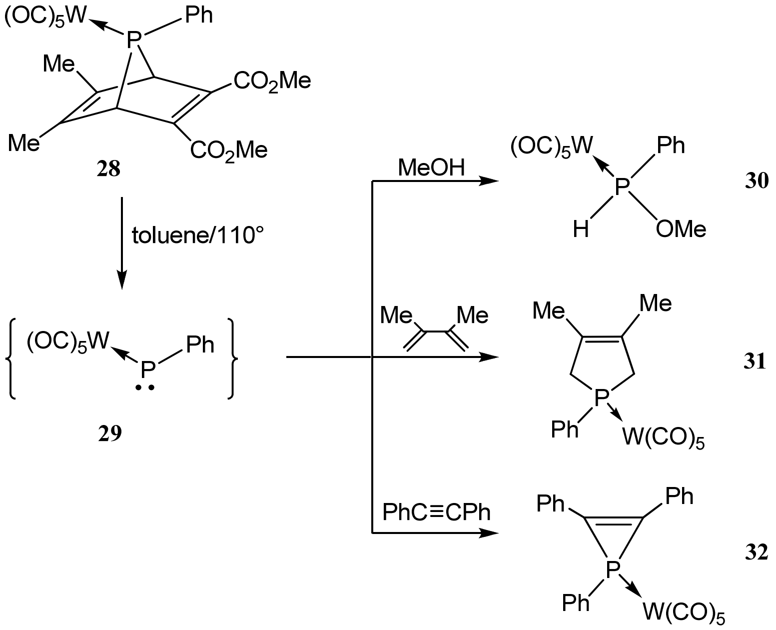
Using the knowledge about carbenoids and silylenoids as background, it is now not difficult to describe and compare the constitution/bonding and reactivity of phosphinidenes, phosphinidenoids[46] and their complexes (Figure 4). A compound in which one electronegative atom/group (halide, alkoxy, etc.) and one electropositive atom (Li, Na, K) are bonded to the same phosphorus centre can be named M/X phosphinidenoid **V** or complex **VII** and thus showing a relationship to phosphinidenes RP **VI** and their complexes **VIII** as MX might be regarded as a potential leaving group for the former or/and *vice versa* a substrate for the latter.[47]



V **VI** **VII** **VIII**

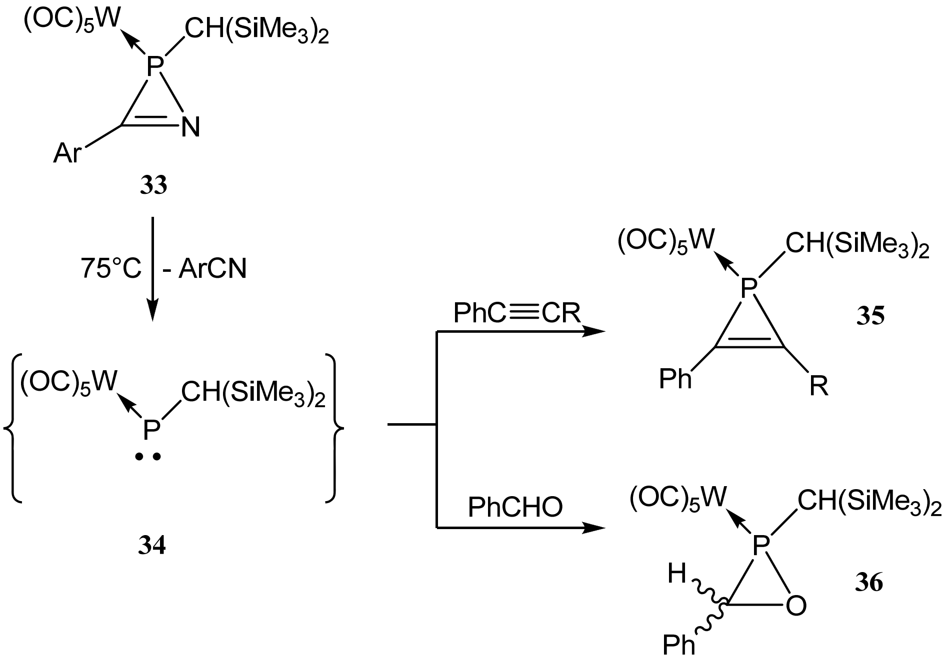
Figure 4. Structures of phosphinidenoids **V**, phosphinidenes **VI**, M/X phosphinidenoid complexes **VII** and terminal phosphinidene complexes **VIII**.

The chemistry of phosphinidenes RP (IUPAC: "phosphandiyls"), with or without transition metal groups, attract the attention of experimental and theoretical chemists over the decades as building blocks[48–50] in organophosphorus chemistry. Especially, as they are accessible from a variety of precursors, although most of them still being proposed only as short-lived intermediates.[51] Since the early nineties, the chemistry has become much more vibrant for the so-called terminal complexes in which the transition metal group controls the reactivity of the phosphinidene.[52–54] In most cases, terminal phosphinidenes and their complexes can be obtained by thermal or photochemical reactions,[55] and many examples of nucleophilic phosphinidene transition metal complexes are known.[56,57] Hereafter, only a few examples will be given to illustrate some important achievements. The occurrence of phosphinidene intermediateswas made plausible by Schmidt's work at an early stage[47a] and later on theoretical studies on related phosphinidenes and complexes emerged.[58] In the case of metal complexes it was Huttner in 1975, who in an attempt to achieve a chlorine/lithium exchange in the complex ($C_5H_5(CO)_2MnP(C_6H_5)Li_2$) to prepare the first Li/Cl phosphinidenoid complex or the terminal phosphinidene complex, showed that a trigonal planar dinuclear μ_2-phosphinidene complex[47b] was obtained, instead. The isolated bridged phosphinidene complex was the first compound in which phosphorus possesses a trigonal planar coordination. Later on, in 1982, Mathey reported first indirect but strong evidence for the formation of a terminal phosphinidene complex[47c] (Scheme 12) by using thermal decomposition of 7–phosphanorbornadiene complex **28**. Quenching experiments with different trapping agents led to the insertion product **30**, the phosphol-3-ene complex **31** and the 1*H*-phosphirene complex **32,** the latter via [2+1] cycloaddition reaction. Especially the latter, served as the strong argument for the intermediate formation of the phosphinidene complex **29**.



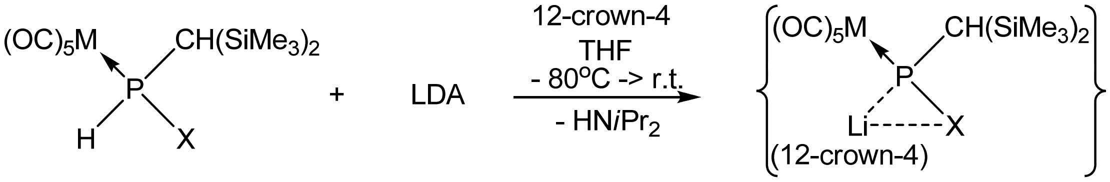
Scheme 12. Proposed formation of terminal phosphinidene complex **29** and trapping reactions using a wide variety of substrates.[47c]

Since then other approaches to terminal phosphinidene complexes were described and among them, in 1994, Streubel et al. described the formation of a transient phosphinidene complex in the thermal reaction of 2*H*-azaphosphirene complex **33**[59] with benzaldehyde or phenylacetylene. Here, a ring cleavage led to the elimination of benzonitrile (PhCN) and the phosphinidene complex intermediate **34** (cf.[60]) (Scheme 13). Complex **34** reacted with benzaldehyde or acetylene derivatives in a [2+1] cycloaddition to give the three-membered heterocycle complexes (cf.[61]) **35** and **36**.



Scheme 13. Proposed formation of the terminal phosphinidene complex **34** and its trapping.[59–61]

Since then, two more important routes have been established: first the thermal cleavage of phosphepine complexes[62] (Lammertsma, 2005) and, second, the hydrogen-atom abstraction from precursors to give the first example of a stable terminal phosphinidene complex[63] that possesses a metal centre (nickel) in the (formal) oxidation state zero and exhibits electrophilic reactivity (Hillhouse, 2002). In 2007, Streubel et al. developed a reliable protocol to generate Li/X phosphinidenoid complexes[64,65] using the following protocol: freshly prepared LDA (lithium diisopropylamide) reacted with chloro or fluorophosphane complex **37** in the presence of 12-crown-4 at –78 °C, which led to the Li/X phosphinidenoid complexes **38a,b** (Scheme 14). Meanwhile, a lot more of such complexes[66] were unambigously identified for the same substituent at phosphorus and the group 6 metal triad (Cr, Mo, W; X = F) as well as for the tungsten complexes (X = F, Cl, Br, I).



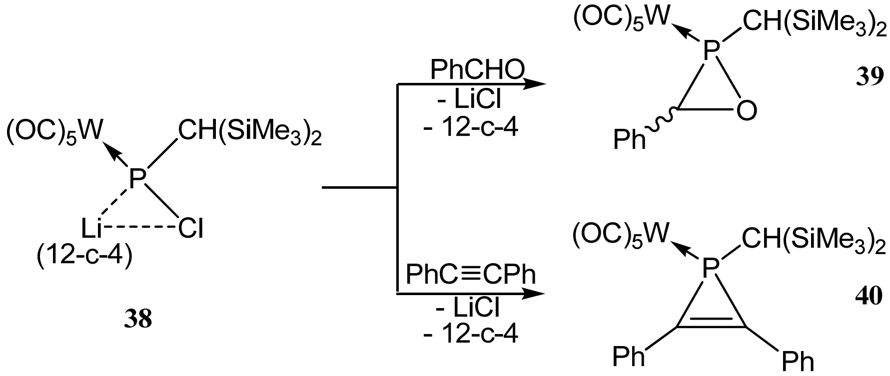
37 **38a,b**

Scheme 14. Generation of Li/X phosphinidenoid complex **38a,b** (**38a**: M = W, Mo, Cr, X = F; **38b**: M = W, X = F, Cl, Br, I).[64,65]

Some aspects concerning scheme 14 need to be emphasized: 1) a co-ligand such as crown ether must be used to stabilize the phosphinidenoid complexes. 2) Only lithium diisopropylamide works selectively. 3) Most of the Li/X phosphinidenoid complexes are stable below –45 °C only, except for the Li/F derivative which is stable up to 10 °C. So and in going from iodine to fluorine, the stabilities of the corresponding Li/X phosphinidenoid complexes vary significantly. If warmed up to ambient temperature all derivatives form *E* and/or *Z* diphosphene complexes, so consequently all NMR spectra were measured at low temperature. 4) DOSY NMR experiments[66] and single-crystal X-ray structure data of a Li/F phosphinidenoid complex showed that there is no covalent bond between phosphorus and lithium, thereby representing an ion pair in the solid state and solution.

^{31}P NMR spectroscopic data showed a very lowfield chemical resonance as compared to the precursor complexes. For example, the Li/Cl phosphinidenoid complex **38** resonated at 212.9 ppm, together with a typically small phosphorus-tungsten coupling constant of $^{1}J_{(W,P)}$ = 67.4 Hz, thus exhibiting the same *downfield* chemical shift trend as carbenoids and silylenoids.

The reactivity of the Li/Cl phosphinidenoid complex was explored in some detail[64] and the reactions implied a "phosphinidene-like" reactivity as illustrated by the formation of complexes **39** and **40** (Scheme 15) but also "phosphanide-like" reactivity with methyl iodide.



Scheme 15. Examples of the reactivity of the Li/Cl phosphinidenoid complex **38**.

The reactions shown in scheme 15 could be interpreted as [2+1] cycloaddition reactions, although some evidences were obtained recently that these might be multi-step reactions that start with a nucleophilic attack of complex **38** onto a π-system in the case of aldimines.[67] Besides, the Li/Cl phosphinidenoid complex **38** also showed *amphiphilic* properties as it also reacted with other nucleophiles[68] (such as *n*BuLi, etc. in an electrophilic manner. Furthermore, there was some indirect evidence for radical reactions[69] and **38** was used to generate the fist *P*-functional *P*-centered phosphanyl complexes.[70]

Chapter 2. Objectives

The objectives of this thesis are:

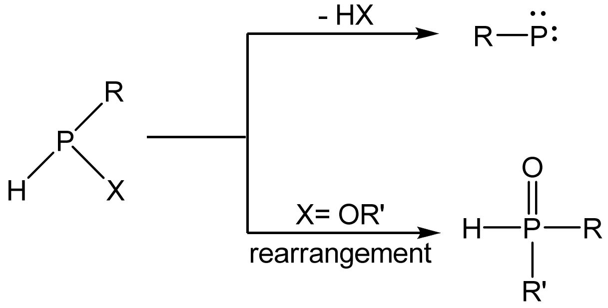
- synthesis of a broad set of *P*-1,1’-bifunctional organophosphane metal complexes of group 6 metals that bear *P*-NR_2 or *P*-OR substituents
- generation/synthesis of lithium *P*-NR_2 and *P*-OR substituted phosphinidenoid complexes via deprotonation of *P*-1,1’-bifunctional organophosphane metal complexes
- studies of physical properties predominantly NMR spectroscopic features
- studies on counter cation and co-ligand effects
- studies on the reactivity of phosphinidenoid metal complexes

The more distant aim was to achieve understanding of the boundary between phosphanide and phosphinidenoid complex chemistry.

Chapter 3. Synthesis and reactions of *P*-amino and *P*-alkoxy phosphane complexes and their corresponding phosphinidenoid complexes

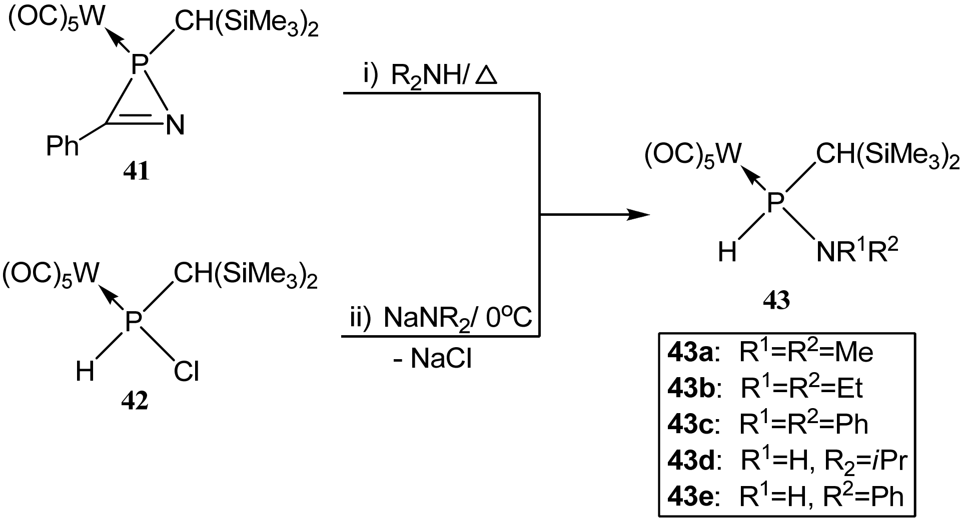
3.1 Synthesis of *P*-dialkyl/arylamino phosphane tungsten complexes 43a–e

Secondary phosphane derivatives as represented by the formula RP(H)X, which contain both a P–H bond and a P–X bond (X = Cl, OR, NR_2, NHR, etc.) are relatively rare, and it has been proposed by many authors that they decompose to yield phosphinidenes or diphosphanes via HX elimination[71] and/or undergo rearrangement reactions to form *P*-oxide derivatives (X = OR)[72] (Scheme 16). Therefore, no direct complexation is available as methodology for the synthesis of the targeted phosphane tungsten/molybdenum/chromium complexes, desired as starting materials for the study presented here.



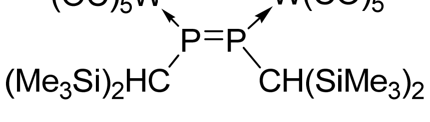
Scheme 16. Formal elimination and rearrangement reactions of secondary phosphane compounds.[71,72]

Therefore, the first aim was to develop an appropriate methodology to access a series of *P*-functional (pentacarbonyltungsten/molybdenum/chromium) phosphane complexes. Scheme 17 displays that the *P*-organoamino substituted phosphane complexes can be prepared via two different pathways: i) via thermal reactions of 2*H*-azaphosphirene complex **41**[73] with amine derivatives in toluene at 75°C (3 hours) or ii) using *P*-chlorophosphane complex **42**[74] and the appropriate sodium salts in diethyl ether at – 30°C.



Scheme 17. Synthetic routes i-ii) to *P*-organoamino substituted phosphane complexes **43** via two different pathways.

One point which deserves mention is that in the synthesis of complex **43c** the formation of the *Z*-diphosphene complex **44** was observed (Figure 5).[66]



44

Figure 5. Formula of Z-diphosphene complex **44**.

Using the methodologies (i, ii) shown above, complexes **43a–e** were synthesized and isolated in good yields (> 60%) by column chromatography at low temperature. As it can be seen from table 1, all ^{31}P NMR resonances appeared at high field, within the range from ca. 46 to 5 ppm, with a tungsten-phosphorus coupling constant of about 250–260 Hz. On the other hand, the ^{31}P nuclei chemical shift decreased from **43a** to **43e** as the electron density at the phosphorus atom increased, which is largely in accordance with the *P*-amino phosphane complex derivatives[75] reported earlier by Mathey. The ^{13}C NMR data of the carbon atoms (abbr. C^P) directly bound to the phosphorus centre showed a δ value around 22 ppm, accompanying a very small phosphorus, carbon coupling constants, ca. $^1J_{(P,C)}$ = 4~5 Hz. The IR spectra of complexes **43a–e** were recorded from KBr pellets, and all the ν(P–H) stretching absorptions appeared around 2200–2400 cm^{-1}, which also match with the reported values by Mathey and Hoge.[75a,76]

Table 1. Selected NMR data of *P*-(organo)aminophosphane complexes **43a–e**

Complexes	δ (^{31}P)[a]/ $^1J_{(W,P)}$[b]	δ (^{13}C)/ $^1J_{(P,C^{p[c]})}$
43a ($R^1 = R^2$ = Me)	46.1/249.2	22.6/3.9
43b ($R^1 = R^2$ = Et)	31.0/249.2	22.7/3.9
43c ($R^1 = R^2$ = Ph)	23.7/263.2	—
43d (R^1 = *i*Pr, R^2 = H)	11.4/255.6	22.3/7.8
43e (R^1 = Ph, R^2 = H)	5.3/253.0	22.4/br

[a]: δ/[ppm], [b]: $^1J_{(W,P)}$/[Hz], *[c]: C^P: carbon atoms which are directly bound to the phosphorus centre

A comparison of the ^{31}P NMR data of complexes **43a–e** with those of the complexes, reported by Mathey (Table 2), revealed that the *P*-diorganoamino phosphane complexes **43a–c** have more upfield ^{31}P resonances than *P*-monoamino phosphane complexes **43d**,**e**, which is also consistent with the trend in complexes in Table 2.

Table 2. ^{31}P NMR data of complexes, reported by F. Mathey

Complex	$[PhP(H)(NEt_2)]W(CO)_5$	$[PhP(H)(NHPh)]W(CO)_5$
δ (^{31}P)/ $^{1}J_{(W,P)}$	47.4 / 253.9	12.1 / 253.9

The molecular structures of complexes **43c–e** were unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 6). Here, complexes **43c** and **43e** were shown for comparison, and all crystallographic parameters are within the normal range.

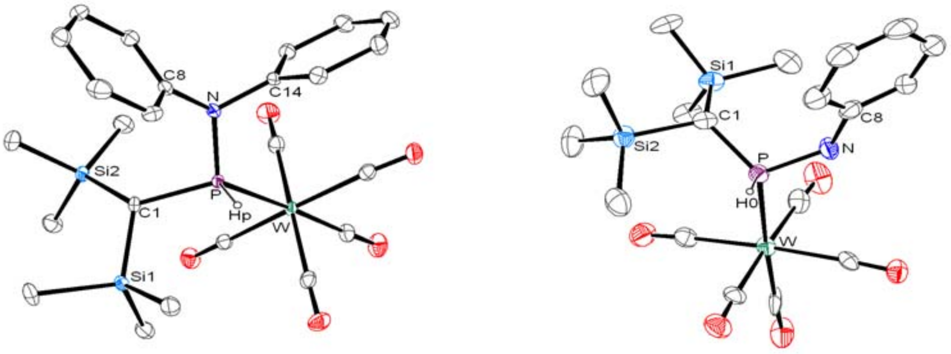
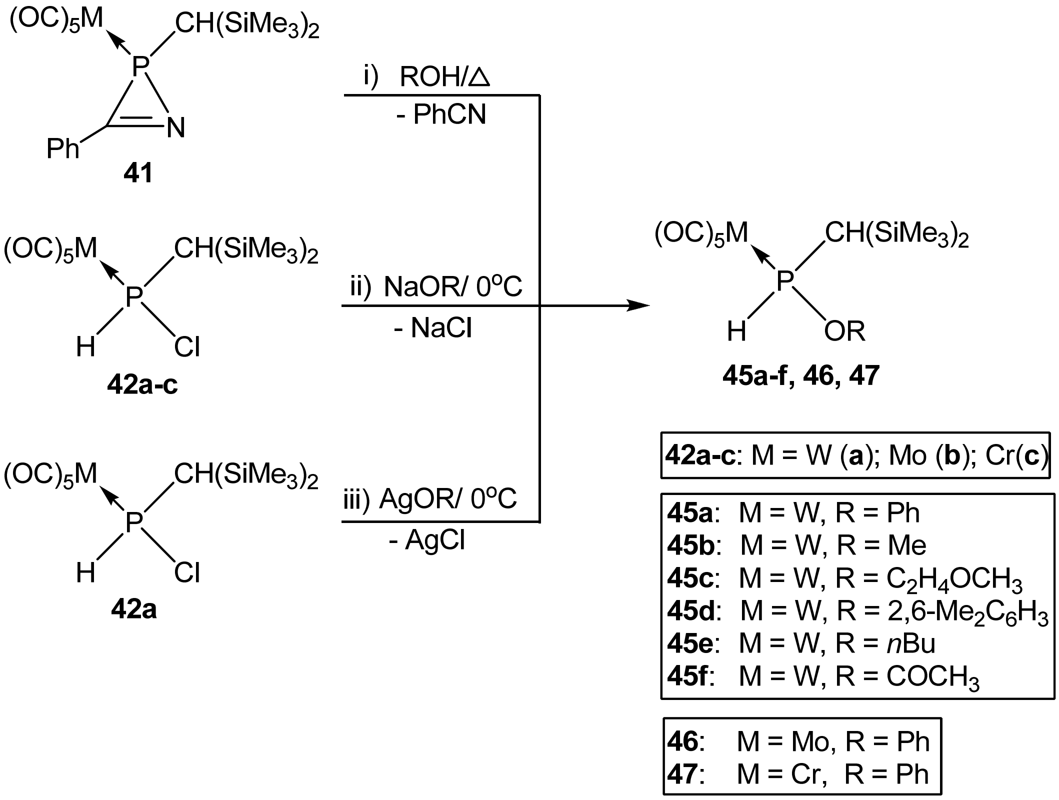


Figure 6. Molecular structure of complex **43c** (left side) and **43e** (right side) in the crystal (hydrogen atoms omitted for clarity). Here, only selected bond length[Å] and bond angles [°] are given: data for **43c**: P–H_p 1.29(3), P–W 2.5305(7), P–N 1.717(2), P–C(1) 1.819(3), N–C(8) 1.448(3), N–C(14) 1.449(3), N–P–W 118.13(8), N–P–C(1) 104.09(11), C(1)–P–W 121.58(9); data for **43e**: P–W 2.516(3), P–C(1) 1.835(13), P–N 1.691(11), N–C(8) 1.430(18) , W–P–N 108.0(4), N–P–C(1) 107.8(6), W–P–C(1) 127.1(4).

3.2 Synthesis of *P*-alkoxy/aryloxy phosphane tungsten complexes 45a–f and molybdenum, chromium complexes 46, 47

The *P*-alkoxy phosphane complexes **45a–f** were obtained using three synthetic routes shown in scheme 18: i) via thermal reaction of 2*H*-azaphosphirene complexes **41** with alcohols in toluene at 75 °C for 3 hours, ii) through reaction of *P*-chlorophosphane complexes **42a–c** with appropriate sodium salts in diethyl ether at –30 °C or iii) using *P*-chlorophosphane complex **42a** with corresponding silver salts in methylenechloride at 0 °C. All complexes were obtained in good yields (> 60%) after purification by column chromatography at low temperature (–20 °C) or just washing with *n*-pentane at low temperature (–90 °C).



Scheme 18: Synthetic routes i–iii) to *P*–alkoxy phosphane complexes **45a–f**,**46**,**47**

In table 3, selected ^{31}P and ^{13}C NMR data are given. Apparently the ^{31}P resonances of complexes **45** are in a small range that is 60–80 ppm downfield to the series of *P*-amino phosphane complexes **43**, due to the more electronegative oxygen atom and the thus more electron-withdrawing alkoxy groups. In much the same vein the tungsten-phosphorus coupling constants were influenced by the nature of the alkoxy groups. In the ^{13}C{^{1}H} NMR spectra all C^{P} atoms appeared within the range of 21–24 ppm ($^{1}J_{(P,C)}$ ca. 10–14 Hz), which (again) is due to the presence of the directly bound oxygen. In the ^{1}H NMR spectra the proton bound directly to the phosphorus appeared in the range of 7.85–8.47 ppm, which significantly depended on the substituent of the alkoxy group. For aromatic substituent the range is about 8.40–8.50 ppm, while for alkyl groups, the range was 7.80–7.90 ppm. The resonances of the proton of the C*H*(SiMe$_3$)$_2$ group were measured at about 0.80–0.90 ppm, which is very much upfield from other known complexes bearing this particular group.

Table 3. Selected NMR data of *P*-alkoxy phosphane complexes **45a–f**

Complexes	δ (^{31}P)$^{[a]}$/ $^{1}J_{(W,P)}{}^{[b]}$	δ (^{13}C)/ $^{1}J_{(P,C^{p[c]})}$
45a (R = Ph)	106.8/275.9	22.6/13.7
45b (R = Me)	109.7/267.0	21.4/13.6
45c (R = C_2H_4OMe)	107.3/267.0	23.4/13.6
45d (R = 2,6-$Me_2C_6H_3$)	99.0/274.7	24.2/9.7
45e (R = *n*Bu)	102.5/267.0	21.3/13.6
45f (R = $COCH_3$)	88.6/275.8	21.7/9.1

[a]: δ/[ppm], [b]: $^{1}J_{(W,P)}$/[Hz], [c]: C^{P}: carbon atoms which are bound directly to the phosphorus centre

For all *P*-H phosphane complexes **45a–f**, the absorptions due to the ν(P–H) stretching mode was within the range of 2200–2400 cm^{-1} like the *P*-amino analogues (**43a–e**) (Table 4). One point which needs to be mentioned is for complex **43b**, no P–H stretching absorption was observed. The same phenomenon appeared in complex $[(CO)_5W(Ph)P(H)(NEt_2)]$[75a] reported by Mathey, although the reason is not clear.

Table 4. Selected IR absorption values of complexes **43**, **45**

Complexes	ν(P–H)/cm^{-1}	ν(CO)[a]/cm^{-1}
43a	2270	2069
43b	not observed	2069
43c	--	--
43d	2226	2068
43e	2310	2071
45a	2290	2073
45b	2265	2070
45c	2260	2073
45d	2367	2072
45e	2265	2070
45f	2366	2075

[a]: highest (nu tilde ῦ) value of CO stretching modes (A_1)

The structures of **45a**, **45d**, **45e** and **45f** were unambiguously confirmed by single-crystal

X-ray diffraction analysis (Figures 7–9). For the discussion complexes **45a** and **45f** will be taken as examples (see Figure 7).

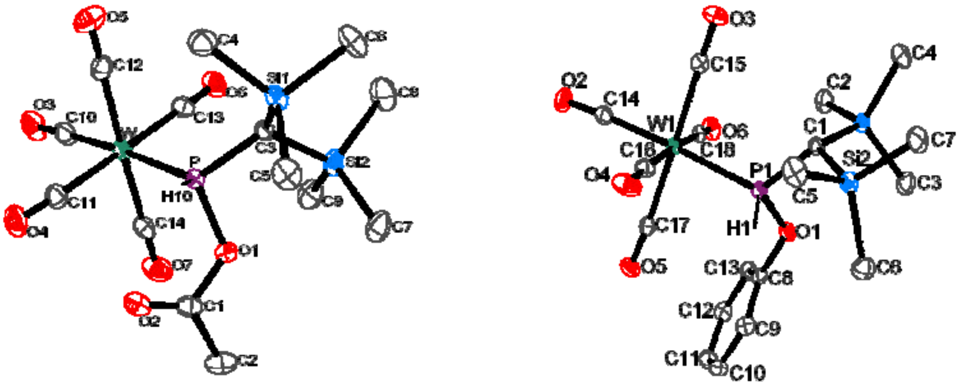


Figure 7. Molecular structures of complex **45a** (right side) and **45f** (left side) in the crystal (hydrogen atoms except H1 (**45a**) and H10 (**45f**) omitted for clarity). Selected bond length [Å] and bond angles [°]: Data for **45f**: P–W 2.4780(8), P–H(10) 1.35(3), P–O(1) 1.676(2), H(10)–P–O(1) 96.8(13), O(1)–P–W 115.68(8), O(1)–P–C(3) 99.66(14); Data for **45a**: P(1)–H(1) 1.40(3), P(1)–O(1) 1.6520(18), P(1)–C(1) 1.811(2), P(1)–W(1) 2.4790(6), O(1)–C(8) 1.397(3), O(1)–P(1)–H(1) 104.1, C(1)–P(1)–H(1) 104.1, W(1)–P(1)–H(1) 104.1.

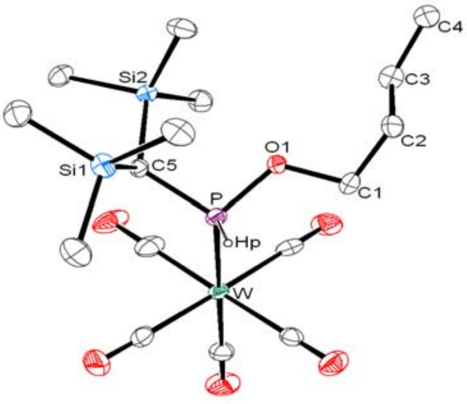


Figure 8. Molecular structure of complex **45e** in the crystal (hydrogen atoms except Hp omitted for clarity). Selected bond length [Å] and bond angles [°]: P–W 2.4750(8), P–Hp 1.34(3), P–O(1) 1.621(2), P–C(5) 1.807(3), O(1)–C(1) 1.448(4); Hp–P–O(1) 95.9(13), O(1)–P–W 121.39(9), O(1)–P–C(5) 99.33(13), Hp–P–C(5) 105.2(13), Hp–P–W 111.0(12), C(5)–P–W 120.38(11).

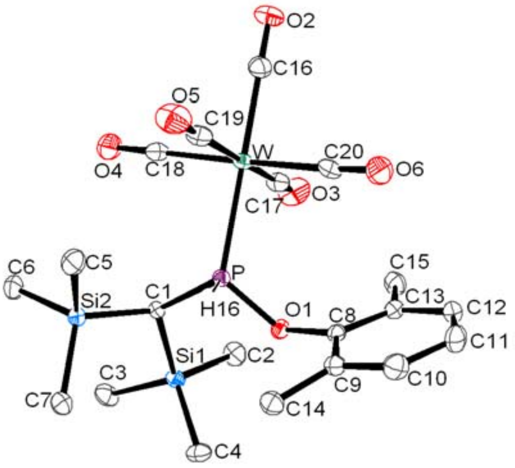


Figure 9. Molecular structure of complex **45d** in the crystal (hydrogen atoms except H16 omitted for clarity). Selected bond length [Å] and bond angles [°]: P–W 2.4918(6), P–H(16) 1.27(3), P–O(1) 1.6571(18), P–C(1) 1.810(3), C(1)–P–H(16) 103.3(16), W–P–H(16) 114.9(16), W–P–O(1) 119.03(7), W–P–C(1) 117.04(8).

In the case of complex **45a** two independent molecules (unit cell of complex **45a**: a = 12.8195(2), b = 13.38630(10), c = 14.26660(10), α = 103.8230(10) deg, β = 92.7380(10) deg, γ = 90.3910(10) deg) were found per asymmetric unit but the differences are negligible so that they will not be discussed further. The noteworthy point here is the P–H bond distances in two independent molecules of complex **45a**. Compared to complex **45c**, one P–H bond length in complex **45a** is longer by 5 pm, while the other shorter by 10 pm. Some selected bond lengths of complexes **45a,d–f** are displayed in table 5.

Table 5. Selected bond distances of complexes **45a**, **45d**, **45e** and **45f**.

bond lengths[a]	**45a**	**45d**	**45e**	**45f**
P–O	1.6522(17)/1.6466(18)	1.676(2)	1.621(2)	1.6571(18)
P–W	2.4791(6)/2.4842(6)	2.4780(8)	2.4750(8)	2.4918(6)

[a]: Å

In order to enable comparative studies later on, some of the corresponding chromium and molybdenum complexes were synthesized using the same protocol, in general. For the chromium and molybdenum derivatives, a lower temperature was used to obtain the *O*-phenyl phosphane complexes **46**, **47**. The selected data of these new complexes are shown in table 6. Obviously, the ^{31}P resonance shift values increased (shifted downfield) in going from tungsten to molybdenum and chromium. This trend has been established before for various classes of *P*-ligands and is known as coordination shift or $\Delta\delta$ value. Interestingly, within a given class of compounds it seems to be largely independent from the actual structural features and possesses very often values 20–30 ppm[77] for the two respective homologues (Cr/Mo or Mo/W). As to the IR spectrum, all stretching or vibration absorption of functional groups (like ν(P–H) and ν(CO)) appeared in the normal range (Table 6).

Table 6. Selected NMR data and IR absorption values of complexes [RP(H)OPh]M(CO)$_5$ (R = CH(SiMe$_3$)$_2$) **45a**, **46** and **47**.

Complexes	δ (^{1}H)[a]/ $^{1}J_{(\mathrm{P,H})}$[b]	δ (^{31}P)/ $^{1}J_{(\mathrm{W,P})}$	δ (^{13}C)[a]/ $^{1}J_{(\mathrm{P,Cp}}$[c]$_{)}$	ν(P–H)[d]	ν(CO)[e]
45a	8.42/325.5	106.8/275.9	22.6/13.7	2290	2073
46	8.06/309.0	135.4/–	21.7/8.4	2287	2075
47	8.02/317.3	161.8/–	22.7/9.1	2348	2065

[a]: ppm; [b]: Hz; [c]: carbons which are directly attached to the phosphorus atoms; [d]: cm^{-1}; [e]: highest (nu tilde ʋ̃) value of CO stretching modes (A$_1$) ; **45a**: M = W, **46**: M = Mo, **47**: M = Cr.

In the case of complex **47** (M = Cr) suitable single-crystal for X-ray diffraction analysis (Figure 10) were grown from diethyl ether.

The comparison of the molecular structural parameters of the *O*-phenyl-substituted phosphane tungsten **45a** and chromium complex **47** revealed little differences: 1) both phosphorus centers have a pyramidal geometry (sum of bond angles around phosphorus atom are 342.2° (**45a**) and 342.5, 341.9° (**47**); 2) bond distances such as the P–O, P–C, P–W and P–Cr are as observed before. 3) The P–H bond in tungsten complex **45a** is slightly elongated by ca. 5 pm than the related P–H bond in chromium complex **47**.

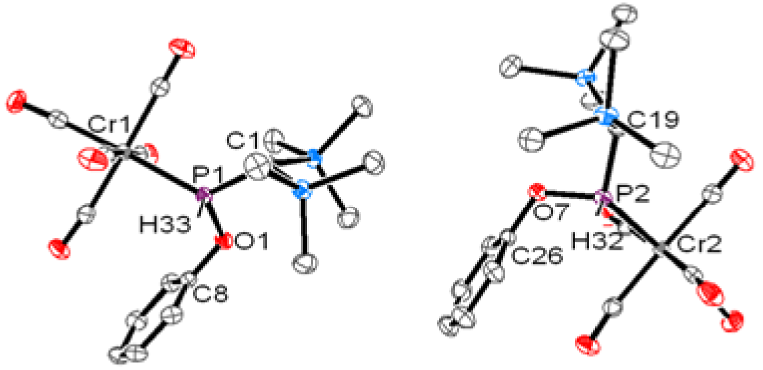
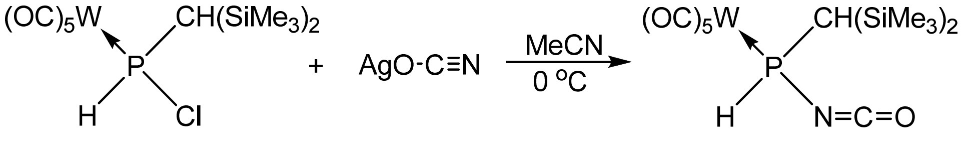


Figure 10. Molecular structure of complex **47** in the crystal, showing the two independent molecules in the unit cell (hydrogen atoms except H33 and H32 omitted for clarity). Selected bond length [Å] and bond angles [°]:P–H 1.369(18), 1.364(18); P–$C_{(silyl)}$ 1.8149(17), 1.8131(17); P–Cr 2.3368(5), 2.3408(5); P–O 1.6488(12), 1.6498(12); P–O–$C_{(ring)}$ 118.53(10), 118.29(11); Cr–P–$C_{(silyl)}$ 124.17(6), 124.35(6); $C_{(silyl)}$–P–O 99.71(7), 99.44(7); O–P–Cr 118.61(5), 118.07(5).

Besides *P*-amino- and *P*-alkoxy-substituted phosphane complexes, an attempt was made to synthesize a complex bearing the P–OCN as structural unit, which would be an interesting candidate for the planned follow-up study. The treatment of *P*-chlorophosphane complex **42** with silver cyanate (AgOCN) in acetonitrile at 0 °C led to an unexpected result (Scheme 19). In contrast to the targeted *P*-cyanate phosphane complex $[RP(H)(OCN)]W(CO)_5$ (R = $CH(SiMe_3)_2$), for which a ^{31}P resonance at low field was expected, the product showed an upfield chemical shift at 29.1 ppm ($^{1}J_{(W,P)}$ = 265.8 Hz, $^{1}J_{(P,H)}$ = 359.8Hz).



Scheme 19. Synthesis of *P*-isocyanate phosphane complex **48**.

The complex **48** was obtained as brownish yellow powder in 55.1% yield. The ^{31}P NMR data of **48** were quite different from the complex [$Ph_2P(NCO)$]$W(CO)_5$ that was reported by Bertrand in 1985, which displayed a ^{31}P NMR resonance at 70 ppm, with a $^{1}J_{(W,P)}$ = 276 Hz, due to the comparatively electron-withdrawing two phenyl groups. One prominent absorption in the IR spectrum of complex **48** is due to the valence stretch vibration of the CO moiety of the isocyanate group, which was assigned to the absorption at 2253 cm^{-1} (Figure 11), having a strong intensity. This assignment is further supported by IR data for the complex [$Ph_2P(NCO)$]$W(CO)_5$ (ν(NCO): 2250 cm^{-1}); (ν(NCO) value of 2280 cm^{-1} was reported for corresponding chromium complex.[78]

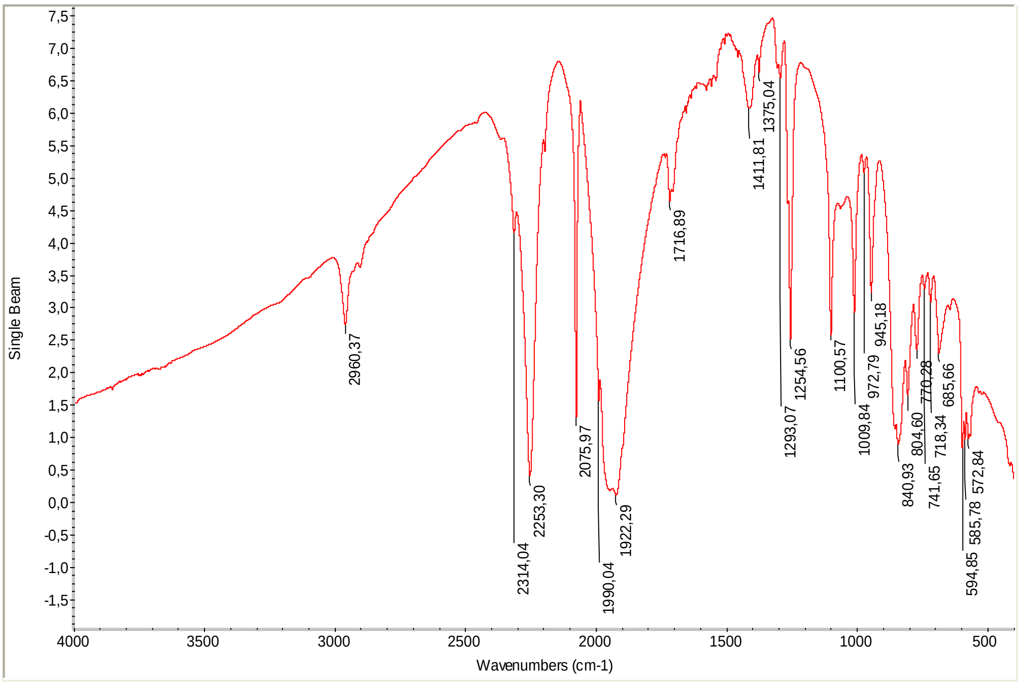


Figure 11. IR spectrum of complex **48** (from KBr pellets).

All attempts to grow single-crystals of complex **48** suitable for X-ray diffraction analysis turned out as a failure. Instead, the crystal structure that was obtained for crystals grown from a diethyl ether solution at +4 °C revealed the constitution of an NCO ethanol addition product **48’** (Figure 12) – although ethanol was not present. All analytical means including multiple NMR, IR, MS and EA confirmed strongly the constitution of complex **48**. Furthermore, ^{1}H NMR and ^{13}C NMR spectra revealed no evidence for ethanol in solution. So here it was deduced a cleavage of diethyl ether must have occurred thus yielding ethanol.

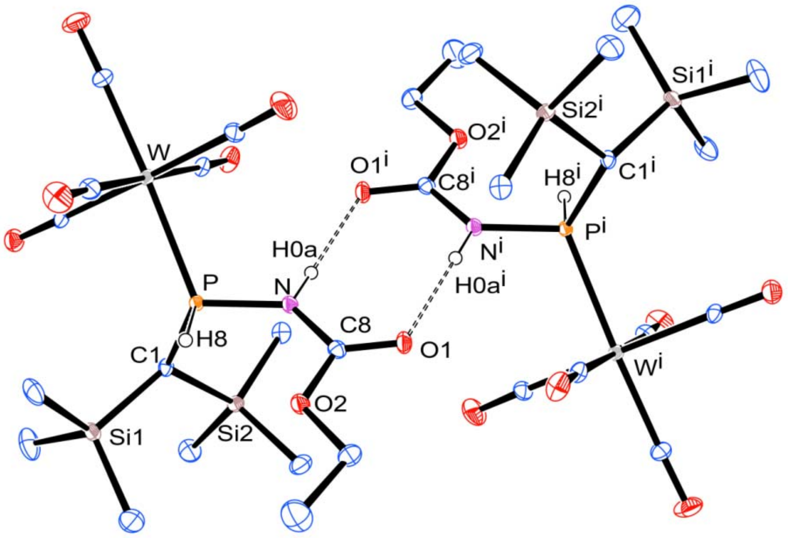


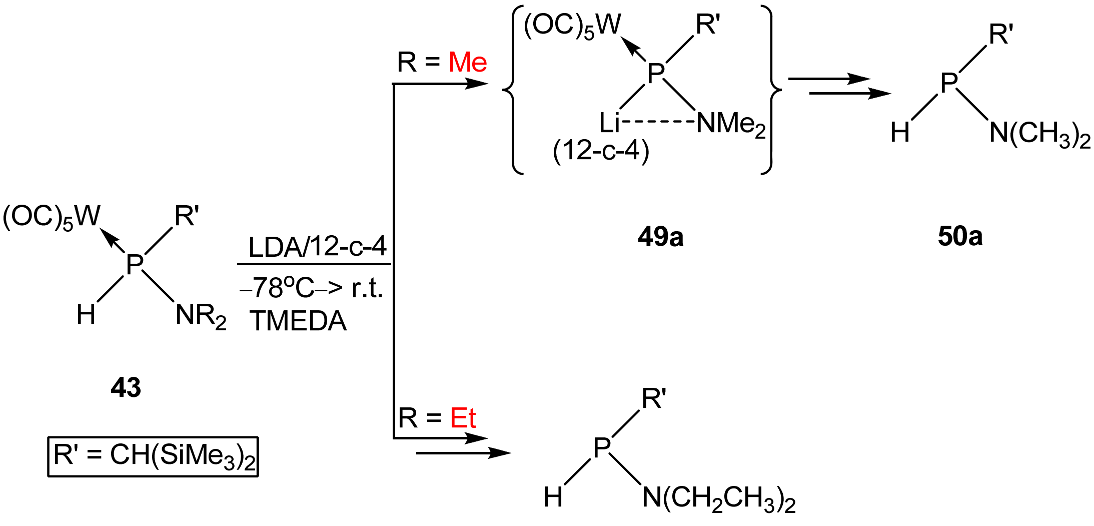
Figure 12. Molecular structure of complex **48'** in the crystal (hydrogen atoms except H8 and H8^i are omitted for clarity). Selected bond length [Å] and bond angles [°]: P–C(1) 1.829(3), P–W 2.4932(8), P–N 1.708(2), P–H(8) 1.41(3), N–C(8) 1.367(4), W–P–C(1) 116.64(10), W–P–N 112.82(8), N–P–C(1) 109.73(13), N–P–H(8) 94.3(12), C(1)–P–H(8) 103.9(11), W–P–H(8) 117.0(11).

Complex **48'** is a dimer, in which two molecules are connected via two hydrogen bonds. Besides, a hydrogen bond interaction exists between H8 and O1, (bond distance of O2–H8 is 2.33(3) Å), however, the bond angle of P–H8–O2 displays an atypical hydrogen bond.[79] The structural differences between complex **48'** and **43c**, the bond distance of P–H in **48'** was about 13 pm longer than that in **43c**, while the bond length of N–C (from carbonyl group) in **48'** was shortened by ca. 8 pm than the corresponding N–C (from phenyl group) in **43c**.

Chapter 4. Studies on lithium/*P*-organoamino and lithium/ *P*-alkoxy phosphinidenoid complexes

4.1 Attempted synthesis of lithium/amino phosphinidenoid complexes 49

In the following chapter 4 deprotonation reactions of the new *P*-bifunctional phosphane complexes **43** and **45** were studied with the emphasis to generate Li/X (X = NR_2, OR) phosphinidenoid complexes and to elucidate properties of the latter. As a protocol to generate Li/X phosphinidenoid complexes (X = F–I) was developed recently by Aysel Özbolat-Schön[66] it was decided to examine here first the transferability to the new chemical system. The reaction of the *P*-organoamino-substituted phosphane complexes **43a–e** with freshly prepared lithium diisopropylamide (LDA), in the presence of 12-crown-4, was carried out at low temperature. In contrast to the previous case of the *P*-X-substituted complexes, the results were disappointing, somehow. In each and every case, ^{31}P NMR resonances having an upfield chemical shift and a large phosphorus-proton coupling constant was observed, which seemed as if the deprotonation at phosphorus didn't take place. To discuss this further complex **43a,b** might serve as good case in point. When complex **43b** was reacted with LDA in diethyl ether at –78 °C with a ratio of 1:5, an intense signal (δ =19.0 ppm, $^{1}J_{(P,H)}$ = 210.0 Hz, and no $^{1}J_{(W,P)}$) was observed in the ^{31}P NMR spectrum. This may be assigned to a product resulting from a deprotonation of the proton atom of the α-C atom of the NCH_2CH_3 group (Scheme 20). As no tungsten-phosphorus coupling constant could be detected decomplexation reaction must have taken place at some point. The observed ^{31}P NMR data were close to the reported phosphane compound $CHR_2P(H)NR_2$ ($R = SiMe_3$),[80] $\delta = 5.9$ ppm, $^1J_{(P,H)} = 210.0$ Hz. As all attempts to isolate compounds via crystallization failed, the nature of the products obtained remained largely unclear. But when *P*-dimethylamino phosphane complex **43a** was reacted with LDA in TMEDA (used as solvent) at low temperature, a quartet due to phosphorus-lithium coupling at 101.8 ppm with a $^1J_{(P,Li)} = 62.1$ Hz was detected in the ^{31}P NMR spectrum at ambient temperature (Figure 13), which was time-dependent. After 50 hours, the intensity of this signal decreased and converted to the decomplexation compound at 39.1 ppm, with $^1J_{(P,H)} = 195.9$ Hz via an unknown pathway (Scheme 20). From these two examples, it is apparent that the preparation of Li/NR_2 phosphinidenoid complexes is largely dependent on the *P*-amino substituent.



Scheme 20. Proposed pathway for the formation and decomposition of Li/NR_2 (R = Me, Et) phosphinidenoid complexes **49a,b** leading to the products **50a,b**.

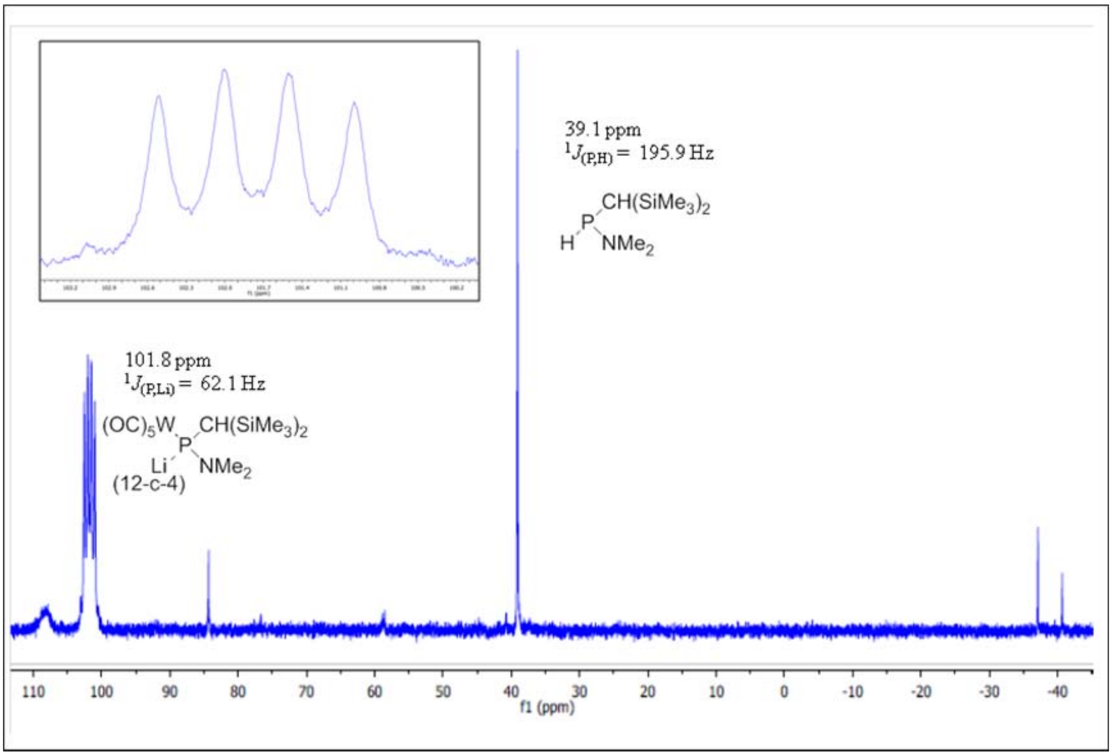
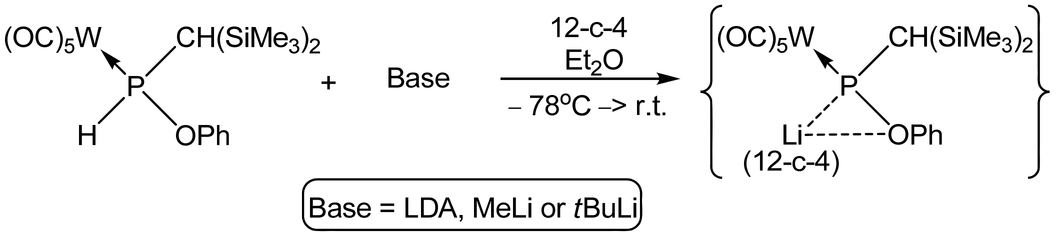


Figure 13. ^{31}P NMR spectrum of the reaction of complex **43a** with lithium diisopropylamide.

If the reaction of complex **43d** with *n*-BuLi was performed and examined by ^{31}P NMR spectroscopy, again a phosphorus-proton coupling but no tungsten-phosphorus coupling was detected. Compared to the situation of complex **43b**, the decomplexation took place predominantly. After addition of MeI at –60 °C, the appearance of a new signal was detected showing a resonance at 10.3 ppm ($^1J_{(P,W)}$ = 258.1 Hz, $^1J_{(P,H)}$ = 342.1 Hz), which was assigned to the *N*-methyl-*N*-isopropylamino phosphane pentacarbonyltungsten complex.

4.2 Synthesis of lithium/alkoxy phosphinidenoid complexes 51

As the preparation of Li/NR$_2$ phosphinidenoid complexes seemed to have one or more intrinsic problems, due to the high acidity of α-CH protons in *N*-alkyl groups, the metalation/deprotonation reaction of *P*-alkoxy phosphane complexes were tested using , predominantly **45a**, and different bases at low temperature (Scheme 21).



45a **51a**

Scheme 21. Synthesis of Li/OPh phosphinidenoid complex **51a**.

At low and ambient temperature a single resonance signal at low field with a small tungsten-phosphorus coupling constant (δ = 209.1 ppm, $^1J_{(W,P)}$ = 76.2 Hz) was observed in the ^{31}P NMR spectra. These data were close to those reported for Li/Cl phosphinidenoid complexes[81] (Li/Cl (R = CH(SiMe$_3$)$_2$: δ = 212.9 ppm, $^1J_{(W,P)}$ = 67.4 Hz; Li/Cl (R = C$_p$*): δ = 279.4 ppm, $^1J_{(W,P)}$ = 80 Hz), thus possessing the same ^{31}P NMR signature. As it was emphasized in the chapter 1, 12-crown-4 is inevitable for Li/Cl phosphinidenoid complex to stabilize. Against this background it seemed interesting to study these particular aspects for Li/OR phosphinidenoid complexes. Therefore, the reaction was also carried out without 12-crown-4 (as co-ligand) which resulted in a ^{31}P NMR spectrum (Figure 14) that revealed a selective reaction by showing just one signal (δ = 200.4 ppm, $^1J_{(W,P)}$ = 71.3 Hz). This not only successfully and strongly confirms that this *P*-alkoxy substituted phosphinidenoid complex can exist without special co-ligands but also that the thermal stability is enhanced as compared to the *P*-halogen derivatives. Therefore, all NMR spectra were measured at ambient temperature. Furthermore, besides the bulky base lithium diisopropyl amide (LDA), other bases such as MeLi and *t*BuLi are also usable to synthesize Li/OR phosphinidenoid complexes as it will be shown hereafter.

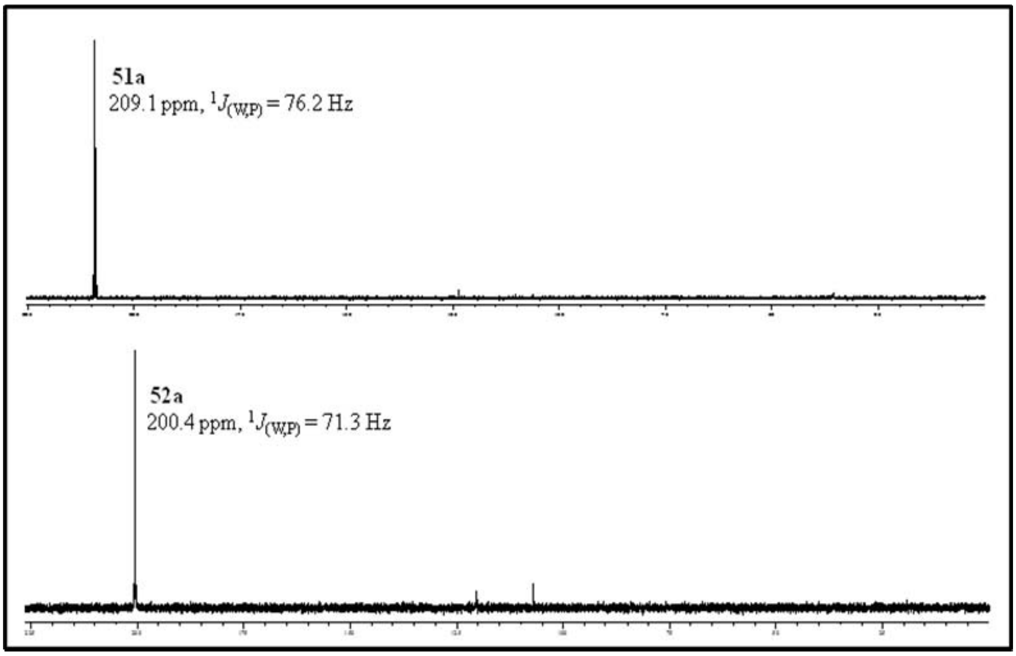


Figure 14. The $^{31}P\{^{1}H\}$ NMR spectra of the reaction solution of Li/OPh phosphinidenoid complex **51a** with and without 12-crown-4 **52a**

The chemical shift value of the Li/OPh phosphinidenoid complex **52a** (without 12-crown-4) is ca. 10 ppm more upfield shifted to the corresponding value of **51a** (with 12-crown-4). Power had shown for various classes of lithium compounds that 12-crown-4 is very effective in removing lithium and coordinating to Li^{+} ions.[82] In transferring these results one might conclude that this ability will lead to an enhanced electron density at the phosphorus centre and thus leading to an upfield shift of its ^{31}P resonance. In total, the observation of this significantly *downfield shifted* ^{31}P resonance (from the precursor complexes) parallels the NMR shift trends in carbenoids and silylenoids and thus the naming of phosphinidenoid complexes seems to be spectroscopically justified. Using the same protocol (with 12-crown-4) it was possible to synthesize a variety of *P*-alkoxy phosphinidenoid complexes; selected NMR data of the isolated Li/OR phosphinidenoid complexes **51a–e** are collected in table 7.

Table 7. Selected NMR data of Li/OR phosphinidenoid complexes **51** in THF-d8

Complexes	δ (^{31}P)[a]/ $^{1}J_{(W,P)}$[b]	δ (^{13}C$_p$)/ $^{1}J_{(P,Cp)}$
51a (R = Ph)	209.1/76.2	25.4/75.0
51b (R = Me)	209.6/68.7	25.8/66.6
51c (R = C_2H_4OMe)	208.8/69.0	24.3/68.5
51d (R =2,6-$Me_2C_6H_3$)	215.3/69.9	22.7/78.8
51e (R = *n*Bu)[c]	201.1/68.7	—

[a]: ppm; [b]: Hz; [c]: in reaction solution.

All ^{31}P resonances were observed at low field between 201 and 215 ppm with characteristic tungsten-phosphorus coupling constants between 70 and 80 Hz, which together resembles the NMR signatures of the Li/Cl phosphinidenoid complexes. The ^{13}C NMR spectra showed larger phosphorus-carbon (C^{P}) coupling constants than their precursors *P*-alkoxy phosphane complexes **45**, but no big differences in the δ value of the C^{P} atoms compared to those of the corresponding precursor phosphane complexes. In contrast, the ^{1}H NMR values of the proton bound to the bis(trimethylsilyl)methyl carbon atoms showed shifts downfield by more than 2 ppm.

The deprotonation protocol using LDA was also transferred successfully to the molybdenum and chromium *P*-phenoxy-substituted phosphane complexes **46** and **47** to yield the phosphinidenoid complexes **53** and **54**, although only in the case of chromium, the phosphinidenoid complex **54** was selectively formed and observed in the ^{31}P NMR spectrum at 248.8 ppm as a singlet. If the reaction was performed in the absence of 12-crown-4, the chemical shift value of the product **55** was invariant (δ = 248.7 ppm) (Figure 15), there was no obvious reason for this result.

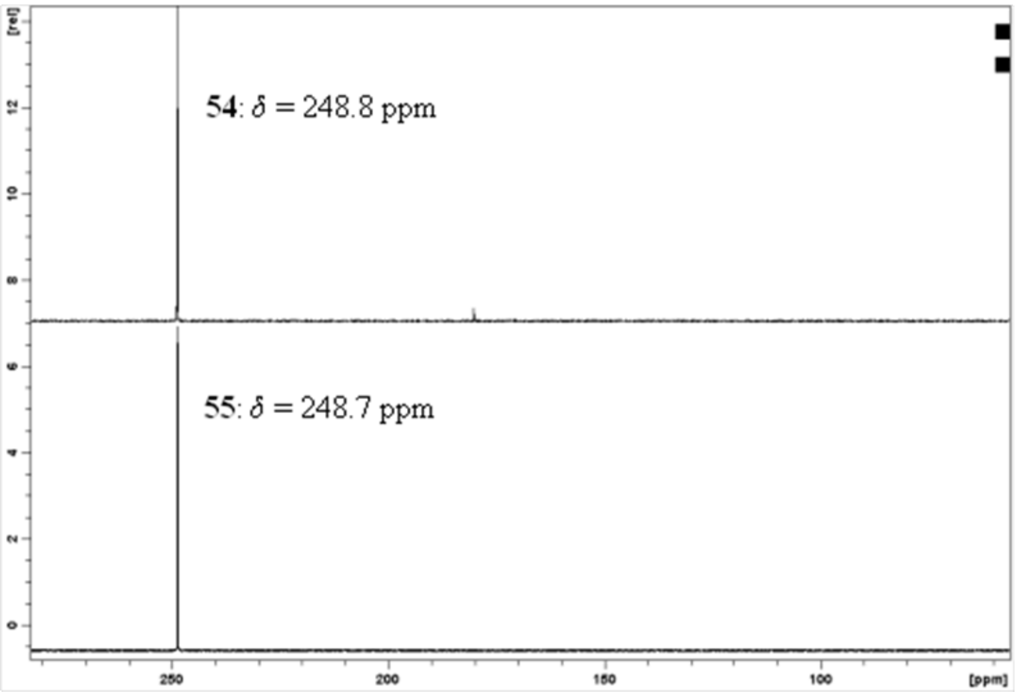


Figure 15. ^{31}P NMR spectrum of Li/OPh phosphinidenoid chromium complex **54**,**55** in the presence of 12-crown-4 (top) or absence (bottom).

In the case of the molybdenum complex **46** an unselective reaction occurred under the same conditions. If the reaction was performed in the presence of 12-crown-4 a product mixture was obtained at ambient temperature and the ^{31}P NMR spectrum included the Li/OPh phosphinidenoid molybdenum complex **53** (236.2 ppm) and the precursor complex **46** (133.9

ppm) and a small amount of the cyclotriphosphane[83] (R = $CH(SiMe_3)_2$) **16** (–126.7, –154.8 ppm, $^1J_{(P,P)}$ = 200.3 Hz) and some other unknown compounds (Figure 16). In order to examine the reaction course an NMR spectrum was recorded at –70 °C, which revealed an unexpected unselective reaction.

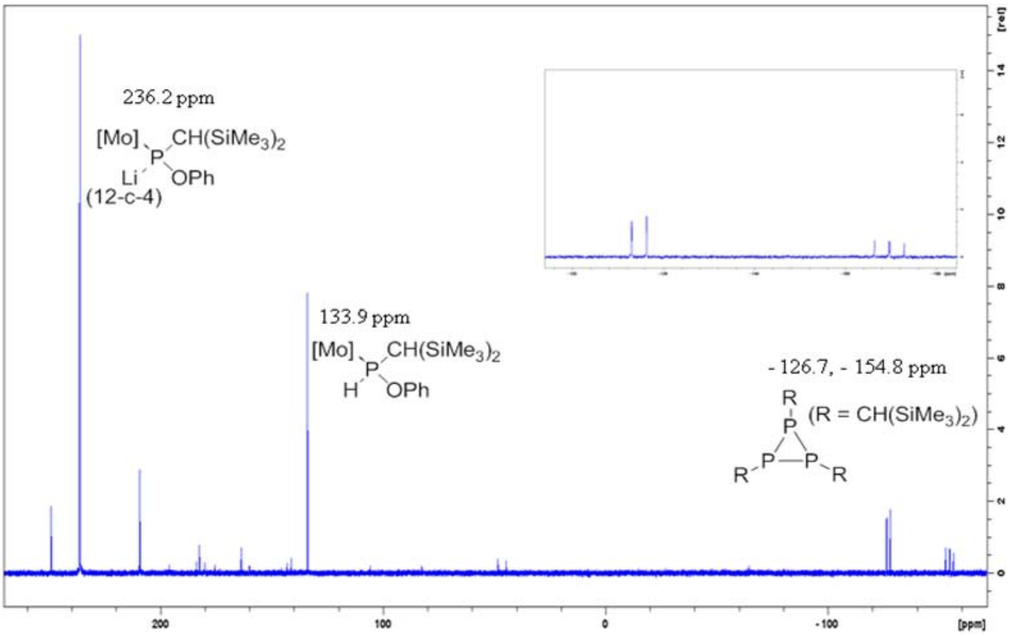


Figure 16. ^{31}P NMR spectrum of the reaction solution of complex **46** with lithium diisopropyl amide with 12-crown-4.

When the deprotonation reaction of **46** was carried out without 12-crown-4, the outcome was selective and an AB-type spin system was observed in the ^{31}P NMR spectrum (Figure 17) (A: –28.9 and B: –198.3 ppm) having a large phosphorus-phosphorus coupling constant ($^1J_{(P,P)}$ = 495.6 Hz). In addition, the ^1H NMR spectrum displayed the signals of three different trimethylsilyl groups (ratio: 1:2:1).

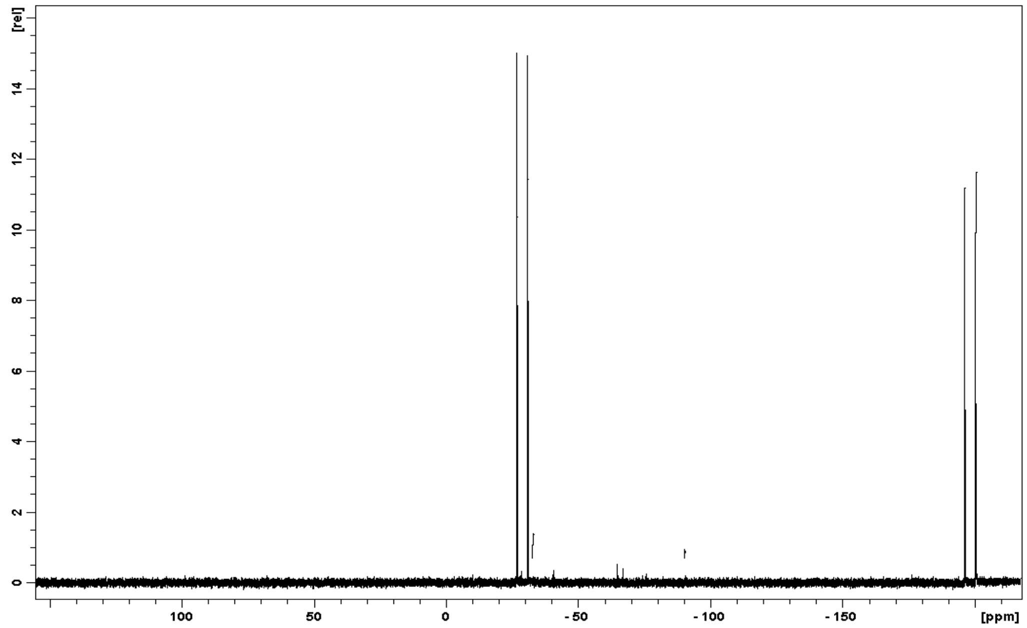
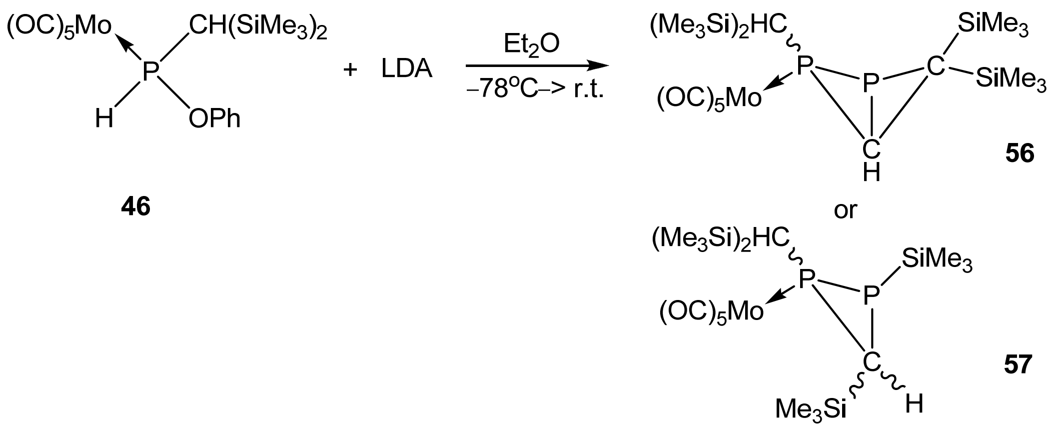


Figure 17. ^{31}P NMR spectrum of the reaction solution of complex **46** with lithium diisopropyl amide without 12-crown-4.

Based on these results a “butterfly type” complex **56** or the diphosphirane complex **57** (Scheme 22) might be tentatively deduced due to its similarity to known free ligands. The butterfly ligand[84] was reported by Niecke and Streubel in 1990 and here has two chemically non-equivalent phosphorus nuclei (–120.2 and –160.2 ppm) and a $^{1}J_{(P,P)}$ coupling of 240.9 Hz. In complex **56** (and **57**) the molybdenum moiety is attached to one phosphorus atom thus leading to a downfield shift of the corresponding center (–28.9 ppm), whereas the other is either found in a bridge-type position (**56**) or connected to a trimethylsilyl group[85] (**57**); both would support a resonance at high field. But there is a significant problem with the first proposal of **56** as there is no obvious reason and source for the extra carbon atom! Therefore, **57** seems to represent a more reasonable proposal although also here no explanation for the formation of **57** can be given.



Scheme 22. Reaction of *P*-OPh-substituted phosphane complex **46** with LDA to yield complex **56,57**.

4.3 Decomposition of a transient lithium/acyloxyl phosphinidenoid complex

When *P*-acyloxy phosphane complex **45f** was treated with lithium diisopropyl amide and 12-crown-4 at –78 °C and slowly warmed up to ambient temperature, the ^{31}P NMR spectrum (Figure 18) displayed a selective reaction yielding just one phosphorus-containing product: a singlet at 45.8 ppm ($^{1}J_{(\mathrm{W,P})}$ = 242.9 Hz, $^{1}J_{(\mathrm{P,H})}$ = 301.4 Hz).

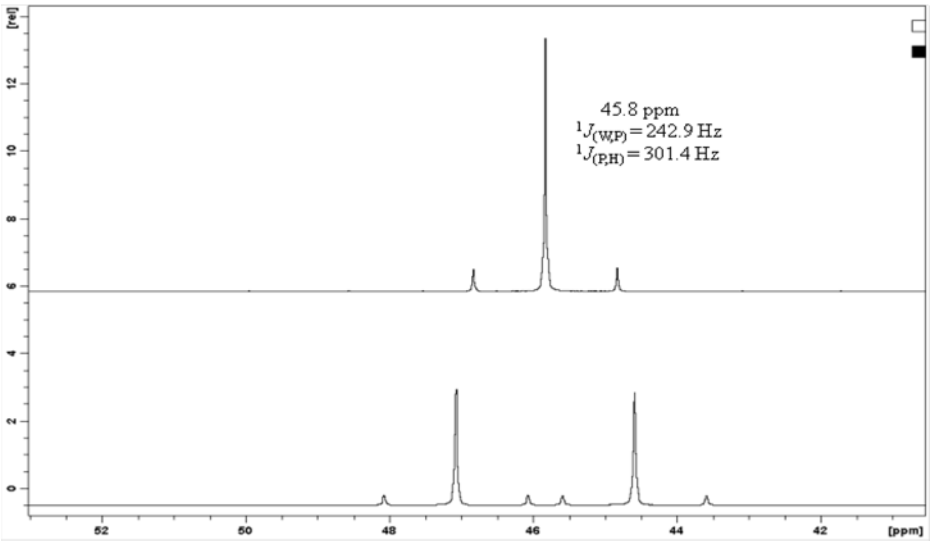


Figure 18. ^{31}P Spectrum of complex **58** in solution showing tungsten-phosphorus (top) and phosphorus-proton couplings (bottom).

In order to examine the reaction course, a ^{31}P NMR reaction monitoring (−80 to 25 °C) was performed that revealed a broad peak at 205.5 ppm of low intensity (−80 to −30 °C), which then disappeared above −30 °C to give the final product **58**. The resonance signal of **58** was found to be temperature dependent, varying from 43.8 ppm at −78 °C to 45.8 ppm at 25 °C.

Complex **58** was purified by washing with *n*-pentane at low temperature (−60 °C), and single-crystals suitable for X-ray crystallography were grown from diethyl ether solution at + 4°C. The molecular structure of **58** (Figure 19) features an unprecedented combination of a P–H and P–O–Li unit.

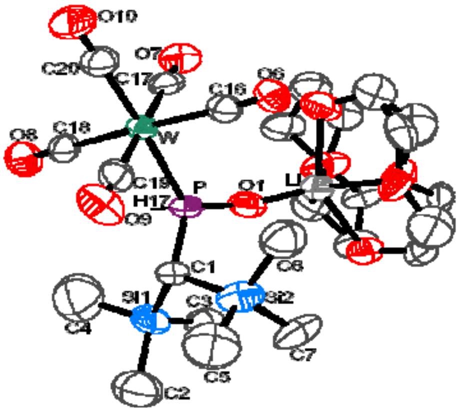
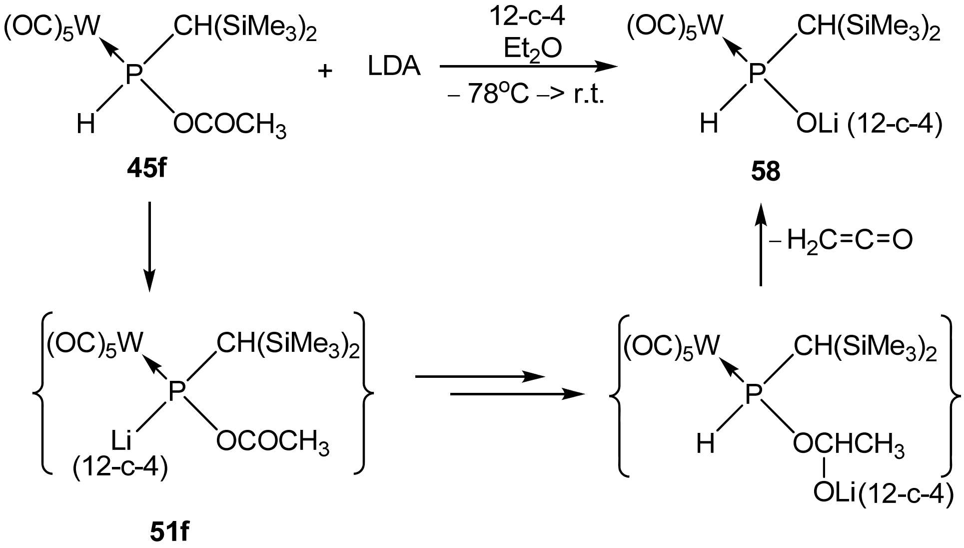


Figure 19. Molecular structure of complex **58** in the crystal (hydrogen atoms except H17 are omitted for clarity). Selected bond length [Å] and bond angles [°]: P–O(1) 1.505(6), P–H(17) 1.50(8), O(1)–Li 1.777(14), P–W 2.5483(17), P–C(1) 1.822(7), W–P–O(1) 121.4(2), W–P–C(1) 115.9(3), C(1)–P–O(1) 109.1(3), P–O(1) –Li 166.7(5).

The phosphorus in **58** has a pyramidal geometry (sum of the bond angles at P: 346.4(4)°). Remarkable is that the P–O bond distance was shortened by about 18 pm compared to the precursor **45f**, while the P–W bond was elongated by about 7 pm. and the P–H bond length in complex **58** is ca. 1.51 Å, about 16 pm longer than the *P*-alkoxyl phosphane derivative **45f** (1.35 Å). Another interesting aspect is that the bond angle of P–O(1)–Li is close to linearity (166.7(5) °), which is in strong contrast to the bond angle P–O(1)–C(1) in complex **45f** (118.5(2) °). The IR spectrum of complex **58** showed an absorption band at 2185 cm^{-1} due to the P–H valence stretch, which was bluefield shifted compared to complex **45f**. The carbonyl absorption bands of the pentacarbonyl tungsten moieties in both complex **45f** and **58** were observed in the typical range (**45f**: 1915, 1929, 1941, 1988, 2075; and **58**: 1909, 1959, 2054 cm^{-1}), the carbonyl stretch of the acyloxy group of complex **45f** was observed at 1740 cm^{-1}.

Although no further information about the decomposition was obtained, the following mechanism is tentatively proposed (Scheme 23): after primary formation of the phosphinidenoid complex **51f** it might be transformed into the *C*-lithiated phosphane complex via rearrangement, which eliminates ketene to give the final product **58**.



Scheme 23. Tentative mechanism for the formation of complex **58**.

As a Li–P interaction could not be spectroscopically identified for complex **51f**, it was interesting to perform the deprotonation in the absence of 12-crown-4. The $^{31}P\{^{1}H\}$ NMR spectroscopic monitoring (Figure 20) revealed a phosphorus-lithium coupling constant (δ = 182.0 ppm, $^{1}J_{(P,Li)}$ = 66.1 Hz) in complex **52f** (analogue of complex **51f**, without 12-crown-4). The observed quartet was also temperature dependent and varied between 180.2 ppm (−80 °C) to 188.5 ppm (−30 °C). Upon temperature increase, the phosphorus-lithium coupling disappeared, a phenomenon which was also reported by other authors like Power.[86]

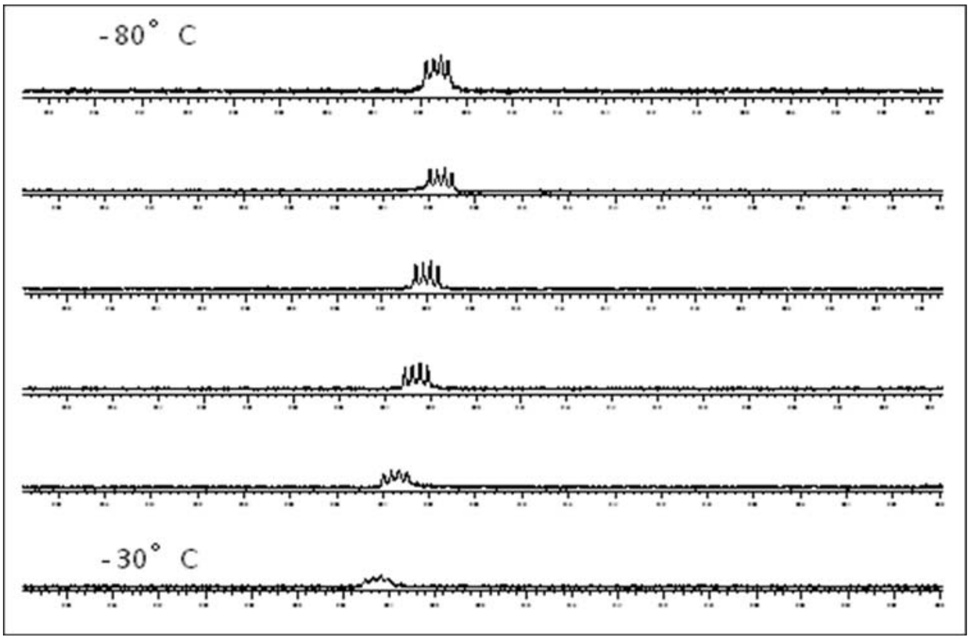
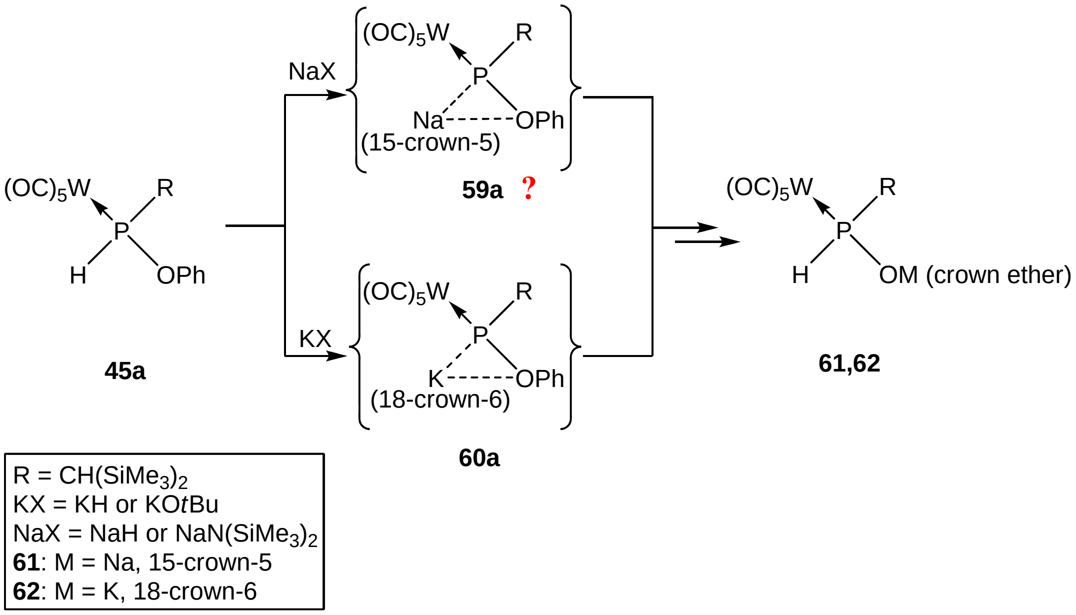


Figure 20. ^{31}P NMR spectroscopic reaction monitoring showing direct phosphorus-lithium coupling in **52f**.

Chapter 5. Investigations on the countercation dependency of stability and NMR signatures of *P*-alkoxy phosphinidenoid complexes

5.1 Investigations on *P*-alkoxy phosphinidenoid complexes having different counter cations

As the effects of counterions on stability and/or NMR signatures of M/X phosphinidenoid complexes are unknown, it was decided to investigate this aspect taking the M/OPh phosphinidenoid complex as a good case in point, especially as the system had tolerated the exchange of LDA for other bases such as MeLi and *t*BuLi. When various sodium and potassium bases were used to affect the deprotonation of phosphane complex **45a** (Scheme 24), the outcome was somehow disappointing. All attempts to obtain Na/OPh phosphinidenoid complex **59a** always led to the product [RP(H)ONa(15-crown-5)]W(CO)$_5$ **61** related to complex **58**. Interestingly, this was completely independent from the nature of the sodium base employed as sterically demanding bases such as NaN(SiMe$_3$)$_2$ gave the same result as NaH that has no steric hinderance. Even at low temperature no ^{31}P resonance signal of the corresponding Na/OPh phosphinidenoid complex **59a** could be detected.



R = $CH(SiMe_3)_2$
KX = KH or KO*t*Bu
NaX = NaH or $NaN(SiMe_3)_2$
61: M = Na, 15-crown-5
62: M = K, 18-crown-6

Scheme 24. Synthesis of complexes **61**, **62** via transient M/OPh phosphinidenoid complexes

Surprisingly, potassium-containing bases such as KH or KO*t*Bu enabled formation of the K/OPh phosphinidenoid complex **60a**, observed in the ^{31}P NMR spectrum (δ = 209.6 ppm). Apparently, the chemical shift of the potassium phosphinidenoid complex was very close to that of the lithium analogue, thus revealing a negligible effect of the counterion. Furthermore, the K/OPh phosphinidenoid complex **60a** was not as stable as the lithium analogue **51a**: the ^{31}P NMR spectrum revealed decomposition of **60a** (δ = 209.6 ppm) within a span of 15 hours to give the final product **62** at 35.4 ppm ($^{1}J_{(W,P)}$ = 228.9 Hz, $^{1}J_{(P,H)}$ = 303.9 Hz), which was then identified as $[RP(H)OK(18\text{-crown-}6)]W(CO)_5$ **62** (Figure 21).

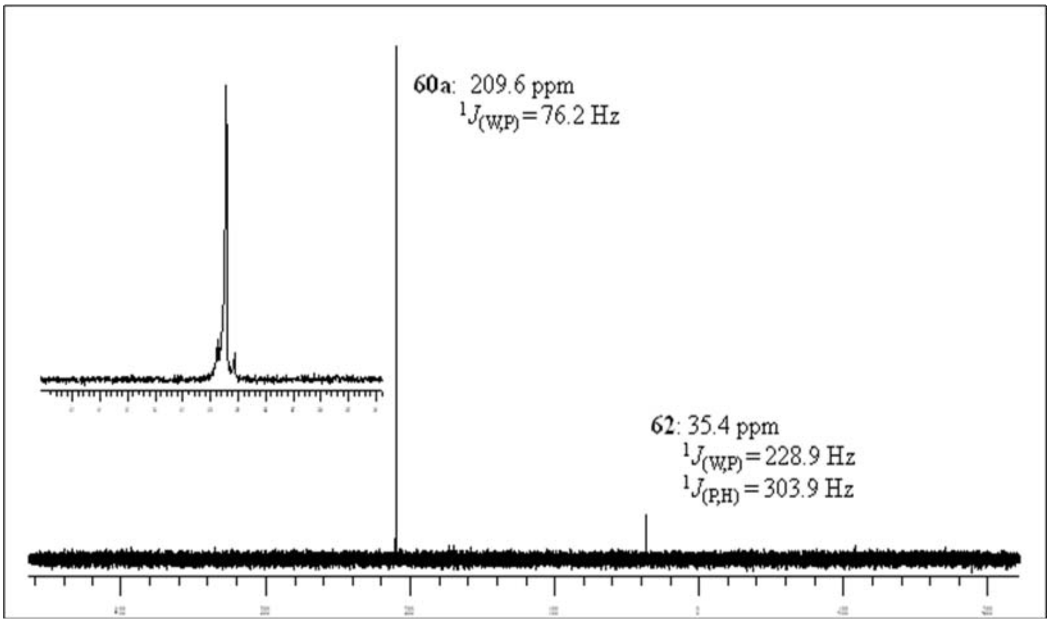


Figure 21. ^{31}P NMR spectrum of the K/OPh phosphinidenoid complex **60a** and its decomposition product **62**.

The outcome of these reactions revealed that the nature of the metal cations have little (to no) effect on the ^{31}P NMR signature of the corresponding phosphinidenoid complexes, which points to well separated metal cations bearing co-ligands such as crown ethers and/or solvent molecules and *P*-OPh phosphanide complexes as anions. In addition and, somehow, in contrast, different metal ions led to *P*-phenoxy phosphinidenoid complexes that possess different thermal stabilities. To examine this point in more detail the dependency of Li/OPh phosphinidenoide complexes from co-ligands was investigated further.

5.2 Investigation on the stability of lithium/alkoxy phosphinidenoid complexes having different co-ligands

As emphasized and described beforehand, the lithium *P*-phenoxy phosphinidenoid complex

51a was stable in solution even in the absence of 12-crown-4. Nevertheless, the question appeared what kind of co-ligands apart from crown ethers could be used? As it is well established, cryptands[87] are more effective reagents (as crown ethers) as they enable to encapsulate alkali metal ions through its nitrogen and/or oxygen donors, thus offering much better selectivity and binding strength for guest cations. Therefore, the appropriate [2,1,1]-cryptand (for lithium) was used instead of 12-crown-4 while keeping LDA as base to yield the corresponding Li/OPh phosphinidenoid complex **63**. The ^{31}P NMR spectrum displayed very similar data as those obtained previously in case of the crown ether which again supported the view of a largely independent cation. In a similar manner, it was then tried to synthesize the potassium derivative using LDA and the [2,2,2]-cryptand under same conditions, but, again a similar value was observed (209.3 ppm) in the ^{31}P NMR spectrum for the K/OPh phosphinidenoid complex **64**.

Besides these studies on the effect of co-ligands on NMR signature and stability of M/OPh phosphinidenoid complexes solvents were also tested with regard to their polarity and donor properties (Table 8).

In a nonpolar solvent such as *n*-pentane the formation of Li/OR phosphinidenoid complexes was not observed. If the polarity was increased, namely toluene was taken, the reaction led to little conversion of the starting material, the phosphane complex **45a** but the targeted Li/OPh phosphinidenoid complex **51a** was observed. When more polar solvents such as Et_2O, THF or tetramethylethylenediamine (TMEDA) were used, the phosphinidenoid complex **51a** was produced predominantly so apparently polar solvents favored this product. When TMEDA was used as solvent (or co-ligand), the tetramer of lithium phenoxide $[(Et_2O)LiOPh]_4$ **65** crystallized from the reaction solution at –30 °C (Figure 22). The similar cubic structures, such as lithium 3,5-dimethylphenolate $[(sol)LiO\text{-}(3,5\text{-}Me_2C_6H_3)]_4$ with different solvents,[88] have been established before. All Li–O bond distances and O–Li–O bond angles are within normal range.

Table 8. Effect of solvents on the formation of Li/OPh phosphinidenoid complex

Solvents	^{31}P NMR: $\delta^{[a]}$ ($^1J_{(W,P)}{}^{[b]}$ / $^1J_{(P,H)}$)	Percentage of final products	
		Phosphinidenoid complex **51a**	Phosphane complex **45a**
n-pentane	105.7 (274.7 / 331.9)	--	100%
toluene	107.1 (274.8 / 329.5) 209.1 (76.4 / --)	16.7%	83.3%
Et_2O/THF/TMEDA	209.2 (76.2 / --)	100%	--

[a]: ppm; [b]: Hz.

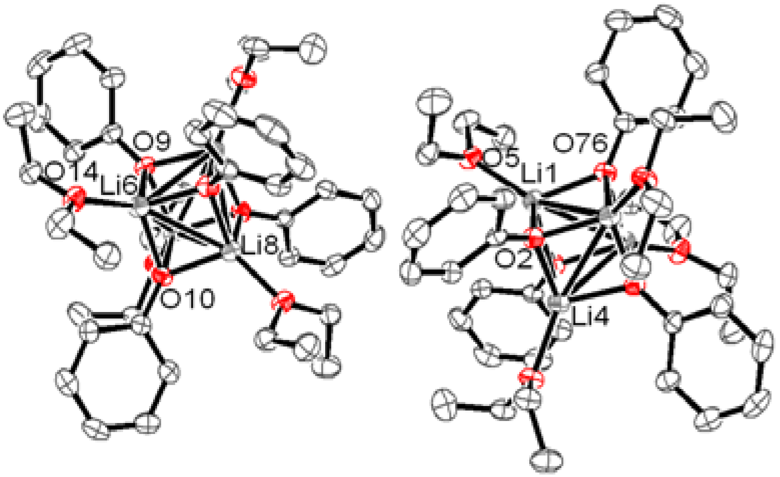
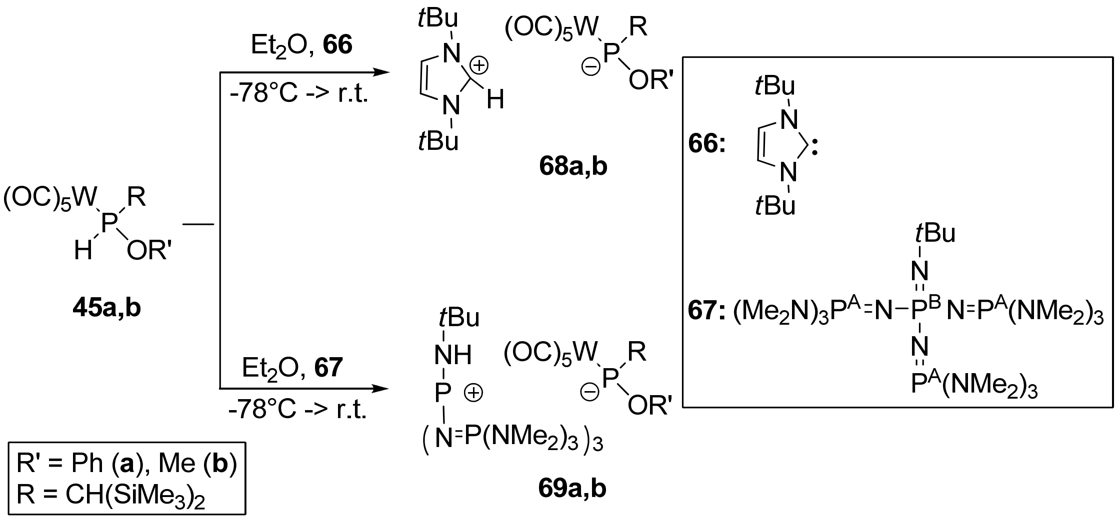


Figure 22. Molecular structure of compound **65** $[(Et_2O)LiOPh]_4$

5.3 Investigation on *P*-OR phosphinidenoid complexes stabilized by weakly coordinating cations

Although, and to the best of my knowledge, the chemistry of alkali metal cations coordinated carbenoids and silylenoids is substantially developed, the use of an organic base was far less studied, which holds true especially for weakly coordinating cations. Therefore, it became interesting to explore this area for the case of alkoxy and aryloxy-substituted phosphinidenoid complexes regarding stability and/or NMR signatures.

When complexes **45a,b** were reacted with the sterically hindered N-heterocyclic carbene **66**[89] and the phosphazene **67**[90] as organic bases, instead of organolithium base, the formation of complexes **68a,b** and **69a,b** were observed (Scheme 25).



Scheme 25. Synthesis of phosphinidenoid complexes **68a,b** and **69a,b** having weakly coordinating counter-cations.

The NHC **66** deprotonated complex **45a**, to yield selectively a signal at 209 ppm in the ^{31}P NMR spectrum, with a typical small tungsten-phosphorus coupling constant of about 75 Hz. The ^{13}C NMR spectra of **68a** revealed a resonance for the carbon atom directly bound to phosphorus (C^P) around 23.9 ppm as doublets ($^1J_{(P,C)}$ ca. 70 Hz), the imidazolium C^2 carbon atoms resonated as singlet around 130 ppm, which is ca. 80 ppm upfield from derivative **66**. On the other hand, the ^{1}H NMR spectra of complexes **68a** showed broad singlet at ca. δ 8.0–8.1 ppm easily attributed to the H atoms at C$^{4/5}$ of the imidazolium ring and, thus, being downfield from carbene **66** (δ: 6.99). When *P*-methoxy substituted phosphane complex **45b** was used to react with **66**, it always led to a mixture of NHC/OMe phosphinidenoid complex **68b** and precursor **45b** with a ratio of 1:10 at ambient temperature. A reaction monitoring the NMR (–70 to 25 °C) (Figure 23) revealed a temperature-dependent ratio between complex **68b** and complex **45b**, whereby higher temperature favoured **45b** over **68b**, while lower temperature led to quantitative formation of **68b**.

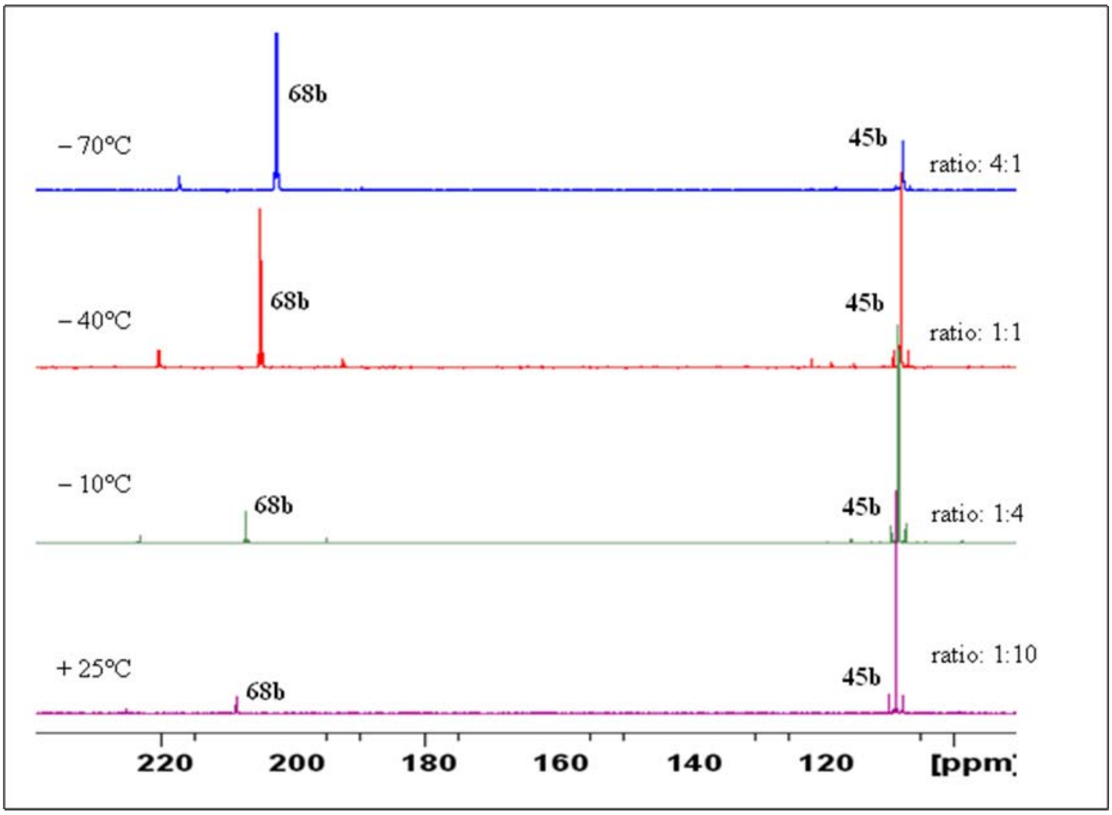


Figure 23. ^{31}P NMR spectroscopic monitoring of the equilibrium between complex **45b** and **68b**.

Single-crystals suitable for X-ray diffraction analysis of complex **68a** were grown from diethyl ether at −60 °C and the molecular structure is shown in figure 24.

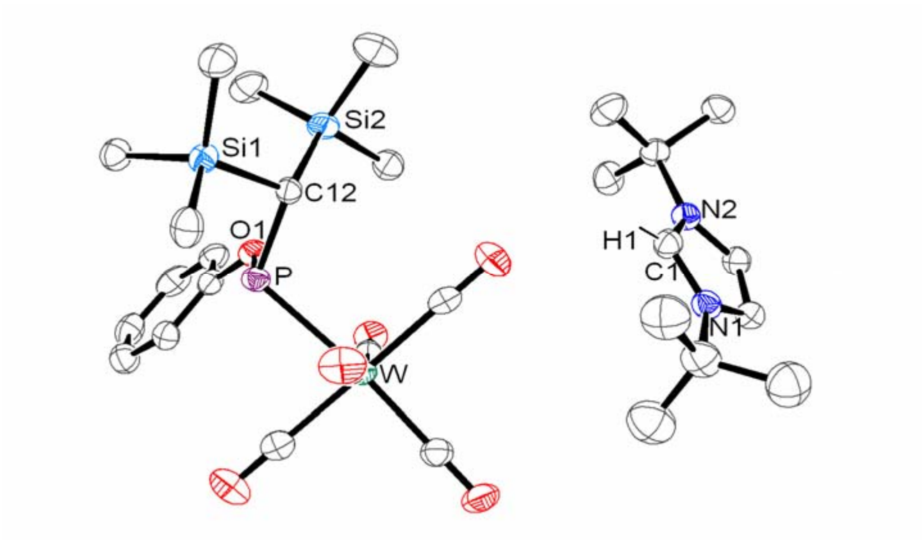


Figure 24. Molecular structure of complex **68a** in the crystal (except for H1, hydrogen atoms are omitted for clarity). Selected bond length [Å] and bond angles [°]: P–O(1) 1.730(3), O(1)–C(19) 1.362(5), P–W 2.5980(11), P–C(12) 1.870(4), C(1)–N(1) 1.320(5), C(1)–N(2) 1.334(5), W–P–O(1) 107.70(10), W–P–C(12) 110.08(13), C(12)–P–O(1) 95.39(16), N(1)–C(1)–N(2) 110.0(4).

A comparison of the crystallographic data of complex **68a** and its precursor **45a** revealed a significant bond elongation of the P–O(1) and P–W bond by 8 pm (5.0%) and 12 pm (4.8%), respectively, which resembles the bond lengthening trend of C–O bonds seen in Li/OR carbenoids.[91] The phosphorus centre of the anionic complex had a trigonal pyramidal environment (sum of bond angles at phosphorus = 313.17 °), thus revealing a stereochemically active lone-pair and the structure displayed an ion pair without any further inter-ion interactions. Although the structural data point to some residual electron density at phosphorus there is also some electron delocalization over the adjacent bonds apparent.

In the second case, the use of the phosphazene base **67** ("P_4-t-Bu" for short) for the deprotonation reaction was also very selective and only three signals appeared in the ^{31}P NMR spectrum (Figure 25): one at 209.7 ppm that was assigned to the phosphinidenoid complex phosphorus atom and two at high field at 13.5 and –22.9 ppm, which resulted from the phosphazenium cation (H-P$_4$-t-Bu) having an increased phosphorus-phosphorus coupling constant ($^2J_{(P,P)}$ = 49.6 Hz) (P^A: d; P^B: quart) compared with phosphazene **67** (δ: 5.9 (P^A) and –24.6 ppm (P^B), $^2J_{(P,P)}$ = 10.2 Hz). In the ^{13}C NMR spectra of **69a,b** the carbon atoms directly bound to phosphorus (C^P) appeared around 24 ppm having phosphorus-carbon coupling constants around 67 Hz.

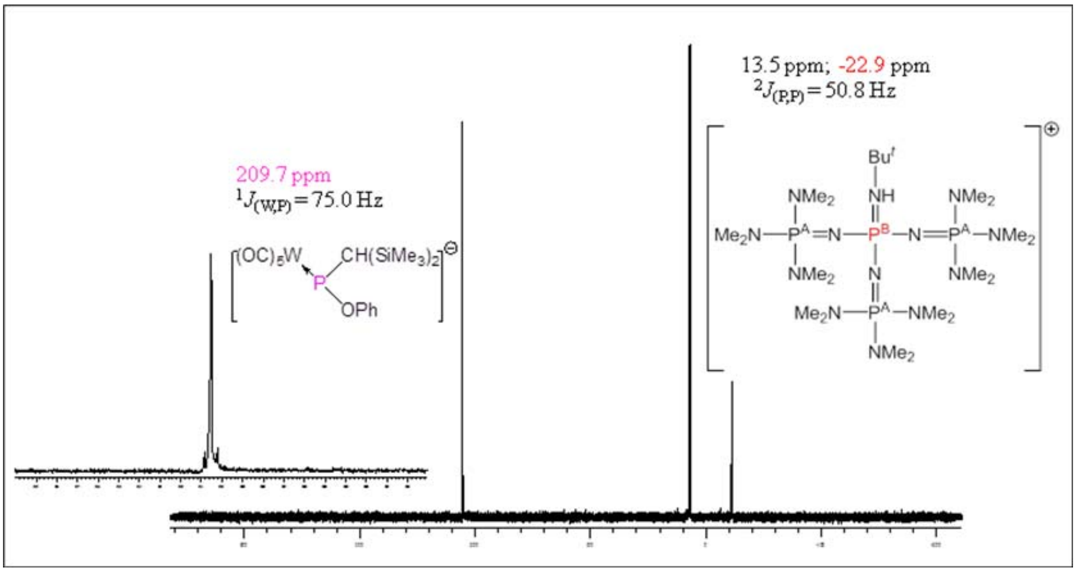
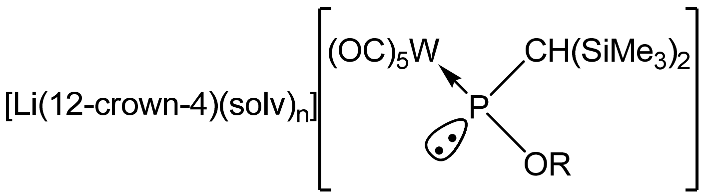


Figure 25. ^{31}P NMR spectrum of the [H-P$_4$-t-Bu]$^+$ stabilized phosphinidenoid complex **69a**.

In a short summary, all new alkoxy and aryloxy phosphinidenoid complexes have strikingly similar ^{31}P NMR data with chemical shifts between 200 and 210 ppm that are accompanied by a typical small tungsten-phosphorus coupling constant of about 75–80 Hz. As all phosphinidenoid complexes show the same NMR signatures it seems that the origin is the insignificance of the cation onto the anion because of a missing interaction. In the same vein this view is supported by the ion pair structure of imidazolium-phosphinidenoid complex **68a** in the crystal.

From all these studies and especially the crystal structure of the imidazolium stabilized phosphinidenoid complex **68a**, the following ion pair chemical formula (Figure 26) of *P*-OR phosphinidenoid complexes is concluded and will be used hereafter and thus “replaces” the one used before.



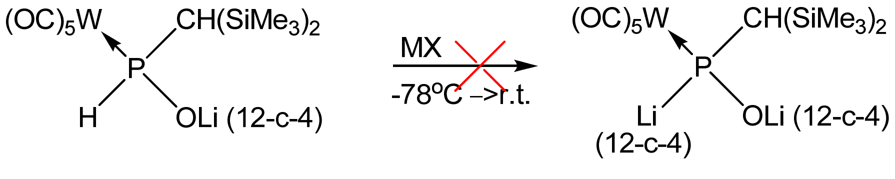
51a-e

Figure 26. Ion pair formula of Li/OR phosphinidenoid complexes **51a–e**.

Chapter 6. Preliminary studies on reactivity of complex 58

The uniqueness of complex **58**, which contains both a P–H and P–O–Li unit in one molecule, was the motivation to examine its reactivity. One especially attractive aspect was the quest for additional deprotonation, thus establishing an even more unique “Li–P–O–Li” moiety in a structure of molecular compound. One special driving force for getting the dilithium-containing complex **70** (Scheme 26), was the perspective to get access to oxaphosphirane complexes[92,93] by reaction with a 1,1-dihalo-substituted substrate of the formula R_2CX_2.

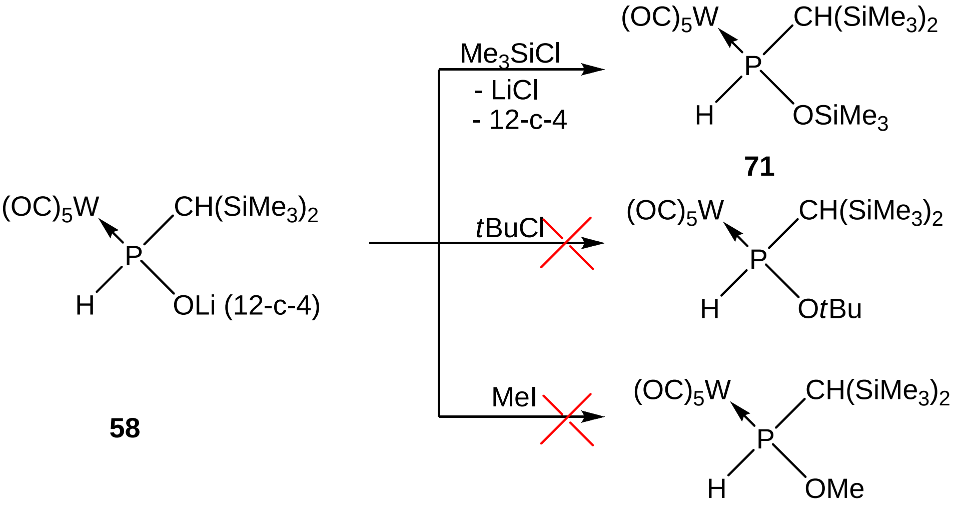
To our surprise and disappointment all bases used such as LDA, *t*BuLi/KO*t*Bu, *n*BuLi/DMPU turned out to be unsuccessful. Although the reason is not apparent it might be a kinetic problem as the OLi(12-crown-4) is quite a bulky substituent at phosphorus and thereby might be effectively blocking the approach of a base. On the other hand, formal anion-anion repulsion might be another argument.



58 **70**

Scheme 26. Attempted deprotonation of **58** to access complex **70** (MX = LDA, *t*BuLi/KO*t*Bu, *n*BuLi/DMPU (= 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone))

Another aspect of interest in complex **58** was its ability for nucleophilic reactions and, therefore, different electrophiles (Scheme 27) such as methyl iodide, chlorotrimethylsilane and *tert*-butyl chloride were tested. But again to our surprise, only the reaction with chlorotrimethylsilane worked out to yield the known *P*-trimethylsiloxyl phosphane complex **71**[94] (δ = 76.8 ppm, $^1J_{(W,P)}$ = 275.1 Hz, $^1J_{(P,H)}$ = 325.5 Hz); in the other two cases, no reaction took place. Under the conditions reported, complex **71** was usually formed as a byproduct in the thermal reaction of 2*H*-azaphosphirene complex **41** in presence of differently substituted nitriles or alkynes via an unknown reaction pathway – but traces of water are required – and the yields varied between 1–10%. Here this complex was very easy to obtain in good yields (71.5%).



Scheme 27. Tested nucleophilic reactions of complex **58** using three different electrophiles.

In order to examine further the aspect of potential kinetic hinderance, the complex **72** having no 12-crown-4 coordinated to the O-Li moiety (analogue of complex **58**) was tried to react with the same electrophiles but no further insight was obtained. If complex **58** was heated in THF at 60 °C for 15 hours, nothing happened; but when the corresponding complex **72** (without crown ether as co-ligand) was heated for 15 hours at 60 °C, an exciting result was obtained by ^{31}P NMR spectroscopy, the spectrum in quest is displayed in figure 27 and shows an AB-type spin system with a doublet in the downfield (A: $\delta = 339.9$ ppm, $^{2}J_{(P,P)} = 82.7$ Hz) and one doublet in the highfield region (B: $\delta = -182.3$ ppm, $^{2}J_{(P,P)} = 82.7$ Hz, $^{1}J_{(W,P)} = 163.8$ Hz, $^{1}J_{(P,H)} = 258.1$ Hz). As the product could not be isolated no further information was obtained and, therefore, no structural assignment could be done.

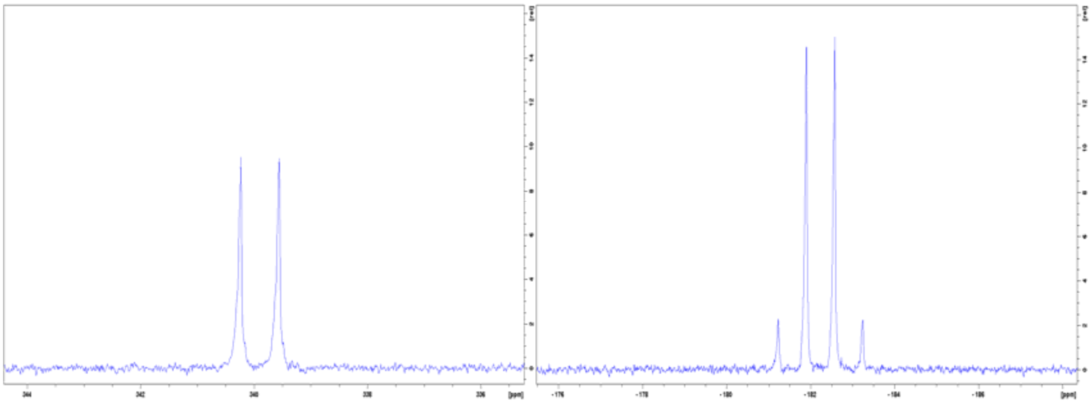


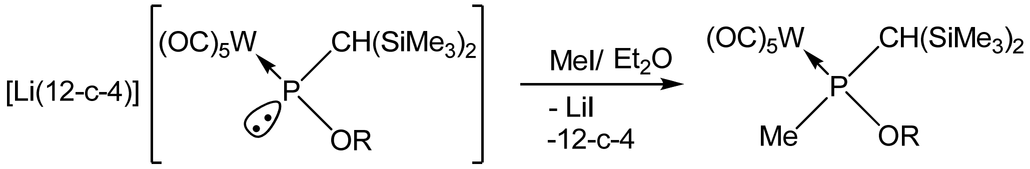
Figure 27. ^{31}P NMR spectrum of complex from thermal reaction of complex **72**

Chapter 7. Studies on reactivity of Li/OR phosphinidenoid complexes 51a–e

7.1 Reaction of lithium/alkoxy phosphinidenoid complexes 51a–d with electrophiles: methyl iodide and deuterated chloroform

As the studies on Li/OR phosphinidenoid complexes had revealed the same NMR signature but higher thermal stabilities, i.e., no diphosphene complexes were observed, the reactivity was brought into the focus of further studies. Firstly, electrophiles such as methyl iodide (Scheme 28), and deuterated chloroform (Scheme 29) were reacted, which, as expected, yielded the corresponding *P*-methyl or *P*-chloro-substituted products **73/74, 75**. With some exceptions (see below) all of them could be isolated after purification by column chromatography and fully characterized.

Except **73b**, all other *P*-methyl-substituted phosphane complexes **73a**, **73c,d** were obtained in good yields. The decreased yield of complex **73b** was largely due to repeated column chromatography at low temperature. It should be noted that in the case of complex **73d**, the reaction was always accompanied by the formation of small amounts (< 10 %) of the cyclotriphosphane **16**, which provided some indirect evidence of a formal elimination of MesOLi on the way to the final product.



51a-d **73a-d**

51, 73a: R = Ph
51, 73b: R = Me
51, 73c: R = $C_2H_4OCH_3$
51, 73d: R = 2,6-$Me_2C_6H_3$.

Scheme 28. Reaction of phosphinidenoid complexes **51a–d** with MeI to obtain the *P*-methylated phosphane complexes **73a–d**.

All *P*-methyl-substituted phosphane complexes **73a–d** showed ^{31}P resonances in the range of 130–140 ppm, tungsten-phosphorus coupling constants magnitudes of about 270 Hz. In the ^{13}C NMR spectra the resonances of the C^p atoms are not significantly affected (24–25 ppm) showing phosphorus-carbon coupling constants ($^1J_{(P,C)}$ = 11–25 Hz) (Table 9).

Table 9. Selected ^{31}P and ^{13}C NMR data and IR absorption values of **73a–d**

Complexes	$\delta(^{31}P)^{[a]}/^1J_{(W,P)}^{[b]}$	$\delta(^{13}C)\ /^1J_{(P,C^p)}^{[c]}$	$\nu(CO)^{[d]}$
73a (R = Ph)	142.4/279.2	30.0/11.1	2068
73b (R = Me)	130.4/269.6	24.2/18.7	2069
73c (R = C_2H_4OMe)	130.2/269.9	23.8/18.9	2069
73d (R = 2,6-$Me_2C_6H_3$)	134.0/273.4	30.2/25.4	--

[a]: ppm; [b]: Hz; [c]: carbon atoms which bound directly to the phosphorus center; [d]: highest (nu tilde $\tilde{\upsilon}$) value of CO stretching modes (A_1).

Single-crystals suitable for X-ray diffraction could be obtained for complex **73a** from diethyl ether solution at −30 °C, the molecular structure of **73a** is shown in figure 28. A comparison of the structural data of complex **73a** with its precursor **45a** showed that all bond angles and bond distances are within the expected range. The only difference concerns the sum of bond angles at phosphorus (without the metal unit) which is 331.51 ° for complex **73a** but 342.30 ° for its precursor **45a**.

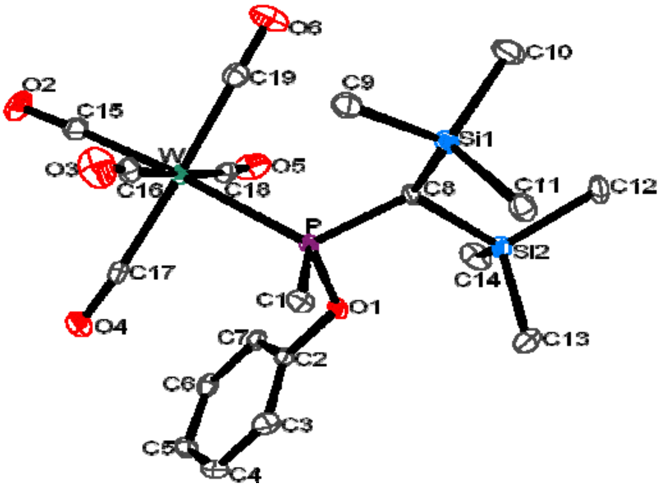
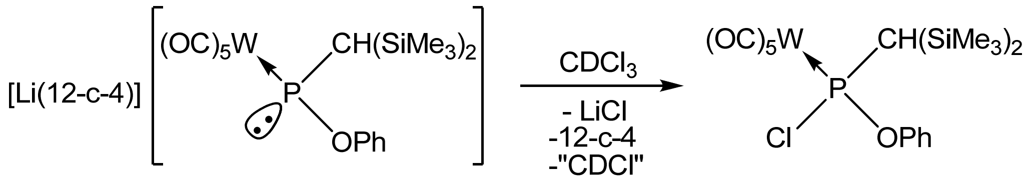


Figure 28. Molecular structure of complex **73a** in the crystal (hydrogen atoms omitted for clarity). Selected bond length [Å] and bond angles [°]: P–O(1) 1.649(2), P–C(1) 1.814(3), P–W 2.5045(7), P–C(8) 1.819(3), O(1)–C(2) 1.398(3), W–P–O(1) 114.80(8), W–P–C(1) 115.28(10), W–P–C(8) 119.05(9), C(1)–P–O(1) 100.28(12), C(8)–P–O(1) 97.66(12), C(1)–P–C(8) 106.89(13).

To complete this series, the reaction of the Li/OPh phosphinidenoid chromium complex **54** with methyl iodide was also investigated and revealed a clean conversion into the *P*-methylated phosphane chromium complex **74** (δ = 139.1 ppm), within the range of the *P*-methylated phosphane tungsten complexes **73a–d**; complex **74** was also characterized by

IR, mass spectrometry. As a clean synthesis of the Li/OPh phosphinidenoid molybdenum complex **53** represented an unsolved problem, the reaction with methyl iodide was not investigated.

When $CDCl_3$ was employed as deuterated solvent to spectroscopically characterize the phosphinidenoid complex **51a** a reaction occurred that led to complex **75a** (Scheme 29). **75a** was obtained as very bright yellow crystalline powder in high yield (90%) and which was fully characterized and unambiguously confirmed by single-crystal X-ray structure analysis.

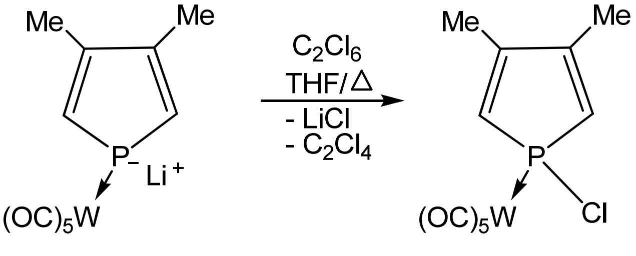


51a

75a

Scheme 29. Synthesis of *P*-chloro-alkoxyl phosphane complex **75a**.

Complex **75a** showed a ^{31}P resonance at 186.7 ppm ($^{1}J_{(W,P)}$ = 335.7 Hz), which is ca. 30 ppm downfield to the known dichlorophosphane complex **78**[95] (δ = 157.0 ppm). Although no intermediate was detected by ^{31}P NMR spectroscopy, the formation of **75a** implies formal elimination of CDCl from a primarily formed *P*-$CDCl_2$ complex derivative via a (C->P) chlorine shift, and although this doesn't seem thermodynamically feasible (at low temperature), it formally resembles a thermal decomposition of a iodo(organo)phosphane tungsten complex (R = $CH(SiMe_3)_2$) bearing a *P*-CH_3 unit.[96] On the other hand, reactions of phosphanides and phospholides with organochlorides are very common. For example, Mathey reported in 2009 the synthesis of 1-chloro-3,4-dimethylphosphole tungsten complex **77**[97] (Scheme 30) via reaction of the lithium phospholide complex **76** with hexachloroethane under formation of lithium chloride and C_2Cl_4.



76 **77**

Scheme 30. Preparation of 1-chloro-3,4-dimethylphosphole tungsten complex **77**.

A comparison of the molecular features of complex **75a** (in Figure 29) with both reported dichlorophosphane complexes $[RPCl_2]W(CO)_5$ (R = $CH(SiMe_3)_2$) **78** and complex **77** reveals for **75a** a W–P bond distance of 2.4731(6) Å, which is slightly longer than in complex **78** (2.458 Å)[95] and in complex **77** (2.452 Å).[97] Complex **75a** has a slightly longer P–Cl bond (2.092 Å) than in both complexes **77** and **78** (**78**: 2.058 Å, **77**: 2.055 Å), probably due to weaker π-donor ability of phenyl group in complex **75a** than other two complexes. The Cl–P–O(1) bond angle in complex **75a** (99.0 °) is larger than corresponding bond angle in complex **78** (Cl–P–Cl: 96.9 °), which could be due to the repulsion force of benzene ring. While comparison of **75a** with its precursor **45a** in correlated bond lengths resulted in slightly shorter P–O and P–C (from $CH(SiMe_3)_2$ group) in complex **75a**. On the other hand, the bond angle of P–O(1)–C(8) in **75a** is bit larger than that in complex **45a**.

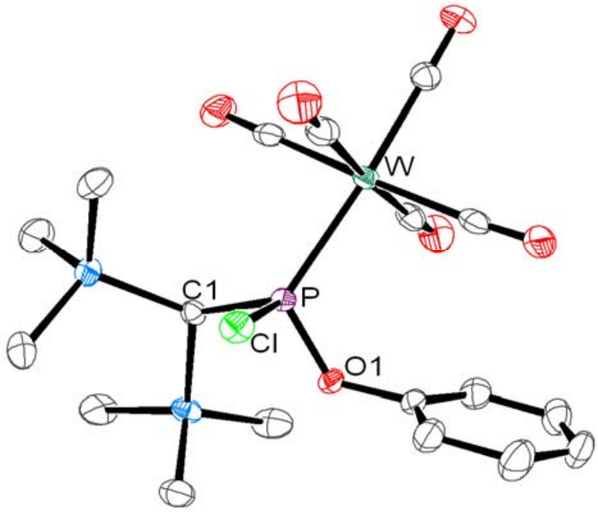
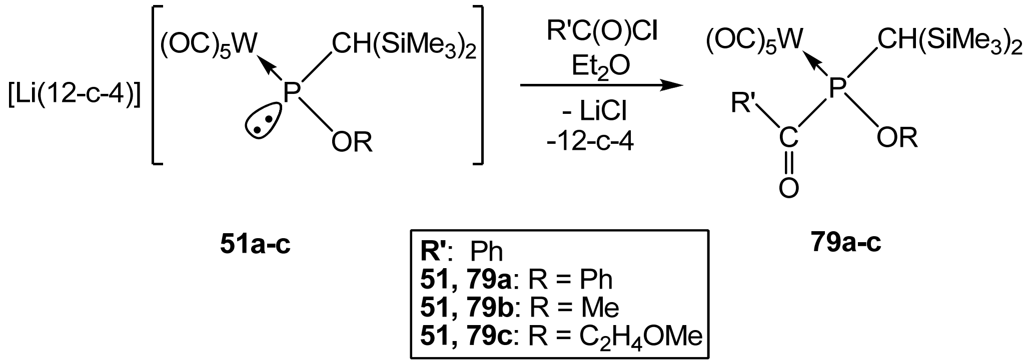


Figure 29. Molecular structure of complex **75a** in the crystal (hydrogen atoms are omitted for clarity). Selected bond length [Å] and bond angles [°]: P–O(1) 1.6187(16), P–C(1) 1.799(2), P–W 2.4731(6), P–Cl 2.0918(9), O(1)–C(8) 1.411(3), W–P–O(1) 117.48(7), W–P–C(1) 120.18(8), W–P–Cl 114.08(3), C(1)–P–O(1) 99.58(10), Cl–P–O(1) 99.00(7), P–O(1)–C(8) 124.35(16).

7.2 Reactivity of lithium/alkoxy phosphinidenoid complexes 51a–c toward acyl chlorides

Among the organophosphorus compounds containing a carbonyl group directly bound to a phosphorus atom, the most important examples are mono- and bis-(acyl) phosphane oxides, which proved to be effective photoinitiators[98] and therefore attracted great attention of chemists. However, acylphosphanes coordinated to a transition-metal center are less studied and their potential is substantially unexplored, although the known stabilizing ability of transition metal complexes could be safely assumed. Hence, it was decided to investigate the synthesis and reactivity of acylphosphane complexes. The synthesis followed the straightforward protocol: treatment of Li/X phosphinidenoid complexes with differently substituted acylchloride to yield the products (Scheme 31). The reactivity of the complexes **51a–c** largely depended on the nature of the substituent OR. An interesting insight was gained through a comparative study between complexes **51a–c** and *P*-halogeno substituted complexes. The former appeared to be far less reactive than those complexes bearing *P*-halogen.[99]



Scheme 31. Synthesis of *P*-functional (acylphosphane) tungsten complexes **79a–c**.

Complexes **79a–c**[99] were obtained in good yields (70–85 %) after purification by column chromatography at low temperature and were fully characterized, pure **79a–c** are stable under inert gas conditions. The ^{31}P NMR resonances of complexes **79a–c** were at ca. 153.5–159.0 ppm, with a $^{1}J_{(W,P)}$ = 273.4–289.9 Hz (Table 10). Both the ^{31}P nuclei chemical shift (δ) and tungsten-phosphorus coupling constants (J) were larger than the *P*-methyl complexes **73a–d**, which is interpretable in terms of the sp^2 hybridization of the carbonyl carbon atoms attached to the phosphorus centre. In the ^{13}C NMR spectra of complexes **79a–c** the signals of the carbonyl carbon atoms, which directly bonded to the phosphorus atom appeared at δ = 202.3–216.6 ppm. Interestingly, in the case of the *P*-alkoxy-substituted acylphosphane complexes **79a–c**, these signals of carbon atoms of the acyl groups displayed larger phosphorus-carbon coupling constants.

Table 10. Selected NMR data and IR absorption values of complexes **79a–c**

Complexes	δ (^{31}P)[a]/$^{1}J_{(W,P)}$[b]	δ (^{13}C)[c]/$^{1}J_{(P,C)}$	δ (^{13}C)[d]/$^{1}J_{(P,C)}$	ν(CO)[e]
79a	159.0/289.9	--	--	--
79b	154.1/273.4	27.3/3.6	208.8/12.1	1670
79c	153.5/278.5	27.5/5.2	208.4/7.1	1647

[a]: ppm; [b]: Hz; [c]: carbon atoms bound directly to the phosphorus centre; [d]: carbon atoms from acyl carbonyl groups; [e] highest (nu tilde $\tilde{\upsilon}$) value of CO stretching modes (A_1).

The IR spectra exhibited surprisingly weak absorption bands in the range of 1648–1702 cm^{-1} due to the carbonyl stretching mode of the acyl moiety in **79a–c** (Figure 30).

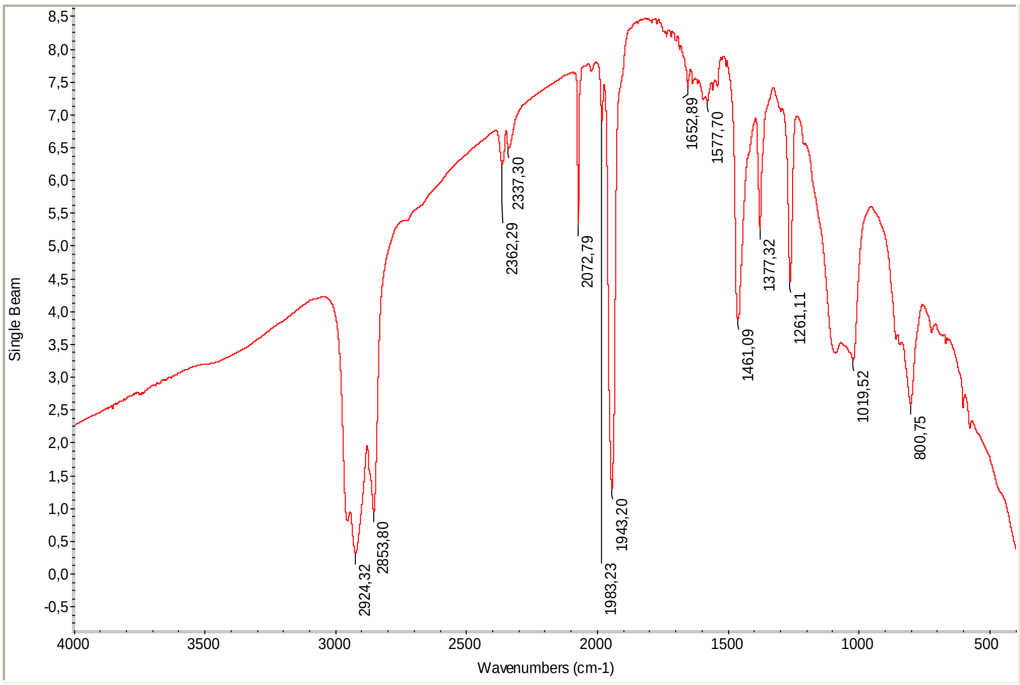
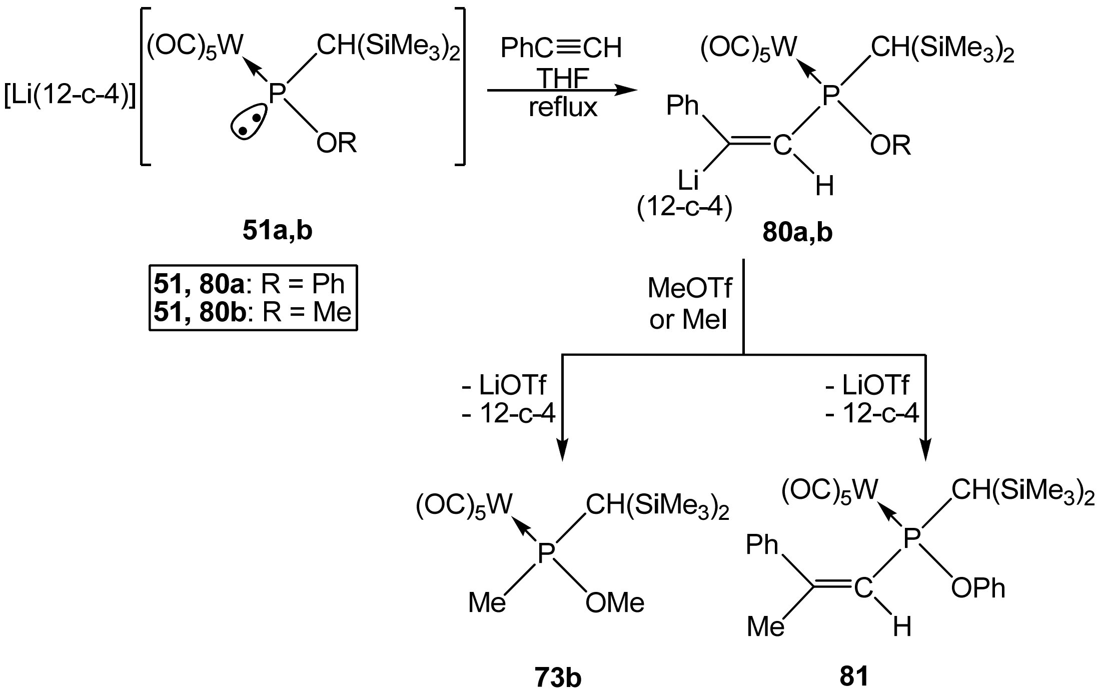


Figure 30. IR spectra of acyl(alkoxy)phosphane complex **79a**

7.3 Reactivity of Li/alkoxy (aryloxy) phosphinidenoid complexes 51a,b towards alkynes

So far, the reactivity studies revealed mostly “phosphanide-type” reactivity of Li/OR phosphinidenoid complexes, although some hints for a “phosphinidene-type” reactivity were also obtained, therefore more in depth investigations of the latter aspect were required. As it was known that Li/Cl phosphinidenoid complexes can undergo the [2+1] cycloaddition reactions to get access to three-membered ring heterocyclic complexes,[64] studies on reactions of the Li/OPh and Li/OMe phosphinidenoid complexes with benzaldehyde and phenylacetylene were carried out.

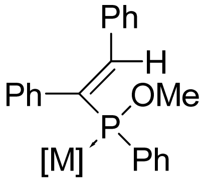
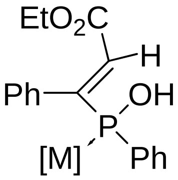
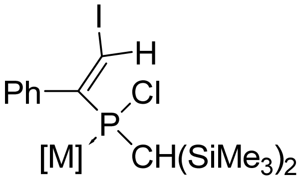
When Li/OPh phosphinidenoid complex **51a** was tried to react with phenylacteylene no reaction was observed at ambient temperature; raising the temperature to reflux conditions yielded the *P*-alkenyl phosphane complex **80** and **81** after subsequent methylation with methyl triflate (Scheme 32). All attempts to find the right conditions to obtain the corresponding 1*H*-phosphirene complex turned out to be unsuccessful.



Scheme 32. Reactions of complex **51a,b** with phenylacetylene to give complexes **81** and **73b** as final products.

The ^{31}P NMR spectroscopic reaction monitoring showed that, after 2 hours, a singlet appeared at δ = 168.9 ppm ($^{1}J_{(W,P)}$ = 289.9 Hz), which was assigned to the intermediate **80** and then trapped with methyl triflate to give the final product **81** (δ = 154.4 ppm, $^{1}J_{(W,P)}$ = 269.1 Hz). Unfortunately, attempts to grow suitable crystals for single X-ray diffraction analysis of **81** were unsuccessful, so the configuration of the C–C double bond is not clear. A comparison of complex **81** with other known *P*-vinyl phosphane complexes derivatives is shown in table 11. The most noteworthy point is that the $^{3}J_{(P,H)}$ coupling constants of ca. 17–22 Hz in these three known *P*-vinyl phosphane complexes (*trans*-configuration) is comparably larger than the value in complex **81**, which is only 4.6 Hz; the CH proton resonates at 7.64 ppm in the ^{1}H NMR spectrum.

Table 11. Selected ^{31}P and ^{1}H NMR data of known *P*-vinyl phosphane complexes

Complexes	$\delta(^{31}P)^{[a]}/^{1}J_{(W,P)}^{[b]}$	$\delta(^{1}H)^{[c]}/^{3}J_{(P,H)}$
 [cf.100]	129.3 / 278	7.78 / 21.8
 [cf.100]	104.3 / 283	6.73 / 17.1
 [cf.101]	89.7 / 283.6	7.40 / 16.8

[a]: ppm; [b]: Hz; [c]: vinyl proton.

As it was noticed several time beforehand the Li/OPh **51a** and Li/OMe phosphinidenoid complexes **51b** showed slightly different reactivity due to different electron-donating effects of the methoxy and phenoxy group. Therefore, reactions of Li/OMe phosphinidenoid complex **51b** were performed using phenylacetylene and ethyl propiolate. The reaction of complex **51b** with phenylacetylene (Scheme 32), under the same conditions as before in the case of the Li/OPh derivative, the *P*-methyl phosphane complex **73b** was always formed as final product, regardless of the nature of the alkylating reagents (MeI or MeOTf).

The final product is substantially different from the result of Li/OPh phosphinidenoid complex case. The ^{31}P NMR revealed the formation of *P*-methyl phosphane complex **73b**. However the reaction without any trapping agents (Figure 31) displayed a new signal at about

162.0 ppm, with ${}^{1}J_{(W,P)}$ = 280.3 Hz, ${}^{3}J_{(P,H)}$ = 15.0 Hz, which can be assigned to be the lithiated intermediate **80b**.

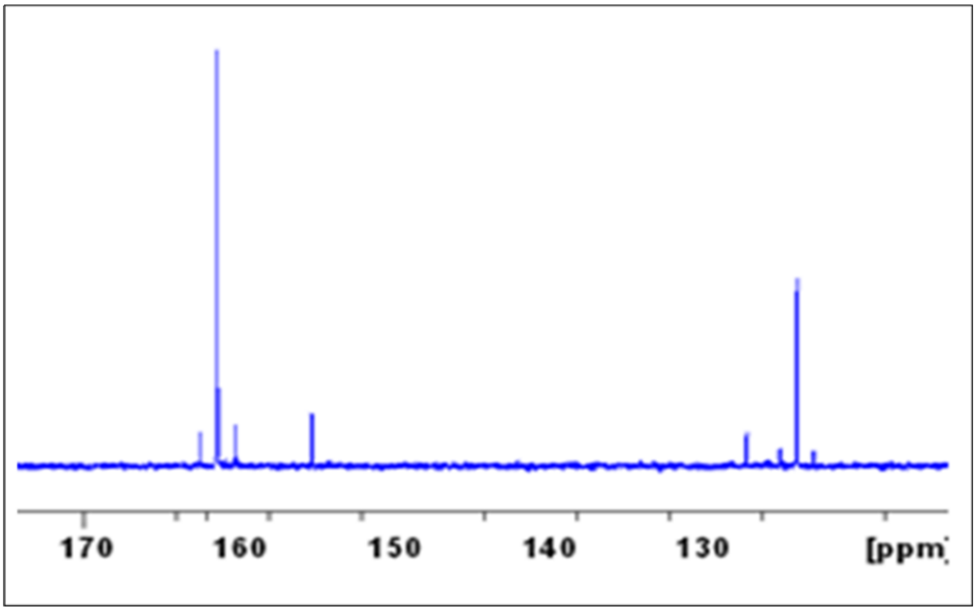
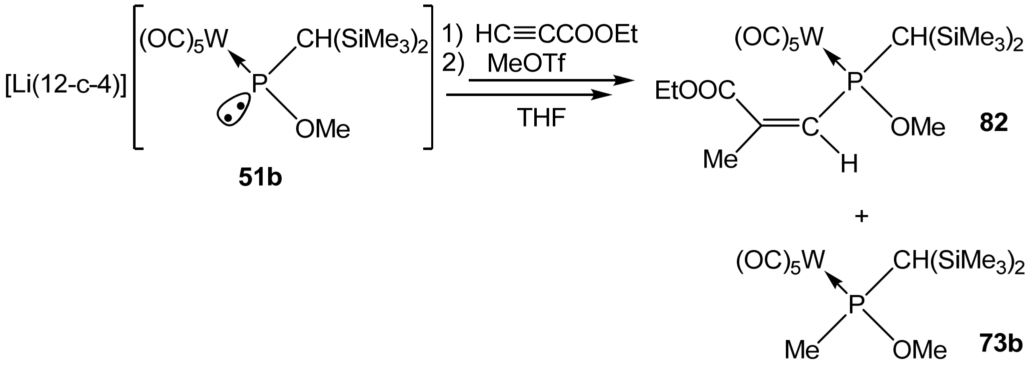


Figure 31. ^{31}P NMR spectrum of the lithiated intermediate complex **80b** without addition of any trapping reagents.

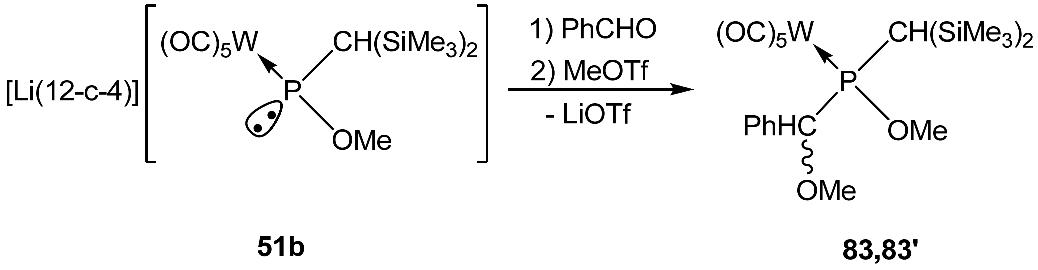
In order to investigate the unusual reactivity of the anionic intermediate complex further, the reaction of complex **51b** with ethyl propiolate and subsequently with MeOTf was also performed. The ^{31}P NMR spectrum revealed that two major products **82** and **73b** were formed (ratio 2:3); **82** showed a resonance at δ = 158.6 ppm (${}^{1}J_{(W,P)}$ = 279.7 Hz, ${}^{3}J_{(P,H)}$ = 15.1 Hz (Scheme 33).



Scheme 33. Reaction of Li/OMe phosphinidenoid complex **51b** with ethyl propiolate and subsequently with MeOTf.

7.4 Reactivity of Li/OR phosphinidenoid complexes 51a,b toward aldehydes

Although the reaction of Li/OR phosphinidenoid complex **51a,b** with different alkynes proceeded differently from that of the corresponding Li/Cl derivatives, studies on the reactivity of complexes **51a,b** towards benzaldehyde seemed especially interesting as the features of a higher polarity combined with the option of creating a P,C and a P,O bond could be favorable. In case of the phosphinidenoid complex **51a** the ^{31}P NMR spectrum revealed no reaction but if it was replaced for the Li/OMe phosphinidenoid complex **51b** a reaction with the system benzaldehyde/MeOTf was observed that yielded the addition complex **83, 83’** as a mixture of diastereomers (ratio 2:3) (Scheme 34).

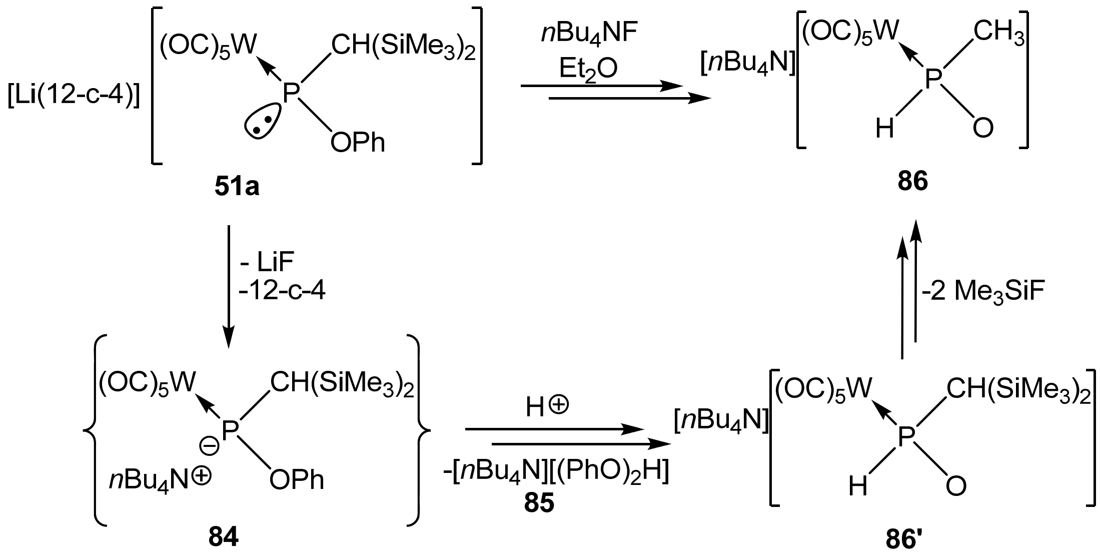


Scheme 34. Reaction of Li/OMe phosphinidenoid complex **51b** with benzaldehyde/MeOTf.

The complexes **83,83’** showed resonances in the ^{31}P NMR spectrum at 161.9 and 162.5 ppm ($^{1}J_{(W,P)}$ = 275.9 Hz). These NMR data are in agreement with those of the complexes[102] [RPX(PhCHOH)]W(CO)$_5$ (R = CH(SiMe$_3$)$_2$; X = Cl, F), and the diastereomers of which have similar data (X = F: δ = 198.1/201 ppm, $^{1}J_{(W,P)}$ = 296.3 Hz; X= Cl, δ = 146.6/138.7 ppm, $^{1}J_{(W,P)}$ = 274 Hz). Further studies showed that different ratios between **51b** and benzaldehyde, i.e., 1:1, 1:3, 1:5, didn’t change the ratio of the two diastereomers. In contrast, the reaction became less selective. The separation and purification of the complexes using column chromatography at low temperature failed, so that only different mixtures were obtained and subjected to various analytical methods. Mass spectrometric experiments (EI) revealed the molecular ion peak (m/z 666.1), which also confirmed the elemental constitution of the products.

7.5 Reaction of lithium/alkoxy phosphinidenoid complexes 51a,b with tetra-*n*-butylammonium fluoride and phosphonium salts

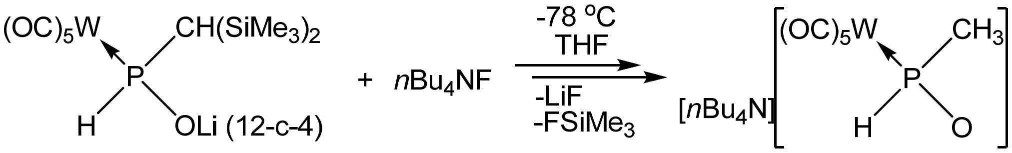
From all reactions reported and discussed so far, no “*phosphinidene*-type” reactivity could be concluded. In order to perform a cation exchange reaction – and to mimic the organic cation phosphinidenoid complexes **68**,**69** – the reaction of complexes **51a** with tetra-*n*-butylammonium fluoride was studied. Surprisingly, the Li/OPh phosphinidenoid complex **51a** reacted with tetra-*n*-butylammonium fluoride to give the final product **86** without any observable intermediate (Scheme 35).



Scheme35. Proposed mechanism for the reaction of Li/OPh phosphinidenoid complex **51a** with tetra-*n*-butylammonium fluoride, yielding complex **86**.

Complexes **86** and **86'**, which are time-dependent, were observed together in the ^{31}P NMR spectrum. But after 24 hours, complex **86'** converted completely to complex **86** by desilylation reaction.[103] In ^{1}H and ^{13}C NMR, there was no related H and C signals of silyl groups. Instead, a doublet quartet was observed in the ^{1}H NMR spectrum due to this P-CH$_3$ coupling. The final product complex **86** displayed a resonance at 35.3 ppm and a large phosphorus-hydrogen coupling constant in the ^{31}P NMR spectrum, thus telling that an unexpected reaction must have taken place. Single-crystal X-ray structure analysis revealed the formation of the salt *n*Bu$_4$N[(PhO)$_2$H] (**85**) (Figure 32) which might have been formed via some kind of elimination reaction from a reactive intermediate. According to this stoichiometry showing two phenyl groups in the product structure one *n*Bu$_4$N unit must be present in the phosphorus-containing product **86**, which therefore is described as the ion pair complex **86**, displaying a ^{31}P resonance at 35.5 ppm ($^{1}J_{(W,P)}$ = 224.6 Hz, $^{1}J_{(P,H)}$ = 300.1 Hz).

In order to confirm this proposal, another independent reaction pathway was tested and, therefore, complex **58** was reacted with tetra-*n*-butylammonium fluoride at low temperature to give complex **86** through elimination of lithium fluoride (Scheme 36).



Scheme 36. Reaction of complex **58** with *n*Bu_4NF to yield complex **86**.

The obtained final product **86** showed the same ^{31}P NMR data (δ = 35.3 ppm, $^1J_{(W,P)}$ = 227.6 Hz, $^1J_{(P,H)}$ = 300.1 Hz), which are very close to the data of complex **58**[104] (δ = 46.0 ppm, $^1J_{(W,P)}$ = 244.1 Hz, $^1J_{(P,H)}$ = 302.6 Hz). Unfortunately, the constitution of this unusual salt structure could not be confirmed as all attempts resulted in the formation of crystals of compound **85** suitable for X-ray diffraction analysis (Figure 32). The molecular structure of **85** shows a linear O1–H···O2[105] hydrogen-bridge with a O1–O2 distance of 2.473(4) Å as the most interesting feature.

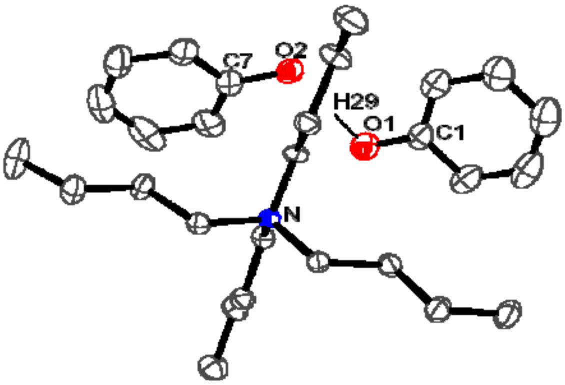
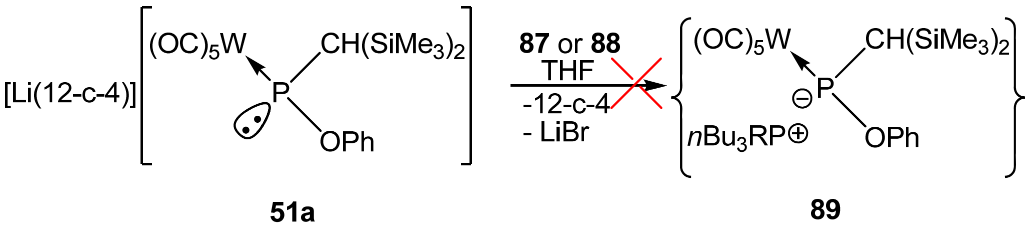


Figure 32. Molecular structure of complex **85** in the crystal (except for H29 hydrogen atoms are

omitted for clarity). Selected bond length [Å] and bond angles [°]: O(1)–H(29) 1.1944, O(1)–C(1) 1.344(6), O(2)–H(29) 1.2861, O(2)–C(7) 1.316(5).

To test the effect of the cation and anion of tetra-*n*-butylammonium fluoride, somehow, the reaction of Li/OPh phosphinidenoid complex **51a** with similar phosphonium salts such as the tetra-*n*-butyl phosphonium bromide and methyl sulfonate were used – the corresponding fluoride is known to exist only as covalent P–F phosphorane and was therefore excluded from this study. Scheme 37 and figure 33 show the reaction were completely unsuccessful.



87: [*n*Bu$_4$P]Br
88: [*n*Bu$_3$(C$_{14}$H$_{29}$)P]SO$_3$Me
89: R = *n*Bu or C$_{14}$H$_{29}$

Scheme 37. Attempted reaction between the Li/OPh phosphinidenoid complex **51a** with phosphonium salts **87,88** to yield the complex **89**.

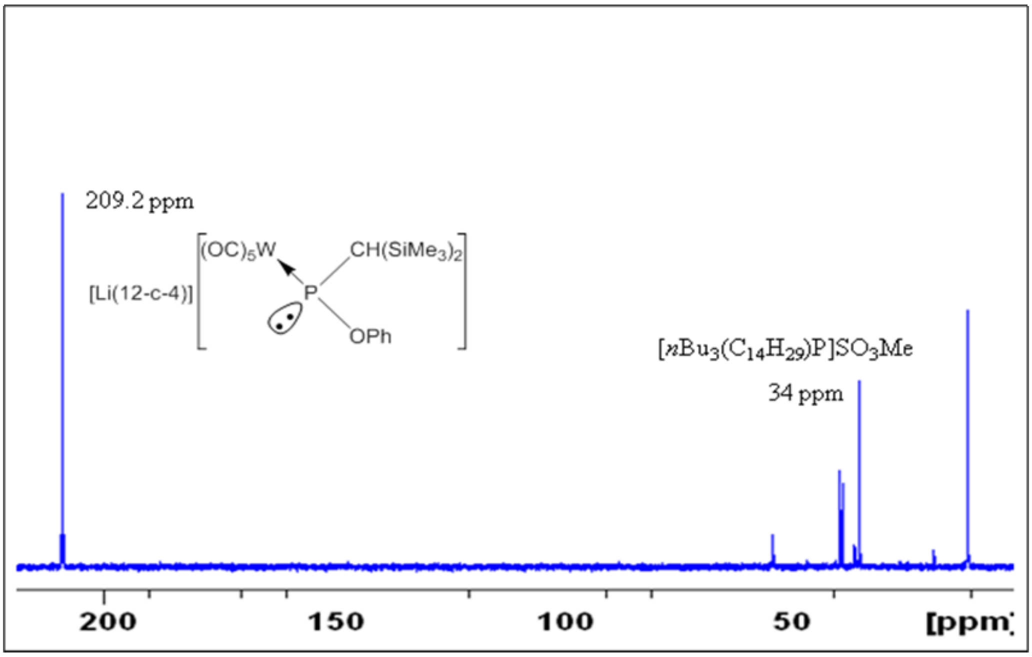
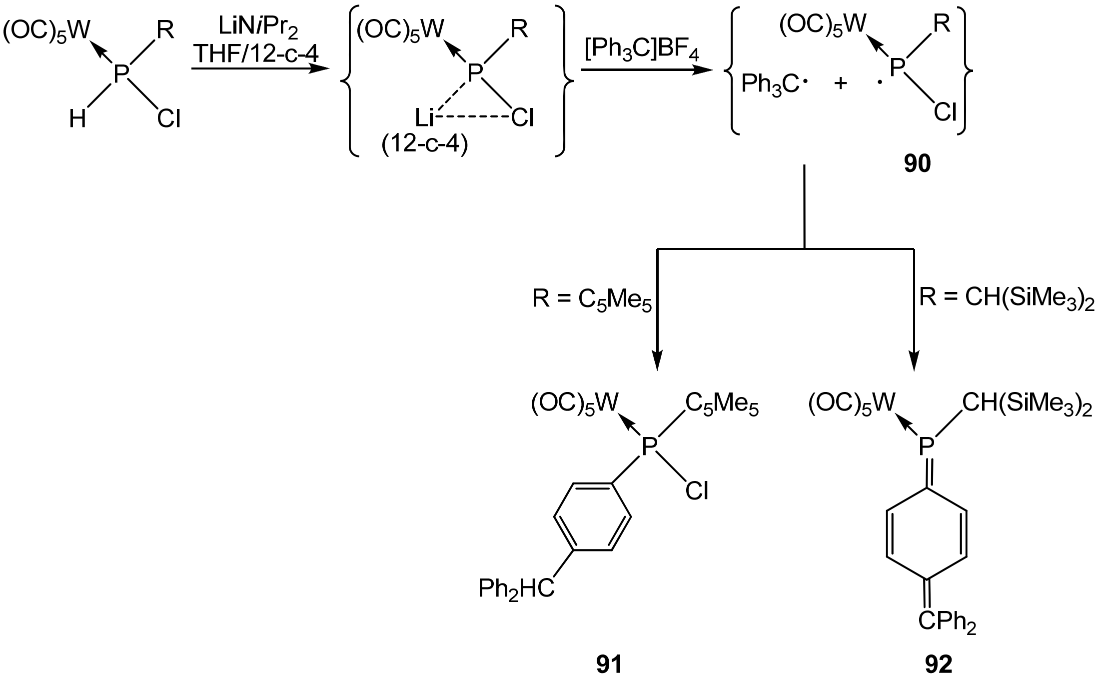


Figure 33. ^{31}P NMR spectrum of the reaction of Li/OPh phosphinidenoid complex **51a** with the phosphonium salt **88** [*n*$Bu_3(C_{14}H_{29})PSO_3Me$)

The ^{31}P NMR spectra showed that the signal at 209.2 ppm, belonging to the Li/OPh phosphinidenoid complex **51a**, didn't vanish (even after hours) after addition of the phosphonium solution and neither did the latter signal at 34 ppm (belonging to unreacted methyl sulfonate), meaning that there was no (or extremely slow) reaction; even heating overnight didn't change the picture. No change occurred either if [*n*Bu_4P]Br was used, instead.

7.6 Reaction of lithium/alkoxy phosphinidenoid complexes 51a,b with tritylium tetrafluoroborate

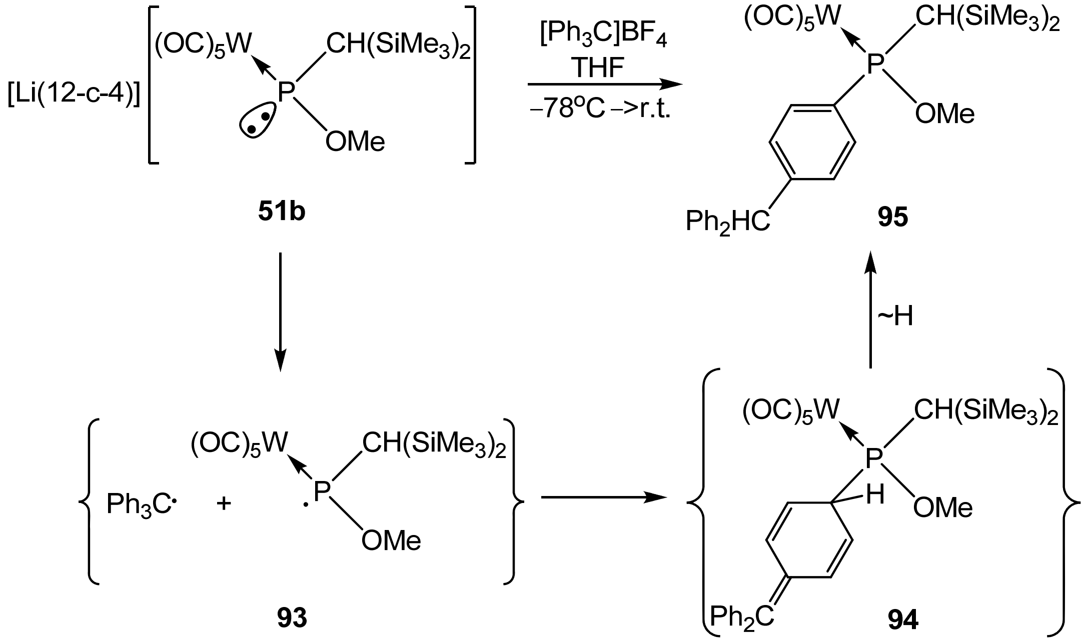
Previous studies on reactions of Li/Cl phosphinidenoid complexes bearing different substituents ($CH(SiMe_3)_2$ and C_5Me_5) with tritylium salt led to the final products **91** and **92** via the transient *P*-chlorophosphanyl radical **90** as confirmed by EPR spectroscopic data and DFT calculations (Scheme 38); both of the final products were unequivocally confirmed by X-ray diffraction analysis.[70]



Scheme 38. Reaction of Li/Cl phosphinidenoid complexes with tritylium tetrafluoroborate to yield complexes **91** and **92**.[70]

On the basis of these fascinating results, the quest for cation exchange *versus* redox reaction of Li/OR phosphinidenoid complexes was open for exploration. First, the Li/OPh phosphinidenoid complex **51a** was tested, but the ^{31}P NMR spectrum revealed that there was no reaction (within 24 h) between complex **51a** and tritylium tetrafluoroborate. To examine if kinetic reasons might be responsible, Li/OMe phosphinidenoid complex **51b** was employed and the ^{31}P NMR spectrum showed that a resonance at δ = 141.7 ppm ($^{1}J_{(W,P)}$ = 277.8 Hz, $^{3}J_{(P,H)}$ = 12.4 Hz), implying that a (redox) reaction had occurred. The product, complex **95**, showed a resonance at δ = 5.62 ppm (singlet) in the ^{1}H NMR spectrum, which is close to the

NMR data of *P*–C_5Me_5 complex **91** (5.64 ppm). After column chromatography, the constitution of complex **95** was established by NMR, and IR spectroscopic measurements as well as mass spectrometry and elemental analysis. The initial step might be the SET oxidation of complex **51b** with tritylium tetrafluoroborate to yield the transient *P*-OMe phosphanyl complex **93** (Scheme 39) which subsequently coupled with the Ph_3C radical to give **94** and then rearranged to give the final product **95**.



Scheme 39. Proposed pathway for the reaction of Li/OMe phosphinidenoid complex **51b** with tritylium tetrafluoroborate to yield complex **95** via oxidative SET reaction.

EPR spectroscopic investigations using the thaw-freeze technique showed that various radicals were involved (Figure 34).

Although a clear-cut picture was not obtained from these preliminary studies the main observations shall be briefly described. From these EPR spectra of frozen and thawing samples (for temperatures see Figure 34), it was straightforward that the reaction still proceeded inside the EPR tube, involving creation and annihilation of radicals. After 4 hours at room temperature, two strong signals remained, one from the stable tritylium carbon-centered radical, and the other most probably stemming from a paramagnetic tungsten complex. This observation implied that this reaction might be not a simple reaction in the sense that a radical pair is formed and then combines.

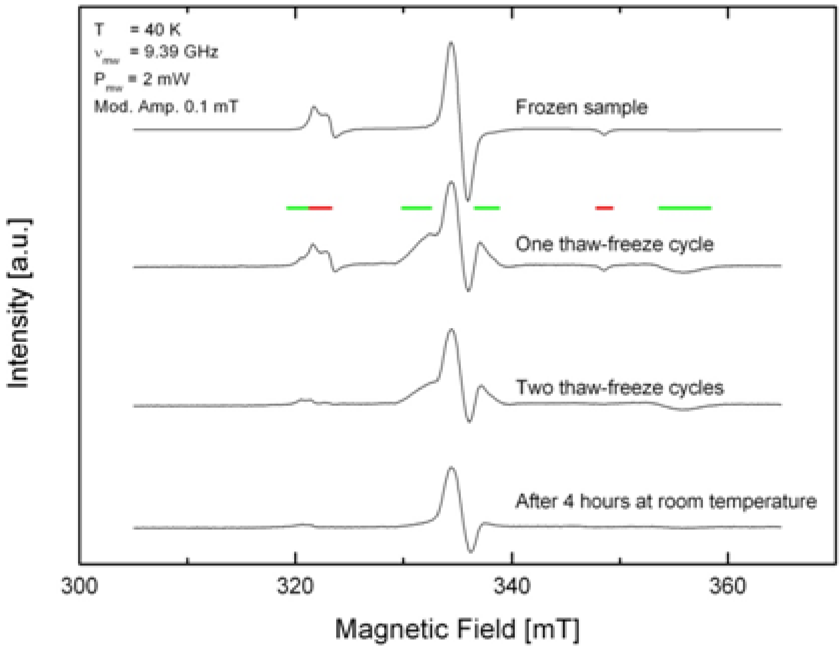


Figure 34. EPR spectrum of the reaction solution of the SET reaction between Li/OMe phosphinidenoid complex **51b** and tritylium tetrafluoroborate.

7.7 Thermal reaction of lithium/alkoxy phosphinidenoid complex 51a

From the reactions we discussed before, it is apparent that the *P*-alkoxy-substituted phosphinidenoid complexes **51a,b** showed “phosphanide-type” reactivity in most cases. One of the most compelling evidence for "phosphinidene-type" reactivity obtained is shown in figure 35. Upon warming up to room temperature, Li/Cl phosphinidenoid complex **38b** led to the formation of diphosphene complex,[64] which gave strong evidence for the generation of terminal phosphinidene complex. However, the thermal reaction of Li/OPh phosphinidenoid complex **51a** (refluxing in THF for 2 hours) resulted in the formation of the cyclotriphosphane **16** (Figure 35) together with the *P*-phenoxy-substituted phosphane complex **45a**. The mechanism for the formation of the cyclotriphosphane **16** is not clear, but phosphinidene complexes might be involved.

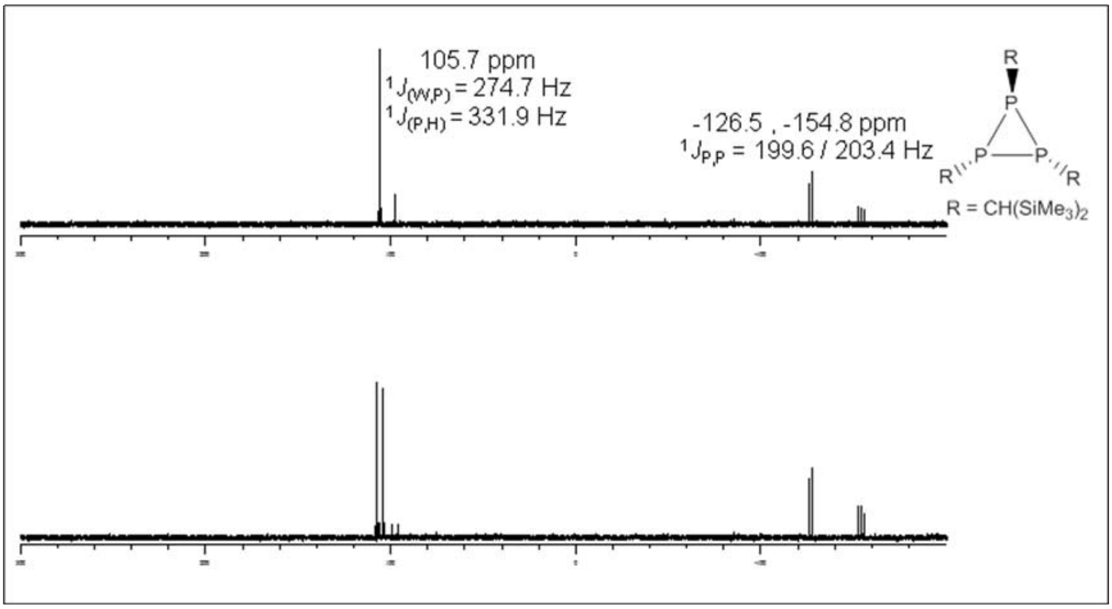
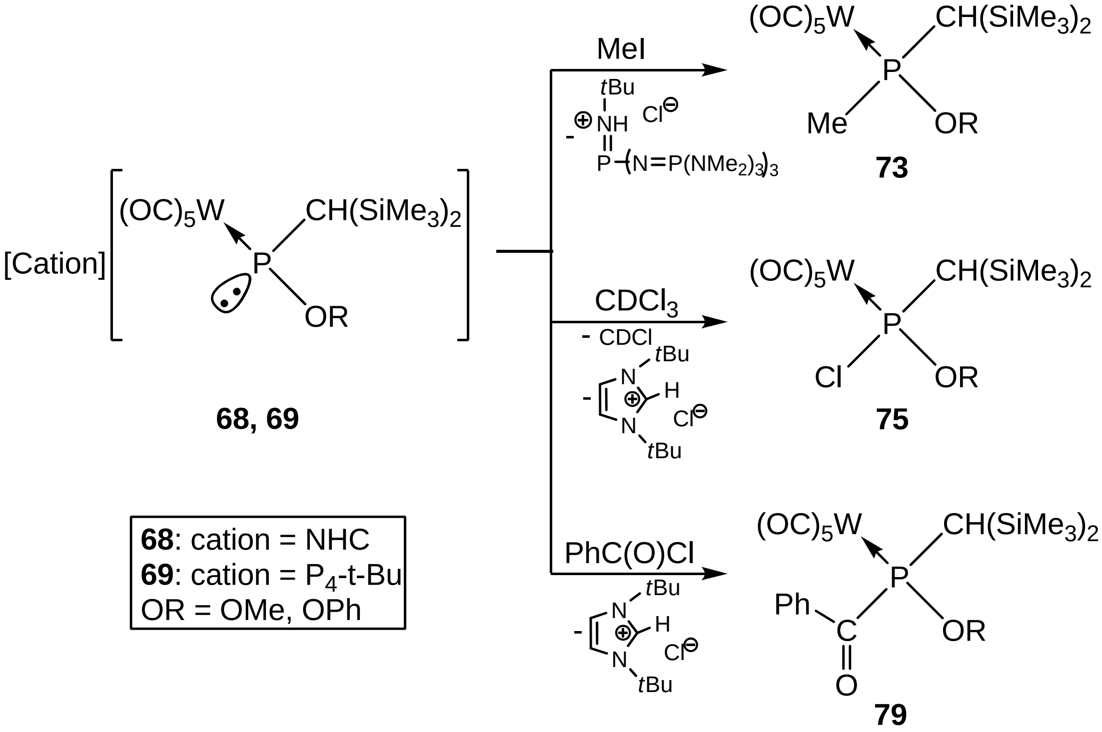


Figure 35. ^{31}P NMR spectrum of thermal reaction of Li/OPh phosphinidenoid complex **51a**.

7.8 Reactions of cation/alkoxy phosphinidenoid complexes 68,69a,b with electrophiles

In chapter 7.1–7.7, the reactivity of Li/OR phosphinidenoid complexes was described, especially those of the Li/OPh and Li/OMe phosphinidenoid complexes **51a,b**. As both of them showed largely “phosphanide-type” reactivity, e.g. demonstrated in reactions with electrophiles such as MeI, benzoylchloride and with phenylacetylene, etc., and the only evidence for a “phosphinidene-type” reactivity was the thermal reaction of Li/OPh phosphinidenoid complex **51a**. Another attempt to investigate the influence of the organic cations on chemical properties of the phosphinidenoid complexes **68**,**69a**,**b** was made, and the reactions of complexes **68**,**69a**,**b** with methyl iodide, benzoylchloride and $CDCl_3$ investigated (Scheme 40).



Scheme 40. Reaction of cation/OR phosphinidenoid complexes **68,69** with methyl iodide, benzoyl chloride and deuterochloroform.

When the imidazolium/OR phosphinidenoid complexes **68a,b** were reacted with methyl iodide, the reactions were selective and thus very similar to the case of the Li/OR phosphinidenoid complexes **51a,b**. While when H-P_4-*t*-Bu/OR phosphinidenoid complex

69a,b were reacted with methyl iodide, non-identified byproducts were formed beside the *P*-methyl-phosphane complex as the major product **73a,b**. The reaction of complexes **68a,b** with deuterated chloroform yielded the *P*-chloro-substituted phosphane complex **75a,b** (Scheme 40, the middle one) which proceeded in much the same way as in the case of the Li/OR phosphinidenoid complexes **51a,b**.

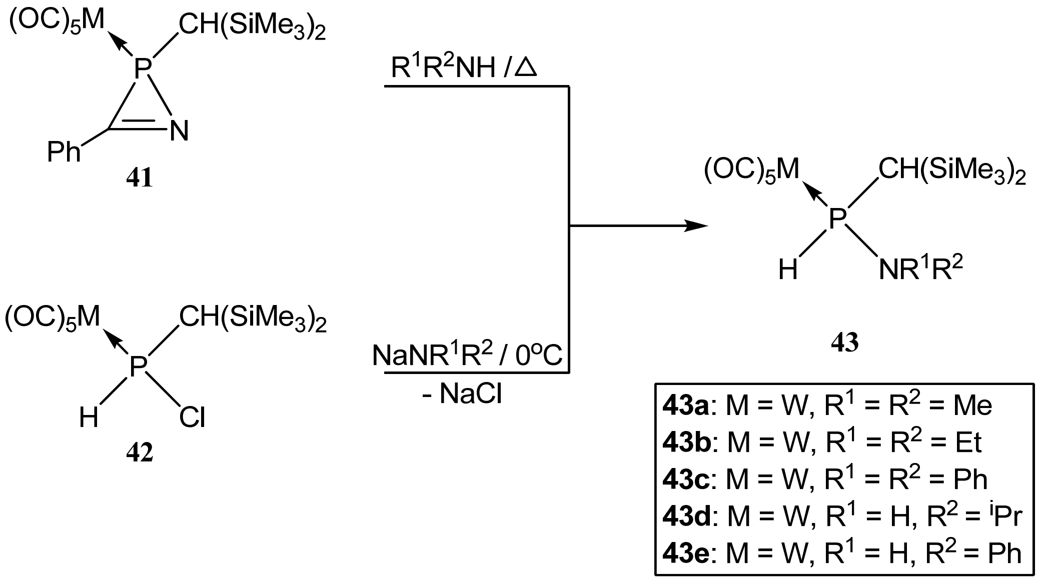
To test the reactivity of the imidazolium phosphinidenoid complex **68** towards benzoyl choride, the reaction was carried out under the same conditions as in the reaction of the lithium derivative **51a,b** (Scheme 40). Here, the selectivity of **68b** was much enhanced in comparison to **51b** (cf. Chapter 7.2), as only the *P*-benzoyl phosphane complex **79b** was observed in the ^{31}P NMR spectrum and its identity checked using an authentic sample. Although the reason is not strictly apparent, the nucleophilicity of complex **68b** was superior to that of the lithium derivative **51b**.

Chapter 8. Summary

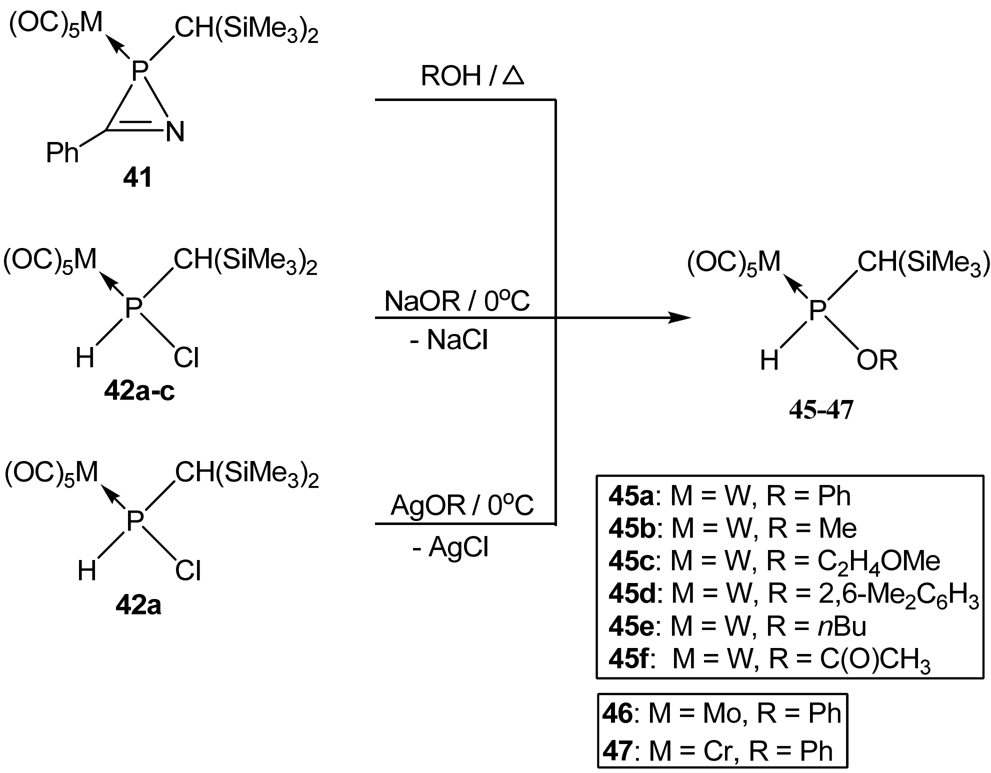
This thesis presents studies on *P*-NR_2 and *P*-OR phosphinidenoid complexes in order to understand the influences of *P*-heteroatom substituent as well as the nature of counterions. It contributes to improve understanding of the boundary between phosphanide and phosphinidenoid complex chemistry.

In chapter 3 the synthesis of *P*-1,1'-bifunctional organophosphane complexes is described using three newly modified methodologies (Scheme 41 and 42):

- thermal reaction of 2*H*-azaphosphirene complexes **41** with different amines and alcohols
- reaction of *P*-chloro phosphane complexes **42a-c** with sodium salts
- reaction of *P*-chloro phosphane complexes **42a** with silver salts.



Scheme 41. Synthesis routes to *P*-amino phosphane complexes **43a–e**.



Scheme 42. Synthesis of *P*-alkoxyl phosphane complexes **45a–f, 46** and **47**.

All of these *P*-1,1'-bifunctional phosphane complexes were obtained in good yields, and fully characterized by various means (NMR, MS, EA, IR). In addition, complexes **43c–d**, **45a**, **45d–f** and **47** were unambiguously confirmed by single-crystal X-ray diffraction analysis, of which the two examples **45a** and **45f** are shown here as examples (Figure 36).

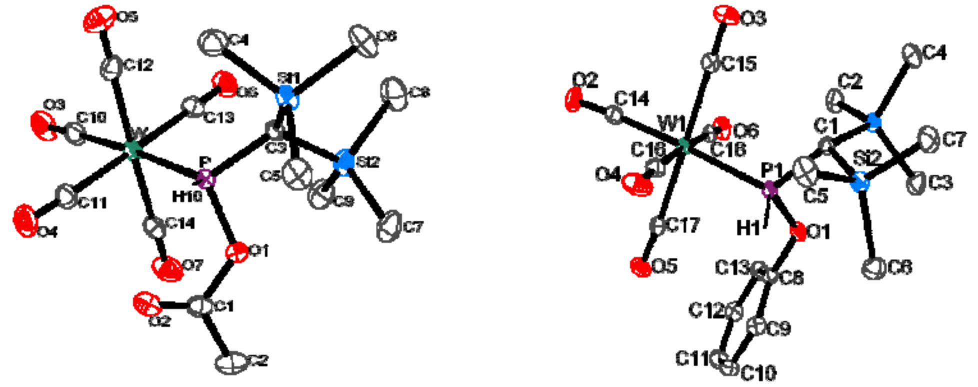
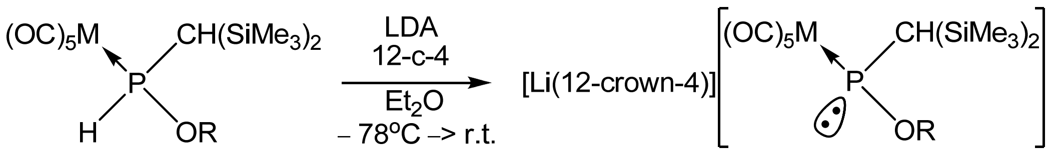


Figure 36. Molecular structures of complex **45f** (left) and **45a** (right) (except for H10 (left) and H1 (right) hydrogen were omitted for clarity).

In chapter 4 studies on one of the major aims, the synthesis and characterization of Li/NR$_2$ and Li/OR phosphinidenoid complexes are described using the very recently established protocol: deprotonation in polar solvents such as diethyl ether and THF using lithium diisopropyl amide (LDA) in the presence of 12-crown-4. The attempts to get the first Li/NR$_2$ phosphinidenoid complexes turned out to be unsuccessful, except for the case of complex **49a** for which a typical NMR signature (δ = 101.8 ppm, $^1J_{(P,Li)}$ = 62.1 Hz) and P-Li coupling was established. All other cases led to decomplexation via an unknown reaction pathway.

The first examples of *P*-OR and *P*-OAr substituted phosphinidenoid complexes **51** were obtained via the same deprotonation methodology using complexes **45** (Scheme 43).



45a-e,46,47

51a-e,53,54

51a: M = W, R = Ph
51b: M = W, R = Me
51c: M = W, R = C_2H_4OMe
51d: M = W, R = 2,6-$Me_2C_6H_3$
51e: M = W, R = *n*Bu

53: M = Mo, R = Ph
54: M = Cr, R = Ph

Scheme 43. Preparation of first Li/OR phosphinidenoid complex **51a–e**,**53** and **54**.

As Li/X phosphinidenoid complexes (X = F–I) the derivatives, complexes **51a–e** possessed the same NMR signature in having a resonance at low field in the ^{31}P NMR spectrum in the range of 201.1–215.3 ppm and a small tungsten-phosphorus coupling constant magnitude of about 68.5–78.8 Hz (Table 12). Here, and as recognized before by Özbolat-Schön, no ^{31}P–^{6}Li couplings could be observed, and, therefore, the constitution of a salt-like structure is proposed for all Li/*P*-OR phosphinidenoid complexes. In contrast to the Li/Cl derivatives, they displayed a superior thermal stability being stable in solution at ambient temperature, which enabled full characterization including NMR and IR spectroscopy; elemental analysis could be obtained for the Li/OPh substituted complex.

Table 12. Selected ^{31}P and ^{13}C NMR data of *P*-alkoxy phosphinidenoid complexes **51**

Complexes	δ (^{31}P)$^{[a]}$/ $^{1}J_{(W,P)}$$^{[b]}$	δ ($^{13}C_p$)/ $^{1}J_{(P,Cp)}$
51a (R = Ph)	209.1/76.2	25.4/75.0
51b (R = Me)	209.6/68.7	25.8/66.6
51c (R = C_2H_4OMe)	208.8/69.0	24.3/68.5
51d (R = 2,6-$Me_2C_6H_3$)	215.3/69.9	22.7/78.8
51e (R = *n*Bu)	201.1/68.7	--

[a]: ppm; [b]: Hz.

The deprotonation of *P*-acetyl phosphane complex **45f** using LDA turned out as a surprise as the decomposition product **58**, featuring both a P–H and a P–O–Li units in one molecular compound, was obtained and unambiguously confirmed by the result of the single-crystal X-ray diffraction analysis (Figure 37).

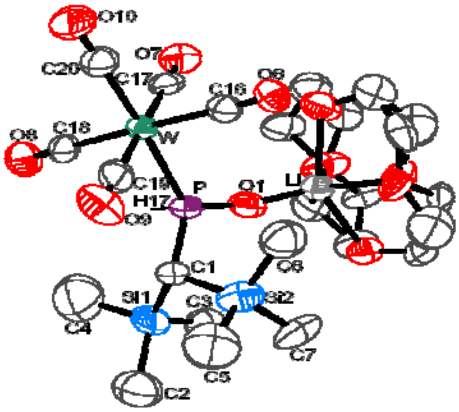


Figure 37. Molecular structure of complex **58** in the crystal (except for H17, hydrogen atoms were omitted for clarity).

In order to study the decomposition and to gain more insight into the bonding, the *deprotonation was repeated in the absence of 12-crown-4*. The ^{31}P NMR reaction monitoring at low temperature revealed a phosphorus-lithium coupling constant ($^{1}J_{(P,Li)}$ = 66.1 Hz) that was observable from –80 °C until –30 °C.

Besides the polarity of the solvent, several aspects of the deprotonation were studied such as substituent effects of the OR group, the nature of the bases and various co-ligands but the differences had no significant effect on the NMR signature. Therefore, other bases such NaH, KH that would lead to different counter metal cations as well as N-heterocyclic carbenes and the phosphazene base "P_4-t-Bu" were examined in the deprotonation of *P*-OPh phosphane complex **45a**. Whereas sodium and potassium led to a decreased stability of phosphinidenoid complexes **59**,**60**, phosphinidenoid complexes **68**,**69a–b** appeared to be more stable. Furthermore, of complex **68a** single-crystals suitable for X-ray diffraction analysis were obtained and the structure of which showed well separated ions with an imidazolium cation and a *P*-OPh phosphanide complex anion (Figure 38).

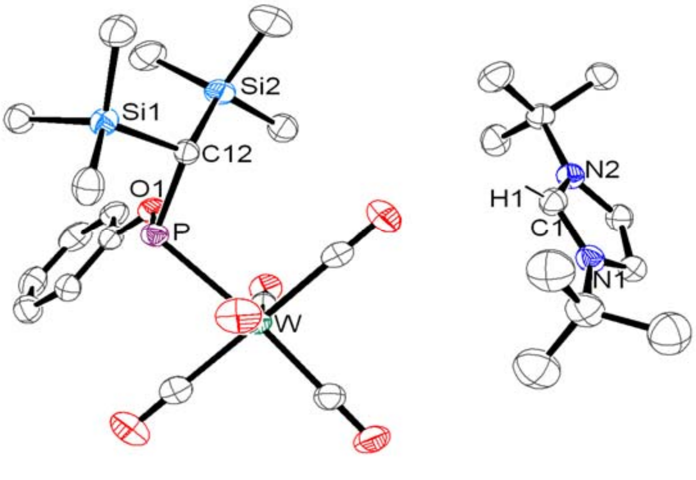
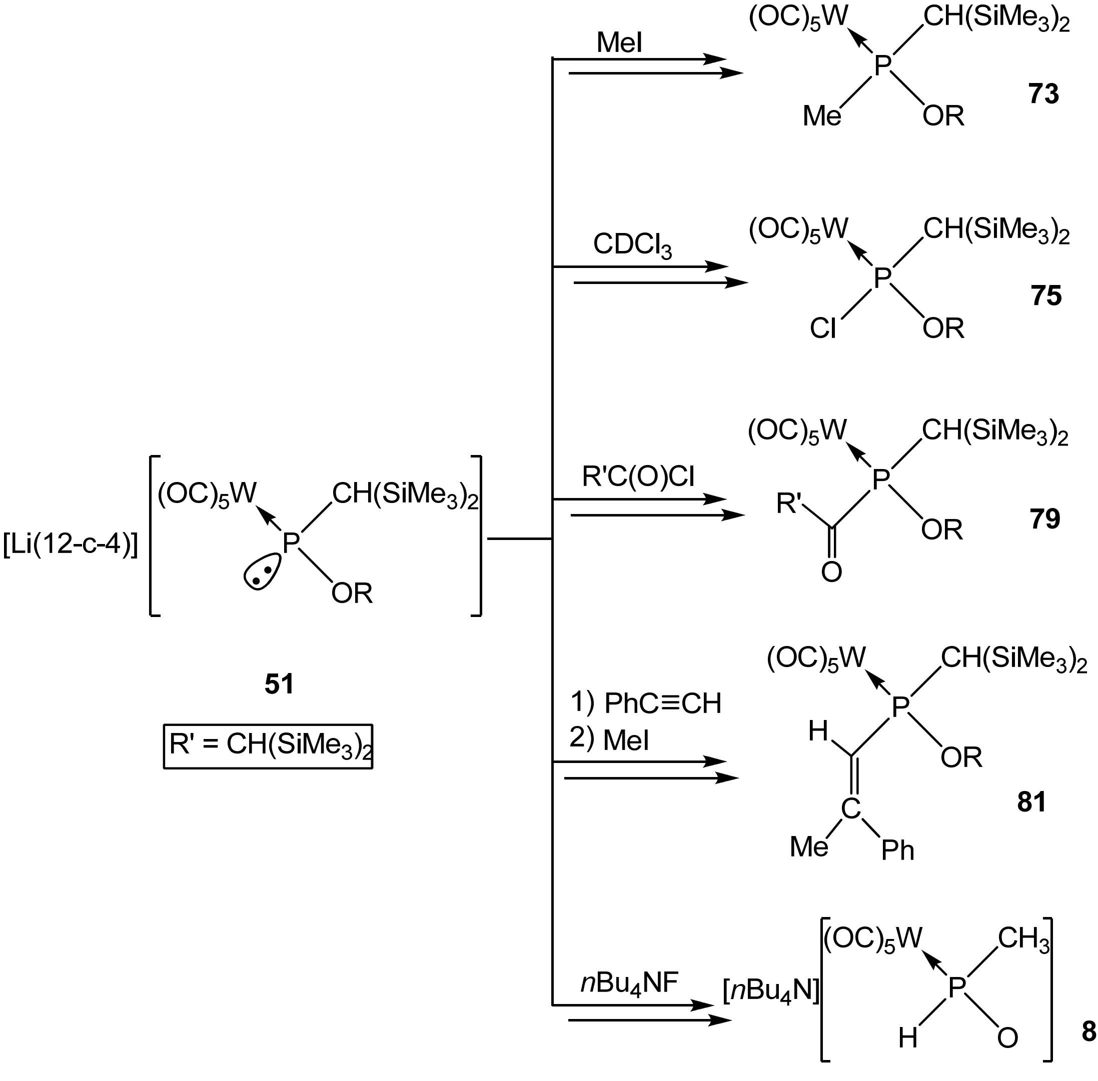


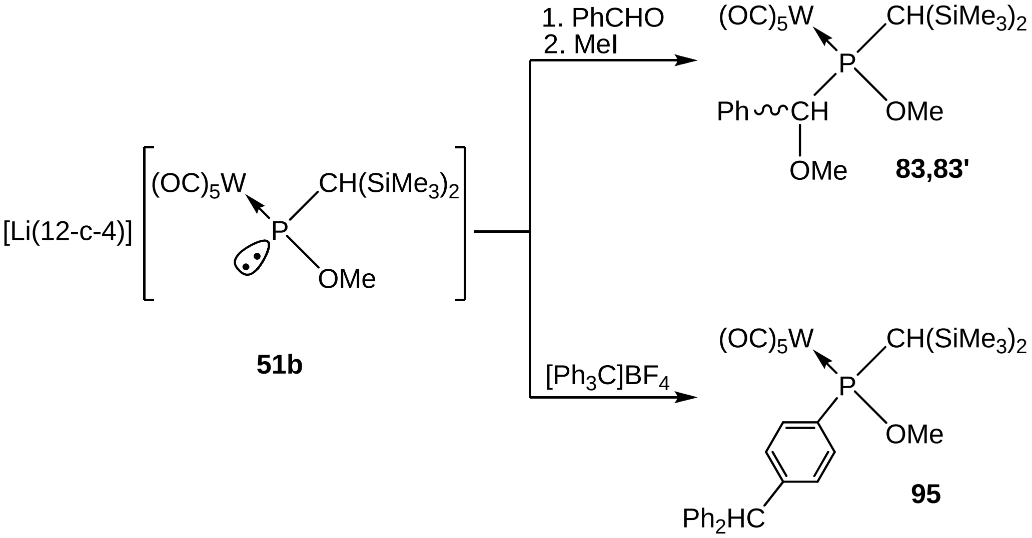
Figure 38. Molecular structure of complex **68a** in the crystal (except for H1, all hydrogen were omitted for clarity).

An important part of this thesis was devoted to reactivity studies, thus trying to elucidate the predominant reaction behavior. The reactions were performed using the Li/OR phosphinidenoid complexes **51a,b** and various substrates as depicted in scheme 44. The outcome was clear-cut: all reactions proceeded in a nucleophilic manner; in some cases the final products were obtained after quenching with methyl iodide. But in none of these experiments a "phosphinidene-type" reactivity, e.g. [2+1] cycloaddition reactions with benzaldehyde or phenylacteylene to yield products having three-membered ring structures could be detected.



Scheme 44. Reactions of Li/OR phosphinidenoid complexes **51** with various trapping reagents.

In most of the reactions the Li/OPh phosphinidenoid complex was less reactive than the *P*-OMe derivative, especially in the case of benzaldehyde that might be kinetically explained by increased steric hinderance caused by the phenyl group together with a more electron-withdrawing effect of the phenyl group. Therefore, the following experiments were performed only with the Li/OMe phosphinidenoid complex **51b** using methyl iodide as quenching reagent, except for the case of the tritylium salt (**95**); here an interesting oxidative SET reaction was observed.



Scheme 45. Reactions of Li/OMe phosphinidenoid complex **51b** with benzaldehyde and tritylium tetrafluroborate

To test the dependency of the reactivity on the nature of the cations a first comparative study was undertaken using complex **68a,b** and MeI and PhC(O)Cl. But here a similar reactivity was observed; an improved selectivity was revealed in the case of imidazolium *P*-OMe phosphanide complex **68b** with benzoyl chloride PhC(O)Cl to yield **79b**.

Besides the typical NMR signature of cation/*P*-OR phosphinidenoid complexes only weak evidence for a “phosphinidene-type” reactivity could be deduced from the thermal reaction of the Li/OPh phosphinidenoid complex **51a,** in which the cyclotriphosphane **16** together with the *P*-phenoxy phosphane complex **45a** were observed by ^{31}P NMR spectroscopy.

Chapter 9. Experimental Part

9.1 General Procedures

All operations were carried out under the atmosphere of deoxygenated and dried Argon (BTS catalysts (Merck) heated at 100–130 °C, phosphorus pentoxide and silical gel) using standard Schlenk techniques and conventional glassware. All solvents were dried over sodium wire or calcium hydride and stored in brown bottles with sodium wire inside and under inert gas atmosphere. Most products were purified by low temperature column chromatography using chromatography columns equipped with integrated cooling mantels cooled with ethanol via a connected cryostat. All glass apparatuses were evacuated and filled with Argon (three times) before usage to remove (mainly) oxygen and moisture.

9.1.1 Analytical Devices and Methods

Melting Point (M.P.) determination were recorded with a Büchi (530 or S) capillary apparatus.

Elemental Analysis (EA) was determined by an elementary vario EL analytical gas chromatography.

Electron Ionization Mass spectra (MS (EI)) were recorded on a Kratos MS 50 spectrometer (70 eV); ESI mass spectra (positive mode) were recorded on a Bruker APEX IV Fourier transform cyclotron resonance (FT-ICR) mass spectrometer equipped with an Apollo ESI source.

Infrared spectra (IR) were recorded on a Thermo Nicolet 380 spectrometer using KBr pellets or nujol or a CH_2Cl_2 solution as samples.

UV/vis spectra (UV/vis) were recorded on a UV-1650PC Shimadzu spectrometer (λ = 190–1100 nm) using dichloromethane or *n*-pentane as solvent. Quartz glass cells were from the company Hellma with an optical path length of 1cm at ambient temperature.

Nuclear Magnet Resonance (NMR) spectra were recorded on a Bruker AX 300 spectrometer (^{1}H: 300.13 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121.5 MHz; ^{29}Si: 59.6 MHz) or on a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz; ^{13}C: 100.6 MHz; ^{31}P: 161.9 MHz; ^{29}Si: 79.5 MHz) at 25 °C using $CDCl_3$, CD_2Cl_2 or THF-d8 as solvents. Shifts are given relative to tetramethylsilane (^{1}H, ^{13}C, ^{29}Si) and 85% H_3PO_4 (^{31}P).

Single-crystal X-ray diffraction data were recorded on a Nonius Kappa CCD diffractometer,[106] Nonius MACH3 diffractometer or a Bruker APEX-II CCD diffractometer with Mokα-10829. The structures were solved by Patterson methods or Direct Methods (SHELXS-97)[107][108] and refined by full-matrix least squares on F^2 (SHELXL-97).[108][109] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included isotropically using the riding model on the bound atoms; in some (denoted) cases hydrogen atoms were located in the Fourier difference electron density. Absorption corrections were carried out analytically or semi-empirically from equivalents.

9.1.2 Purchased Chemicals

The following reagents and solvent are available commercially and some are purified before usage (company name in brackets):

- Tungsten hexacarbonyl (Aldrich)
- Chromium hexacarbonyl (Aldrich or Merck)

- Molybdenum hexacarbonyl (ABCR)
- *n*-Butyllithium (1.6 M in hexane, Aldrich or Acros)
- *t*-Butyllithium (1.6 M in hexane, Aldrich or Acros)
- Methyllithium (1.6 M in diethyl ether, Acros)
- Silical gel merck 60 (0.063–0.02 mm, PH = 6.5–7.5, Merck)
- 12-crown-4 (Merck)
- Acetaldehyde (Acros)
- Benzaldehyde (KMF)
- Diisopropylamine (Aldrich)
- Diethylamine (Riedel)
- Dimethylamine (Riedel)
- Diphenylamine (Acros)
- Isopropylamine (Merck)
- Aniline (Acros)
- Methanol (Sigma-Aldrich)
- *n*-Butanol (Merck)
- Phenol (Acros)
- Ethylene glycol (Riedel)
- Diethylene glycol (Merck)
- 2, 6-dimethylphenol (Acros)
- Silver acetate (Acros)
- Tritylium tetrafluoroborate (Acros)

- Phenylacetylene (Acros)
- Tetrabutylammonium fluoride (1 M solution in THF, Alfa Aesar or Aldrich)
- Phosphazene base “P_4-*t*-Bu” (~1 M solution in hexane, Aldrich)
- Silver cyanate (Acros)
- Potassium hydride (Acros)
- Methyltriflate (Acros)
- Potassium *tert*-butoxide (Merck)

9.1.3 Synthesized chemicals

The following chemicals were synthesized by published procedures.

- [2-Bis(trimethylsilyl)methyl-3-phenyl-2*H*-azaphosphirene-κP] pentacarbonyltungsten(0) complex[73]
- {[Bis(trimethylsilyl)methylene]chlorophosphane}pentacarbonyltungsten(0)[74]
- {[Bis(trimethylsilyl)methylene]chlorophosphane}pentacarbonylmolybdenum(0)[66]
- {[Bis(trimethylsilyl)methylene]chlorophosphane}pentacarbonylchromium(0)[66]
- *N,N*-1,3-di-*tert*-butyl-imidazolyl-2-ylidene[89]

9.2 Syntheses of [{bis(trimethylsilyl)methyl}alkoxyl/amino phosphane]pentacarbonyltungsten(0), molybdenum(0) and chromium(0) complexes

9.2.1 Synthesis of [{bis(trimethylsilyl)methyl}dimethylaminophosphane] pentacarbonyltungsten(0) 43a

To a stirred solution of 617 mg (1.0 mmol) of 2*H*-azaphosphirene complex **41** in 30 mL of toluene, 0.5 mL (1.0 mmol) of dimethylamine were added and heated at 75 °C for 3 hours while stirring. After removal of all volatiles in *vacuo* (~ 10^{-2} mbar), the final product **43a** was purified by washing with little amounts of *n*-pentane at low temperature (–60 °C). (NMR code: 02m3a005.08)

Yellow solid, yield: 173 mg (0.31 mmol, 31%); m.p. 35 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.25 (s, 9H, $Si(CH_3)_3$), 0.26 (d, 9H, $^4J_{(P,H)}$ = 0.6 Hz, $Si(CH_3)_3$), 1.16 (dd, 1H, $^2J_{(P,H)}$ = 6.0 Hz, $^4J_{(H,H)}$ = 2.5 Hz, PCH), 2.76 (d, 6H, $^3J_{(P,H)}$ = 10.9 Hz, $N(CH_3)_2$), 7.03 (d, 1H, $^1J_{(P,H)}$ = 342.9 Hz, P-H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 0.0 (d, $^3J_{(P,C)}$ = 2.6 Hz, $Si(CH_3)_3$), 0.5 (d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$), 22.6 (d, $^1J_{(P,C)}$ = 3.9 Hz, *C*H($SiMe_3)_2$), 42.8 (d, $^2J_{(P,C)}$ = 5.2 Hz, $N(CH_3)_2$), 195.1 (d, $^2J_{(P,C)}$ = 7.1 Hz, $^1J_{(W,C)}$ = 126.0 Hz, *cis*-CO), 201.8 (d, $^2J_{(P,C)}$ = 22.6 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 46.1 (d_{sat}, $^1J_{(W,P)}$ = 249.2 Hz, $^1J_{(P,H)}$ = 342.1 Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ = 0.2 (d_{sat}, $^2J_{(P,Si)}$ = 3.8 Hz), 2.0 (d_{sat}, $^2J_{(P,Si)}$ = 7.6 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 1917 (vs, ν(CO)), 2069 (s, ν(CO)), 2270 (w, ν(PH)), 2958 (w, ν(CH/CH_3)); MS (EI, ^{184}W): m/z (%): 559.06 ($M^{\cdot+}$, 38), 531.1 ($[M-CO]^{\cdot+}$, 30), 503.1 ($[M-2CO]^{\cdot+}$, 34), 475.0 ($[M-3CO]^{\cdot+}$, 100), 417.0 ($[M-5CO]^{\cdot+}$, 80), 234.1 ($[M-W(CO)_5]^{\cdot+}$, 52), 73.0 ($SiMe_3^{\cdot+}$, 70);

elemental analysis (%) calcd. for $C_{14}H_{26}NO_5PSi_2W$: C 30.06, H 4.69, N 2.50; found: C 30.88, H 4.39, N 2.56.

9.2.2 Synthesis of [{bis(trimethylsilyl)methyl}diethylaminophosphane] pentacarbonyltungsten(0) 43b

To a stirred solution of 617 mg (1.0 mmol) of 2*H*-azaphosphirene complex **41** in 30 mL of toluene were added 0.1 mL (1.0 mmol) of diethylamine at 75 °C. The reaction mixture was heated for 3 hours while stirring. After removal of all volatiles in *vacuo* (~ 10^{-2} mbar), the final product was purified by column chromotagraphy on silical gel (–20 °C, 2 × 11 cm, petroleum ether / Et_2O : 9 / 1). And evaporation of the solvent of first fraction yielded complex **43b**. (NMR code: 44m3b025.07)

Yellow viscous oil, yield: 123 mg (0.21 mmol, 21%); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.25 (s, 9H, $Si(CH_3)_3$), 0.26 (s, 9H, $Si(CH_3)_3$), 1.08 (d, 1H, $^2J_{(P,H)}$ = 1.7 Hz, PCH), 1.13 (t, 6H, $^3J_{(H,H)}$ = 14.2 Hz, NCH_2CH_3), 3.10 (m, 4H, NCH_2), 7.18 (d, 1H, $^1J_{(P,H)}$ = 342.5 Hz, P-H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 0.0 (d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$), 0.2 (d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$), 11.2 (d, $^3J_{(P,C)}$ = 4.5 Hz, NCH_2CH_3), 22.7 (d, $^1J_{(P,C)}$= 3.9 Hz, PCH), 43.4 (d, $^2J_{(P,C)}$ = 5.2 Hz, NCH_2CH_3), 196.0 (d, $^1J_{(W,C)}$ = 125.4 Hz, $^2J_{(P,C)}$ = 6.5Hz, *cis*-CO), 197.0 (d, $^2J_{(P,C)}$ = 23.3 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 31.0 (d_{sat}, $^1J_{(W,P)}$ = 249.2 Hz, $^1J_{(P,H)}$ = 342.0 Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ = –0.2 (d_{sat}, $^2J_{(P,Si)}$ = 7.1 Hz), 2.2 (d_{sat}, $^2J_{(P,Si)}$ = 4.2 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2069 (m, ν(CO)), 1932 (vs, ν(CO)); MS (EI, ^{184}W): m/z (%): 587.1($M^{\cdot+}$, 40), 559.1 ($[M-CO]^{\cdot+}$, 8), 531.1 ($[M-2CO]^{\cdot+}$, 18), 503.1 ($[M-3CO]^{\cdot+}$, 95), 445.1 ($[M -5CO]^{\cdot+}$, 38), 262.1 ($[M-W(CO)_5]^{\cdot+}$, 90), 73.0 ($Me_3Si^{\cdot+}$, 58); elemental analysis (%)

calcd. for $C_{16}H_{30}NO_5PSi_2W$: C 32.72, H 5.15, N 2.38; found: C 33.25, H 5.23, N 2.29.

9.2.3 Synthesis of [{bis(trimethylsilyl)methyl}diphenylaminophosphane] pentacarbonyltungsten(0) 43c

To a stirred solution of 210 mg (1.1 mmol) of diphenylamide sodium salt in 10 mL of ditheyl ether were added a solution of 550 mg (1.0 mmol) of chlorophosphane complex **42** in 10 mL of diethyl ether at –30 °C. Then immediately the solution color changed to black red, and the reaction mixture was stirred for 3 hours. After removal of all volatiles in *vacuo* (~ 10^{-2} mbar), the final product was purified by column chromotagraphy on silica gel (–20 °C, 2 × 9 cm, petroleum ether / Et_2O with different ratios). After evaporation of solvent of first fraction yielded complexes **43c** together with diphosphene complex. (NMR code: 46m3a041.08)

Yellow solid, crystallized from Et_2O at –30 °C, $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 23.7$ (d_{sat}, $^1J_{(W,P)} = 263.2$ Hz, $^1J_{(P,H)} = 330.6$ Hz).

9.2.4 Synthesis of [{bis(trimethylsilyl)methyl}isopropylaminophosphane] pentacarbonyltungsten(0) 43d

To a stirred solution of 617 mg (1.0 mmol) of 2*H*-azaphosphirene complex **41** in 30 mL of toluene were added 0.14 mL (1.0 mmol) of isopropylamine at 75 °C. The reaction mixture was heated for 3 hours while stirring. After removal of all volatiles in *vacuo* (~ 10^{-2} mbar), the final product was purified by washing with *n*-pentane at low temperature (–60 °C). After filtration and evaporation of the solvent, complex **43d** was yielded. (NMR code:

47m3a053.07)

Yellow solid, crystallized from *n*-pentane at –30 °C; yield: 200 mg (0.33 mmol, 33%); m.p. 73 °C; ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.25 (d, 9H, $^4J_{(P,H)}$ = 0.6 Hz, Si(CH$_3$)$_3$), 0.29 (d, 9H, $^4J_{(P,H)}$ = 0.4 Hz, Si(CH$_3$)$_3$), 0.96 (d, 1H, $^3J_{(H,H)}$ = 6.2 Hz, C*H*(SiMe$_3$)$_2$), 1.18 (d, 6H, $^2J_{(H,H)}$ = 6.4 Hz, CH$_3$), 3.26 (br, 1H, NH), 3.40 (q, 1H, $^3J_{(P,H)}$ = 7.0 Hz, C*H*(CH$_3$)$_2$), 7.09 (d, 1H, $^1J_{(P, H)}$ = 320.2 Hz, PH); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ = –1.3 (d, $^3J_{(P,C)}$ = 2.3 Hz, Si(CH$_3$)$_3$), 0.0 (d, $^3J_{(P,C)}$ = 3.2 Hz, Si(CH$_3$)$_3$), 22.3 (d, $^1J_{(P,C)}$ = 7.8 Hz, *C*H(SiMe$_3$)$_2$), 22.7 (d, $^3J_{(P,C)}$ = 4.5 Hz, CH(*C*H$_3$)$_2$), 46.2 (d, $^2J_{(P,C)}$ = 3.2 Hz, N*C*H(CH$_3$)$_2$), 195.1 (d, $^2J_{(P,C)}$ = 7.1 Hz, *cis*-CO), 197.4 (d, $^2J_{(P,C)}$ = 22.0 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 11.4 (d$_{sat}$, $^1J_{(W,P)}$ = 255.6 Hz, $^1J_{(P,H)}$ = 320.4 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, CDCl$_3$): δ = 0.5 (d$_{sat}$, $^2J_{(P,Si)}$ = 3.8 Hz), 2.3 (d$_{sat}$, $^2J_{(P,Si)}$ = 7.6 Hz); IR (KBr, cm^{-1}): ῦ = 2956 (w, ν(CH/CH$_3$)), 2226 (w, ν(PH)), 2068 (s, ν(CO)), 1920 (vs, ν(CO)); MS (EI, ^{184}W): m/z (%): 573.0 (M$^{\cdot+}$, 49), 545.0 ([M-CO]$^{\cdot+}$, 41), 517.0 ([M -2CO]$^{\cdot+}$, 39), 489.0 ([M-3CO]$^{\cdot+}$, 85), 461.0 ([M-4CO]$^{\cdot+}$, 20), 433.0 ([M-5CO]$^{\cdot+}$, 71), 73.0 (Me$_3$Si$^{\cdot+}$, 82); elemental analysis (%) calcd for $C_{15}H_{28}NO_5PSi_2W$: C 31.42, H 4.92, N 2.44; found: C 31.80, H 4.98, N 2.21.

9.2.5 Synthesis of [{bis(trimethylsilyl)methyl}phenylaminophosphane] pentacarbonyltungsten(0) 43e

To a stirred solution of 617 mg (1.0 mmol) of 2*H*-azaphosphirene complex **41** in 30 mL of toluene were added 92 µL (1.0 mmol) of phenylamine at 75 °C. The reaction mixture was heated for 3 hours while stirring. After removal of all volatiles in *vacuo* (~ 10^{-2} mbar), the final product was purified by column chromotagraphy on silica gel (–20 °C, 2 × 9.5 cm, petroleum ether / Et_2O : 9 / 1). After evaporation of solvent of first fraction, complex **43e** was obtained. (NMR code: 04m3a011.08)

Yellow solid, crystallized from *n*-pentane at –30 °C; yield: 297 mg (0.49 mmol, 49%); m.p. 90 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.20 (d, 9H, $^4J_{(P,H)}$ = 0.4 Hz, $Si(CH_3)_3$), 0.28 (d, 9H, $^4J_{(P,H)}$ = 0.8 Hz, $Si(CH_3)_3$), 1.83 (dd, 1H, $^2J_{(P,H)}$ = 13.6 Hz, $^3J_{(H,H)}$ = 3.3 Hz, PCH), 3.97 (br, 1H, NH), 6.85 (d, 2H, $^3J_{(H,H)}$ = 7.5Hz, *o*-Ph), 7.00 (t, 1H, $^3J_{(H,H)}$ = 7.6 Hz, *p*-Ph), 7.33 (t, 2H, $^3J_{(H,H)}$ = 7.4 Hz, *m*-Ph), 7.49 (dd, 1H, $^1J_{(P,H)}$ = 357.7 Hz, PH); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 0.0 (d, $^3J_{(P,C)}$ = 1.3 Hz, $Si(CH_3)_3$), 15.1 (d, CH), 115.9 (d, $^3J_{(P,C)}$ = 4.5 Hz, *o*-Ph), 120.0 (s, *p*-Ph), 128.1 (s, *m*-Ph), 141.2 (d, $^2J_{(P,C)}$ = 9.7 Hz, N-C), 195.1 (d, $^2J_{(P,C)}$ = 6.5 Hz, *cis*-*C*O), 196.6 (d, $^2J_{(P,C)}$ = 23.2 Hz, *trans*-*C*O); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 5.3 (d_{sat}, $^1J_{(W,P)}$ = 253.0 Hz, $^1J_{(P,H)}$ = 357.3 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = 0.5 (d_{sat}, $^2J_{(P,Si)}$ = 1.3 Hz), 1.5 (d_{sat}, $^2J_{(P,Si)}$ = 1.3 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 3419 (w, ν(NH)), 2960 (w, ν(CH/CH_3)), 2310 (w, ν(PH)), 2071 (m, ν(CO)), 1986 (m, ν(CO)), 1946 (vs, ν(CO)), 1918 (m, ν(CO)), 1904 (m, ν(CO)); MS (EI, ^{184}W): m/z (%): 607.1 ($M^{\cdot+}$, 40), 579.1 ($[M-CO]^{\cdot+}$, 9), 551.1 ($[M-2CO]^{\cdot+}$, 8), 523.1 ($[M-3CO]^{\cdot+}$, 100), 73 ($Me_3Si^{\cdot+}$, 42); elemental analysis (%) calcd for $C_{18}H_{26}NO_5PSi_2W$: C 35.59, H 4.31, N 2.31; found: C 35.73, H 4.61, N 2.06.

9.2.6 Synthesis of [{bis(trimethylsilyl)methyl}phenoxyphosphane]pentacarbonyltungsten(0) 45a

To a stirred solution of 150 mg (1.3 mmol) sodium phenolate in 10 mL of Et_2O were added 550 mg (1.0 mmol) of chlorophosphane complex **42** at –78 °C. Then the reaction solution was stirred overnight. Then solvent was evaporated in *vacuo* (~10^{-2} mbar) and then washed with *n*-pentane (10 mL × 3) at ambient temperature. After filtration of liquid from solid, the yellow crystals of complex **45a** were grown from *n*-pentane solution at –30 °C. (NMR code: 08m3a019.08)

Yellow solid, yield: 377 mg (0.62 mmol, 62 %); m.p. 78 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.30 (d, 9H, $^{4}J_{(H,H)}$ = 0.6 Hz, $SiMe_3$), 0.40 (s, 9H, $SiMe_3$), 1.12 (dd, 1H, $^{3}J_{(H,H)}$ =1.9 Hz, $^{2}J_{(P,H)}$ = 2.8 Hz, CH), 7.10 (d, 2H, $^{3}J_{(H,H)}$ = 7.6 Hz, *o*-Ph), 7.19 (t, 1H, $^{3}J_{(H,H)}$ =7.6 Hz, *p*-Ph), 7.38 (t, 2H, $^{3}J_{(H,H)}$ =7.5 Hz, *m*-Ph), 8.42 (d, 1H, $^{1}J_{(P,H)}$ = 325.2 Hz, $^{3}J_{(H,H)}$ = 1.7 Hz, P–H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 0.0 (d, $^{3}J_{(P,C)}$ = 2.6 Hz, $Si(CH_3)_3$), 1.9 (s, $Si(CH_3)_3$), 22.6 (d, $^{1}J_{(P,C)}$ = 13.7 Hz, PCH), 120.0 (d, $^{4}J_{(P,C)}$ = 6.5 Hz, *m*-Ph), 124.1 (d, $^{5}J_{(P,C)}$ = 1.3 Hz, *p*-Ph), 129.7 (s, *o*-Ph), 153.7 (d, $^{2}J_{(P,C)}$ = 6.5Hz, *i*-Ph), 195.8 (d, $^{2}J_{(P,C)}$ = 7.8 Hz, *cis*-CO), 198.3 (d, $^{2}J_{(P,C)}$ = 27.2 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 106.8 (d_{sat}, $^{1}J_{(W,P)}$ = 275.9 Hz, $^{1}J_{(P,H)}$ = 325.5 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = 1.9 (d_{sat}, $^{2}J_{(P,Si)}$ = 5.8 Hz), 3.5 (d_{sat}, $^{2}J_{(P,Si)}$ = 8.5 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 3420 (br, ν(OH)), 2953 (w, ν(CH/CH_3)), 2290 (w, ν(PH)), 2073 (m, ν(CO)), 1979 (m, ν(CO)), 1957 (s, ν(CO)), 1920 (vs, ν(CO)), 1910 (vs, ν(CO)); MS (EI, ^{184}W): m/z (%): 609.0 ($M^{\cdot+}$, 65), 580. 0 ($[M-CO]^{\cdot+}$, 10), 524.0 ($[M-3CO]^{\cdot+}$, 78), 73.0 ($SiMe^{\cdot+}$, 100); elemental analysis (%) calcd. for $C_{18}H_{25}O_6PSi_2W$: C 35.54, H 4.14; found: C 34.40, H 3.96.

9.2.7 Synthesis of [{bis(trimethylsilyl)methyl}methoxyphosphane] pentacarbonyltungsten(0) 45b

To a stirred solution of 617 mg (1.0 mmol) of 2*H*-azaphosphirene complex **41** in 30 mL of toluene were added 41 µL (1.1 mmol) of methanol at 75 °C. The reaction mixture was stirred for 3 hours while stirring. After removal of all volatiles in *vacuo* (~10^{-2} mbar), the final product was purified by column chromotagraphy on silical gel (–20 °C, 2 × 7 cm, petroleum ether). And evaporation of the solvent of first fraction yielded complex **45b**. (NMR code: 05m3a003.09)

Yellow solid, yield: 293 mg (0.53 mmol, 53%); m.p. 62 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.12 (s, 9H, $SiMe_3$), 0.18 (s, 9H, $SiMe_3$), 0.86 (d, 1H, $^2J_{(P,H)}$ = 1.5 Hz, PCH), 3.43 (d, 3H, $^3J_{(P,H)}$ =14.7 Hz, OCH_3), 7.80 (d, 1H, $^1J_{(P,H)}$ = 320.7 Hz, $^3J_{(H,H)}$ = 1.5 Hz, PH); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = –1.9 (d, $^3J_{(P,C)}$ = 2.6 Hz, $Si(CH_3)_3$), 0.0 (d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$), 21.4 (d, $^1J_{(P,C)}$ = 13.6 Hz, P*C*H($SiMe_3$)$_2$), 54.1 (d, $^2J_{(P,C)}$ = 3.9 Hz, PO*C*H$_3$), 194.6 (d, $^2J_{(P,C)}$ = 7.1 Hz, $^1J_{(W,C)}$ = 125.4 Hz, *cis*-CO), 197.3 (d, $^2J_{(P,C)}$ = 24.6 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 109.7 (d_{sat}, $^1J_{(W,P)}$ = 267.0 Hz, $^1J_{(P,H)}$ = 320.4 Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ = 1.0 (d_{sat}, $^2J_{(P,Si)}$ = 5.8 Hz), 2.5 (d_{sat}, $^2J_{(P,Si)}$ = 8.7 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2962 (w, ν(CH/CH_3)), 2265 (w, ν(PH)), 2070 (m, ν(CO)), 1921 (m, ν(CO)); MS (EI, ^{184}W): m/z (%): 546.0 ($M^{\cdot+}$, 60), 518.0([M-CO]$^{\cdot+}$, 49), 490.0([M-2CO]$^{\cdot+}$, 72), 404.0([M-5CO]$^{\cdot+}$, 74), 73.0 ($Me_3Si^{\cdot+}$, 100); elemental analysis (%) calcd. for $C_{13}H_{23}O_6PSi_2W$: C 28.58, H 4.24; found: C 28.74, H 4.31.

9.2.8 Synthesis of [{bis(trimethylsilyl)methyl}(2-methoxyethan-1-oxyl phosphane]pentacarbonyltungsten(0) 45c

To a stirred solution of 1.23 g (2.0 mmol) of 2*H*-azaphosphirene complex **41** in 30 mL of toluene were added 0.17 mL (2.1 mmol) of 2-methoxyethan-1-ol at 75 °C. The reaction mixture was stirred for 3 hours. After removal of all volatiles in *vacuo* (~ 10^{-2} mbar), the final product was purified by column chromotagraphy on silical gel (–20 °C, 3 × 13 cm, petroleum ether / Et_2O: first pure petroleum ether, then 50/1, 50/3). And evaporation of the solvent of fourth fraction gave complex **45c**. (NMR code: 02m3a020.10)

Yellow viscous oil, yield: 0.73 g (1.24 mmol, 62%); ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 0.21$ (s, 9H, $SiMe_3$), 0.27 (s, 9H, $SiMe_3$), 0.93 (b, 1H, $C\mathit{H}(SiMe_3)_2$), 3.35 (s, 3H, OCH_3), 3.57 (t, 2H, $^2J_{(H,H)}$ = 4.3 Hz, $OCH_2C\mathit{H}_2OCH_3$), 3.78 (m, 2H, $OC\mathit{H}_2CH_2OCH_3$), 7.90 (dd, 1H, $^1J_{(P,H)}$ = 324.1 Hz, $^4J_{(H,H)}$ = 1.3 Hz, PH); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): $\delta = 0.2$ (d, $^3J_{(P,C)}$ = 2.6 Hz, $SiMe_3$), 2.0 (d, $^3J_{(P,C)}$ = 3.2 Hz, $SiMe_3$), 23.4 (d, $^1J_{(P,C)}$ = 13.6 Hz, PCH), 58.7 (s, OCH_3), 68.0 (d, $^3J_{(P,C)}$ = 3.9 Hz, $OCH_2\mathit{C}H_2OCH_3$), 71.6 (d, $^2J_{(P,C)}$ = 7.8 Hz, $O\mathit{C}H_2CH_2OCH_3$), 196.6 (dd, $^2J_{(P,C)}$ = 7.1 Hz, $^1J_{(W,C)}$ = 125.4 Hz, *cis*-CO), 199.4 (d, $^2J_{(P,C)}$ = 24.6 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): $\delta = 107.3$ (d_{sat}, $^1J_{(W,P)}$ = 267.0 Hz, $^1J_{(P,H)}$ = 324.2 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): $\delta = 1.1$ (d_{sat}, $^2J_{(P,Si)}$ = 6.0 Hz), 2.7 (d_{sat}, $^2J_{(P,Si)}$ = 8.9 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2260 (w, ν(PH)), 2072 (s, ν(CO)), 1936 (s, ν(CO)); MS (EI, ^{184}W): m/z (%): 589.9 ($M^{+\cdot}$, 30), 562.0 ($[M-CO]^{+\cdot}$, 25), 534.0 ($[M-2CO]^{+\cdot}$, 30), 506.0 ($[M-3CO]^{+\cdot}$, 80), 478.0 ($[M-4CO]^{+\cdot}$, 60), 73.0 ($SiMe_3^{+\cdot}$, 100); elemental analysis (%) calcd. for $C_{15}H_{27}O_7PSi_2W$: C 30.52, H 4.61; found: C 30.79, H 4.24.

9.2.9 Synthesis of [{bis(trimethylsilyl)methyl}-2,6-dimethylphenoxy phosphane]pentacarbonyltungsten(0) 45d

To a stirred solution of 160 mg (1.1 mmol) sodium 2,6-dimethylphenolate in 10 mL of Et_2O were added 550 mg (1.0 mmol) of chlorophosphane complex **42** at –78 °C. The reaction solution was stirred overnight. Then solvent was evaporated in *vacuo* (~10^{-2} mbar) and washed with *n*-pentane (10 mL × 3) at ambient temperature. After filtration of liquid from solid, the yellow crystals of complex **45d** were grown from *n*-pentane solution at –30 °C. (NMR code: 50m3a014.08)

Yellow solid, yield: 453 mg (0.71 mmol, 71%); m.p. 88–90 °C; ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.35 (d, 18H, $^{2}J_{(H,H)}$ = 11.1 Hz, SiMe$_3$), 1.36 (dd, 1H, $^{2}J_{(P,H)}$ = 5.1 Hz, $^{3}J_{(H,H)}$ = 3.1 Hz, PCH), 2.39 (s, 6H, PhMe_2), 7.01 (s, 3H, Ph), 8.47 (dd, 1H, $^{1}J_{(P,H)}$ = 336.3 Hz, $^{3}J_{(H,H)}$ = 4.5 Hz, PH); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ = 1.2 (d, $^{3}J_{(P,C)}$ = 3.2 Hz, SiMe$_3$), 3.0 (d, $^{3}J_{(P,C)}$ = 2.6 Hz, SiMe$_3$), 18.7 (s, 2,6-Me_2C$_6$H$_3$), 24.2 (d, $^{1}J_{(P,C)}$ = 9.7 Hz, PCH), 124.9 (d, $^{5}J_{(P,C)}$ = 1.9 Hz, *p*-Ph), 130.0 (d, $^{4}J_{(P,C)}$ = 1.9 Hz, *m*-Ph), 130.6 (d, $^{3}J_{(P,C)}$ = 4.5 Hz, *o*-Ph), 150.4 (d, $^{2}J_{(P,C)}$ = 7.8 Hz, POC), 196.3 (d, $^{2}J_{(P,C)}$ = 6.5 Hz, *cis*-CO), 198.4 (d, $^{2}J_{(P,C)}$ = 27.2 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 99.0 (d$_{sat}$, $^{1}J_{(W,P)}$ = 274.7 Hz, $^{1}J_{(P,H)}$ = 335.7 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, CDCl$_3$): δ = 1.6 (d$_{sat}$, $^{2}J_{(P,Si)}$ = 5.8 Hz), 1.9 (d$_{sat}$, $^{2}J_{(P,Si)}$ = 4.7 Hz); IR (KBr, cm^{-1}): ῦ = 2959 (w, ν(CH/CH$_3$)), 2367 (w, ν(PH)), 2072 (m, ν(CO)), 1985 (m, ν(CO)), 1915 (s, ν(CO)); MS (EI, ^{184}W): m/z (%): 636.1 (M$^{\cdot+}$, 48), 552.1 ([M-3CO]$^{\cdot+}$, 57), 515.0 ([M-2,6-Me$_2$C$_6$H$_3$O]$^{\cdot+}$, 61), 73.0 (SiMe$^{\cdot+}$, 100); elemental analysis (%) calcd. for C$_{20}$H$_{29}$O$_6$PSi$_2$W: C 37.74, H 4.59, found: C 37.76, H 4.64.

9.2.10 Synthesis of [{bis(trimethylsilyl)methyl}-*n*-butoxyphosphane] pentacarbonyltungsten(0) 45e

To a stirred solution of 617 mg (1.0 mmol) of 2*H*-azaphosphirene complex **41** in 30 mL of toluene were added 90 μL (1.0 mmol) of *n*-butanol at 75 °C. The reaction mixture was heated for 3 hours while stirring. After removal of all volatiles in *vacuo* (~10^{-2} mbar), the final product was purified by washing with *n*-pentane at low temperature (–60 °C). After filtration complex **45e** was yielded. (NMR code: 51m3a025.07)

Yellow solid, crystallized from *n*-pentane at –30 °C; yield: 253 mg (0.43 mmol, 43%); m.p. 62 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.23 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$), 0.93 (d, 1H, $^{4}J_{(H,H)}$ = 1.3 Hz, PC*H*), 0.97 (t, 3H, $^{2}J_{(H,H)}$ = 7.4 Hz, $OC_3H_6CH_3$), 1.44 (m, 2H, $^{2}J_{(H,H)}$ = 7.4 Hz, $OC_2H_4CH_2CH_3$), 1.68 (m, 2H, $^{2}J_{(H,H)}$ = 6.4 Hz, $OCH_2CH_2C_2H_5$), 3.68 (m, 2H, $^{2}J_{(H,H)}$ = 6.5 Hz, $OCH_2C_3H_7$), 7.85 (d, 1H, $^{1}J_{(P,H)}$ = 319.7 Hz, P–H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = –1.8 (d, $^{3}J_{(P,C)}$ = 1.9 Hz, $Si(CH_3)_3$), 0.0 (d, $^{3}J_{(P,C)}$ = 2.6 Hz, $Si(CH_3)_3$), 11.5 (s, CH_3), 17.1 (s, CH_2CH_3), 21.3 (d, $^{1}J_{(P,C)}$ = 13.6 Hz, PCH), 30.4 (d, $^{3}J_{(P,C)}$ = 8.4 Hz, OCH_2CH_2), 67.3 (d, $^{2}J_{(P,C)}$ = 4.5 Hz, OCH_2CH_2), 195.6 (d, $^{2}J_{(P,C)}$ = 7.8 Hz, $^{1}J_{(W,C)}$ = 125.4 Hz, *cis*-CO), 197.3 (d, $^{2}J_{(P,C)}$ = 24.6 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 102.5 (d_{sat}, $^{1}J_{(W,P)}$ = 267.0 Hz, $^{1}J_{(P,H)}$ = 320.4 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = 1.3 (d_{sat}, $^{2}J_{(P,Si)}$ = 5.8 Hz), 3.0 (d_{sat}, $^{2}J_{(P,Si)}$ = 9.1 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2962 (w, ν(CH/CH_3)), 2265 (w, ν(PH)), 2070 (m, ν(CO)), 1921 (s, ν(CO)); MS (EI, ^{184}W): m/z (%): 588.0 (M$^{\cdot+}$, 68), 560.0([M-CO]$^{\cdot+}$, 32), 504.0([M-3CO]$^{\cdot+}$, 35), 448.0 ([M-5CO]$^{\cdot+}$, 40), 73.0 ($Me_3Si^{\cdot+}$, 100); elemental analysis (%) calcd. for $C_{16}H_{29}O_6PSi_2W$: C 32.66, H 4.97; found C 32.79, H 5.14.

9.2.11 Synthesis of [{bis(trimethylsilyl)methyl}-*O*-acetyl-phosphane] pentacarbonyltungsten(0) 45f

To a stirred solution of 184 mg (1.1 mmol) silver acetate in 10 mL of CH_2Cl_2 were added 550 mg (1.0 mmol) of chlorophosphane complex **42** at 0 °C. Then the reaction solution was stirred overnight. Then solvent was evaporated in *vacuo* (~10^{-2} mbar) and final product was purified by column chromotagraphy on silical gel (–20 °C, 2 × 9.5 cm, petroleum ether / diethyl ether: 10/1 and 1/1). Evaporation of second fraction gave complex **45f**. (NMR code: 37m3b022.08)

White solid, crystallized from Et_2O at –30 °C; yield: 345 mg, (0.6 mmol, 60%); m.p. 50–51 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.22 (s, 9H, $SiMe_3$), 0.31 (s, 9H, $SiMe_3$), 0.88 (dd, 1H, $^2J_{(P,H)}$ = 7.2 Hz, $^4J_{(H,H)}$ = 2.5 Hz, PCH), 2.18 (d, 3H, $^4J_{(P,H)}$ = 1,3 Hz, CH_3), 8.21 (dd, $^1J_{(P,H)}$ = 354.8 Hz, $^3J_{(H,H)}$ = 2.5 Hz, P–H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 1.0 (s, $SiMe_3$), 2.1 (d, $^3J_{(P,C)}$ = 2.6 Hz, $SiMe_3$), 21.7 (d, $^1J_{(P,C)}$ = 9.1Hz, PCH), 22.3 (s, *C*H_3CO), 168.5 (d, $^2J_{(P,C)}$ = 7.8 Hz, CH_3*C*O), 195.9 (d, $^2J_{(P,C)}$ = 7.5 Hz, *cis*-CO), 198.8 (d, $^2J_{(P,C)}$ = 28.8 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 88.6 (d_{sat}, $^1J_{(W,P)}$ = 275.8 Hz, $^1J_{(P,H)}$ = 354.2 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = 1.4 (d_{sat}, $^2J_{(P,Si)}$ = 6.2 Hz), 2.7 (d_{sat}, $^2J_{(P,Si)}$ = 7.9 Hz); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2959 (w, ν(CH/CH_3)), 2366 (w, ν(PH)), 2075 (s, ν(CO)), 1988 (s, ν(CO)), 1941 (vs, ν(CO)), 1929 (vs, ν(CO)), 1915 (s, ν(CO)), 1740 (m, ν(*CO*CH_3)); MS (EI, ^{184}W): m/z (%): 573.9 ($M^{\cdot +}$, 51), 545.9 ($[M-CO]^{\cdot +}$, 48), 517.9 ($[M-2CO]^{\cdot +}$, 10), 489.9 ($[M-3CO]^{\cdot +}$, 100), 432.0 ($[M-5CO]^{\cdot +}$, 42), 73 ($SiMe^{\cdot +}$, 91); elemental analysis (%) calcd. for $C_{14}H_{23}O_7PSi_2W$: C 29.28, H 4.04; found: C 29.33, H 4.15.

9.2.12 Synthesis of [{bis(trimethylsilyl)methyl}phenoxyphosphane] pentacarbonylmolybdenum(0) 46

To a solution of 351 mg (4.5 mmol) sodium phenolate in 10 mL of Et_2O at –30 °C were added a solution of chlorophosphane molybdenum complex **42b** 1.4 g (3.0 mmol) in 10 mL of Et_2O. The mixture was stirred overnight. After evaporation of solvent in *vacuo* (~10^{-2} mbar), the raw product was purified by column chromatography on silica gel at low temperature (SiO_2,

–20 °C, 2 × 5.5 cm, petroleum ether, petroleum ether/Et_2O) and then washed with *n*-pentane at ambeint temperature. Then filttration and removal of the volatiles led to the yellow powder **46**. (NMR code: 19m3c027.09)

Yellow solid, crystallized from the *n*-pentane at –30 °C. Yield: 1.13 g (72.3%, 2.2 mmol); m.p. 63 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.29 (s, 9H, $Si(CH_3)_3$), 0.40 (s, 9H, $Si(CH_3)_3$), 0.96 (dd, 1H, $^2J_{(P,H)}$ = 4.8 Hz, $^3J_{(H,H)}$ = 1.8 Hz, PCH), 7.08 (d, 2H, $^3J_{(H,H)}$ = 7.3 Hz, Ph), 7.17 (t, 1H, $^3J_{(H,H)}$ = 7.3 Hz, Ph), 7.38 (t, 2H, $^3J_{(H,H)}$ = 7.8 Hz, Ph), 8.06 (dd, 1H, $^1J_{(P,H)}$ = 309.0 Hz, $^3J_{(H,H)}$ = 2.1 Hz, PH); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 0.1 (d, $^3J_{(P,C)}$ = 4.7 Hz, $Si(CH_3)_3$), 1.2 (d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$), 21.7 (d, $^1J_{(P,C)}$ = 8.4 Hz, PCH), 119.2 (d, $^4J_{(P,C)}$ = 6.3 Hz, *m*-Ph), 123.3 (d, $^5J_{(P,C)}$ = 1.6 Hz, *p*-Ph), 128.9 (s, *o*-Ph), 153.1 (d, $^2J_{(P.C)}$ = 5.8 Hz, *i*-Ph), 203.9 (d, $^2J_{(P,C)}$ = 9.5 Hz, *cis*-CO), 208.3 (d, $^2J_{(P,C)}$ = 28.9 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 135.4 (s, $^1J_{(P,H)}$ = 309.0 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = 0.8 (d, $^2J_{(P,Si)}$ = 5.5 Hz, $PCH(SiMe_3)_2$), 1.8 (d, $^2J_{(P,Si)}$ = 8.7 Hz, $PCH(SiMe_3)_2$); IR (KBr, cm^{-1}): ῡ = 2955 (w, ν(CH/CH_3)), 2287 (w, ν(PH)), 2075 (m, ν(CO)), 1998 (m, ν(CO)), 1945 (vs, ν(CO)), 1910 (vs, ν(CO)); MS (EI, 70eV, ^{98}Mo): m/z (%): 521.9 ($M^{+\cdot}$, 30), 494.0 ($[M-CO]^{+\cdot}$, 22), 438.0 ($[M-3CO]^{+\cdot}$, 93), 410.0 ($[M-4CO]^{+\cdot}$, 60), 382.0 ($[M-5CO]^{+\cdot}$, 22), 307.9 ($[M-5CO-SiMe_3]^{+\cdot}$, 51), 73.0 ($SiMe_3^{+\cdot}$, 100); elemental analysis (%) calcd. for $C_{18}H_{25}O_6PSi_2Mo$: C 41.54, H 4.84; found: C 39.47, H 5.66.

9.2.13 Synthesis of [{bis(trimethylsilyl)methyl}phenoxyphosphane] pentacarbonylchromium(0) 47

To a solution of 150 mg (1.3 mmol) sodium phenolate in 10 mL of Et_2O at –30 °C were added a solution of chlorophosphane chromium complex **42c** 418 mg (1.0 mmol) in 10 mL of Et_2O. The mixture was stirred overnight. After evaporation of solvent, the raw product was washed with *n*-pentane at ambient temperature. Then filtration and removal of the volatiles led to the yellow powder of complex **47**. (NMR code: 04m3b033.11)

Yellow solid, crystallized from the Et_2O at –30 °C. Yield: 297 mg (71%, 0.71 mmol); m.p. 80 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 0.20$ (s, 9H, $Si(CH_3)_3$), 0.30 (s, 9H, $Si(CH_3)_3$), 0.88 (dd, 1H, $^2J_{(P,H)} = 3.6$ Hz, PCH), 7.05 (m, 3H, Ph), 7.29 (m, 2H, Ph), 8.02 (dd, 1H, $^1J_{(P,H)} = 317.3$ Hz, $^3J_{(H,H)} = 1.5$ Hz, PH); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = –0.0$ (d, $^3J_{(P,C)} = 2.6$ Hz, $Si(CH_3)_3$), 1.8 (d, $^3J_{(P,C)} = 3.2$ Hz, $Si(CH_3)_3$), 22.7 (d, $^1J_{(P,C)} = 9.1$ Hz, PCH), 119.8 (d, $^4J_{(P,C)} = 5.8$ Hz, *m*-Ph), 124.0 (d, $^5J_{(P,C)} = 1.3$ Hz, *p*-Ph), 129.5 (s, *o*-Ph), 153.3 (d, $^2J_{(P.C)} = 7.1$ Hz, *ipso*-Ph), 215.3 (d, $^2J_{(P,C)} = 14.2$ Hz, *cis*-CO), 219.8 (d, $^2J_{(P,C)} = 6.5$ Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 161.8$ (s, $^1J_{(P,H)} = 317.9$ Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): $\delta = 1.2$ (d, $^2J_{(P,Si)} = 5.8$ Hz, $PCH(SiMe_3)_2$), 2.0 (d, $^2J_{(P,Si)} = 9.5$ Hz, $PCH(SiMe_3)_2$); IR (KBr, cm^{-1}): $\tilde{\upsilon} = 2956$ (w, ν(CH/CH_3)), 2348 (w, ν(PH)), 2065 (s, ν(CO)), 1929 (vs, ν(CO)); MS (EI, 70eV, ^{52}Cr): m/z (%): 476.1 ($M^{+\cdot}$, 10), 448.1 ($[M\text{-}CO]^{+\cdot}$, 4), 392.1 ($[M\text{-}3CO]^{+\cdot}$, 18), 364.1 ($[M\text{-}4CO]^{+\cdot}$, 25), 336.1 ($[M\text{-}5CO]^{+\cdot}$, 100), 73.1 ($SiMe_3^{+\cdot}$, 61); elemental analysis (%) calcd. for $C_{18}H_{25}O_6PSi_2Cr$: C 45.37, H 5.29; found: C 44.11, H 5.49.

9.2.14 Syntheses of [{bis(trimethylsilyl)methyl}isocyanatophosphane] pentacarbonyltungsten(0) 48

A solution of 550 mg (1.0 mmol) chlorophosphane complex **42** in 10 mL of acetonitrile was added to a solution of 150 mg (1.1 mmol) silver cyanate in 10 mL of acetonitrile at ambient temperature. The solution mixture was stirred for 3 hours, and the solvent was evaporated in *vacuo* (~ 0.01 mbar). The raw product was purified by column chromotagraphy (–20 °C, SiO_2, 2×8, petroleum ether/diethyl ether = 100/1). The final product **48** was contained in the first fraction. (NMR code: 33m3b054.10)

Brownish yellow solid, crystallized from the mixture of Et_2O and CH_2Cl_2 at +4 °C; Yield: 307 mg (55%, 0.55 mmol); m.p. 68–70 °C; ^1H NMR (300.13 MHz, CD_2Cl_2): $\delta = 0.25$ (s, 9H, $Si(CH_3)_3$), 0.33 (s, 9H, $Si(CH_3)_3$), 0.88 (br, 1H, PCH), 7.70 (dd, 1H, $^1J_{(P,H)} = 359.0$ Hz, $^3J_{(H,H)} = 1.5$ Hz, PH); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): $\delta = 0.0$ (d, $^3J_{(P,C)} = 3.2$ Hz, $Si(CH_3)_3$), 1.9 (d, $^3J_{(P,C)} = 3.9$ Hz, $Si(CH_3)_3$), 21.2 (d, $^1J_{(P,C)} = 10.3$ Hz, PCH), 196.4 (d, $^2J_{(P,C)} = 6.5$ Hz, $^1J_{(W,C)} = 126.1$ Hz, *cis*-CO), 199.1 (d, $^2J_{(P,C)} = 27.8$ Hz, *trans*-CO), 221.8 (s, P-N=*C*); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta = 29.1$ (d_{sat}, $^1J_{(W,P)} = 265.8$ Hz, $^1J_{(P,H)} = 359.8$ Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, CD_2Cl_2): $\delta = 1.2$ (d, $^2J_{(P,Si)} = 6.0$ Hz, $PCHSi(Me_3)_2$), 3.1 (d, $^2J_{(P,Si)} = 8.7$ Hz, $PCHSi(Me_3)_2$); IR (KBr, cm^{-1}): $\tilde{\upsilon} = 2960$ (w, ν(CH/CH_3)), 2314 (w, ν(PH)), 2253 (s, ν(N=C=O)), 2076 (s, ν(CO)), 1990 (s, ν(CO)), 1922 (vs, ν(CO)); MS (EI, 70eV, ^{184}W): m/z (%): 557.0 ($M^{+\cdot}$, 30), 501.0 ($[M\text{-}2CO]^{+\cdot}$, 22), 473.0 ($[M\text{-}3CO]^{+\cdot}$, 70), 445.0 ($[M\text{-}4CO]^{+\cdot}$, 17), 417.0 ($[M\text{-}5CO]^{+\cdot}$, 38), 73.1 ($SiMe_3^{+\cdot}$, 100); elemental analysis (%) calcd. for $C_{13}H_{20}NO_6PSi_2W$: C 28.02, H 3.62, N 2.51; found: C 28.13, H 3.85, N 2.65.

9.3 Syntheses of [lithium(12-crown-4)][{bis(trimethylsilyl) methyl}alkoxyphosphinidenoid)]pentacarbonyltungsten(0), molybdenum(0) and chromium(0)

9.3.1 Synthesis of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl} phenoxyphosphinidenoid]pentacarbonyltungsten(0) 51a

To a solution of 0.22 mmol lithium diisopropylamide (LDA), freshly prepared from 0.14 mL (1.6 M, 0.22 mmol) of *n*-butyllithium and 30 µL (0.2 mmol) of diisopropylamine in 2 mL of diethyl ether and cooled to −78 °C, a solution of 122 mg (0.2 mmol) **45a** and 32 µL (0.2 mmol) of 12-crown-4 in 2 mL of diethyl ether was dropwise added and the reaction mixture was stirred for 2 hours. Then the solvent was evaporated in *vacuo* (~ 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon, and the complex **51a** was obtainded as orange solid after drying in *vacuo*. (NMR code: 38m3b036.08)

Orange solid, yield: 400 mg (0.51mmol, 51%); m.p. 75°C; ^{1}H NMR (300.13 MHz, THF-d8): δ = 0.08 (d, 9H, $^4J_{(P,H)}$ = 1.7 Hz, Si(CH$_3$)$_3$), 0.17 (s, 9H, Si(CH$_3$)$_3$), 2.28 (d, 1H, $^2J_{(P,H)}$ = 1.7 Hz, PCH), 3.76 (s, 16 H, 12-crown-4), 7.02 (m, 5H, Ph); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = 1.7 (d, $^3J_{(P,C)}$ = 4.5 Hz, Si(CH$_3$)$_3$), 4.0 (d, $^3J_{(P,C)}$ = 1.3 Hz, Si(CH$_3$)$_3$), 25.4 (d, $^1J_{(P,C)}$ = 75.0 Hz, PCH), 68.6 (s, 12-crown-4), 118.1 (d, $^5J_{(P,C)}$ = 1.9 Hz, *p*-Ph), 119.4 (d, $^3J_{(P,C)}$ = 15.5 Hz, *o*-Ph), 128.8 (d, $^4J_{(P,C)}$ = 1.9 Hz, *m*-Ph), 162.2 (d, $^2J_{(P,C)}$ = 9.1 Hz, *i*-Ph), 206.4 (d, $^2J_{(P,C)}$ = 5.2 Hz, *cis*-CO), 210.3 (d, $^2J_{(P,C)}$ = 14.9 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 209.1 (s$_{sat}$, $^1J_{(W,P)}$ = 76.2 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, THF-d8): δ = −5.9 (d$_{sat}$, $^2J_{(P,Si)}$ = 32.7 Hz), −2.3 (d$_{sat}$, $^2J_{(P,Si)}$ = 25.8 Hz); IR (nujol, cm^{-1}): ῦ = 2058 (m, ν(CO)), 2044 (m, ν(CO)), 1916 (s, ν(CO)); elemental analysis calcd (%) for $C_{26}H_{40}LiO_{10}PSi_2W$: C 39.50, H 5.10; found C 40.57, H 5.61.

9.3.2 Synthesis of [lithium(Et_2O)$_n$][{bis(trimethylsilyl)methyl}phenoxyl phosphinidenoid]pentacarbonyltungsten(0) 52a

To a solution of 0.11 mmol lithium diisopropylamide (LDA, freshly prepared from 70 µL (1.6 M, 0.11 mmol) of *n*-butyllithium and 20 µL (0.1 mmol) of diisopropylamine in 1 mL of diethyl ether and cooled to –78 °C, a solution of 61 mg (0.1 mmol) **45a** in 1 mL of diethyl ether was dropwise added and the reaction mixture was stirred for 1 hour. Then the ^{31}P NMR spectroscopy in reaction solution showed formation of complex **52a** as a singlet.

^{31}P NMR (75.5 MHz, reaction solution): δ = 200.4 ppm (s_{sat}, $^1J_{(W,P)}$ = 70.8 Hz)

9.3.3 Synthesis of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl} methoxyphosphinidenoid]pentacarbonyltungsten(0) 51b

To a solution of 0.22 mmol lithium diisopropylamide (LDA), freshly prepared from 0.14 mL (1.6 M, 0.22 mmol) of *n*-butyllithium and 30 µL (0.2 mmol) of diisopropylamine in 2 mL of diethyl ether and cooled to –78 °C, a solution of 109 mg (0.2 mmol) **45b** and 32 µL (0.2 mmol) of 12-crown-4 in 2 mL of diethyl ether was dropwise added and the reaction mixture stirred for 2 hours. Then the solvent was evaporated in *vacuo* (~ 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon, and the complex **51b** was obtainded as orange oil after drying in *vacuo*. (NMR code: 10m3b060.09)

^{1}H NMR (300.13 MHz, THF-d8): δ = 0.04 (s, 9H, $SiMe_3$), 0.11 (d, 9H, $^4J_{(P,H)}$ = 1.5 Hz, $SiMe_3$), 2.09 (s, 1H, PC*H*), 3.13 (d, 3H, $^3J_{(P,H)}$ = 14.9 Hz, POC*H*$_3$), 3.77 (s, 16H, 12-crown-4);

$^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d8): $\delta = 1.4$ (d, $^3J_{(P,C)} = 12.3$ Hz, Si(*C*H$_3$)$_3$), 4.0 (s, Si(*C*H$_3$)$_3$), 25.8 (d, $^1J_{(P,C)} = 66.6$ Hz, P*C*H), 58.0 (d, $^2J_{(P,C)} = 29.1$ Hz, PO*C*H$_3$), 69.1 (s, 12-crown-4), 208.1 (d, $^2J_{(P,C)} = 5.7$ Hz, *cis*-CO), 212.1 (d, $^2J_{(P,C)} = 14.2$ Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d8): $\delta = 209.6$ (s$_{sat}$, $^1J_{(W,P)} = 68.7$ Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, THF-d8): $\delta = -6.1$ (d$_{sat}$, $^2J_{(P,Si)} = 30.9$ Hz), -2.1 (d$_{sat}$, $^2J_{(P,Si)} = 62.1$ Hz).

9.3.4 Synthesis of [lithium(Et$_2$O)$_n$][{bis(trimethylsilyl)methyl}methoxy phosphinidenoid]pentacarbonyltungsten(0) 52b

To a solution of 0.11 mmol lithium diisopropylamide (LDA), freshly prepared from 70 µL (1.6 M, 0.11 mmol) of *n*-butyllithium and 20 µL (0.1 mmol) of diisopropylamine in 1 mL of diethyl ether and cooled to −78 °C, a solution of 55 mg (0.1 mmol) **45b** in 1 mL of diethyl ether was dropwise added and the reaction mixture stirred for 1 hour. Then the resulting orange-red solution of complex **52b** was characterized by ^{31}P NMR.

Red solution, ^{31}P NMR (75.5 MHz, in reaction solution): $\delta = 200.3$ ppm (s$_{sat}$, $^1J_{(W,P)} = 67.4$ Hz, $^3J_{(P,H)} = 15.3$ Hz)

9.3.5 Synthesis of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl} (2-methoxyethan-1-oxy)phosphinidenoid]pentacarbonyltungsten (0) 51c

To a solution of .022 mmol lithium diisopropylamide (LDA, freshly prepared from 0.14 mL (1.6 M, 0.22 mmol) of *n*-butyllithium and 30 µL (0.2 mmol) of diisopropylamine in 2 mL of diethyl ether and cooled to −78 °C, a solution of 118 mg (0.2 mmol) **45c** and 32 µL (0.2 mmol) of 12-crown-4 in 2 mL of diethyl ether was dropwise added and the reaction mixture was stirred for 2 hours. Then the solvent was evaporated in *vacuo* (~ 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon, and the complex **51c** was obtainded as orange oil after drying in *vacuo*. (NMR code: 36m3b011.10)

^{1}H NMR (300.13 MHz, THF-d8): δ = 0.00 (d, 9H, $^{4}J_{(P,H)}$ = 1.5 Hz, $Si(CH_3)_3$), 0.10 (s, 9H, $Si(CH_3)_3$), 1.86 (br, 1H, PCH), 3.18 (s, 3H, $POC_2H_4OCH_3$), 3.45 (m, 2H, $POCH_2CH_2OCH_3$), 3.50 (m, 2H, $POCH_2CH_2OCH_3$), 3.69 (s, 16H, 12-crown-4); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = –0.1 (d, $^{3}J_{(P,C)}$ = 4.5 Hz, $Si(CH_3)_3$), 2.4 (s, $Si(CH_3)_3$), 24.3 (d, $^{1}J_{(P,C)}$ = 68.5 Hz, PCH), 57.2 (s, $POC_2H_4OCH_3$), 67.0 (s, 12-crown-4), 68.1 (d, $^{2}J_{(P,C)}$ = 23.9 Hz, $POCH_2CH_2OCH_3$), 72.3 (d, $^{3}J_{(P,C)}$ = 9.7 Hz, $POCH_2CH_2OCH_3$), 206.3 (d, $^{2}J_{(P,C)}$ = 5.2 Hz, *cis*-CO), 210.2 (d, $^{2}J_{(P,C)}$ = 14.2 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 208.8 (s_{sat}, $^{1}J_{(W,P)}$ = 69.0 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, THF-d8): δ = –6.4 (d_{sat}, $^{2}J_{(P,Si)}$ = 28.3 Hz), –2.1 (s_{sat}).

9.3.6 Synthesis of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl}(2,6-dimethyl-phenoxyphosphinidenoid]pentacarbonyltungsten(0) 51d

To a solution of .022 mmol lithium diisopropylamide (LDA, freshly prepared from 0.14 mL (1.6 M, 0.22 mmol) *n*-butyllithium and 30 µL (0.2 mmol) diisopropylamine in 2 mL of diethyl ether cooled to –78 °C, a solution of 127 mg (0.2 mmol) **45d** and 32 μL (0.2 mmol) of 12-crown-4 in 2 mL of diethyl ether was dropwise added. Then the reaction mixture was stirred for 2 hours. Then the solvent was evaporated in *vacuo* (~ 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon, and the complex **51d** was obtainded as orange oil after drying in *vacuo*. The NMR of complex **51d** was fully characterized at–40 °C. (NMR code: 40m3mTT2.09)

^{1}H NMR (300.13 MHz, THF-d8, –40 °C): δ = –0.08 (s, 9H, SiMe$_3$), 0.10 (s, 9H, SiMe$_3$), 0.95 (d, 12H, $^{2}J_{(H,H)}$ = 6.0 Hz, HN^{i}Pr$_2$-*H*), 2.08 (d, 3H, $^{2}J_{(H,H)}$ = 13.0 Hz, PO-2,6-*Me*$_2$C$_6$H$_3$), 2.17 (s, 3H, PO-2,6-*Me*$_2$C$_6$H$_3$), 2.32 (br, 1H, PCH), 2.85 (octet, 2H, $^{2}J_{(H,H)}$ = 6.2 Hz, NH(C*H*(CH$_3$)$_2$)$_2$), 3.74 (s, 16H, 12-crown-4), 6.75 (m, 2H, $^{3}J_{(H,H)}$ = 7.3 Hz, *m*-Ph), 6.93 (d, 1H, $^{3}J_{(H,H)}$ = 7.4 Hz, *p*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8, –40 °C): δ = 1.3 (d, $^{3}J_{(P,C)}$ = 10.3 Hz, Si(CH$_3$)$_3$), 2.9 (s, Si(CH$_3$)$_3$), 20.8 (s, 2,6-*Me*$_2$C$_6$H$_3$), 22.7 (d, $^{1}J_{(P,C)}$ = 78.8 Hz, P*C*H), 68.7 (s, 12-crown-4), 126.2 (d, $^{5}J_{(P,C)}$ = 1.9 Hz, *p*-Ph), 131.1 (d, $^{4}J_{(P,C)}$ = 1.9 Hz, *m*-Ph), 131.5 (d, $^{3}J_{(P,C)}$ = 3.9 Hz, *o*-Ph), 153.5 (d, $^{2}J_{(P,C)}$ = 8.4 Hz, P-O-*C*), 219.7 (d, $^{2}J_{(P,C)}$ = 12.9 Hz, *cis*-CO), 223.4 (d, $^{2}J_{(P,C)}$ = 21.3 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8, –40 °C): δ = 215.3 (s$_{sat}$, $^{1}J_{(W,P)}$ = 69.9 Hz).

9.3.7 Synthesis of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl}*n*-butoxyphosphinidenoid]pentacarbonyltungsten(0) 51e

To a solution of 0.22 mmol lithium diisopropylamide (LDA, freshly prepared from 0.14 ml (1.6 M, 0.22 mmol) *n*-butyllithium and 30 μL (0.2 mmol) diisopropylamine in 2 mL of diethyl ether cooled to **–78** °C, a solution of 118 mg (0.2 mmol) **45e** and 32 µL (0.2 mmol) of 12-crown-4 in 2 mL of diethyl ether was slowly added. Then the reaction mixture was stirred for 2 hours. Then the yellow solution of complex **51e** was characterized only by ^{31}P NMR.

^{31}P {^{1}H} NMR (75.5 MHz, in reaction solution): $\delta = 201.3$ (s_{sat}, $^{1}J_{(W,P)} = 68.7$ Hz).

9.3.8 Synthesis of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl} phenoxyphosphinidenoid]pentacarbonylmolybdenum(0) 53

To a solution of 0.12 mmol of freshly prepared LDA (lithium diisopropylamide) from 75 µL (1.6 M, 0.12 mmol) of *n*-butyllithium and 14 µL (0.1 mmol) of diisopropylamine in 0.4 mL of diethyl ether was added 52 mg (0.1 mmol) *P*-phenoxy phosphane complex of **46** and 19 µL (0.12 mmol) of 12-crown-4 in 0.3 mL of Et_2O at –78 °C. The solution mixture was stirred for 1 hour, then removed all volatiles in *vacuo* (ca. 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon. The complex **53** was obtained after drying in *vacuo*. (NMR code: 08m3b045.11)

From ^{31}P NMR (in THF-d8 at 25 °C), the peaks of phosphinidenoid complex **53** ($\delta = 236.2$ ppm) and starting material phosphane complex **46** ($\delta = 133.9$ ppm) both showed up with a ratio of 1:0.3. Moreover, the cyclotriphosphane $(PR)_3$ **16** was also observed at high filed. The selected data were given as follows.

Black red solution, ^{1}H NMR (300.13 MHz, THF-d8): $\delta = 0.11$ (d, 18H, $^{4}J_{(P,H)} = 1.9$ Hz, $SiMe_3$), 0.99 (d, $^{2}J_{(H,H)} = 6.2$ Hz, $HN(CH(CH_3)_2)_2$), 2.20 (d, 1H, $^{2}J_{(P,H)} = 1.9$ Hz, PCH), 2.88

(m, $^{2}J_{(H,H)}$ = 6.2 Hz, HN(C*H*(CH$_3$)$_2$)$_2$), 3.72 (s, 16H, 12-crown-4), 7.04 (m, 5H, Ph); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = 0.0 (s, Si(CH$_3$)$_3$), 20.9 (d, $^{1}J_{(P,C)}$ = 41.0 Hz, PCH), 21.9 (s, HN(CH(*C*H$_3$)$_2$)$_2$), 44.6 (s, HN(*C*H(*C*H$_3$)$_2$)$_2$), 68.2 (s, 12-crown-4), 127.2 (d, $^{5}J_{(P,C)}$ = 1.5 Hz, *p*-Ph), 127.8 (d, $^{3}J_{(P,C)}$ = 6.6 Hz, *o*-Ph), 129.4 (s, Ph), 160.5 (s, P-O-*C*), 209.5 (d, $^{2}J_{(P,C)}$ = 11.4 Hz, *cis*-CO), 212.9 (d, $^{2}J_{(P,C)}$ = 3.4 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 236.2 (s, no P,Mo coupling).

9.3.9 Synthesis of [lithium(thf)$_n$][{bis(trimethylsilyl)methyl}phenoxy phosphinidenoid]pentacarbonyltmolybdenum(0) 56,57

To a solution of 0.12 mmol of freshly prepared LDA (lithium diisopropylamide) from 75 µL (1.6 M, 0.12 mmol) of *n*-butyllithium and 14 µL (0.1 mmol) of diisopropylamine in 0.4 mL of diethyl ether was added 52 mg (0.1 mmol) *P*-phenoxy phosphane complex **46** in 0.3 mL of THF at –78 °C. The solution mixture was stirred for 1 hour, then removed all volatiles in *vacuo* (ca. 10^{-2} mbar). The final product **56** or **57** was fully characterized by multiple NMR in THF-d8 at ambient temperature. (NMR code: 08m3c027.11)

Yellow solution, ^{1}H NMR (300.13 MHz, THF-d8): δ = –0.35 (dd, 1H, $^{2}J_{(P,H)}$ = 10.0 Hz, $^{3}J_{(H,H)}$ = 7.4 Hz), 0.13 (s, 9H, Si(CH$_3$)$_3$), 0.17 (s, 18H, Si(CH$_3$)$_3$), 0.24 (s, 9H, Si(CH$_3$)$_3$), 0.63 (d, 1H, *J* = 14.1 Hz), 1.60 (d, 3H, *J* = 6.3 Hz); ^{31}P{^{1}H} NMR (75.5 MHz, THF-d8): δ = –28.9 (P^{A}, $^{1}J_{(P,P)}$ = 495.6 Hz), –198.3 (P^{B}, $^{1}J_{(P,P)}$ = 495.6 Hz)

9.3.10 Synthesis of [lithium(12-crown-4)][{bis(trimethysilyl)methyl}phenoxyphosphinidenoid]pentacarbonylchromium(0) 54

To a solution of 0.12 mmol of freshly prepared LDA (lithium diisopropylamide) from 75 µL (1.6 M, 0.12 mmol) of *n*-butyllithium and 14 µL (0.1 mmol) of diisopropylamine in 0.4 mL of diethyl ether was added 47 mg (0.1 mmol) phenoxyl phosphane chromium complex **47** and 19 µL (0.12 mmol) of 12-crown-4 in 0.3 mL of Et_2O at –78 °C. The solution mixture was stirred for 1 hour, then removed all volatile *in vacuo* (~ 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon, and the complex **54** was obtainded as orange viscous after drying in *vacuo*. (NMR code: 21m3b030.09)

^{1}H NMR (300.13 MHz, THF-d8): δ = 0.00 (d, 9H, $^4J_{(P,H)}$ = 1.1 Hz, Si(CH$_3$)$_3$), 0.10 (s, 9H, Si(CH$_3$)$_3$), 1.85 (br, 1H, PCH), 3.67 (s, 16H, 12-crown-4), 6.95 (m, 5H, Ph); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = 0.1 (d, $^3J_{(P,C)}$ = 10.3 Hz, Si(CH$_3$)$_3$), 4.0 (s, Si(CH$_3$)$_3$), 23.4 (d, $^1J_{(P,C)}$ = 73.1 Hz, PCH), 65.8 (s, 12-crown-4), 116.7 (d, $^5J_{(P,C)}$ = 1.9 Hz, *p*-Ph), 118.1 (d, $^3J_{(P,C)}$ = 15.5 Hz, *o*-Ph), 127.3 (d, $^4J_{(P,C)}$ = 1.9 Hz, *m*-Ph), 160.5 (d, $^2J_{(P,C)}$ = 9.1 Hz, *i*-Ph), 224.2 (d, $^2J_{(P,C)}$ = 3.2 Hz, *cis*-CO), 229.8 (s, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 248.8 (s); ^{29}Si{^{1}H} NMR (59.6 MHz, THF-d8): δ = –6.6 (d$_{sat}$, $^2J_{(P,Si)}$ = 33.8 Hz), –2.4 (s).

9.3.11 Synthesis of [lithium(thf)$_n$][{bis(trimethylsilyl)methyl}phenoxyphosphinidenoid]pentacarbonylchromium(0) 55

Method A: To a solution of 0.12 mmol of freshly prepared LDA (lithium diisopropylamide) from 75 µL (1.6 M, 0.12 mmol) of *n*-butyllithium and 14 µL (0.1 mmol) of diisopropylamine in 0.4 mL of diethyl ether was added 47 mg (0.1 mmol) phenoxyl phosphane chromium complex **47** in 0.3 mL of THF at –78 °C. The reaction mixture was stirred for 1 hour, then removed all volatile in *vacuo* (ca. 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon, and the complex **55** was obtainded.

Method B: To a solution of 48 mg (0.1 mmol) phenoxyl phosphane chromium complex **47** in 0.5 mL of THF was added 70 µL(1.6 M in diethyl ether, 0.12 mmol) MeLi at –78 °C. The reaction mixture was stirred for 0.5 hour, then evaporated all volatiles in *vacuo* (~ 10^{-2} mbar) and the residue was washed with *n*-pentane at low temperature under Argon. The complex **55** was yielded as viscous after drying in *vacuo*. (NMR code: 12m3b031.11)

^{1}H NMR (300.13 MHz, THF-d8): δ = 0.00 (d, 9H, $^{4}J_{(P,H)}$ = 1.6 Hz, $Si(CH_3)_3$), 0.10 (s, 9H, $Si(CH_3)_3$), 1.86 (br, 1H, PCH), 6.49 (t, 1H, $^{3}J_{(H,H)}$ = 6.6 Hz, *p*-Ph), 6.94 (m, 4H, $^{3}J_{(H,H)}$ = 8.4 Hz, Ph); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = –0.1 (d, $^{3}J_{(P,C)}$ = 12.0 Hz, $Si(CH_3)_3$), 2.5 (s, $Si(CH_3)_3$), 23.3 (d, $^{1}J_{(P,C)}$ = 72.8 Hz, PCH), 116.5 (d, $^{5}J_{(P,C)}$ = 1.7 Hz, *p*-Ph), 118.1 (d, $^{3}J_{(P,C)}$ = 15.0 Hz, *o*-Ph), 127.2 (d, $^{4}J_{(P,C)}$ = 1.7 Hz, *m*-Ph), 160.4 (d, $^{2}J_{(P,C)}$ = 9.0 Hz, *i*-Ph), 224.1 (d, $^{2}J_{(P,C)}$ = 3.3 Hz, *cis*-CO), 229.7 (s, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 248.7 (s, no P, Cr coupling); ^{29}Si{^{1}H} NMR (59.6 MHz, THF-d8): δ = –6.5 (d_{sat}, $^{2}J_{(P,Si)}$ = 33.8 Hz), –2.3 (s).

9.4 Syntheses of [{bis(trimethylsilyl)methyl}-alkoxylphosphinidenoid]pentacarbonyltungsten (0) complexes having organic counter cations

9.4.1 Synthesis of [(*N,N*-di-tert-butyl-imidazolium)][{bis(trimethylsilyl) methyl}phenoxyphosphinidenoid]pentacarbonyltungsten (0) 68a

A solution of 160 mg (0.8 mmol) *N,N*-1,3-di-*tert*-butyl-imidazolyl-2-ylidene in 1 mL of diethyl ether was added dropwise to the solution of 490 mg (0.8 mmol) phosphane complex **45a** in 1 mL of diethyl ether at –78 °C. The reaction solution was stirred for 0.5 hour and yellow solid were precipitated. Filtration and evaporation of solvent in *vacuo* ($\sim 10^{-2}$ mbar) led to the yellow powder of complex **68a**. (NMR code: 42m3b034.10)

Yellow solid, Yield: 474 mg (60%, 0.48 mmol); crystallized from Et_2O at –60 °C; m.p. 100 °C; ^{1}H NMR (300.13 MHz, THF-d8): δ = 0.10 (d, 9H, $^{4}J_{(P,H)}$ = 1.7 Hz, $Si(CH_3)_3$), 0.19 (s, 9H, $Si(CH_3)_3$), 1.67 (s, 18H, $NC(CMe_3)$), 2.30 (d, 1H, $^{2}J_{(P,H)}$ = 1.5 Hz, PCH), 6.60 (m, 1H, *p*-Ph), 7.05 (m, 4H, *m*-Ph and *o*-Ph), 7.83 (br, 2H, $C^{4,5}$-H), 8.85 (br, 1H, C^{2}-H); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, THF-d8): δ = 1.2 (d, $^{3}J_{(P,C)}$ = 12.3 Hz, $Si(CH_3)_3$), 2.5 (s, $Si(CH_3)_3$), 23.9 (d, $^{1}J_{(P,C)}$ = 70.5 Hz, PCH), 28.3 (s, $NC(\mathit{C}H_3)_3$), 60.0 (s, $N\mathit{C}(CH_3)_3$), 116.6 (d, $^{5}J_{(P,C)}$ = 1.9 Hz, *p*-Ph), 117.9 (s, Ph), 118.0 (s, N*CC*N), 127.4 (s, Ph), 131.1 (s, N*C*N), 160.7 (d, $^{2}J_{(P,C)}$ = 8.4 Hz, POC), 204.9 (d, $^{2}J_{(P,C)}$ = 5.0 Hz, $^{1}J_{(W,C)}$ = 127.1 Hz, *cis*-CO), 209.1 (d, $^{2}J_{(P,C)}$ = 15.0 Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, THF-d8): δ = 208.6 (s_{sat}, $^{1}J_{(W,P)}$ = 75.5 Hz); $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, THF-d8): δ = –5.9 (d, $^{2}J_{(P,Si)}$ = 32.9 Hz, $PCH(SiMe_3)_2$), –2.1 (s, $PCH(SiMe_3)_2$).

9.4.2 Synthesis of [(*N,N*-di-tert-butyl-imidazolium)][{bis(trimethylsilyl) methyl}methoxyphosphinidenoid]pentacarbonyltungsten(0) 68b

A solution of 160 mg (0.8 mmol) *N,N*-1,3-di-tert-butyl-imidazolyl-2-ylidene in 1 mL of diethyl ether was added dropwise to the solution of 437 mg (0.8 mmol) phosphane complex **45b** in 1 mL of diethyl ether at –78 °C. The reaction solution was stirred for 0.5 hour and yellow solids were precipitated. Then filtration and evaporation of the solvent in *vacuo* (ca. 0.01 mbar) led to the mixture of yellow solid of complex **68b** and *P*-methoxyphosphane complex **45b**. (NMR code: 04m3mTT1.11 and 03m3mTT1.11)

Yellow solid, Yield: 337 mg (58%, 0.47 mmol); m.p. 95 °C; ^{1}H NMR (300.13 MHz, THF-d8): $\delta = 0.00$ (s, 9H, $Si(CH_3)_3$), 0.07 (s, 9H, $Si(CH_3)_3$), 1.66 (s, 18H, $N(CMe_3)$), 2.22 (br, 1H, PCH), 3.09 (d, 3H, $^3J_{(P,H)} = 15.2$ Hz, POMe), 8.07 (s, 2H, $C^{4,5}$-H), 9.07 (br, 1H, C^2-H); $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d8): $\delta = 0.1$ (d, $^3J_{(P,C)} = 11.4$ Hz, $Si(CH_3)_3$), 2.9 (s, $Si(CH_3)_3$), 24.5 (d, $^1J_{(P,C)} =$ 66.1 Hz, PCH), 28.6 (s, $NC(CH_3)_3$), 57.5 (d, $^2J_{(P,C)} = 28.5$ Hz, $POCH_3$), 59.9 (s, $NC(CH_3)_3$), 120.5 (s, NCCN), 132.4 (s, NCN), 196.9 (d, $J_{(P,C)} = 8.1$ Hz, NCN), 207.0 (d, $^2J_{(P,C)} = 2.6$ Hz, $^1J_{(W,C)} = 127.9$ Hz, *cis*-CO), 211.3 (d, $^2J_{(P,C)} = 14.5$ Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d8): $\delta = 202.9$ (s_{sat}, $^1J_{(W,P)} = 68.9$ Hz).

9.4.3 Synthesis of [1-*tert*-butyl-4,4,4-*tris*(dimethylamino)-2,2-*bis*{*tris*(dimethylamino)}phosphoranylidenammonium][{bis(trimethylsilyl)methyl}phenoxyphosphinidenoid]pentacarbonyltungsten(0) 69a

To a solution of 61 mg (0.1 mmol) *P*-phenoxy phosphane complex **45a** in 1.0 mL of THF was added 0.1 mL (1.0 M in *n*-pentane) „P_4-*t*-Bu" phosphazene at –78 °C. The reaction mixture was stirred for 1 hour, and then all volatiles were removed in vacuo (~ 10^{-2} mbar). The final complex **69a** was obtained as red solid after purification by washing with *n*-pentane at low temperature (–60 °C). (NMR code: 43m3c009.10)

Red solid, Yield: 90 mg (72%, 0.072 mmol); m.p. 93 °C; ^{1}H NMR (300.13 MHz, THF-d8): δ = 0.08 (d, 9H, $^{4}J_{(P,H)}$ = 1.7 Hz, Si(CH$_3$)$_3$), 0.17 (s, 9H, Si(CH$_3$)$_3$), 1.33 (d, 9H, $^{3}J_{(P,H)}$ = 0.8 Hz, PNC(CH$_3$)$_3$), 2.22 (d, 1H, $^{2}J_{(P,H)}$ = 7.2 Hz, PCH), 2.63 (d, 54H, $^{2}J_{(H,H)}$ = 9.8 Hz, N(CH$_3$)$_2$), 6.48 (m, 1H, *p*-Ph), 6.95 (m, 4H, *m*-Ph and *o*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = 2.5 (d, $^{3}J_{(P,C)}$ = 12.2 Hz, Si(CH$_3$)$_3$), 4.1 (s, Si(CH$_3$)$_3$), 23.8 (d, $^{1}J_{(P,C)}$ = 67.9 Hz, PCH), 32.4 (d, $^{3}J_{(P,C)}$ = 5.1 Hz, PNC(*C*H$_3$)$_3$), 37.9 (d, $^{2}J_{(P,C)}$ = 4.7 Hz, P(NMe$_2$)$_3$), 51.4 (d, $^{2}J_{(P,C)}$ = 3.5 Hz, PN*C*(CH$_3$)$_3$), 118.0 (d, $^{5}J_{(P,C)}$ = 1.9 Hz, *p*-Ph), 119.4 (d, $^{3}J_{(P,C)}$ = 15.7 Hz, *o*-Ph), 129.9 (d, $^{4}J_{(P,C)}$ = 1.5 Hz, *m*-Ph), 162.2 (d, $^{2}J_{(P,C)}$ = 8.7 Hz, *i*-Ph), 206.3 (d, $^{1}J_{(W,C)}$ = 126.7 Hz, $^{2}J_{(P,C)}$ = 4.9 Hz, *cis*-CO), 210.3 (d, $^{2}J_{(P,C)}$ = 14.5 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 209.7 (s$_{sat}$, $^{1}J_{(W,P)}$ = 76.3 Hz), 13.5 (d, $^{2}J_{(P,P)}$ = 49.6 Hz, 3P, P^{A}), –22.9 (quart, $^{2}J_{(P,P)}$ = 49.6 Hz, 1P, P^{B}); ^{29}Si{^{1}H} NMR (59.6 MHz, THF-d8): δ = –6.0 (d, $^{2}J_{(P,Si)}$ = 32.1 Hz, PCH(SiMe$_3$)$_2$), –2.1 (s, PCH(SiMe$_3$)$_2$).

9.4.4 Synthesis of [1-*tert*-butyl-4,4,4-*tris*(dimethylamino)-2,2-*bis*{*tris* (dimethylamino)}phosphoranylidenammonium][{bis(trimethylsilyl) methyl}methoxyphosphinidenoid]pentacarbonyltungsten 69b

To a solution of 56 mg (0.1 mmol) *P*-methoxy phosphane complex **45b** in 1.0 mL of THF was added 0.1 mL (1.0 M in *n*-pentane) P$_4$-*t*-Bu phosphazene (short for S. B.) at –78 °C. The reaction mixture was stirred for 1 hour, and then evaporated solvent in *vacuo* (~ 10^{-2} mbar). The pure complex **69b** was obtained as orange viscous after purification by washing with *n*-pentane at low temperature (–60 °C). (NMR code: 45m3c016.10)

Red viscous oil, Yield: 74 mg (63%, 0.063 mmol); ^{1}H NMR (300.13 MHz, THF-d8): δ = 0.00

(d, 9H, ${}^{4}J_{(P,H)}$ = 1.6 Hz, Si(CH$_3$)$_3$), 0.07 (s, 9H, Si(CH$_3$)$_3$), 1.29 (d, 9H, ${}^{3}J_{(P,H)}$ = 0.8 Hz, PNC(CH$_3$)$_3$), 2.04 (br, 1H, PCH), 2.63 (d, 54H, ${}^{2}J_{(H,H)}$ = 10.0 Hz, N(CH$_3$)$_2$), 3.08 (d, 3H, ${}^{3}J_{(P,H)}$ = 15.0 Hz, PO(CH$_3$)); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = –0.1 (d, ${}^{3}J_{(P,C)}$ = 12.3 Hz, Si(CH$_3$)$_3$), 2.5 (s, Si(CH$_3$)$_3$), 24.2 (d, ${}^{1}J_{(P,C)}$ = 67.0 Hz, PCH), 30.8 (d, ${}^{3}J_{(P,C)}$ = 5.1 Hz, PNC(*C*H$_3$)$_3$), 36.3 (d, ${}^{2}J_{(P,C)}$ = 4.6 Hz, P(NMe$_2$)$_3$), 49.9 (d, ${}^{2}J_{(P,C)}$ = 3.9 Hz, PN*C*(CH$_3$)$_3$), 56.5 (d, ${}^{2}J_{(P,C)}$ = 28.9 Hz, POCH$_3$), 206.5 (d, ${}^{1}J_{(W,C)}$ = 127.6 Hz, ${}^{2}J_{(P,C)}$ = 4.9 Hz, *cis*-CO), 210.4 (d, ${}^{2}J_{(P,C)}$ = 14.2 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 210.7 (s$_{sat}$, ${}^{1}J_{(W,P)}$ = 69.8 Hz), 13.5 (d, ${}^{2}J_{(P,P)}$ = 49.6 Hz, 3P, P^{A}), –22.9 (quart, ${}^{2}J_{(P,P)}$ = 49.6 Hz, 1P, P^{B}); ^{29}Si{^{1}H} NMR (59.6 MHz, THF-d8): δ = –10.5 (d, ${}^{2}J_{(P,Si)}$ = 29.5 Hz, PCH(SiMe$_3$)$_2$), –2.6 (s, PCH(SiMe$_3$)$_2$).

9.5 Synthesis and Reactivity of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl}-oxanido-phosphane]pentacarbonyl tungsten(0) 58

9.5.1 Synthesis of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl} oxanido-phosphane]pentacarbonyltungsten(0) 58

A solution of 115 mg (0.22 mmol) of **45f** in 2 mL of Et$_2$O was added to a solution of LDA, freshly prepared from 0.14 mL (1.6 M in *n*-hexane, 0.22 mmol) of *n*-butyllithium and 30 µL (0.22 mml) of diisopropylamine in 2 mL Et$_2$O at –78 °C and the reaction solution was stirred for 2 hours. The solvent was evaporated in *vacuo* (ca. 10^{-2} mbar) and the residue was washed with *n*-pentane (0.5 mL × 3) at –30 °C. The yellow powder of complex **58** was yielded after drying in *vacuo*. (NMR code: 17m3c013.09)

Yellow solid, yield: 51 mg (0.08 mmol, 36%); m.p. 84–86 °C; ^{1}H NMR (300.13 MHz, THF-d8): δ = 0.15 (s, 9H, Si(CH$_3$)$_3$), 0.25 (s, 9H, Si(CH$_3$)$_3$), 0.82 (br, 1H, PCH), 1.29 (d, 3H, $^{2}J_{(\mathrm{H,H})}$ = 7.0 Hz, ^{i}Pr$_2$NCOC*H*$_3$), 3.66 (s, 16H, 12-crown-4), 8.59 (d, 1H, $^{1}J_{(\mathrm{P,H})}$ = 301.8 Hz, P*H*); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = 1.3 (d, $^{3}J_{(\mathrm{P,C})}$ = 1.9 Hz, Si(CH$_3$)$_3$), 3.1 (d, $^{3}J_{(\mathrm{P,C})}$ = 2.6 Hz, Si(CH$_3$)$_3$), 29.7 (d, $^{1}J_{(\mathrm{P,C})}$ = 3.2 Hz, PCH), 70.1 (s, 12-crown-4), 202.1 (d, $^{2}J_{(\mathrm{P,C})}$ = 9.1 Hz, *cis*-CO), 205.1 (d, $^{2}J_{(\mathrm{P,C})}$ = 13.6 Hz, *trans*-*C*O); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 45.8 (d$_{\mathrm{sat}}$, $^{1}J_{(\mathrm{W,P})}$ = 242.9 Hz, $^{1}J_{(\mathrm{P,H})}$ = 301.4 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, THF-d8): δ = –1.4 (d$_{\mathrm{sat}}$, $^{2}J_{(\mathrm{P,Si})}$ = 8.7 Hz, *Si*(CH$_3$)$_3$), –0.9 (d$_{\mathrm{sat}}$, $^{2}J_{(\mathrm{P,Si})}$ = 5.5 Hz, *Si*(CH$_3$)$_3$); IR (nujol, cm^{-1}): $\tilde{\upsilon}$ = 2185 (w, ν(PH)), 2054 (s, ν(CO)), 1959 (s, ν(CO)), 1909 (s, ν(CO)); elemental analysis (%) calcd. for $C_{20}H_{36}LiO_{10}PSi_2W$: C 33.62, H 5.08; found: C 33.14, H 4.77.

9.5.2 Reactivity of [lithium(12-crown-4)][{bis(trimethylsilyl)methyl} oxanido-phosphane]pentacarbonyltungsten(0) 58

9.5.2.1 Reaction with trimethylchlorosilane to yield complex 71

A solution of 115 mg (0.22 mmol) of **45f** in 2 mL of Et$_2$O was added to a solution of LDA, freshly prepared from 0.14 mL (1.6 M in *n*-hexane, 0.22 mmol) of *n*-butyllithium and 30 µL (0.22 mml) of diisopropylamine in 2 mL Et$_2$O at **–**7**8** °C and the reaction solution was stirred for 30 minutes, then 26 µL(0.2 mmol) trimethylchlorosilane was added by syringe. After another 1 hour stirring, the solvent was evaporated in *vacuo* (~ 10^{-2} mbar) and the residue was washed with *n*-pentane at –30 °C. The ^{31}P NMR displayed a signal at 76.9 ppm, which proved to be trimethylsiloxyl phosphane complex **71**[8]. (NMR code: 14m3a029.09)

Yellow solid, Yield: 87 mg (0.14 mmol, 71.5%); $^{31}P\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 76.9$ ppm (d_{sat}, $^{1}J_{(W,P)} = 274.7$ Hz, $^{1}J_{(P,H)} = 325.5$ Hz)

9.5.2.2 Thermal reaction of complex 72

To a solution of 115 mg (0.22 mmol) of phosphane complex **45f** in 2 mL of THF was added a solution of MeLi (1.6 M in diethyl ether, 0.15 mL) at −78 °C. After 30 minutes stirring, remove the cooling bath and heat the solution at 60 °C for overnight (~13 hours). The solution color changed to black red from pale yellow. The ^{31}P NMR spectra showed signals as AB spin system at both highfield and lowfield. (NMR code: 01m3a028.11)

^{31}P NMR (75.5 MHz, in reaction solution): A: $\delta = 399.9$ (d, $^{2}J_{(P,P)} = 78.8$ Hz, $J_{(P,H)} = 20.0$ Hz), B: $\delta = -182.2$ (d, $^{2}J_{(P,P)} = 78.8$ Hz, $^{1}J_{(W,P)} = 164.0$ Hz, $^{1}J_{(P,H)} = 258.1$ Hz)

9.6 Reactivity of [lithium(12-crown-4)][{bis(trimethylsilyl) methyl}alkoxyphosphinidenoid]pentacarbonyltungsten (0), -molybdenum (0) and chromium (0)

9.6.1 Synthesis of [{bis(trimethylsilyl)methyl}phenoxymethylphosphane] pentacarbonyltungsten(0) 73a

To a solution of freshly prepared phosphinidenoid complex **51a**, 12 µL (0.2 mmol) of methyl iodide was added via a syringe. The reaction mixture was stirred for another 2 hours, and then subjected to filtration. Removal of solvent in *vacuo* (~10^{-2} mbar) led to the raw product of complex **73a**. The raw product **73a** was then purified further by column chromatography (SiO_2, –20 °C, 2 x 12 cm, using petroleum ether). (NMR code: 46m3b042.08)

Yellow solid, crystallized from Et_2O solution at –30 °C, yield: 470 mg (0.86 mmol, 43%); m.p. 127–130 °C; ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.27 (s, 9H, $Si(CH_3)_3$), 0.29 (s, 9H, $Si(CH_3)_3$), 1.79 (d, 1H, $^2J_{(P,H)}$ = 10.3 Hz, PCH), 2.20 (d, 3H, $^2J_{(P,H)}$ = 4.7 Hz, PCH_3), 7.02 (d, 2H, $^3J_{(H,H)}$ = 8.7 Hz, *m*-Ph), 7.16 (t, 1H, $^3J_{(H,H)}$ = 7.3 Hz, *p*-Ph), 7.27 (t, 2H, $^3J_{(H,H)}$ = 8.1 Hz, *o*-Ph); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 1.9 (d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$), 2.5 (d, $^2J_{(P,C)}$ = 2.0 Hz, $Si(CH_3)_3$), 26.4 (d, $^1J_{(P,C)}$ = 18.1 Hz, PCH_3), 30.0 (d, $^1J_{(P,C)}$ = 11.1 Hz, PCH), 121.7 (d, $^4J_{(P,C)}$ = 3.6 Hz, *m*-Ph), 124.0 (d, $^5J_{(P,C)}$ = 1.9 Hz, *p*-Ph), 129.0 (d, $^3J_{(P,C)}$ = 1.4 Hz, *o*-Ph), 151.9 (d, $^2J_{(P,C)}$ = 6.6 Hz, POC), 196.2 (d, $^2J_{(P,C)}$ = 7.5 Hz, *cis*-CO), 198.1 (d, $^2J_{(P,C)}$ = 25.7 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 142.4 (s_{sat}, $^1J_{(W,P)}$ = 279.2 Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ = –3.0 (s, $PCH(SiMe_3)_2$), 0.1 (d, $^2J_{(P,Si)}$ = 6.9 Hz, $PCH(SiMe_3)_2$); MS(EI, ^{184}W): m/z (%): 622.0 ($M^{+\cdot}$, 26), 594.0 ($[M\text{-}CO]^{+\cdot}$, 15), 538.1 ($[M\text{-}3CO]^{+\cdot}$, 100), 482.0 ($[M\text{-}5CO]^{+\cdot}$, 43), 73.0 ($SiMe^{+\cdot}$, 98); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 3440 (br, ν(aromatic-H)), 2961 (w, ν(CH/CH_3)), 2068 (s, ν(CO)), 1984 (m, ν(CO)), 1920 (vs, ν(CO)); elemental analysis calcd (%) for $C_{19}H_{27}O_6PSi_2W$: C 36.67, H 4.37; found: C 36.58, H 4.64.

9.6.2 Synthesis of [{bis(trimethylsilyl)methyl}methoxyl-methylphosphane] pentacarbonyltungsten(0) 73b

To a solution of freshly generated phosphinidenoid complex **51b**, 12 μL (0.2 mmol) of methyl iodide was added via a syringe. The reaction mixture was stirred for another 2 h, then subjected to the filtration. Then solvent was removed in *vacuo* (ca. 0.01 mbar) and the raw product **73b** was further purified by column chromotagraphy (SiO_2, −20 °C, 1 x 8 cm, using only petroleum ether). (NMR code: 15m3b051.09)

Orange solid, yield: 34 mg (0.06 mmol, 30%); m.p. 125°C; ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.24 (s, 9H, $Si(CH_3)_3$), 0.28 (s, 9H, $Si(CH_3)_3$), 1.61 (d, 1H, $^2J_{(P,H)}$ = 10.8 Hz, PC*H*), 1.94 (d, 3H, $^2J_{(P,H)}$ = 4.9 Hz, PCH_3), 3.46 (d, 3H, $^3J_{(P,H)}$ = 13.0 Hz, $POCH_3$), $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 2.8 (d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$), 3.4 (d, $^3J_{(P,C)}$ = 1.9 Hz, $Si(CH_3)_3$), 24.2 (d, $^1J_{(P,C)}$ = 18.7 Hz, PCH_3), 29.8 (d, $^1J_{(P,C)}$ = 11.6 Hz, PCH), 52.9 (d, $^2J_{(P,C)}$ = 3.2 Hz, $POCH_3$), 197.7 (d, $^2J_{(P,C)}$ = 7.1 Hz, *cis*-CO), 199.6 (d, $^2J_{(P,C)}$ = 23.9 Hz, *trans*-CO), $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 130.4 (s_{sat}, $^1J_{(W,P)}$ = 269.6 Hz); MS (EI, 70eV, ^{184}W): m/z(%): 560.1 ($M^{+\cdot}$, 22), 532.1 ($[M-CO]^{+\cdot}$, 20), 504.1 ($[M-2CO]^{+\cdot}$, 30), 476.0 ($[M-3CO]^{+\cdot}$, 28), 420.1 ($[M-5CO]^{+\cdot}$, 50), 374.0 ($[M-5CO-(CH_3)_2O]^{+\cdot}$, 32), 223.1 ($[M-W(CO)_5-CH_3]^{+\cdot}$, 50), 73.0 ($SiMe_3^{+\cdot}$, 100); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2963 (m, ν(CH/CH_3)), 2069 (m, ν(CO)), 1933 (s, ν(CO)); elemental analysis calcd (%) for $C_{14}H_{25}O_6PSi_2W$: C 30.01, H 4.50; found: C 30.42, H 4.65.

9.6.3 Synthesis of [{bis(trimethylsilyl)methyl}-2-methoxyethan-1-oxy-methyl-phosphane]pentacarbonyltungsten(0) 73c

To a solution of freshly generated phosphinidenoid complex **51c**, 12 μL of methyl iodide was added via a syringe. The reaction mixture was stirred for another 2 h, and then the liquid was filtered from the solid and the solvent was removed in *vacuo* (ca. 0.01 mbar). The raw product of **73c** was further purified by column chromotagraphy (SiO_2, −20 °C, using petroleum ether).

After three times of column chromotagraphy, the final viscous product **73c** was obtained. (NMR code: 39m3b017.10)

Orange viscous, yield: 43 mg (0.07 mmol, 35%); ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.26 (s, 9H, Si(CH$_3$)$_3$), 0.28 (s, 9H, Si(CH$_3$)$_3$), 1.61 (d, 1H, $^2J_{(P,H)}$ = 10.2 Hz, PC*H*), 1.97 (d, 3H, $^2J_{(P,H)}$ = 4.9 Hz, PCH$_3$), 3.32 (s, 3H, POC$_2$H$_4$OC*H*$_3$), 3.56 (m, 2H, POCH$_2$C*H*$_2$OCH$_3$), 3.79 (m, 2H, POC*H*$_2$CH$_2$OCH$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ = 1.8 (d, $^3J_{(P,C)}$ = 3.1 Hz, Si(CH$_3$)$_3$), 2.3 (d, $^3J_{(P,C)}$ = 2.1 Hz, Si(CH$_3$)$_3$), 23.8 (d, $^1J_{(P,C)}$ = 18.9 Hz, PCH), 28.9 (d, $^1J_{(P,C)}$ = 12.4 Hz, PCH$_3$), 57.6 (s, POC$_2$H$_4$O*C*H$_3$), 64.8 (d, $^3J_{(P,C)}$ = 3.2 Hz, POCH$_2$*C*H$_2$OCH$_3$), 70.7 (d, $^2J_{(P,C)}$ = 8.1 Hz, PO*C*H$_2$CH$_2$OCH$_3$), 197.2 (d, $^2J_{(P,C)}$ = 8.0 Hz, $^1J_{(W,C)}$ = 125.5 Hz, *cis*-CO), 199.1 (d, $^2J_{(P,C)}$ = 23.2 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 130.2 (s$_{sat}$, $^1J_{(W,P)}$ = 269.6 Hz); MS (EI, 70 eV, ^{184}W): m/z (%): 604.0 (M$^{+\cdot}$, 16), 576.0 ([M-CO]$^{+\cdot}$, 16), 548.0 ([M-2CO]$^{+\cdot}$, 40), 520.0 ([M-3CO]$^{+\cdot}$, 65), 464.1 ([M-5CO)$^{+\cdot}$, 25), 73.1 (SiMe$_3$$^{+\cdot}$, 100); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2959 (w, ν(CH/CH$_3$)), 2069 (s, ν(CO)), 1921 (vs, ν(CO)); elemental analysis calcd (%) for C$_{16}$H$_{29}$O$_7$PSi$_2$W: C 31.80, H 4.84; found: C 32.51, H 5.05.

9.6.4 Synthesis of [{bis(trimethylsilyl)methyl}-2,6-dimethylphenoxy methylphosphane]pentacarbonyltungsten(0) 73d

To a solution of freshly prepared phosphinidenoid complex **51d**, 12 μL of methyl iodide was added via a syringe. Then the reaction mixture was stirred for another 1 hour. After filtration and removal of solvent in *vacuo* (ca. 0.01 mbar), the mixture of raw product **73d** and complex **45d** was obtained, which was purified further by twice column chromatography (SiO$_2$, −20 °C, using petroleum ether). The mixture of **73d** and **45d** was still not separated. (NMR code: 39m3c055.09)

Yellow viscous, ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.27 (d, 18H, $^{2}J_{(H,H)}$ = 8.4 Hz, SiMe$_3$), 1.28 (d, $^{2}J_{(P,H)}$ = 10.4 Hz, PCH), 2.21 (d, 3H, $^{2}J_{(P,H)}$ = 6.0 Hz, PCH$_3$), 2.26 (s, 6H, 2,6-*Me*$_2$C$_6$H$_3$), 6.80 (d, 1H, $^{3}J_{(H,H)}$ = 7.5 Hz, *p*-Ph), 6.93 (d, 2H, $^{3}J_{(H,H)}$ = 7.5 Hz, *m*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ = –0.1 (s, Si(CH$_3$)$_3$), 1.9 (d, $^{3}J_{(P,C)}$ = 2.5 Hz, Si(CH$_3$)$_3$), 17.1 (s, PO-2,6-(*C*H$_3$)$_2$C$_6$H$_3$), 28.6 (d, $^{1}J_{(P,C)}$ = 16.8 Hz, PCH$_3$), 30.2 (d, $^{1}J_{(P,C)}$ = 25.4 Hz, PCH), 120.3 (s, *p*-aryl), 127.4 (s, *m*-aryl), 128.5 (d, $^{3}J_{(P,C)}$ = 2.3 Hz, *o*-aryl), 151.5 (d, $^{2}J_{(P,C)}$ = 9.3 Hz, POC), 195.3 (d, $^{2}J_{(P,C)}$ = 6.8 Hz, *cis*-CO), 198.1 (d, $^{2}J_{(P,C)}$ = 25.0 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 134.0 (s$_{sat}$, $^{1}J_{(W,P)}$ = 273.4 Hz).

9.6.5 Synthesis of [{bis(trimethylsilyl)methyl}phenoxymethylphosphane] pentacarbonylchromium(0) 74

To a solution of freshly prepared Li/OPh phosphiniednoid chromium complex **54**, 12 µL of methyl iodide was added via a syringe. The reaction mixture was stirred for another 2 hours and then subjected to filtration. Removal of solvent in *vacuo* (ca. 0.01 mbar) led to the raw product **74**, which was purified further by column chromatography (SiO$_2$, –20 °C, using petroleum ether). Evaporation of the solvent in the first fraction gave the final product **74**. (NMR code: 20m3a055.09)

Yellow solid, ^{31}P NMR (75.5 MHz, in reaction solution): δ = 139.1 (s, no P,Cr and P, H coupling); IR(KBr, cm^{-1}): $\tilde{\upsilon}$ = 2963 (w, ν(CH/CH$_3$)), 2060 (s, ν(CO)), 1984 (vs, ν(CO)), 1925 (vs, ν(CO)); MS(EI, 70 eV, ^{52}Cr): 490.0 (M$^{+\cdot}$, 10), 462.1 ([M-CO]$^{+\cdot}$, 8), 406.0 ([M-3CO]$^{+\cdot}$, 22), 378.0 ([M-4CO]$^{+\cdot}$, 20), 350.1 ([M-5CO)$^{+\cdot}$, 100), 73.0 (SiMe$_3^{+\cdot}$, 21).

9.7.1 Synthesis of [{bis(trimethylsilyl)methyl}phenoxychlorophosphane] pentacarbonyltungsten(0) 75a

A solution of 20 mg (0.11 mmol) *N,N*-di-*tert*-butyl heterocyclic carbene (NHC) in 0.5 mL of diethyl ether (or a solution of 0.11 mmol freshly prepared lithium diisopropyl amide, from 70 µL of *n*-butyllithium solution and 15 µL of diisopropylamine in 1 mL of diethyl ether) was added dropwise to the solution of 61 mg (0.1 mmol) phosphane complex **45a** in 0.5 mL of diethyl ether at –78 °C. The reaction solution was stirred for 40 minutes and then evaporated solvent in *vacuo* (ca. 0.01 mbar) and the residue was dissolved in $CDCl_3$, the solution color changed immediately to black red from yellow. Removal of solvent in *vacuo* and purification by washing with *n*-pentane at low temperature (–60 °C) gave the complex **75a** as orange powder. (NMR code: 46m3a023.10)

Orange solid, crystallized from Et_2O at ambient temperature; yield: 58 mg (0.09 mmol, 90%); m.p. 100 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.30 (s, 9H, $Si(CH_3)_3$), 0.34 (s, 9H, $Si(CH_3)_3$), 1.72 (s, 18H, $NC(CH_3)_3$), 1.98 (d, 1H, $^2J_{(P,H)}$ = 7.0 Hz, PCH), 7.27 (m, 5H, Ph), 7.68 (s, 2H, NC*H*); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 1.7 (d, $^3J_{(P,C)}$ = 3.6 Hz, $Si(CH_3)_3$), 2.0 (d, $^3J_{(P,C)}$ = 2.4 Hz, $Si(CH_3)_3$), 29.3 (s, NC(*C*H$_3$)$_3$), 59.7 (s, N*C*(CH$_3$)$_3$), 118.9 (s, N*CC*N), 121.1 (d, $^3J_{(P,C)}$ = 5.3 Hz, *o*-Ph), 125.1 (d, $^4J_{(P,C)}$ = 2.2 Hz, *m*-Ph), 129.1 (d, $^5J_{(P,C)}$ = 1.0 Hz, *p*-Ph), 151.5 (d, $^2J_{(P,C)}$ = 7.2 Hz, POC), 195.0 (d, $^2J_{(P,C)}$ = 7.9 Hz, $^1J_{(W,C)}$ = 126.9 Hz, *cis*-CO), 197.2 (d, $^2J_{(P,C)}$ = 39.8, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): $\delta = 186.7$ (s$_{sat}$, $^{1}J_{(W,P)} = 335.7$ Hz, $^{2}J_{(P,H)} = 6.4$ Hz); IR (KBr, cm^{-1}): ῦ = 2970 (w, ν(CH/CH$_3$)), 2078 (m, ν(CO)), 1999 (m, ν(CO)), 1942 (vs, ν(CO)), 1915 (s, ν(CO)); MS (EI, 70 eV, ^{184}W): m/z (%): 641.9 ($M^{+\cdot}$, 30), 544.8 ($[M\text{-}OPh]^{+\cdot}$, 50), 501.9 ($[M\text{-}5CO]^{+\cdot}$, 17), 283.1 ($[M\text{-}5CO\text{-}Cl]^{+\cdot}$, 100), 73.0 ($SiMe_3^{+\cdot}$, 60); elemental analysis (%) calcd. for $C_{18}H_{24}ClO_6PSi_2W$: C 33.63, H 3.76; found: C 33.97, H 3.79.

9.7.2 Synthesis of [{bis(trimethylsilyl)methyl}methoxychlorophosphane] pentacarbonyltungsten(0) 75b

A solution of 20 mg (0.11 mmol) *N,N*-di-tetra-butyl heterocyclic carbene (NHC) in 0.5 mL of diethyl ether (or a solution of 0.11 mmol freshly prepared lithium diisopropyl amide, from 70 µL of *n*-butyllithium solution and 15 µL of diisopropylamine in 1 mL of diethyl ether) was added dropwise to the solution of 55 mg (0.1 mmol) phosphane complex **45b** in 0.5 mL of diethyl ether at –78 °C. The reaction solution was stirred for 0.5 hour, then evaporated solvent in *vacuo* (ca. 0.01 mbar) and the residue was dissolved in $CDCl_3$. Complex **75b** was obtained after removal of solvent in *vacuo*. (NMR code: 18m3b026.11)

^{31}P{^{1}H} NMR (121.5 MHz, in reaction solution): $\delta = 189.8$ (s$_{sat}$, $^{1}J_{(W,P)} = 328.2$ Hz, $^{3}J_{(P,H)} = 15.4$ Hz)

9.8.1 Synthesis of [{bis(trimethylsilyl)methyl}phenoxylbenzoylphosphane] pentacarbonyltungsten(0) 79a

A cooled solution (–50 °C) of the appropriate phosphane complex **45a** (487 mg, 0.8 mmol) in 4 mL of THF was added dropwise to a stirred solution of freshly prepared LDA (0.84 mmol) in 9 mL of THF at –78 ºC. After 30 min at –78 ºC the acyl chloride PhC(O)Cl (0.98 mL, 0.84 mmol) was added and the reaction mixtures were allowed to warm up to 10 ºC (~2 h) in a cooling bath. Volatiles were evaporated in *vacuo* (~10^{-2} mbar), *n*-pentane (15 mL) was added and the precipitate was filtered off. The solvent was then removed and the residue subjected to column chromatography (SiO_2, –20 °C, petrol ether, petrol ether/diethyl ether = 10/0.5). Eluation of the second band yielded mixture of complex **79a** and *P*-phenoxy-phosphane complex **45a**. (NMR code: 40m3b010.09)

$^{31}P\{^1H\}$ NMR (121.5 MHz, in reaction solution): **79a**: δ = 159.0 (s_{sat}, $^1J_{(W,P)}$ = 289.9 Hz); **45a**: δ = 106.8 (s_{sat}, $^1J_{(W,P)}$ = 275.9 Hz, $^1J_{(P,H)}$ = 325.5 Hz)

9.8.2 Synthesis of [{bis(trimethylsilyl)methyl}methoxylbenzoylphosphane] pentacarbonyltungsten(0) 79b

A cooled solution (–50 °C) of the appropriate phosphane complex **45b** (437 mg, 0.8 mmol) in 4 mL of THF was added dropwise to a stirred solution of freshly prepared LDA (0.84 mmol) in 9 mL of THF at –78 ºC. After 30 min at –78 ºC the acyl chloride PhC(O)Cl (0.98 mL, 0.84 mmol) was added and the reaction mixtures were allowed to warm up to 10 ºC (~2 h) in a cooling bath. Volatiles were evaporated in *vacuo* (~10^{-2} mbar), *n*-pentane (15 mL) was added and the precipitate was filtered off. The solvent was then removed and the residue subjected to column chromatography (SiO_2, –20 °C, silical gel, petrol ether/diethyl ether = 10/0.5). Eluation of the second band yielded complex **79b**. (NMR code: 07m3b040.10)

Yellow viscous; yield: 338 mg (0.52 mmol, 65%); ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.21 (s, 9H, Si(CH$_3$)$_3$), 0.32 (s, 9H, Si(CH$_3$)$_3$), 2.06 (d, 1H, $^{2}J_{(P,H)}$ = 11.7 Hz, PCH), 3.60 (d, 3H, $^{3}J_{(P,H)}$ = 13.0 Hz, POCH$_3$), 7.51 (t, 2H, $^{3}J_{(H,H)}$ = 7.7 Hz, *m*-Ph), 7.62 (t, 1H, $^{3}J_{(H,H)}$ = 7.7 Hz, *p*-Ph), 8.05 (d, 2H, $^{3}J_{(H,H)}$ = 7.4 Hz, *o*-Ph). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ = 2.9 (d, $^{3}J_{(P,C)}$ = 3.1 Hz, Si(CH$_3$)$_3$), 3.4 (d, $^{3}J_{(P,C)}$ = 2.8 Hz, Si(CH$_3$)$_3$), 27.3 (d, $^{1}J_{(P,C)}$ = 3.6 Hz, PCH), 56.3 (d, $^{2}J_{(P,C)}$ = 3.3 Hz, POCH$_3$), 128.9 (s, Ph), 129.0 (s, Ph), 133.6 (s, Ph), 135.3 (d, $^{2}J_{(P,C)}$ = 36.5 Hz, Ph), 196.9 (d, $^{2}J_{(P,C)}$ = 7.1 Hz, $^{1}J_{(W,C)}$ = 118.2 Hz, *cis*-CO), 198.0 (d, $^{2}J_{(P,C)}$ = 26.8 Hz, *trans*-CO), 208.8 (d, $^{1}J_{(P,C)}$ = 12.1 Hz, C(O)P). ^{31}P {^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 154.1 (s$_{sat}$, $^{1}J_{(W,P)}$ = 273.4 Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2072 (s, ν(CO)), 1929 (m, ν(CO)), 1670 (s, ν(PC(O)). UV/vis (*n*-pentane): λ (abs) = 231.5 nm (1.703). MS (EI, 70 eV, ^{184}W): m/z (%): 650.1(M$^{+\cdot}$, 6), 622.2 ([M-CO]$^{+\cdot}$, 28), 594.2 ([M-2CO]$^{+\cdot}$, 20), 566.1 ([M-3CO]$^{+\cdot}$, 40), 105.1 ([M-W(CO)$_5$-PhC(O)-OMe-CHSiMe$_3$]$^{+\cdot}$, 100), 73.1 (SiMe$_3$$^{+\cdot}$, 77); elemental analysis (%) calcd. for $C_{20}H_{27}O_7PSi_2W$: C 36.93, H 4.18; found: C 37.93, H 5.05.

9.8.3 Synthesis of [{bis(trimethylsilyl)methyl}-2-methoxyethan-1-oxy-benzoylphosphane]pentacarbonyltungsten(0) 79c

A cooled solution (–50 °C) of the appropriate phosphane complex **45c** (472 mg, 0.8 mmol) in 4 mL of THF was added dropwise to a stirred solution of freshly prepared LDA (0.84 mmol) in 9 mL of THF at –78 ºC. After 30 min at –78 ºC the acyl chloride PhC(O)Cl (0.98 mL, 0.84 mmol) was added and the reaction mixtures were allowed to warm up to 10 ºC (~2 h) in a cooling bath. Volatiles were evaporated in *vacuo* (~10^{-2} mbar), *n*-pentane (15 mL) was added and the precipitate was filtered off. The solvent was then removed and the residue subjected to column chromatography (–20 °C, petrol ether, petrol ether/diethyl ether = 10/0.5). Eluation of the second band afforded target complex **79c**. (NMR code: 04m3c040.10)

Yellow viscous; yield: 344 mg (0.50 mmol, 62%); ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 0.17$ (s, 9H, $Si(CH_3)_3$), 0.30 (s, 9H, $Si(CH_3)_3$), 2.16 (d, 1H, $^2J_{(P,H)} = 12.7$ Hz, PCH), 3.26 (s, 3H, OCH_3), 3.59 (m. 2H, CH_2OCH_3), 3.91 (m, 2H, OCH_2CH_2), 7.52 (t, 2H, $^3J_{(H,H)} = 7.9$ Hz, *m*-Ph), 7.61 (t, 1H, $^3J_{(H,H)} = 7.7$ Hz, *p*-Ph), 8.17 (d, 2H, $^3J_{(H,H)} = 8.1$ Hz, *o*-Ph); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 2.8$ (d, $^3J_{(P,C)} = 3.1$ Hz, $Si(CH_3)_3$), 3.4 (d, $^3J_{(P,C)} = 2.8$ Hz, $Si(CH_3)_3$), 27.5 (d, $^1J_{(P,C)} = 5.2$ Hz, PCH), 58.3 (s, $POC_2H_4OCH_3$), 68.1 (d, $^3J_{(P,C)} = 3.2$ Hz, OCH_2CH_2), 71.3 (d, $^2J_{(P,C)} = 8.4$ Hz, OCH_2CH_2), 128.8 (s, Ph), 129.4 (s, Ph), 133.6 (s, Ph), 135.8 (d, $^2J_{(P,C)} = 35.5$ Hz, *i*-Ph), 197.1 (d, $^2J_{(P,C)} = 7.1$ Hz, *cis*-CO), 198.0 (d, $^2J_{(P,C)} = 27.2$ Hz, *trans*-CO), 208.4 (d, $^1J_{(P,C)} = 7.1$ Hz, C(O)P). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 153.5$ (s_{sat}, $^1J_{(W,P)} = 278.5$ Hz). IR (KBr, cm^{-1}): $\tilde{\upsilon} = 2072$ (s, ν(CO)), 1931 (m, ν(CO)), 1647 (s, ν(PC(O)). UV/vis (*n*-pentane): λ (abs) = 232.0 nm (1.314). MS (EI, 70 eV, ^{184}W): m/z (%): 694.1 ($M^{+\cdot}$, 12), 679.0 ($[M-CH_3]^{+\cdot}$, 21), 666.1 ($[M-CO]^{+\cdot}$, 11), 610.1 ($[M-3CO]^{+\cdot}$, 12), 582.1 ($[M-4CO]^{+\cdot}$, 22), 73.1 ($SiMe_3^{+\cdot}$, 100); elemental analysis (%) calcd. for $C_{22}H_{31}O_8PSi_2W$: C 38.05, H 4.50; found: C 38.17, H 5.28.

9.9.1 Synthesis of [{bis(trimethylsilyl)methyl}{1(2)-phenyl-2(1)-methyl vinyl}phenoxyphosphane]pentacarbonyltungsten(0) 81

To a solution of 608 mg (1.0 mmol) phosphane complex **45a** in 5 mL of THF was added dropwise a solution of 0.65 mL MeLi (1.6 M in hexane) at –78 °C. The solution color changed to red immediately and stirred for 30 minutes. Then 0.1 mL of phenylacetylene was added and refluxed for 2 hours, and solution color changed to black red. When it cooled down to room temperature, MeOTf was used to quench reaction. The raw product of complex **81** was purified by column chromatography (SiO_2, –20 °C, 2 × 11 cm, petroleum ether and Et_2O = 10:1). Evaporation of the second fraction gave complex **81**. (NMR code: 05m3b012.10 and 05m3c016.10)

Brownish yellow solid, yield: 449 mg (62%, 0.62 mmol); ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 0.36 (s, 9H, $Si(CH_3)_3$), 0.43 (s, 9H, $Si(CH_3)_3$), 1.23 (s, 1H, PCH), 1.31 (br, 3H, Me), 7.22 (m, 5H, Ph), 7.41 (t, 5H, $^3J_{(H,H)}$ = 3.9 Hz, Ph), 7.64 (d, 1H, $^2J_{(P,H)}$ = 4.6 Hz, PC*H*=C); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 2.8 (d, $^3J_{(P,C)}$ = 3.9 Hz, $Si(CH_3)_3$), 3.6 (d, $^3J_{(P,C)}$ = 1.9 Hz, $Si(CH_3)_3$), 22.7 (s, C=C*C*H_3), 25.8 (d, $^1J_{(P,C)}$ = 11.0 Hz, PCH), 123.1 (d, $^4J_{(P,C)}$ = 3.9 Hz, Ph), 125.3 (d, $^5J_{(P,C)}$ = 1.9 Hz, Ph), 127.3 (d, $^3J_{(P,C)}$ = 18.8 Hz, Ph), 129.3 (s, Ph), 130.2 (d, $^5J_{(P,C)}$ = 1.9 Hz, Ph), 135.9 (d, $^3J_{(P,C)}$ = 16.2 Hz, Ph), 150.9 (d, $^2J_{(P,C)}$ = 18.7 Hz, *i*-Ph), 154.0 (d, $^2J_{(P,C)}$ = 5.8 Hz, *i*-Ph), 175.7 (d, $^1J_{(P,C)}$ = 26.5 Hz, P*C*=C), 205.2 (d, $^2J_{(P,C)}$ = 5.2 Hz, *cis*-CO), 208.8 (d, $^2J_{(P,C)}$ = 30.1 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 154.1 (s_{sat}, $^1J_{(W,P)}$ = 269.6 Hz); $^{29}Si\{^1H\}$ NMR (59.6 MHz, CD_2Cl_2): δ = 0.1 (d, $^2J_{(P,Si)}$ = 10.1 Hz, $PCHSi(CH_3)_3$), 0.3 (d, $^2J_{(P,Si)}$ = 3.4 Hz, $PCHSi(CH_3)_3$); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2960 (s, ν(CH/CH_3)), 2070 (s, ν(CO)), 2019 (vs, ν(CO)), 1932 (vs, ν(CO)), 1592 (w, ν(*trans* C=C)); MS (EI, 70eV, ^{184}W): m/z (%): 724.1 ($M^{+\cdot}$, 10), 696.1 ($[M\text{-}CO]^{+\cdot}$, 19), 640.1 ($[M\text{-}3CO]^{+\cdot}$, 50), 612.1 ($[M\text{-}4CO]^{+\cdot}$, 23), 597.1 ($[M\text{-}4CO\text{-}Me)^{+\cdot}$, 24), 367.1 ($[M\text{-}W(CO)_5\text{-}P]^{+\cdot}$, 39), 73.0 ($SiMe_3^{+\cdot}$, 100).

9.9.2 Synthesis of [{bis(trimethylsilyl)methyl}-(1,1-methoxyphenylmethyl) methoxylphosphane]pentacarbonyltungsten(0) 83,83’

To a solution of 221 mg (0.4 mmol) *P*-methoxyl phosphane complex **45b** and 67 µL (0.42

mmol) of 12-crown-4 in 3 mL of THF cooled to –78 °C, then 0.25 mL (1.6 M in hexane, 0.4 mmol) MeLi was dropwise added. After the reaction mixture was stirred for 30 minutes, 40 µL (0.4 mmol) PhCHO were syringed to the freshly prepared phosphinidenoid complex solution. The reaction solution didn't have obvious color change. After another 30 minites stirring, 44 µL of MeOTf (or 24 µL of MeI) was added to quench. The volatiles were evaporated in *vacuo* (ca. 0.01 mbar), and then the raw product was purified by column chromatography (–20 °C, SiO_2, 2 × 5 cm, petroleum ether). The second fraction gave the aiming products **83,83'** as mixture. This fraction was subjected to another column chromatography, but the mixture of complexes **83,83'**(again) was obtained. (NMR code: 51×3a009.10)

^{31}P NMR (121.5 MHz, THF solution): δ = 161.8 (s_{sat}, $^{1}J_{(W,P)}$ = 275.9 Hz, $^{3}J_{(P,H)}$ = 15.3 Hz); MS(EI, 70eV, ^{184}W): 666.1 ($M^{+\cdot}$, 10), 582.1 ($[M\text{-}3CO]^{+\cdot}$, 39), 526.1 ($[M\text{-}5CO]^{+\cdot}$, 21), 179.0 ($[M\text{-}W(CO)_5\text{-}CH(SiMe_3)_2]^{+\cdot}$, 100), 73.0 ($SiMe_3^{+\cdot}$, 48).

9.9.3 Synthesis of [tetra-*n*-butylammonium][{bis(trimethylsilyl)methyl} oxanido-phosphane]pentacarbonyltungsten(0) 86

To a solution of 122 (0.2 mmol) *P*-phenyl phosphane complex **45a** and 35 µL (0.21 mmol) of 12-crown-4 in 2 mL of THF cooled to –78 °C, then 0.15 mL (1.6 M in hexane) MeLi was dropwise added. After the reaction mixture was stirred for 0.5 hour, 0.2 mL (1M in THF, 0.2 mmol) $^{n}Bu_4NF$ were added dropwise to the freshly prepared phosphinidenoid complex solution. The reaction color changed to very pale yellow. After stirring for another 1 hour, the volatiles were evaporated in *vacuo* (ca. 0.01 mbar), and final product **86** was purified by washing with *n*-pentane at low temperature (–60 °C). (NMR code: 43m3c018.09)

Yellow solid, ^{1}H NMR (300.13 MHz, THF-d8): δ = 0.92 (t, 24H, $^2J_{(H,H)}$ = 7.4 Hz, $CH_3(CH_2)_3N^+$), 1.33 (m, 16H, $^2J_{(H,H)}$ = 7.4 Hz, $CH_3CH_2(CH_2)_2N^+$), 1.57 (m, 16H, $^2J_{(H,H)}$ = 7.4 Hz, $C_2H_5CH_2CH_2N^+$), 1.73 (dd, 3H, $^2J_{(P,H)}$ = 5.3 Hz, PCH_3), 3.31 (m, 16H, $^2J_{(H,H)}$ = 7.2 Hz, $C_3H_5CH_2N^+$), 6.33 (t, 1H, $^3J_{(H,H)}$ = 7.4 Hz, *p*-Ph), 6.67 (d, 2H, $^3J_{(H,H)}$ = 7.4 Hz, *m*-Ph), 6.87 (d, 2H, $^3J_{(H,H)}$ = 7.6 Hz, *o*-Ph), 8.11 (qd, $^1J_{(P,H)}$ = 300.6 Hz, $^2J_{(P,H)}$ = 5.3 Hz, PH); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d8): δ = 14.2 (s, $NC_3H_7CH_3$), 20.8 (s, $NC_2H_5CH_2CH_3$), 24.9 (s, $NCH_2CH_2C_2H_5$), 28.1 (d, $^1J_{(P,C)}$ = 22.6 Hz, PCH_3), 59.4 (s, $NCH_2C_3H_7$), 200.0 (d, $^2J_{(P,C)}$ = 9.7 Hz, *cis*-CO), 204.0 (d, $^2J_{(P,C)}$ = 10.5 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF-d8): δ = 33.2 (d_{sat}, $^1J_{(W,P)}$ = 227.6 Hz, $^1J_{(P,H)}$ = 300.1 Hz).

9.9.4 Synthesis of [{bis(trimethylsilyl)methyl}methoxy-(*p*-diphenyl methylenephenyl)phosphane]pentacarbonyltungsten(0) 95

To a solution of 165 mg (0.3 mmol) *P*-methoxyl phosphane complex **45b** and 51 µL of 12-crown-4 in 1 mL of THF cooled to –78 °C, then 0.2 mL (1.6 M in hexane) MeLi was dropwise added. After the reaction mixture was stirred for 0.5 hour, 110 mg (0.33 mmol) $Ph_3C[BF_4]$ were transfered to the freshly prepared phosphinidenoid complex solution. The reaction color firstly changed to purple, then gradually to black red. The volatiles were evaporated in *vacuo* (~ 0.01 mbar), and final product **95** was purified by column chromotagraphy (–20 °C, SiO_2, 2 × 11 cm, petroleum ether). Removal of solvent in the third fraction yielded complex **95**. (NMR code: 14m3a053.10)

Yellow solid, Yield: 418 mg (53%, 0.16 mmol); m.p. 155 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.09 (s, 9H, $Si(CH_3)_3$), 0.24 (s, 9H, $Si(CH_3)_3$), 2.06 (d, 1H, $^2J_{(P,H)}$ = 11.1 Hz, PCH), 3.18 (d, 3H, $^{3}J_{(P,H)}$ = 13.6 Hz, POCH$_3$), 5.62 (s, 1H, PPh-C*H*Ph$_2$), 7.25 (m, Ph), 7.72 (dd, 2H, $^{3}J_{(P,H)}$ = 10.6 Hz, P-*o*-Ph*H*); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ = 2.5 (d, $^{3}J_{(P,C)}$ = 3.2 Hz, Si(CH$_3$)$_3$), 3.6 (d, $^{3}J_{(P,C)}$ = 1.9 Hz, Si(CH$_3$)$_3$), 33.1 (d, $^{1}J_{(P,C)}$ = 11.0 Hz, PCH), 52.8 (s, *C*HArPh$_2$), 56.7 (d, $^{2}J_{(P,C)}$ = 18.1 Hz, POCH$_3$), 126.2 (s, *p*-Ph), 127.9 (d, $^{3}J_{(P,C)}$ = 6.5 Hz, Ar-*m*), 128.5 (s, *o*-Ph), 129.3 (s, *m*-Ph), 132.8 (d, $^{2}J_{(P,C)}$ = 14.8 Hz, *o*-Ar), 136.1 (d, $^{1}J_{(P,C)}$ = 29.1 Hz, *i*-Ar), 143.1 (s, *i*-Ph), 147.9 (d, $^{4}J_{(P,C)}$ = 1.9 Hz, *p*-Ar), 197.5 (d, $^{2}J_{(P,C)}$ = 7.8 Hz, $^{1}J_{(W,C)}$ = 125.4 Hz, *cis*-CO), 198.8 (d, $^{2}J_{(P,C)}$ = 24.6 Hz, *trans*-CO); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 141.7 (s$_{sat}$, $^{1}J_{(W,P)}$ = 277.8 Hz, $^{2}J_{(P,H)}$ = 12.4 Hz); ^{29}Si{^{1}H} NMR (59.6 MHz, CDCl$_3$): δ = –1.7 (d, $^{2}J_{(P,Si)}$ = 2.0 Hz, PCH(SiMe$_3$)$_2$), –0.6 (d, $^{2}J_{(P,Si)}$ = 3.6 Hz, PCH(SiMe$_3$)$_2$); IR (KBr, cm^{-1}): $\tilde{\upsilon}$ = 2924 (s, ν(CH/CH$_3$)), 2853 (s, ν(CH)), 2067 (m, ν(CO)), 1973 (s, ν(CO)), 1933 (s, ν(CO)); MS (EI, 70eV, ^{184}W): m/z (%): 788.2 (M$^{+\cdot}$, 18), 760.2 ([M-CO]$^{+\cdot}$, 50), 704.2 ([M-3CO]$^{+\cdot}$, 100), 648.2 ([M-5CO]$^{+\cdot}$, 14), 243.1 (Ph$_3$C$^{+\cdot}$, 40), 73.0 (SiMe$_3$$^{+\cdot}$, 57); elemental analysis (%) calcd. for C$_{32}$H$_{37}$O$_6$PSi$_2$W: C 48.74, H 4.73; found: C 47.99, H 5.19.

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Appendix

I Abbreviations used

t-BuLi: *tert*-butyllithium

n-BuLi: *n*-butyllithium

LDA: lithium diisopropylamide

Ph: Phenyl

Me: Methyl

M: Metal

TfOMe: Methyl triflate

h: hour

min: minutes

THF: tetrahydrofuran

Et_2O: diethyl ether

M: mol/L

MS: Mass spectrometry

IR: Infred spectrometry

EI: Electron collision ionization

EA: Elemental analysis

NMR: Nuclear Magnetic Resonance

EPR: Elelctron Paramagnetic Resonance

s: singlet

d: doblet

t: triplet

m: multiplet

s_{sat}: singlet with satellites

r.t.: room temperature

w: weak

m: medium

s: strong

vs: very strong

Å: Angstrom (= 10^{-10} m)

pm: picometer (= 10^{-12} m)

Cp*: 1,2,3,4,5-Pentamethylcyclopenta-2,4-dien-1-yl

g: gramme

Hz: Herz

ppm: part per million

m/z: Mass to charge ratio

$^{n}J_{(X,Y)}$: Coupling constants (X, Y: nuclei for coupling; n: number of bonds)

II Crystal data

1. Crystal data of molecule [{bis(trimethylsily)methyl}phenylaminophosphane] pentacarbonyl tungsten complex (**43e**) (GSTR044).

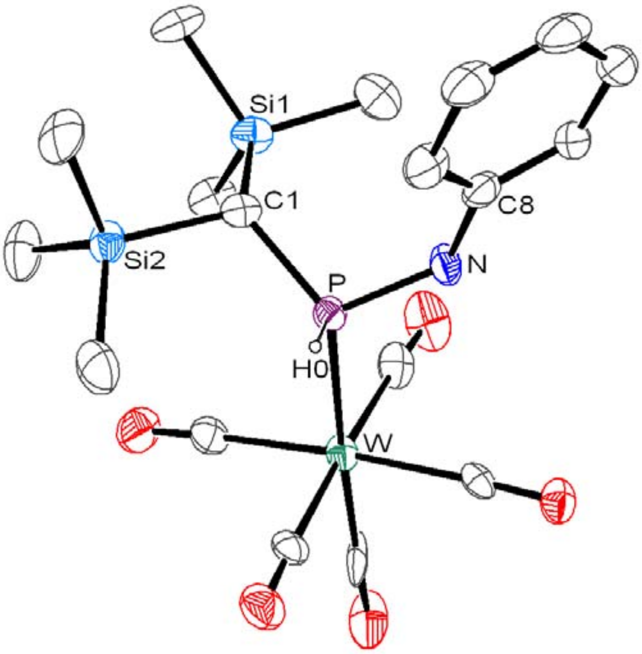

Table 1. Crystal data and structure refinement for **43e**.

Identification code	GSTR044/LDU-HPNH-Ph
Empirical formula	C18 H26 N O5 P Si2 W
Formula weight	607.40
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 11.9647(2) A alpha = 90 deg. b = 9.7457(2) A beta = 90.9460(10) deg. c = 21.1753(4) A gamma = 90 deg.

Volume	2468.80(8) A^3
Z, Calculated density	4, 1.634 Mg/m^3
Absorption coefficient	4.866 mm^-1
F(000)	1192
Crystal size	0.39 x 0.19 x 0.12 mm
Theta range for data collection	1.70 to 27.50 deg.
Limiting indices	-14<=h<=15, -12<=k<=12, -25<=l<=27
Reflections collected / unique	29461 / 5605 [R(int) = 0.1026]
Completeness to theta = 27.50	98.9 %
Absorption correction	Analytical
Max. and min. transmission	0.6045 and 0.2527
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5605 / 0 / 260
Goodness-of-fit on F^2	1.173
Final R indices [I>2sigma(I)]	R1 = 0.0789, wR2 = 0.2134
R indices (all data)	R1 = 0.0871, wR2 = 0.2191
Extinction coefficient	0.0069(6)
Largest diff. peak and hole	6.233 and -3.339 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **43e**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

W	7200(1)	9539(1)	5430(1)	23(1)
P	7999(3)	7301(3)	5821(2)	22(1)
Si(1)	8102(3)	7368(4)	7320(2)	30(1)
Si(2)	6300(3)	5484(4)	6558(2)	27(1)
O(1)	6304(10)	12294(12)	4827(8)	57(4)
O(2)	5858(9)	7867(12)	4368(6)	39(2)
O(3)	9169(8)	9783(10)	4450(5)	31(2)
O(4)	8707(11)	11205(14)	6409(7)	54(3)
O(5)	5075(10)	9547(14)	6323(6)	50(3)
N	9403(9)	7370(12)	5751(6)	29(3)
C(1)	7695(11)	6434(13)	6568(6)	23(2)
C(2)	5674(15)	5336(19)	5754(9)	45(4)
C(3)	5230(14)	6305(19)	7064(10)	48(4)
C(4)	6588(15)	3721(16)	6844(10)	48(4)
C(5)	7190(14)	8863(15)	7493(7)	36(3)
C(6)	8009(16)	6088(17)	7974(7)	41(4)
C(7)	9588(14)	8000(20)	7294(9)	47(4)
C(8)	10172(12)	6250(16)	5803(6)	30(3)
C(9)	9814(14)	4900(17)	5765(7)	34(3)
C(10)	10611(15)	3825(17)	5808(7)	40(4)
C(11)	11708(16)	4111(19)	5884(8)	44(4)
C(12)	12066(14)	5489(18)	5903(8)	41(4)
C(13)	11292(12)	6530(20)	5879(7)	37(4)
C(14)	6621(12)	11287(17)	5063(9)	41(4)
C(15)	6325(11)	8470(14)	4765(6)	25(3)
C(16)	8474(10)	9656(13)	4811(7)	23(3)
C(17)	8150(13)	10601(15)	6072(8)	34(3)
C(18)	5847(12)	9526(15)	6016(7)	32(3)

Table 3. Bond lengths [A] and angles [deg] for **43e**.

W-C(14)	1.992(16)
W-C(15)	2.028(14)
W-C(16)	2.029(14)
W-C(17)	2.040(17)
W-C(18)	2.056(15)
W-P	2.516(3)
P-N	1.691(11)
P-C(1)	1.835(13)
P-H(0)	1.0000
Si(1)-C(5)	1.861(15)
Si(1)-C(6)	1.869(15)

Si(1)-C(7)	1.882(18)
Si(1)-C(1)	1.891(13)
Si(2)-C(4)	1.852(16)
Si(2)-C(2)	1.855(18)
Si(2)-C(3)	1.863(17)
Si(2)-C(1)	1.908(14)
O(1)-C(14)	1.162(19)
O(2)-C(15)	1.162(18)
O(3)-C(16)	1.146(17)
O(4)-C(17)	1.13(2)
O(5)-C(18)	1.139(19)
N-C(8)	1.430(18)
C(1)-H(1)	1.0000
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(13)	1.37(2)
C(8)-C(9)	1.39(2)
C(9)-C(10)	1.42(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.35(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.41(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.38(2)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500

C(14)-W-C(15)	89.8(7)

C(14)-W-C(16)	87.8(5)
C(15)-W-C(16)	88.0(5)
C(14)-W-C(17)	90.7(7)
C(15)-W-C(17)	177.1(6)
C(16)-W-C(17)	89.2(6)
C(14)-W-C(18)	88.2(6)
C(15)-W-C(18)	90.7(6)
C(16)-W-C(18)	175.8(5)
C(17)-W-C(18)	92.1(6)
C(14)-W-P	176.0(5)
C(15)-W-P	88.4(4)
C(16)-W-P	88.6(4)
C(17)-W-P	90.9(4)
C(18)-W-P	95.4(4)
N-P-C(1)	107.8(6)
N-P-W	108.0(4)
C(1)-P-W	127.1(4)
N-P-H(0)	103.8
C(1)-P-H(0)	103.8
W-P-H(0)	103.8
C(5)-Si(1)-C(6)	109.5(7)
C(5)-Si(1)-C(7)	108.0(8)
C(6)-Si(1)-C(7)	107.8(9)
C(5)-Si(1)-C(1)	113.5(7)
C(6)-Si(1)-C(1)	106.5(7)
C(7)-Si(1)-C(1)	111.3(7)
C(4)-Si(2)-C(2)	107.3(9)
C(4)-Si(2)-C(3)	109.7(9)
C(2)-Si(2)-C(3)	106.8(9)
C(4)-Si(2)-C(1)	106.8(7)
C(2)-Si(2)-C(1)	112.8(7)
C(3)-Si(2)-C(1)	113.3(7)
C(8)-N-P	127.0(10)
P-C(1)-Si(1)	116.9(7)
P-C(1)-Si(2)	113.6(7)
Si(1)-C(1)-Si(2)	117.1(7)
P-C(1)-H(1)	101.9
Si(1)-C(1)-H(1)	101.9
Si(2)-C(1)-H(1)	101.9
Si(2)-C(2)-H(2A)	109.5
Si(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5

H(2B)-C(2)-H(2C)	109.5
Si(2)-C(3)-H(3A)	109.5
Si(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
Si(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
Si(2)-C(4)-H(4A)	109.5
Si(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
Si(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
Si(1)-C(5)-H(5A)	109.5
Si(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Si(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
Si(1)-C(6)-H(6A)	109.5
Si(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
Si(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
Si(1)-C(7)-H(7A)	109.5
Si(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(13)-C(8)-C(9)	119.8(14)
C(13)-C(8)-N	118.7(14)
C(9)-C(8)-N	121.5(13)
C(8)-C(9)-C(10)	119.4(15)
C(8)-C(9)-H(9)	120.3
C(10)-C(9)-H(9)	120.3
C(11)-C(10)-C(9)	120.5(17)
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8
C(10)-C(11)-C(12)	119.6(14)
C(10)-C(11)-H(11)	120.2
C(12)-C(11)-H(11)	120.2
C(13)-C(12)-C(11)	119.9(16)

C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(8)-C(13)-C(12)	120.7(17)
C(8)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
O(1)-C(14)-W	177.2(15)
O(2)-C(15)-W	177.3(12)
O(3)-C(16)-W	176.4(11)
O(4)-C(17)-W	177.1(14)
O(5)-C(18)-W	177.3(13)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **43e**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
W	20(1)	16(1)	33(1)	1(1)	3(1)	3(1)
P	20(2)	22(2)	24(2)	0(1)	3(1)	4(1)
Si(1)	35(2)	30(2)	24(2)	-4(2)	-1(2)	4(2)
Si(2)	26(2)	19(2)	36(2)	2(2)	5(2)	-1(1)
O(1)	38(7)	30(6)	102(11)	34(7)	20(7)	14(5)
O(2)	28(5)	39(6)	49(6)	5(5)	-2(5)	6(5)
O(3)	28(5)	26(5)	40(6)	3(4)	7(4)	-1(4)
O(4)	47(7)	49(8)	67(8)	-27(7)	7(6)	-7(6)
O(5)	37(6)	63(9)	51(7)	16(6)	16(5)	18(6)
N	18(5)	25(6)	45(7)	9(5)	5(5)	2(4)
C(1)	28(6)	18(6)	21(6)	-4(5)	2(5)	10(5)
C(2)	36(8)	47(10)	52(10)	-3(8)	-4(7)	-16(7)
C(3)	38(9)	35(9)	71(12)	1(8)	24(8)	0(7)
C(4)	45(9)	21(7)	78(13)	21(8)	10(9)	1(7)
C(5)	52(9)	25(7)	30(7)	-4(6)	4(6)	10(7)
C(6)	63(11)	36(9)	25(7)	10(6)	1(7)	9(8)
C(7)	37(9)	53(11)	50(10)	-4(8)	-9(7)	-3(8)
C(8)	32(7)	34(7)	24(6)	10(6)	9(5)	10(6)
C(9)	38(8)	33(8)	30(7)	2(6)	11(6)	12(6)
C(10)	51(10)	32(8)	38(8)	11(6)	16(7)	20(7)
C(11)	53(10)	42(9)	36(8)	17(7)	13(7)	28(8)
C(12)	30(8)	53(10)	41(9)	18(8)	11(6)	17(7)
C(13)	24(7)	55(10)	34(7)	16(7)	7(6)	8(7)
C(14)	21(7)	33(8)	69(11)	14(8)	28(7)	3(6)
C(15)	19(6)	23(6)	33(7)	4(5)	-4(5)	5(5)
C(16)	17(6)	16(6)	35(7)	-2(5)	-3(5)	3(5)
C(17)	31(7)	27(7)	45(8)	-6(6)	11(6)	5(6)

C(18)	25(7)	31(8)	40(8)	3(6)	1(6)	9(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **43e**.

	x	y	z	U(eq)
H(0)	7759	6623	5491	26
H(1)	8242	5659	6567	27
H(2A)	6214	4909	5472	67
H(2B)	5479	6251	5596	67
H(2C)	4999	4768	5770	67
H(3A)	4509	5846	6998	72
H(3B)	5158	7277	6951	72
H(3C)	5460	6225	7509	72
H(4A)	5904	3171	6810	72
H(4B)	6843	3755	7285	72
H(4C)	7170	3304	6586	72
H(5A)	6496	8541	7683	54
H(5B)	7014	9355	7100	54
H(5C)	7579	9482	7788	54
H(6A)	8324	6485	8363	62
H(6B)	8431	5262	7863	62
H(6C)	7225	5845	8039	62
H(7A)	9625	8818	7028	70
H(7B)	10064	7278	7118	70
H(7C)	9850	8221	7723	70
H(9)	9042	4695	5711	41
H(10)	10371	2897	5782	48
H(11)	12237	3388	5924	52
H(12)	12840	5698	5933	49
H(13)	11533	7458	5916	45

Table 6. Torsion angles [deg] for **43e**.

C(14)-W-P-N	57(7)
C(15)-W-P-N	119.7(6)
C(16)-W-P-N	1.6(6)
C(17)-W-P-N	-57.5(6)
C(18)-W-P-N	-149.7(7)
C(14)-W-P-C(1)	-173(7)
C(15)-W-P-C(1)	-109.9(7)
C(16)-W-P-C(1)	162.1(7)

C(17)-W-P-C(1)	72.9(7)
C(18)-W-P-C(1)	-19.3(7)
C(1)-P-N-C(8)	52.4(14)
W-P-N-C(8)	-167.2(11)
N-P-C(1)-Si(1)	67.4(8)
W-P-C(1)-Si(1)	-63.1(9)
N-P-C(1)-Si(2)	-151.4(7)
W-P-C(1)-Si(2)	78.0(7)
C(5)-Si(1)-C(1)-P	72.5(9)
C(6)-Si(1)-C(1)-P	-166.8(8)
C(7)-Si(1)-C(1)-P	-49.5(10)
C(5)-Si(1)-C(1)-Si(2)	-67.2(9)
C(6)-Si(1)-C(1)-Si(2)	53.4(9)
C(7)-Si(1)-C(1)-Si(2)	170.7(8)
C(4)-Si(2)-C(1)-P	129.2(9)
C(2)-Si(2)-C(1)-P	11.6(10)
C(3)-Si(2)-C(1)-P	-109.9(9)
C(4)-Si(2)-C(1)-Si(1)	-89.8(10)
C(2)-Si(2)-C(1)-Si(1)	152.6(8)
C(3)-Si(2)-C(1)-Si(1)	31.1(11)
P-N-C(8)-C(13)	-165.1(11)
P-N-C(8)-C(9)	16(2)
C(13)-C(8)-C(9)-C(10)	0(2)
N-C(8)-C(9)-C(10)	178.9(13)
C(8)-C(9)-C(10)-C(11)	0(2)
C(9)-C(10)-C(11)-C(12)	-2(2)
C(10)-C(11)-C(12)-C(13)	3(2)
C(9)-C(8)-C(13)-C(12)	2(2)
N-C(8)-C(13)-C(12)	-177.2(14)
C(11)-C(12)-C(13)-C(8)	-3(2)
C(15)-W-C(14)-O(1)	-63(34)
C(16)-W-C(14)-O(1)	25(34)
C(17)-W-C(14)-O(1)	115(34)
C(18)-W-C(14)-O(1)	-153(34)
P-W-C(14)-O(1)	1(40)
C(14)-W-C(15)-O(2)	82(24)
C(16)-W-C(15)-O(2)	-5(24)
C(17)-W-C(15)-O(2)	-18(32)
C(18)-W-C(15)-O(2)	170(24)
P-W-C(15)-O(2)	-94(24)
C(14)-W-C(16)-O(3)	-1(19)
C(15)-W-C(16)-O(3)	89(19)
C(17)-W-C(16)-O(3)	-91(19)
C(18)-W-C(16)-O(3)	16(24)

P-W-C(16)-O(3)	178(100)
C(14)-W-C(17)-O(4)	-73(28)
C(15)-W-C(17)-O(4)	28(36)
C(16)-W-C(17)-O(4)	15(28)
C(18)-W-C(17)-O(4)	-161(28)
P-W-C(17)-O(4)	104(28)
C(14)-W-C(18)-O(5)	27(32)
C(15)-W-C(18)-O(5)	-63(32)
C(16)-W-C(18)-O(5)	10(38)
C(17)-W-C(18)-O(5)	118(32)
P-W-C(18)-O(5)	-151(32)

2. Crystal data of molecule [{bis(trimethylsily)methyl}diphenylaminophosphane] pentacarbonyl tungsten complex (**43c**) (GSTR047).

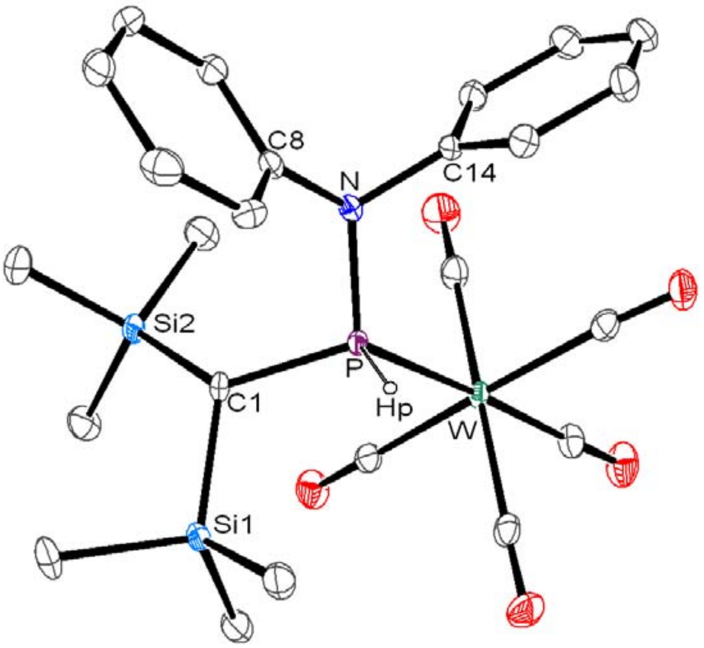

Table 1. Crystal data and structure refinement for **43c**.

Identification code	HPNPh2/GSTR047
Empirical formula	C24 H30 N O5 P Si2 W
Formula weight	683.49

Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.8838(2) A α = 105.8090(10) deg. b = 10.60590(10) A β = 102.5580(10) deg. c = 14.8107(2) A γ = 101.6580(10) deg.
Volume	1400.52(4) A^3
Z, Calculated density	2, 1.621 Mg/m^3
Absorption coefficient	4.299 mm^-1
F(000)	676
Crystal size	0.21 x 0.19 x 0.17 mm
Theta range for data collection	2.95 to 27.49 deg.
Limiting indices	-12<=h<=12, -13<=k<=13, -19<=l<=19
Reflections collected / unique	26215 / 6325 [R(int) = 0.0526]
Completeness to theta = 27.49	98.3 %
Absorption correction	Analytical
Max. and min. transmission	0.5285 and 0.4654
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6325 / 0 / 427
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0261, wR2 = 0.0616
R indices (all data)	R1 = 0.0278, wR2 = 0.0623
Largest diff. peak and hole	1.260 and -2.958 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **43c**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W	5798(1)	9548(1)	6871(1)	11(1)
P	6544(1)	7499(1)	7133(1)	10(1)
Si(1)	3774(1)	5396(1)	7075(1)	12(1)
Si(2)	6088(1)	7328(1)	9176(1)	14(1)
O(1)	4736(3)	11934(2)	6349(2)	29(1)
O(2)	7832(2)	9993(3)	5521(2)	27(1)
O(3)	3750(2)	9597(2)	8255(2)	25(1)
O(4)	8085(3)	11832(2)	8759(2)	29(1)
O(5)	3298(2)	7466(2)	5000(2)	24(1)
N	8350(2)	7673(2)	7582(2)	12(1)
C(1)	5689(3)	6514(3)	7790(2)	11(1)
C(2)	3736(3)	4462(3)	5795(2)	19(1)
C(3)	3336(4)	4100(3)	7684(2)	20(1)
C(4)	2329(3)	6287(3)	6996(2)	20(1)
C(5)	6860(4)	6145(4)	9726(2)	24(1)
C(6)	4462(3)	7514(3)	9590(2)	21(1)
C(7)	7412(3)	9055(3)	9669(2)	22(1)
C(8)	8850(3)	6567(3)	7801(2)	13(1)
C(9)	9917(3)	6877(3)	8678(2)	15(1)
C(10)	10414(3)	5848(3)	8931(2)	19(1)
C(11)	9840(3)	4502(3)	8312(2)	21(1)
C(12)	8796(3)	4197(3)	7425(2)	21(1)
C(13)	8304(3)	5227(3)	7173(2)	17(1)
C(14)	9335(3)	8514(3)	7244(2)	13(1)
C(15)	9622(3)	7962(3)	6369(2)	17(1)
C(16)	10548(3)	8781(3)	6033(2)	21(1)
C(17)	11184(3)	10152(3)	6589(2)	23(1)
C(18)	10923(3)	10685(3)	7470(2)	23(1)
C(19)	10006(3)	9867(3)	7807(2)	17(1)
C(20)	5105(3)	11066(3)	6543(2)	18(1)
C(21)	7148(3)	9774(3)	6011(2)	17(1)
C(22)	7318(3)	10994(3)	8079(2)	19(1)
C(23)	4464(3)	9521(3)	7746(2)	16(1)
C(24)	4199(3)	8188(3)	5672(2)	16(1)

Table 3. Bond lengths [A] and angles [deg] for **43c**

W-C(20)	2.006(3)
W-C(23)	2.041(3)
W-C(24)	2.047(3)
W-C(22)	2.054(3)
W-C(21)	2.058(3)
W-P	2.5305(7)
P-N	1.717(2)
P-C(1)	1.819(3)
P-HP	1.29(3)
Si(1)-C(4)	1.865(3)
Si(1)-C(3)	1.869(3)
Si(1)-C(2)	1.872(3)
Si(1)-C(1)	1.910(3)
Si(2)-C(7)	1.867(3)
Si(2)-C(6)	1.867(3)
Si(2)-C(5)	1.869(3)
Si(2)-C(1)	1.914(3)
O(1)-C(20)	1.139(4)
O(2)-C(21)	1.131(4)
O(3)-C(23)	1.137(4)
O(4)-C(22)	1.133(4)
O(5)-C(24)	1.138(4)
N-C(8)	1.448(3)
N-C(14)	1.449(3)
C(1)-H(1)	0.96(3)
C(2)-H(2A)	0.98(5)
C(2)-H(2B)	0.96(4)
C(2)-H(2C)	0.97(3)
C(3)-H(3A)	0.97(5)
C(3)-H(3B)	0.98(4)
C(3)-H(3C)	0.92(4)
C(4)-H(4A)	0.97(4)
C(4)-H(4B)	0.93(4)
C(4)-H(4C)	0.96(4)
C(5)-H(5A)	1.04(4)
C(5)-H(5B)	0.98(4)
C(5)-H(5C)	0.86(4)
C(6)-H(6A)	0.92(5)
C(6)-H(6B)	0.98(4)
C(6)-H(6C)	0.93(4)
C(7)-H(7A)	0.93(3)
C(7)-H(7B)	0.98(3)

C(7)-H(7C)	0.87(4)
C(8)-C(13)	1.389(4)
C(8)-C(9)	1.393(4)
C(9)-C(10)	1.389(4)
C(9)-H(9)	0.90(4)
C(10)-C(11)	1.390(5)
C(10)-H(10)	0.89(4)
C(11)-C(12)	1.392(4)
C(11)-H(11)	0.89(4)
C(12)-C(13)	1.388(4)
C(12)-H(12)	0.90(4)
C(13)-H(13)	0.78(3)
C(14)-C(15)	1.384(4)
C(14)-C(19)	1.385(4)
C(15)-C(16)	1.398(4)
C(15)-H(15)	0.93(3)
C(16)-C(17)	1.393(5)
C(16)-H(16)	1.01(4)
C(17)-C(18)	1.376(5)
C(17)-H(17)	1.01(4)
C(18)-C(19)	1.391(4)
C(18)-H(18)	0.86(4)
C(19)-H(19)	0.89(3)

C(20)-W-C(23)	88.12(11)
C(20)-W-C(24)	88.73(12)
C(23)-W-C(24)	91.89(11)
C(20)-W-C(22)	88.08(12)
C(23)-W-C(22)	86.26(12)
C(24)-W-C(22)	176.37(10)
C(20)-W-C(21)	86.80(11)
C(23)-W-C(21)	174.34(10)
C(24)-W-C(21)	90.48(12)
C(22)-W-C(21)	91.08(12)
C(20)-W-P	174.96(8)
C(23)-W-P	93.42(8)
C(24)-W-P	86.42(8)
C(22)-W-P	96.80(8)
C(21)-W-P	91.85(8)
N-P-C(1)	104.09(11)
N-P-W	118.13(8)
C(1)-P-W	121.58(9)
N-P-HP	102.9(14)
C(1)-P-HP	99.0(14)

W-P-HP	108.1(14)
C(4)-Si(1)-C(3)	108.49(14)
C(4)-Si(1)-C(2)	107.88(14)
C(3)-Si(1)-C(2)	107.74(14)
C(4)-Si(1)-C(1)	116.38(13)
C(3)-Si(1)-C(1)	106.82(13)
C(2)-Si(1)-C(1)	109.24(13)
C(7)-Si(2)-C(6)	106.95(15)
C(7)-Si(2)-C(5)	109.49(16)
C(6)-Si(2)-C(5)	107.73(15)
C(7)-Si(2)-C(1)	112.71(13)
C(6)-Si(2)-C(1)	114.31(13)
C(5)-Si(2)-C(1)	105.50(14)
C(8)-N-C(14)	113.6(2)
C(8)-N-P	121.13(17)
C(14)-N-P	116.97(16)
P-C(1)-Si(1)	114.23(13)
P-C(1)-Si(2)	118.19(14)
Si(1)-C(1)-Si(2)	117.20(13)
P-C(1)-H(1)	104.0(19)
Si(1)-C(1)-H(1)	96.7(18)
Si(2)-C(1)-H(1)	101.8(18)
Si(1)-C(2)-H(2A)	102(3)
Si(1)-C(2)-H(2B)	112(2)
H(2A)-C(2)-H(2B)	111(3)
Si(1)-C(2)-H(2C)	111.6(19)
H(2A)-C(2)-H(2C)	114(3)
H(2B)-C(2)-H(2C)	107(3)
Si(1)-C(3)-H(3A)	107(3)
Si(1)-C(3)-H(3B)	111(2)
H(3A)-C(3)-H(3B)	114(3)
Si(1)-C(3)-H(3C)	108(2)
H(3A)-C(3)-H(3C)	111(3)
H(3B)-C(3)-H(3C)	105(3)
Si(1)-C(4)-H(4A)	109(2)
Si(1)-C(4)-H(4B)	115(2)
H(4A)-C(4)-H(4B)	110(3)
Si(1)-C(4)-H(4C)	106(2)
H(4A)-C(4)-H(4C)	108(3)
H(4B)-C(4)-H(4C)	109(3)
Si(2)-C(5)-H(5A)	116(2)
Si(2)-C(5)-H(5B)	111(2)
H(5A)-C(5)-H(5B)	104(3)
Si(2)-C(5)-H(5C)	114(2)

H(5A)-C(5)-H(5C)	102(3)
H(5B)-C(5)-H(5C)	109(3)
Si(2)-C(6)-H(6A)	115(3)
Si(2)-C(6)-H(6B)	112(2)
H(6A)-C(6)-H(6B)	106(3)
Si(2)-C(6)-H(6C)	107(2)
H(6A)-C(6)-H(6C)	104(3)
H(6B)-C(6)-H(6C)	111(3)
Si(2)-C(7)-H(7A)	105.3(17)
Si(2)-C(7)-H(7B)	112(2)
H(7A)-C(7)-H(7B)	105(3)
Si(2)-C(7)-H(7C)	109(2)
H(7A)-C(7)-H(7C)	116(3)
H(7B)-C(7)-H(7C)	109(3)
C(13)-C(8)-C(9)	119.5(3)
C(13)-C(8)-N	122.5(2)
C(9)-C(8)-N	118.0(2)
C(10)-C(9)-C(8)	120.2(3)
C(10)-C(9)-H(9)	120(2)
C(8)-C(9)-H(9)	120(2)
C(9)-C(10)-C(11)	120.1(3)
C(9)-C(10)-H(10)	119(3)
C(11)-C(10)-H(10)	121(3)
C(10)-C(11)-C(12)	119.7(3)
C(10)-C(11)-H(11)	117(2)
C(12)-C(11)-H(11)	123(2)
C(13)-C(12)-C(11)	120.1(3)
C(13)-C(12)-H(12)	118(2)
C(11)-C(12)-H(12)	121(2)
C(12)-C(13)-C(8)	120.4(3)
C(12)-C(13)-H(13)	121(3)
C(8)-C(13)-H(13)	118(3)
C(15)-C(14)-C(19)	120.1(3)
C(15)-C(14)-N	120.1(2)
C(19)-C(14)-N	119.8(2)
C(14)-C(15)-C(16)	120.1(3)
C(14)-C(15)-H(15)	122(2)
C(16)-C(15)-H(15)	118(2)
C(17)-C(16)-C(15)	119.4(3)
C(17)-C(16)-H(16)	121(2)
C(15)-C(16)-H(16)	120(2)
C(18)-C(17)-C(16)	120.2(3)
C(18)-C(17)-H(17)	119(2)
C(16)-C(17)-H(17)	121(2)

C(17)-C(18)-C(19)	120.4(3)
C(17)-C(18)-H(18)	121(2)
C(19)-C(18)-H(18)	118(2)
C(14)-C(19)-C(18)	119.8(3)
C(14)-C(19)-H(19)	116(2)
C(18)-C(19)-H(19)	124(2)
O(1)-C(20)-W	178.5(3)
O(2)-C(21)-W	173.4(2)
O(4)-C(22)-W	175.3(3)
O(3)-C(23)-W	175.5(2)
O(5)-C(24)-W	177.8(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **43c**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
W	14(1)	11(1)	11(1)	6(1)	4(1)	3(1)
P	11(1)	11(1)	8(1)	4(1)	3(1)	2(1)
Si(1)	13(1)	12(1)	12(1)	6(1)	4(1)	1(1)
Si(2)	16(1)	18(1)	9(1)	7(1)	5(1)	2(1)
O(1)	40(1)	26(1)	34(1)	19(1)	17(1)	19(1)
O(2)	25(1)	43(1)	27(1)	24(1)	14(1)	14(1)
O(3)	28(1)	30(1)	23(1)	10(1)	15(1)	11(1)
O(4)	34(1)	21(1)	22(1)	1(1)	4(1)	-2(1)
O(5)	25(1)	24(1)	15(1)	4(1)	-1(1)	1(1)
N	10(1)	13(1)	15(1)	8(1)	4(1)	2(1)
C(1)	14(1)	11(1)	10(1)	6(1)	5(1)	4(1)
C(2)	22(2)	16(1)	14(1)	4(1)	4(1)	-1(1)
C(3)	27(2)	16(1)	22(2)	10(1)	12(1)	2(1)
C(4)	16(1)	22(2)	26(2)	12(1)	8(1)	5(1)
C(5)	25(2)	34(2)	21(2)	19(1)	7(1)	7(2)
C(6)	22(2)	25(2)	15(1)	4(1)	9(1)	3(1)
C(7)	22(2)	25(2)	14(2)	2(1)	6(1)	0(1)
C(8)	11(1)	16(1)	16(1)	9(1)	7(1)	4(1)
C(9)	14(1)	16(1)	15(1)	5(1)	4(1)	2(1)
C(10)	13(1)	27(2)	21(2)	15(1)	4(1)	7(1)
C(11)	18(1)	21(2)	32(2)	18(1)	9(1)	9(1)
C(12)	18(1)	13(1)	29(2)	5(1)	6(1)	3(1)
C(13)	13(1)	19(1)	16(1)	6(1)	0(1)	3(1)
C(14)	10(1)	16(1)	16(1)	11(1)	4(1)	4(1)
C(15)	17(1)	17(1)	17(1)	8(1)	5(1)	5(1)
C(16)	20(1)	31(2)	21(2)	16(1)	12(1)	11(1)
C(17)	15(1)	28(2)	31(2)	20(1)	8(1)	3(1)

C(18)	18(1)	18(2)	26(2)	10(1)	2(1)	-5(1)
C(19)	17(1)	18(1)	14(1)	7(1)	2(1)	0(1)
C(20)	22(1)	20(1)	19(1)	9(1)	10(1)	8(1)
C(21)	17(1)	20(2)	19(1)	11(1)	5(1)	9(1)
C(22)	23(2)	16(1)	19(1)	8(1)	7(1)	4(1)
C(23)	17(1)	13(1)	18(1)	7(1)	3(1)	4(1)
C(24)	18(1)	19(1)	18(1)	11(1)	7(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **43c**.

	x	y	z	U(eq)
HP	6190(30)	6560(30)	6290(20)	19(8)
H(1)	6140(30)	5790(30)	7750(20)	17(8)
H(2A)	2880(50)	3670(50)	5590(30)	63(14)
H(2B)	4590(40)	4170(40)	5780(30)	34(10)
H(2C)	3670(30)	5030(30)	5380(20)	21(8)
H(3A)	3250(50)	4580(50)	8310(40)	65(15)
H(3B)	4050(40)	3570(40)	7710(30)	38(10)
H(3C)	2480(40)	3470(40)	7300(30)	21(9)
H(4A)	2480(40)	6860(40)	6600(30)	26(9)
H(4B)	2270(40)	6800(40)	7590(30)	38(10)
H(4C)	1430(40)	5590(40)	6650(30)	32(10)
H(5A)	7170(50)	6450(40)	10490(30)	55(13)
H(5B)	7740(40)	6030(40)	9550(30)	42(11)
H(5C)	6260(40)	5350(40)	9570(30)	29(10)
H(6A)	3740(50)	6720(50)	9410(30)	53(12)
H(6B)	4030(40)	8160(40)	9360(30)	43(11)
H(6C)	4750(40)	7800(40)	10270(30)	36(10)
H(7A)	7590(30)	9320(30)	10350(20)	4(6)
H(7B)	7000(40)	9740(30)	9470(20)	22(8)
H(7C)	8160(40)	9010(30)	9450(30)	23(9)
H(9)	10250(40)	7740(40)	9100(20)	16(8)
H(10)	11080(40)	6070(40)	9500(30)	29(10)
H(11)	10260(40)	3900(40)	8470(30)	26(9)
H(12)	8340(40)	3330(40)	7050(30)	30(10)
H(13)	7760(40)	5080(40)	6660(30)	16(9)
H(15)	9190(30)	7050(40)	5980(20)	17(8)
H(16)	10710(40)	8380(40)	5380(30)	28(9)
H(17)	11850(40)	10760(40)	6350(30)	29(10)
H(18)	11350(40)	11510(40)	7840(30)	27(9)
H(19)	9860(30)	10140(30)	8400(20)	18(8)

Table 6. Torsion angles [deg] for **43c**.

C(20)-W-P-N	128.7(9)
C(23)-W-P-N	-123.65(12)
C(24)-W-P-N	144.67(12)
C(22)-W-P-N	-37.01(12)
C(21)-W-P-N	54.30(12)
C(20)-W-P-C(1)	-100.6(9)
C(23)-W-P-C(1)	7.10(13)
C(24)-W-P-C(1)	-84.59(13)
C(22)-W-P-C(1)	93.74(13)
C(21)-W-P-C(1)	-174.95(13)
C(1)-P-N-C(8)	38.3(2)
W-P-N-C(8)	176.58(17)
C(1)-P-N-C(14)	-175.41(19)
W-P-N-C(14)	-37.1(2)
N-P-C(1)-Si(1)	-150.49(13)
W-P-C(1)-Si(1)	73.05(15)
N-P-C(1)-Si(2)	65.42(17)
W-P-C(1)-Si(2)	-71.04(16)
C(4)-Si(1)-C(1)-P	-76.33(18)
C(3)-Si(1)-C(1)-P	162.36(15)
C(2)-Si(1)-C(1)-P	46.09(18)
C(4)-Si(1)-C(1)-Si(2)	68.14(18)
C(3)-Si(1)-C(1)-Si(2)	-53.18(18)
C(2)-Si(1)-C(1)-Si(2)	-169.44(14)
C(7)-Si(2)-C(1)-P	-2.5(2)
C(6)-Si(2)-C(1)-P	119.87(17)
C(5)-Si(2)-C(1)-P	-121.97(17)
C(7)-Si(2)-C(1)-Si(1)	-145.57(15)
C(6)-Si(2)-C(1)-Si(1)	-23.2(2)
C(5)-Si(2)-C(1)-Si(1)	95.00(17)
C(14)-N-C(8)-C(13)	-103.0(3)
P-N-C(8)-C(13)	44.3(3)
C(14)-N-C(8)-C(9)	77.2(3)
P-N-C(8)-C(9)	-135.5(2)
C(13)-C(8)-C(9)-C(10)	-1.1(4)
N-C(8)-C(9)-C(10)	178.7(2)
C(8)-C(9)-C(10)-C(11)	-0.4(4)
C(9)-C(10)-C(11)-C(12)	1.7(4)
C(10)-C(11)-C(12)-C(13)	-1.6(5)
C(11)-C(12)-C(13)-C(8)	0.2(5)
C(9)-C(8)-C(13)-C(12)	1.2(4)
N-C(8)-C(13)-C(12)	-178.6(3)

C(8)-N-C(14)-C(15)	64.2(3)
P-N-C(14)-C(15)	-84.6(3)
C(8)-N-C(14)-C(19)	-114.9(3)
P-N-C(14)-C(19)	96.4(3)
C(19)-C(14)-C(15)-C(16)	-2.3(4)
N-C(14)-C(15)-C(16)	178.6(2)
C(14)-C(15)-C(16)-C(17)	0.3(4)
C(15)-C(16)-C(17)-C(18)	1.3(4)
C(16)-C(17)-C(18)-C(19)	-1.0(4)
C(15)-C(14)-C(19)-C(18)	2.7(4)
N-C(14)-C(19)-C(18)	-178.3(2)
C(17)-C(18)-C(19)-C(14)	-1.0(4)
C(23)-W-C(20)-O(1)	165(11)
C(24)-W-C(20)-O(1)	-103(11)
C(22)-W-C(20)-O(1)	79(11)
C(21)-W-C(20)-O(1)	-12(11)
P-W-C(20)-O(1)	-87(11)
C(20)-W-C(21)-O(2)	-2(2)
C(23)-W-C(21)-O(2)	-28(3)
C(24)-W-C(21)-O(2)	87(2)
C(22)-W-C(21)-O(2)	-90(2)
P-W-C(21)-O(2)	174(2)
C(20)-W-C(22)-O(4)	46(3)
C(23)-W-C(22)-O(4)	-42(3)
C(24)-W-C(22)-O(4)	17(4)
C(21)-W-C(22)-O(4)	133(3)
P-W-C(22)-O(4)	-135(3)
C(20)-W-C(23)-O(3)	-43(3)
C(24)-W-C(23)-O(3)	-131(3)
C(22)-W-C(23)-O(3)	45(3)
C(21)-W-C(23)-O(3)	-17(4)
P-W-C(23)-O(3)	142(3)
C(20)-W-C(24)-O(5)	0(7)
C(23)-W-C(24)-O(5)	88(7)
C(22)-W-C(24)-O(5)	29(8)
C(21)-W-C(24)-O(5)	-87(7)
P-W-C(24)-O(5)	-179(100)

3. Crystal data of molecule [{bis(trimethylsily)methyl}isopropylaminophosphane] pentacarbonyl tungsten complex (**43d**) (joerg87/GSTR038).

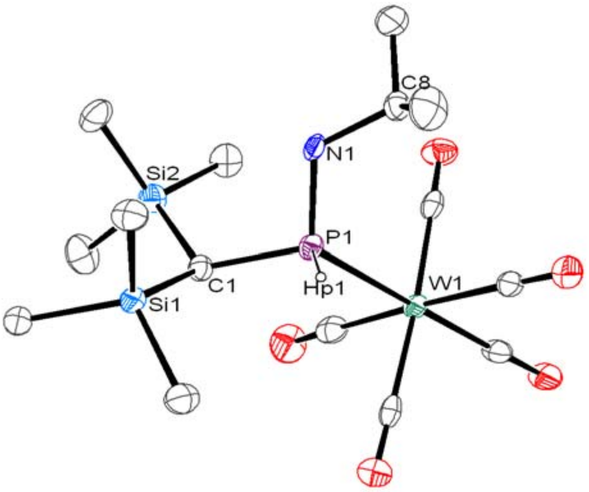

Table 1. Crystal data and structural refinement of **43d**

Identification code	joerg87/GSTR038
Empirical formula	C30 H51 N2 O10 P2 Si4 W2
Formula weight	1141.73
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.6900(2) A, α = 102.9600(10) ° b = 15.7215(3) A, β = 101.9810(10) ° c = 16.2744(3) A, γ = 93.8520(10) °
Volume	2346.60(8) A^3
Z, Calculated density	2, 1.616 Mg/m^3
Absorption coefficient	5.114 mm^-1
F(000)	1118
Crystal size	0.18 x 0.13 x 0.10 mm
Theta range for data collection	2.60 to 27.49 deg.

Limiting indices	-12<=h<=12, -20<=k<=20, -21<=l<=21
Reflections collected / unique	43324 / 10653 [R(int) = 0.0556]
Completeness to theta	27.49 98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6288 and 0.4664
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10653 / 0 / 471
Goodness-of-fit on F^2	0.988
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0614
R indices (all data)	R1 = 0.0475, wR2 = 0.0661
Largest diff. peak and hole	1.796 and -2.289 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **43d**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W(1)	8836(1)	3769(1)	2912(1)	18(1)
W(2)	6677(1)	81(1)	3647(1)	23(1)
P(1)	11456(1)	4153(1)	3113(1)	17(1)
Si(1)	13541(1)	5861(1)	3625(1)	19(1)
Si(2)	12240(1)	4885(1)	1591(1)	23(1)
C(1)	12053(4)	5114(2)	2760(2)	19(1)
C(2)	15111(4)	5267(3)	3903(3)	25(1)
C(3)	14127(4)	6837(3)	3243(3)	28(1)
C(4)	12847(4)	6257(3)	4616(2)	28(1)
C(5)	10967(5)	3947(3)	856(3)	32(1)
C(6)	11802(5)	5885(3)	1196(3)	39(1)
C(7)	14084(4)	4666(3)	1499(3)	32(1)
C(8)	12182(4)	2473(2)	2846(3)	24(1)
C(9)	12604(4)	1800(3)	2137(3)	32(1)
C(10)	12958(5)	2426(3)	3741(3)	40(1)
C(11)	6791(4)	3446(3)	2844(3)	24(1)

C(12)	8334(4)	4551(3)	2076(3)	28(1)
C(13)	8799(4)	2731(3)	1878(3)	22(1)
C(14)	9266(4)	2989(2)	3769(3)	22(1)
C(15)	8917(4)	4849(3)	3903(3)	21(1)
N(1)	12381(3)	3361(2)	2699(2)	19(1)
O(1)	5613(3)	3245(2)	2836(2)	33(1)
O(2)	8034(3)	4999(2)	1618(2)	45(1)
O(3)	8782(3)	2170(2)	1296(2)	32(1)
O(4)	9460(3)	2553(2)	4240(2)	33(1)
O(5)	8945(3)	5462(2)	4436(2)	28(1)
P(2)	6757(1)	-1219(1)	2462(1)	21(1)
Si(3)	5109(1)	-2119(1)	621(1)	25(1)
Si(4)	7998(1)	-760(1)	955(1)	29(1)
C(16)	6386(4)	-1131(3)	1341(2)	23(1)
C(17)	3330(4)	-1987(3)	867(3)	32(1)
C(18)	4911(5)	-2203(3)	-562(2)	36(1)
C(19)	5726(5)	-3176(3)	825(3)	35(1)
C(20)	9335(5)	45(3)	1805(3)	40(1)
C(21)	7325(5)	-191(3)	81(3)	40(1)
C(22)	8925(5)	-1706(3)	516(3)	41(1)
C(23)	9019(4)	-1936(3)	3305(3)	37(1)
C(24)	8290(5)	-2752(3)	3494(3)	50(1)
C(25)	10496(5)	-2067(4)	3219(4)	63(2)
C(26)	6496(5)	1082(3)	4610(3)	39(1)
C(27)	6577(4)	872(3)	2816(3)	27(1)
C(28)	4514(5)	-199(3)	3291(3)	32(1)
C(29)	6735(5)	-732(3)	4461(3)	36(1)
C(30)	8839(5)	365(3)	4004(3)	33(1)
N(2)	8215(4)	-1749(2)	2514(2)	30(1)
O(6)	6367(4)	1636(2)	5175(2)	59(1)
O(7)	6504(4)	1321(2)	2338(2)	41(1)
O(8)	3315(4)	-346(2)	3092(2)	52(1)
O(9)	6746(4)	-1191(3)	4916(2)	61(1)
O(10)	10046(4)	531(2)	4212(2)	50(1)

Table 3. Bond lengths [A] and angles [deg] for **43d**.

W(1)-C(11)	1.987(4)
W(1)-C(12)	2.039(4)
W(1)-C(15)	2.047(4)
W(1)-C(14)	2.053(4)
W(1)-C(13)	2.058(4)
W(1)-P(1)	2.5049(10)
W(2)-C(26)	2.003(5)

W(2)-C(27)	2.026(4)
W(2)-C(29)	2.031(4)
W(2)-C(30)	2.044(5)
W(2)-C(28)	2.044(5)
W(2)-P(2)	2.4935(10)
P(1)-N(1)	1.682(3)
P(1)-C(1)	1.834(4)
P(1)-HP1	1.28(4)
Si(1)-C(2)	1.868(4)
Si(1)-C(4)	1.871(4)
Si(1)-C(3)	1.876(4)
Si(1)-C(1)	1.905(4)
Si(2)-C(5)	1.866(4)
Si(2)-C(6)	1.869(4)
Si(2)-C(7)	1.872(4)
Si(2)-C(1)	1.904(4)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-N(1)	1.476(4)
C(8)-C(10)	1.514(5)
C(8)-C(9)	1.525(5)
C(8)-H(8)	1.0000
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800

C(11)-O(1)	1.160(5)
C(12)-O(2)	1.144(5)
C(13)-O(3)	1.136(5)
C(14)-O(4)	1.133(4)
C(15)-O(5)	1.138(5)
N(1)-HN1	0.8800
P(2)-N(2)	1.685(3)
P(2)-C(16)	1.823(4)
P(2)-HP2	1.0000
Si(3)-C(17)	1.863(4)
Si(3)-C(18)	1.867(4)
Si(3)-C(19)	1.879(4)
Si(3)-C(16)	1.907(4)
Si(4)-C(20)	1.856(5)
Si(4)-C(22)	1.871(4)
Si(4)-C(21)	1.874(4)
Si(4)-C(16)	1.904(4)
C(16)-H(16)	1.0000
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-O(6)	1.150(5)
C(27)-O(7)	1.156(5)
C(28)-O(8)	1.132(5)
C(29)-O(9)	1.144(5)
C(30)-O(10)	1.142(5)
N(2)-HN2	0.8800

C(11)-W(1)-C(12)	90.83(15)
C(11)-W(1)-C(15)	91.06(15)
C(12)-W(1)-C(15)	87.09(15)
C(12)-W(1)-C(14)	177.68(14)
C(15)-W(1)-C(14)	91.26(14)
C(11)-W(1)-C(13)	90.80(15)
C(12)-W(1)-C(13)	89.50(15)
C(15)-W(1)-C(13)	176.72(14)
C(14)-W(1)-C(13)	91.54(14)
C(11)-W(1)-P(1)	175.50(11)

C(12)-W(1)-P(1)	93.21(11)
C(15)-W(1)-P(1)	87.12(10)
C(14)-W(1)-P(1)	88.84(11)
C(13)-W(1)-P(1)	91.22(10)
C(26)-W(2)-C(27)	91.40(17)
C(26)-W(2)-C(29)	89.33(18)
C(27)-W(2)-C(29)	178.63(17)
C(26)-W(2)-C(30)	89.89(19)
C(27)-W(2)-C(30)	90.44(16)
C(29)-W(2)-C(30)	90.72(17)
C(26)-W(2)-C(28)	89.94(18)
C(27)-W(2)-C(28)	89.46(16)
C(29)-W(2)-C(28)	89.38(17)
C(30)-W(2)-C(28)	179.80(19)
C(26)-W(2)-P(2)	176.15(14)
C(27)-W(2)-P(2)	90.68(11)
C(29)-W(2)-P(2)	88.53(13)
C(30)-W(2)-P(2)	93.35(13)
C(28)-W(2)-P(2)	86.83(12)
N(1)-P(1)-C(1)	104.32(16)
N(1)-P(1)-W(1)	117.68(11)
C(1)-P(1)-W(1)	117.79(12)
N(1)-P(1)-HP1	105.0(15)
C(1)-P(1)-HP1	102.4(16)
W(1)-P(1)-HP1	108.0(16)
C(2)-Si(1)-C(4)	109.26(18)
C(2)-Si(1)-C(3)	108.57(19)
C(4)-Si(1)-C(3)	108.76(18)
C(2)-Si(1)-C(1)	111.44(17)
C(4)-Si(1)-C(1)	108.28(18)
C(3)-Si(1)-C(1)	110.50(17)
C(5)-Si(2)-C(6)	106.6(2)
C(5)-Si(2)-C(7)	108.4(2)
C(6)-Si(2)-C(7)	109.6(2)
C(5)-Si(2)-C(1)	113.27(18)
C(6)-Si(2)-C(1)	106.74(18)
C(7)-Si(2)-C(1)	111.96(17)
P(1)-C(1)-Si(2)	115.4(2)
P(1)-C(1)-Si(1)	111.60(18)
Si(2)-C(1)-Si(1)	117.74(19)
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
H(9B)-C(9)-H(9C)	109.5

C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(1)-C(11)-W(1)	177.2(3)
O(2)-C(12)-W(1)	178.6(4)
O(3)-C(13)-W(1)	178.5(3)
O(4)-C(14)-W(1)	177.9(3)
O(5)-C(15)-W(1)	178.0(3)
C(8)-N(1)-P(1)	120.4(2)
C(8)-N(1)-HN1	119.8
P(1)-N(1)-HN1	119.8
N(2)-P(2)-C(16)	101.52(17)
N(2)-P(2)-W(2)	119.84(13)
C(16)-P(2)-W(2)	119.92(13)
N(2)-P(2)-HP2	104.6
C(16)-P(2)-HP2	104.6
W(2)-P(2)-HP2	104.6
C(17)-Si(3)-C(18)	107.6(2)
C(17)-Si(3)-C(19)	110.7(2)
C(18)-Si(3)-C(19)	106.68(19)
C(17)-Si(3)-C(16)	107.30(19)
C(18)-Si(3)-C(16)	113.52(19)
C(19)-Si(3)-C(16)	111.03(19)
C(20)-Si(4)-C(22)	107.7(2)
C(20)-Si(4)-C(21)	106.8(2)
C(22)-Si(4)-C(21)	109.7(2)
C(20)-Si(4)-C(16)	113.82(19)
C(22)-Si(4)-C(16)	112.08(19)
C(21)-Si(4)-C(16)	106.54(19)
P(2)-C(16)-Si(4)	115.0(2)
P(2)-C(16)-Si(3)	109.96(19)
Si(4)-C(16)-Si(3)	118.6(2)
P(2)-C(16)-H(16)	103.7
Si(4)-C(16)-H(16)	103.7
Si(3)-C(16)-H(16)	103.7
Si(3)-C(17)-H(17A)	109.5
Si(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
Si(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Si(3)-C(18)-H(18A)	109.5
Si(3)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
Si(3)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
Si(3)-C(19)-H(19A)	109.5
Si(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(4)-C(20)-H(20A)	109.5
Si(4)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(4)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
Si(4)-C(21)-H(21A)	109.5
Si(4)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(4)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Si(4)-C(22)-H(22A)	109.5
Si(4)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
Si(4)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
N(2)-C(23)-C(25)	109.4(4)
N(2)-C(23)-C(24)	110.9(4)
C(25)-C(23)-C(24)	110.7(4)
N(2)-C(23)-H(23)	108.6
C(25)-C(23)-H(23)	108.6
C(24)-C(23)-H(23)	108.6
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5

H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(6)-C(26)-W(2)	177.6(4)
O(7)-C(27)-W(2)	179.2(4)
O(8)-C(28)-W(2)	179.4(4)
O(9)-C(29)-W(2)	178.9(4)
O(10)-C(30)-W(2)	179.2(5)
C(23)-N(2)-P(2)	124.1(3)
C(23)-N(2)-HN2	118.0
P(2)-N(2)-HN2	118.0

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **43d**. The anisotropic displacement factor exponent takes the form -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
W(1)	11(1)	20(1)	22(1)	4(1)	4(1)	1(1)
W(2)	28(1)	21(1)	20(1)	4(1)	5(1)	2(1)
P(1)	13(1)	20(1)	18(1)	7(1)	3(1)	1(1)
Si(1)	16(1)	19(1)	22(1)	4(1)	7(1)	1(1)
Si(2)	26(1)	25(1)	20(1)	9(1)	5(1)	2(1)
C(1)	16(2)	19(2)	21(2)	7(2)	4(2)	2(2)
C(2)	18(2)	28(2)	27(2)	4(2)	0(2)	4(2)
C(3)	31(2)	22(2)	31(2)	2(2)	15(2)	-2(2)
C(4)	28(2)	28(2)	27(2)	4(2)	8(2)	4(2)
C(5)	35(3)	36(3)	23(2)	7(2)	2(2)	0(2)
C(6)	50(3)	36(3)	32(2)	20(2)	3(2)	2(2)
C(7)	32(2)	41(3)	25(2)	7(2)	14(2)	1(2)
C(8)	17(2)	24(2)	34(2)	15(2)	8(2)	4(2)
C(9)	23(2)	28(2)	46(3)	8(2)	12(2)	3(2)
C(10)	43(3)	46(3)	37(3)	25(2)	5(2)	8(2)
C(11)	22(2)	20(2)	30(2)	2(2)	6(2)	5(2)
C(12)	17(2)	33(2)	32(2)	5(2)	5(2)	4(2)
C(13)	13(2)	30(2)	26(2)	14(2)	5(2)	0(2)
C(14)	18(2)	19(2)	29(2)	2(2)	9(2)	0(2)
C(15)	12(2)	29(2)	24(2)	14(2)	3(2)	-2(2)
N(1)	14(2)	22(2)	26(2)	11(1)	10(1)	2(1)
O(1)	14(2)	28(2)	54(2)	2(2)	11(1)	2(1)
O(2)	42(2)	52(2)	52(2)	34(2)	9(2)	18(2)
O(3)	32(2)	32(2)	29(2)	-1(2)	7(1)	5(1)
O(4)	40(2)	31(2)	37(2)	15(2)	18(1)	8(1)

O(5)	30(2)	26(2)	28(2)	4(1)	6(1)	5(1)
P(2)	24(1)	19(1)	20(1)	8(1)	4(1)	3(1)
Si(3)	29(1)	25(1)	21(1)	7(1)	6(1)	0(1)
Si(4)	31(1)	26(1)	32(1)	8(1)	15(1)	2(1)
C(16)	28(2)	22(2)	21(2)	9(2)	7(2)	3(2)
C(17)	33(2)	31(2)	33(2)	13(2)	3(2)	2(2)
C(18)	49(3)	35(3)	17(2)	2(2)	-1(2)	6(2)
C(19)	46(3)	28(2)	29(2)	4(2)	10(2)	1(2)
C(20)	35(3)	39(3)	49(3)	12(2)	18(2)	-3(2)
C(21)	54(3)	38(3)	37(3)	16(2)	20(2)	4(2)
C(22)	44(3)	41(3)	46(3)	11(2)	24(2)	11(2)
C(23)	23(2)	54(3)	39(3)	25(2)	-2(2)	13(2)
C(24)	49(3)	45(3)	59(3)	31(3)	-1(3)	7(3)
C(25)	36(3)	71(4)	88(4)	39(4)	4(3)	17(3)
C(26)	46(3)	28(2)	39(3)	2(2)	10(2)	-2(2)
C(27)	27(2)	21(2)	32(2)	3(2)	7(2)	3(2)
C(28)	36(3)	27(2)	30(2)	5(2)	7(2)	0(2)
C(29)	37(3)	39(3)	26(2)	8(2)	1(2)	-4(2)
C(30)	37(3)	29(2)	32(2)	10(2)	-2(2)	1(2)
N(2)	29(2)	35(2)	32(2)	14(2)	10(2)	13(2)
O(6)	71(3)	43(2)	50(2)	-19(2)	20(2)	0(2)
O(7)	52(2)	33(2)	46(2)	23(2)	11(2)	10(2)
O(8)	29(2)	59(2)	64(2)	11(2)	11(2)	-1(2)
O(9)	66(3)	75(3)	51(2)	45(2)	2(2)	-5(2)
O(10)	33(2)	51(2)	58(2)	18(2)	-6(2)	-2(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **43d**.

	x	y	z	U(eq)
H(2A)	15817	5649	4389	38
H(2B)	15532	5107	3400	38
H(2C)	14809	4733	4067	38
H(3A)	13310	7151	3087	42
H(3B)	14525	6639	2736	42
H(3C)	14852	7232	3708	42
H(4A)	12577	5754	4836	42
H(4B)	12015	6562	4471	42
H(4C)	13587	6663	5061	42
H(5A)	11074	3884	260	48
H(5B)	9993	4059	885	48
H(5C)	11164	3405	1036	48

H(6A)	12451	6396	1564	59
H(6B)	10821	5983	1221	59
H(6C)	11902	5799	597	59
H(7A)	14280	4112	1656	47
H(7B)	14769	5147	1890	47
H(7C)	14168	4623	901	47
H(8)	11144	2324	2799	28
H(9A)	12046	1828	1570	48
H(9B)	12420	1209	2224	48
H(9C)	13617	1929	2162	48
H(10A)	13984	2549	3801	60
H(10B)	12739	1837	3822	60
H(10C)	12653	2862	4178	60
HN1	12987	3478	2394	23
HP2	5984	-1664	2480	25
H(16)	5803	-629	1345	28
H(17A)	2645	-2485	507	48
H(17B)	3018	-1439	744	48
H(17C)	3392	-1967	1480	48
H(18A)	4207	-2703	-894	53
H(18B)	5827	-2289	-714	53
H(18C)	4595	-1661	-698	53
H(19A)	5819	-3167	1439	52
H(19B)	6648	-3242	676	52
H(19C)	5031	-3671	468	52
H(20A)	10101	236 1	554	60
H(20B)	9728	-231	2272	60
H(20C)	8881	555	2039	60
H(21A)	6835	301	313	60
H(21B)	6662	-608	-401	60
H(21C)	8127	30	-125	60
H(22A)	9552	-1521	171	62
H(22B)	8219	-2191	150	62
H(22C)	9489	-1903	996	62
H(23)	9061	-1418	3800	45
H(24A)	7323	-2653	3550	75
H(24B)	8833	-2855	4035	75
H(24C)	8253	-3267	3018	75
H(25A)	10467	-2551	2715	94
H(25B)	11028	-2209	3743	94
H(25C)	10963	-1527	3142	94
HN2	8511	-1925	2034	36
HP1	12010(40)	4370(20)	3920(20)	21(10

Table 6. Torsion angles [deg] for **43d**.

C(11)-W(1)-P(1)-N(1)	95.2(14)
C(12)-W(1)-P(1)-N(1)	-110.97(17)
C(15)-W(1)-P(1)-N(1)	161.44(15)
C(14)-W(1)-P(1)-N(1)	70.12(16)
C(13)-W(1)-P(1)-N(1)	-21.40(15)
C(11)-W(1)-P(1)-C(1)	-138.5(14)
C(12)-W(1)-P(1)-C(1)	15.35(18)
C(15)-W(1)-P(1)-C(1)	-72.25(17)
C(14)-W(1)-P(1)-C(1)	-163.57(17)
C(13)-W(1)-P(1)-C(1)	104.92(17)
N(1)-P(1)-C(1)-Si(2)	42.7(2)
W(1)-P(1)-C(1)-Si(2)	-89.92(18)
N(1)-P(1)-C(1)-Si(1)	-95.3(2)
W(1)-P(1)-C(1)-Si(1)	132.17(13)
C(5)-Si(2)-C(1)-P(1)	30.6(3)
C(6)-Si(2)-C(1)-P(1)	147.7(2)
C(7)-Si(2)-C(1)-P(1)	-92.3(2)
C(5)-Si(2)-C(1)-Si(1)	165.90(19)
C(6)-Si(2)-C(1)-Si(1)	-77.0(2)
C(7)-Si(2)-C(1)-Si(1)	42.9(3)
C(2)-Si(1)-C(1)-P(1)	59.2(2)
C(4)-Si(1)-C(1)-P(1)	-61.0(2)
C(3)-Si(1)-C(1)-P(1)	179.98(18)
C(2)-Si(1)-C(1)-Si(2)	-77.7(2)
C(4)-Si(1)-C(1)-Si(2)	162.15(19)
C(3)-Si(1)-C(1)-Si(2)	43.1(2)
C(12)-W(1)-C(11)-O(1)	-163(7)
C(15)-W(1)-C(11)-O(1)	-75(7)
C(14)-W(1)-C(11)-O(1)	16(7)
C(13)-W(1)-C(11)-O(1)	107(7)
P(1)-W(1)-C(11)-O(1)	-9(8)
C(11)-W(1)-C(12)-O(2)	51(16)
C(15)-W(1)-C(12)-O(2)	-40(16)
C(14)-W(1)-C(12)-O(2)	25(19)
C(13)-W(1)-C(12)-O(2)	142(16)
P(1)-W(1)-C(12)-O(2)	-127(16)
C(11)-W(1)-C(13)-O(3)	112(13)
C(12)-W(1)-C(13)-O(3)	21(13)
C(15)-W(1)-C(13)-O(3)	-12(14)
C(14)-W(1)-C(13)-O(3)	-161(13)
P(1)-W(1)-C(13)-O(3)	-72(13)
C(11)-W(1)-C(14)-O(4)	-2(9)

C(12)-W(1)-C(14)-O(4)	24(12)
C(15)-W(1)-C(14)-O(4)	89(9)
C(13)-W(1)-C(14)-O(4)	-93(9)
P(1)-W(1)-C(14)-O(4)	176(100)
C(11)-W(1)-C(15)-O(5)	-82(9)
C(12)-W(1)-C(15)-O(5)	9(9)
C(14)-W(1)-C(15)-O(5)	-169(9)
C(13)-W(1)-C(15)-O(5)	42(11)
P(1)-W(1)-C(15)-O(5)	102(9)
C(10)-C(8)-N(1)-P(1)	-78.3(4)
C(9)-C(8)-N(1)-P(1)	156.2(3)
C(1)-P(1)-N(1)-C(8)	-179.8(3)
W(1)-P(1)-N(1)-C(8)	-47.2(3)
C(26)-W(2)-P(2)-N(2)	-122(2)
C(27)-W(2)-P(2)-N(2)	115.40(18)
C(29)-W(2)-P(2)-N(2)	-65.72(19)
C(30)-W(2)-P(2)-N(2)	24.92(18)
C(28)-W(2)-P(2)-N(2)	-155.18(18)
C(26)-W(2)-P(2)-C(16)	111(2)
C(27)-W(2)-P(2)-C(16)	-11.17(19)
C(29)-W(2)-P(2)-C(16)	167.7(2)
C(30)-W(2)-P(2)-C(16)	-101.65(19)
C(28)-W(2)-P(2)-C(16)	78.26(19)
N(2)-P(2)-C(16)-Si(4)	-45.4(2)
W(2)-P(2)-C(16)-Si(4)	89.3(2)
N(2)-P(2)-C(16)-Si(3)	91.6(2)
W(2)-P(2)-C(16)-Si(3)	-133.76(14)
C(20)-Si(4)-C(16)-P(2)	-34.8(3)
C(22)-Si(4)-C(16)-P(2)	87.8(3)
C(21)-Si(4)-C(16)-P(2)	-152.2(2)
C(20)-Si(4)-C(16)-Si(3)	-167.9(2)
C(22)-Si(4)-C(16)-Si(3)	-45.3(3)
C(21)-Si(4)-C(16)-Si(3)	74.7(3)
C(17)-Si(3)-C(16)-P(2)	71.7(2)
C(18)-Si(3)-C(16)-P(2)	-169.6(2)
C(19)-Si(3)-C(16)-P(2)	-49.4(3)
C(17)-Si(3)-C(16)-Si(4)	-153.1(2)
C(18)-Si(3)-C(16)-Si(4)	-34.3(3)
C(19)-Si(3)-C(16)-Si(4)	85.8(2)
C(27)-W(2)-C(26)-O(6)	147(11)
C(29)-W(2)-C(26)-O(6)	-32(11)
C(30)-W(2)-C(26)-O(6)	-122(11)
C(28)-W(2)-C(26)-O(6)	58(11)
P(2)-W(2)-C(26)-O(6)	25(12)

C(26)-W(2)-C(27)-O(7)	-94(25)
C(29)-W(2)-C(27)-O(7)	28(29)
C(30)-W(2)-C(27)-O(7)	176(100)
C(28)-W(2)-C(27)-O(7)	-4(25)
P(2)-W(2)-C(27)-O(7)	83(25)
C(26)-W(2)-C(28)-O(8)	66(43)
C(27)-W(2)-C(28)-O(8)	-26(43)
C(29)-W(2)-C(28)-O(8)	155(43)
C(30)-W(2)-C(28)-O(8)	37(73)
P(2)-W(2)-C(28)-O(8)	-116(43)
C(26)-W(2)-C(29)-O(9)	84(22)
C(27)-W(2)-C(29)-O(9)	-38(27)
C(30)-W(2)-C(29)-O(9)	174(100)
C(28)-W(2)-C(29)-O(9)	-6(22)
P(2)-W(2)-C(29)-O(9)	-92(22)
C(26)-W(2)-C(30)-O(10)	5(32)
C(27)-W(2)-C(30)-O(10)	96(32)
C(29)-W(2)-C(30)-O(10)	-85(32)
C(28)-W(2)-C(30)-O(10)	33(67)
P(2)-W(2)-C(30)-O(10)	-173(100)
C(25)-C(23)-N(2)-P(2)	-157.2(4)
C(24)-C(23)-N(2)-P(2)	80.4(5)
C(16)-P(2)-N(2)-C(23)	175.6(3)
W(2)-P(2)-N(2)-C(23)	40.9(4)

4. Crystal data of molecule [{bis(trimethylsily)methyl}acetatophosphane]pentacarbonyl tungsten complex (**45f**) (GSTR096, Greg919).

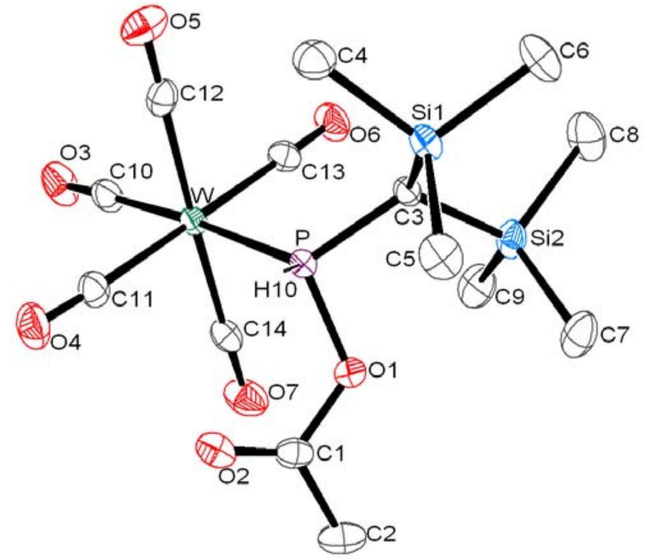

Table 1. Crystal data and structure refinement for **45f**.

Identification code	GSTR096, Greg919
Device Type	Nonius KappaCCD
Empirical formula	C14 H23 O7 P Si2 W
Formula weight	574.32
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, C 2 2 21
Unit cell dimensions	a = 9.1768(3) A α = 90 deg. b = 16.9657(6) A β = 90 deg. c = 27.8831(11) A γ = 90 deg.
Volume	4341.1(3) A^3
Z, Calculated density	8, 1.757 Mg/m^3
Absorption coefficient	5.535 mm^-1
F(000)	2240
Crystal size	0.47 x 0.24 x 0.20 mm

Theta range for data collection	2.81 to 28.00 deg.
Limiting indices	-9<=h<=12, -20<=k<=22, -31<=l<=36
Reflections collected / unique	11916 / 5203 [R(int) = 0.0357]
Completeness to theta = 28.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.35252 and 0.23539
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5203 / 0 / 237
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0201, wR2 = 0.0438
R indices (all data)	R1 = 0.0214, wR2 = 0.0442
Absolute structure parameter	-0.009(5)
Largest diff. peak and hole	0.746 and -0.732 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **45f**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7136(4)	6679(2)	7154(1)	24(1)
C(2)	8015(4)	7412(2)	7220(2)	37(1)
C(3)	5605(3)	5890(2)	5911(1)	18(1)
C(4)	2796(4)	4957(2)	6071(1)	31(1)
C(5)	2815(4)	6734(2)	6289(1)	30(1)
C(6)	2891(4)	6146(2)	5260(1)	36(1)
C(7)	6010(5)	7701(2)	5746(2)	35(1)
C(8)	6398(4)	6524(3)	4926(1)	40(1)
C(9)	8663(4)	6613(2)	5699(2)	37(1)
C(10)	9103(4)	3602(2)	6839(1)	29(1)

C(11)	7009(4)	4490(2)	7355(1)	25(1)
C(12)	6169(4)	3774(2)	6458(1)	26(1)
C(13)	8611(3)	4532(2)	5984(1)	25(1)
C(14)	9421(4)	5288(2)	6862(1)	25(1)
O(1)	6868(2)	6541(1)	6677(1)	23(1)
O(2)	6719(3)	6245(2)	7461(1)	31(1)
O(3)	9841(3)	3090(2)	6948(1)	40(1)
O(4)	6576(3)	4438(2)	7733(1)	36(1)
O(5)	5263(3)	3359(2)	6339(1)	40(1)
O(6)	9082(3)	4532(2)	5602(1)	35(1)
O(7)	10291(3)	5735(2)	6966(1)	41(1)
P	6198(1)	5661(1)	6516(1)	17(1)
Si(1)	3521(1)	5943(1)	5886(1)	21(1)
Si(2)	6660(1)	6692(1)	5584(1)	24(1)
W	7812(1)	4516(1)	6667(1)	18(1)

Table 3. Bond lengths [A] and angles [deg] for **45f**.

C(1)-O(2)	1.191(4)
C(1)-O(1)	1.375(4)
C(1)-C(2)	1.492(5)
C(2)-H(2C)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2A)	0.9800
C(3)-P	1.813(3)
C(3)-Si(2)	1.904(3)
C(3)-Si(1)	1.916(3)
C(3)-H(3A)	1.0000
C(4)-Si(1)	1.872(4)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-Si(1)	1.865(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-Si(1)	1.872(4)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-Si(2)	1.868(4)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800

C(7)-H(7C)	0.9800
C(8)-Si(2)	1.870(4)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-Si(2)	1.871(4)
C(9)-H(9C)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9A)	0.9800
C(10)-O(3)	1.143(4)
C(10)-W	2.010(4)
C(11)-O(4)	1.130(4)
C(11)-W	2.054(3)
C(12)-O(5)	1.138(4)
C(12)-W	2.050(4)
C(13)-O(6)	1.149(4)
C(13)-W	2.042(3)
C(14)-O(7)	1.138(4)
C(14)-W	2.047(4)
O(1)-P	1.676(2)
P-W	2.4780(8)
P-H(10)	1.35(3)

O(2)-C(1)-O(1)	122.1(3)
O(2)-C(1)-C(2)	126.9(3)
O(1)-C(1)-C(2)	111.0(3)
C(1)-C(2)-H(2C)	109.5
C(1)-C(2)-H(2B)	109.5
H(2C)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2A)	109.5
H(2C)-C(2)-H(2A)	109.5
H(2B)-C(2)-H(2A)	109.5
P-C(3)-Si(2)	116.52(17)
P-C(3)-Si(1)	110.12(16)
Si(2)-C(3)-Si(1)	117.14(16)
P-C(3)-H(3A)	103.7
Si(2)-C(3)-H(3A)	103.7
Si(1)-C(3)-H(3A)	103.7
Si(1)-C(4)-H(4A)	109.5
Si(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
Si(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5

Si(1)-C(5)-H(5A)	109.5
Si(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Si(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
Si(1)-C(6)-H(6A)	109.5
Si(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
Si(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
Si(2)-C(7)-H(7A)	109.5
Si(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
Si(2)-C(8)-H(8A)	109.5
Si(2)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
Si(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
Si(2)-C(9)-H(9C)	109.5
Si(2)-C(9)-H(9B)	109.5
H(9C)-C(9)-H(9B)	109.5
Si(2)-C(9)-H(9A)	109.5
H(9C)-C(9)-H(9A)	109.5
H(9B)-C(9)-H(9A)	109.5
O(3)-C(10)-W	178.3(3)
O(4)-C(11)-W	176.8(3)
O(5)-C(12)-W	179.6(4)
O(6)-C(13)-W	178.8(3)
O(7)-C(14)-W	178.0(3)
C(1)-O(1)-P	118.5(2)
O(1)-P-C(3)	99.66(14)
O(1)-P-W	115.68(8)
C(3)-P-W	120.37(11)
O(1)-P-H(10)	96.8(13)
C(3)-P-H(10)	101.3(13)
W-P-H(10)	118.9(13)
C(5)-Si(1)-C(6)	108.81(18)
C(5)-Si(1)-C(4)	110.71(17)

C(6)-Si(1)-C(4)	108.12(18)
C(5)-Si(1)-C(3)	111.01(16)
C(6)-Si(1)-C(3)	110.55(16)
C(4)-Si(1)-C(3)	107.61(16)
C(7)-Si(2)-C(8)	109.64(19)
C(7)-Si(2)-C(9)	109.7(2)
C(8)-Si(2)-C(9)	106.49(19)
C(7)-Si(2)-C(3)	112.10(16)
C(8)-Si(2)-C(3)	107.24(17)
C(9)-Si(2)-C(3)	111.46(16)
C(10)-W-C(13)	91.18(14)
C(10)-W-C(14)	90.27(15)
C(13)-W-C(14)	88.83(14)
C(10)-W-C(12)	91.56(15)
C(13)-W-C(12)	90.34(14)
C(14)-W-C(12)	178.00(15)
C(10)-W-C(11)	88.37(14)
C(13)-W-C(11)	179.47(16)
C(14)-W-C(11)	91.46(14)
C(12)-W-C(11)	89.38(14)
C(10)-W-P	176.00(10)
C(13)-W-P	92.63(10)
C(14)-W-P	88.58(10)
C(12)-W-P	89.64(10)
C(11)-W-P	87.82(10)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **45f**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	22(1)	24(2)	26(2)	-8(1)	-1(2)	4(2)
C(2)	34(2)	35(2)	42(2)	-14(2)	-6(2)	-7(2)
C(3)	21(2)	19(2)	15(2)	-1(1)	-1(1)	2(1)
C(4)	27(2)	36(2)	31(2)	-2(2)	-2(2)	-8(2)
C(5)	25(2)	36(2)	29(2)	-2(2)	3(2)	7(2)
C(6)	34(2)	51(2)	25(2)	3(2)	-11(2)	5(2)
C(7)	46(2)	25(2)	34(2)	5(2)	17(2)	3(2)
C(8)	45(2)	51(3)	25(2)	6(2)	12(2)	4(2)
C(9)	33(2)	37(2)	42(2)	6(2)	9(2)	-9(2)
C(10)	37(2)	29(2)	20(2)	-3(2)	-1(2)	6(2)
C(11)	28(2)	24(2)	22(2)	1(1)	0(1)	6(2)
C(12)	28(2)	20(2)	28(2)	3(1)	3(2)	3(1)

C(13)	22(2)	28(2)	25(2)	-3(2)	-3(1)	0(2)
C(14)	24(2)	34(2)	19(2)	-1(1)	2(1)	3(1)
O(1)	26(1)	19(1)	22(1)	-2(1)	-2(1)	-2(1)
O(2)	35(1)	35(2)	23(1)	-6(1)	-2(1)	0(1)
O(3)	49(2)	42(2)	30(2)	1(1)	-3(1)	26(1)
O(4)	47(2)	37(2)	24(1)	6(1)	9(1)	6(1)
O(5)	35(2)	31(2)	55(2)	-4(1)	-2(1)	-9(1)
O(6)	38(1)	45(2)	22(1)	0(1)	6(1)	-3(1)
O(7)	33(1)	57(2)	33(2)	-8(1)	-2(1)	-14(1)
P	18(1)	18(1)	15(1)	0(1)	-1(1)	0(1)
Si(1)	21(1)	26(1)	17(1)	1(1)	-3(1)	2(1)
Si(2)	29(1)	23(1)	21(1)	4(1)	8(1)	3(1)
W	20(1)	20(1)	16(1)	0(1)	-1(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for**45f**.

	x	y	z	U(eq)
H(2C)	8032	7554	7561	55
H(2B)	7577	7842	7035	55
H(2A)	9013	7320	7108	55
H(3A)	5840	5401	5727	22
H(4A)	3071	4851	6404	47
H(4B)	3205	4548	5862	47
H(4C)	1731	4957	6043	47
H(5A)	3164	7247	6176	45
H(5B)	3163	6642	6616	45
H(5C)	1747	6727	6285	45
H(6A)	3319	5757	5041	55
H(6B)	3199	6676	5164	55
H(6C)	1826	6110	5246	55
H(7A)	6026	7762	6096	53
H(7B)	5013	7774	5628	53
H(7C)	6651	8095	5600	53
H(8A)	5395	6658	4837	60
H(8B)	6585	5969	4851	60
H(8C)	7077	6857	4746	60
H(9C)	9168	7052	5542	56
H(9B)	9026	6113	5570	56
H(9A)	8844	6632	6045	56
H(10)	4930(30)	5716(18)	6760(11)	12(8)

Table 6. Torsion angles [deg] for **45f**.

O(2)-C(1)-O(1)-P	-11.0(4)
C(2)-C(1)-O(1)-P	167.8(2)
C(1)-O(1)-P-C(3)	165.2(2)
C(1)-O(1)-P-W	-64.2(2)
Si(2)-C(3)-P-O(1)	29.17(19)
Si(1)-C(3)-P-O(1)	-107.36(16)
Si(2)-C(3)-P-W	-98.36(17)
Si(1)-C(3)-P-W	125.11(12)
P-C(3)-Si(1)-C(5)	61.0(2)
Si(2)-C(3)-Si(1)-C(5)	-75.2(2)
P-C(3)-Si(1)-C(6)	-178.11(18)
Si(2)-C(3)-Si(1)-C(6)	45.7(2)
P-C(3)-Si(1)-C(4)	-60.2(2)
Si(2)-C(3)-Si(1)-C(4)	163.52(17)
P-C(3)-Si(2)-C(7)	-83.0(2)
Si(1)-C(3)-Si(2)-C(7)	50.5(2)
P-C(3)-Si(2)-C(8)	156.64(19)
Si(1)-C(3)-Si(2)-C(8)	-69.9(2)
P-C(3)-Si(2)-C(9)	40.5(3)
Si(1)-C(3)-Si(2)-C(9)	173.92(19)
O(3)-C(10)-W-C(13)	145(13)
O(3)-C(10)-W-C(14)	56(13)
O(3)-C(10)-W-C(12)	-125(13)
O(3)-C(10)-W-C(11)	-35(13)
O(3)-C(10)-W-P	-17(14)
O(6)-C(13)-W-C(10)	-15(17)
O(6)-C(13)-W-C(14)	75(17)
O(6)-C(13)-W-C(12)	-107(17)
O(6)-C(13)-W-C(11)	-48(26)
O(6)-C(13)-W-P	164(17)
O(7)-C(14)-W-C(10)	176(100)
O(7)-C(14)-W-C(13)	85(9)
O(7)-C(14)-W-C(12)	19(12)
O(7)-C(14)-W-C(11)	-95(9)
O(7)-C(14)-W-P	-8(9)
O(5)-C(12)-W-C(10)	-66(65)
O(5)-C(12)-W-C(13)	25(65)
O(5)-C(12)-W-C(14)	91(65)
O(5)-C(12)-W-C(11)	-154(100)
O(5)-C(12)-W-P	118(100)
O(4)-C(11)-W-C(10)	-34(5)

O(4)-C(11)-W-C(13)	-1(18)
O(4)-C(11)-W-C(14)	-124(5)
O(4)-C(11)-W-C(12)	58(5)
O(4)-C(11)-W-P	148(5)
O(1)-P-W-C(10)	66.6(16)
C(3)-P-W-C(10)	-173.6(16)
O(1)-P-W-C(13)	-95.49(14)
C(3)-P-W-C(13)	24.34(15)
O(1)-P-W-C(14)	-6.72(13)
C(3)-P-W-C(14)	113.11(16)
O(1)-P-W-C(12)	174.19(14)
C(3)-P-W-C(12)	-65.98(15)
O(1)-P-W-C(11)	84.79(14)
C(3)-P-W-C(11)	-155.38(16)

5. Crystal data of molecule [{bis(trimethylsily)methyl}-2,6-dimethylphenoxylphosphane] pentacarbonyl tungsten complex (**45d**) (GSTR082, Greg803).

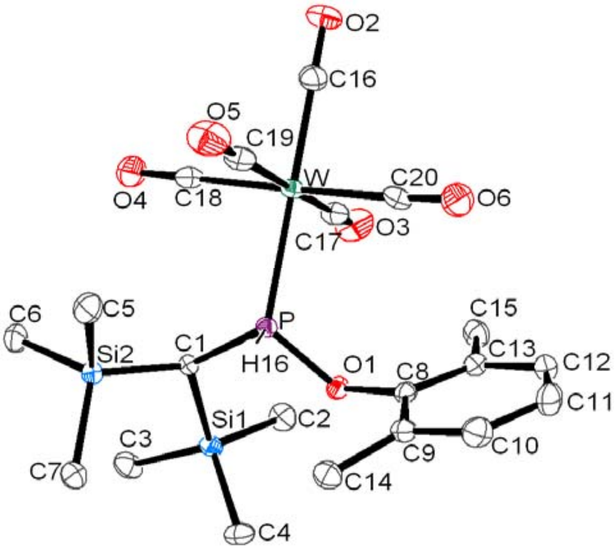

Table 1. Crystal data and structure refinement for **45d**.

Identification code	GSTR082, Greg803
Device Type	Nonius KappaCCD
Empirical formula	C20 H29 O6 P Si2 W
Formula weight	636.43

Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.4714(2) A α = 96.4330(10) ° b = 9.9051(3) A β = 103.0160(10) ° c = 15.0145(3) A γ = 111.9870(10) °
Volume	1242.16(5) A^3
Z, Calculated density	2, 1.702 Mg/m^3
Absorption coefficient	4.842 mm^-1
F(000)	628
Crystal size	0.60 x 0.59 x 0.40 mm
Theta range for data collection	3.15 to 27.99 deg.
Limiting indices	-12<=h<=11, -12<=k<=13, -19<=l<=19
Reflections collected / unique	16042 / 5921 [R(int) = 0.0513]
Completeness to theta = 27.99	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.1423 and 0.0826
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5921 / 0 / 284
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0635
R indices (all data)	R1 = 0.0253, wR2 = 0.0640
Extinction coefficient	0.0151(6)

Largest diff. peak and hole	2.244 and -1.767 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **45d**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	9532(3)	-2814(3)	2553(2)	15(1)
C(2)	11444(3)	-2155(3)	4622(2)	25(1)
C(3)	8281(3)	-4792(3)	3887(2)	26(1)
C(4)	8347(3)	-1699(3)	4189(2)	24(1)
C(5)	7592(4)	-3280(4)	449(2)	28(1)
C(6)	7296(4)	-5910(3)	1329(2)	28(1)
C(7)	5872(3)	-3717(3)	1922(2)	24(1)
C(8)	11629(3)	1671(3)	3318(2)	16(1)
C(9)	10506(3)	2216(3)	2956(2)	18(1)
C(10)	11060(3)	3731(3)	2964(2)	25(1)
C(11)	12651(4)	4690(3)	3356(2)	28(1)
C(12)	13715(3)	4132(3)	3772(2)	23(1)
C(13)	13235(3)	2622(3)	3768(2)	18(1)
C(14)	8736(3)	1255(3)	2604(2)	23(1)
C(15)	14414(3)	2060(3)	4234(2)	24(1)
C(16)	14529(3)	-906(3)	969(2)	25(1)
C(17)	14145(4)	-998(4)	2799(2)	25(1)
C(18)	11849(3)	-3214(4)	1220(2)	24(1)
C(19)	11393(4)	-1027(4)	265(2)	26(1)
C(20)	13595(4)	1311(4)	1762(2)	29(1)
O(1)	11143(2)	142(2)	3301(1)	16(1)
O(2)	15523(3)	-902(3)	664(2)	32(1)
O(3)	14906(3)	-1088(3)	3479(2)	39(1)
O(4)	11310(3)	-4501(3)	1030(2)	35(1)
O(5)	10651(3)	-1070(3)	-453(2)	40(1)
O(6)	14031(4)	2579(3)	1821(2)	45(1)
P	10661(1)	-1049(1)	2301(1)	14(1)
Si(1)	9392(1)	-2818(1)	3805(1)	17(1)
Si(2)	7565(1)	-3923(1)	1575(1)	18(1)
W	12777(1)	-958(1)	1548(1)	17(1)

Table 3. Bond lengths [A] and angles [deg] for **45d**.

C(1)-P	1.810(3)

C(1)-Si(1)	1.914(2)
C(1)-Si(2)	1.926(2)
C(1)-H(1A)	1.0000
C(2)-Si(1)	1.871(3)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-Si(1)	1.875(3)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-Si(1)	1.865(3)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-Si(2)	1.874(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-Si(2)	1.870(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-Si(2)	1.865(3)
C(7)-H(7C)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7A)	0.9800
C(8)-C(9)	1.398(4)
C(8)-O(1)	1.404(3)
C(8)-C(13)	1.407(3)
C(9)-C(10)	1.390(4)
C(9)-C(14)	1.513(3)
C(10)-C(11)	1.387(4)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.387(4)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.390(4)
C(12)-H(12A)	0.9500
C(13)-C(15)	1.499(4)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15C)	0.9800
C(15)-H(15B)	0.9800

C(15)-H(15A)	0.9800
C(16)-O(2)	1.134(4)
C(16)-W	2.027(3)
C(17)-O(3)	1.142(4)
C(17)-W	2.042(3)
C(18)-O(4)	1.155(4)
C(18)-W	2.024(3)
C(19)-O(5)	1.133(4)
C(19)-W	2.050(3)
C(20)-O(6)	1.152(4)
C(20)-W	2.043(3)
O(1)-P	1.6571(18)
P-W	2.4918(6)
P-H(16)	1.27(3)
P-C(1)-Si(1)	117.62(12)
P-C(1)-Si(2)	111.18(13)
Si(1)-C(1)-Si(2)	115.57(12)
P-C(1)-H(1A)	103.4
Si(1)-C(1)-H(1A)	103.4
Si(2)-C(1)-H(1A)	103.4
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
Si(1)-C(3)-H(3A)	109.5
Si(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
Si(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
Si(1)-C(4)-H(4A)	109.5
Si(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
Si(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
Si(2)-C(5)-H(5A)	109.5
Si(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Si(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5

H(5B)-C(5)-H(5C)	109.5
Si(2)-C(6)-H(6A)	109.5
Si(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
Si(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
Si(2)-C(7)-H(7C)	109.5
Si(2)-C(7)-H(7B)	109.5
H(7C)-C(7)-H(7B)	109.5
Si(2)-C(7)-H(7A)	109.5
H(7C)-C(7)-H(7A)	109.5
H(7B)-C(7)-H(7A)	109.5
C(9)-C(8)-O(1)	119.9(2)
C(9)-C(8)-C(13)	122.1(2)
O(1)-C(8)-C(13)	117.9(2)
C(10)-C(9)-C(8)	117.4(2)
C(10)-C(9)-C(14)	119.3(2)
C(8)-C(9)-C(14)	123.2(2)
C(11)-C(10)-C(9)	121.8(3)
C(11)-C(10)-H(10A)	119.1
C(9)-C(10)-H(10A)	119.1
C(12)-C(11)-C(10)	119.3(3)
C(12)-C(11)-H(11A)	120.4
C(10)-C(11)-H(11A)	120.4
C(11)-C(12)-C(13)	121.4(2)
C(11)-C(12)-H(12A)	119.3
C(13)-C(12)-H(12A)	119.3
C(12)-C(13)-C(8)	117.7(2)
C(12)-C(13)-C(15)	120.0(2)
C(8)-C(13)-C(15)	122.4(2)
C(9)-C(14)-H(14A)	109.5
C(9)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(9)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15C)	109.5
C(13)-C(15)-H(15B)	109.5
H(15C)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15A)	109.5
H(15C)-C(15)-H(15A)	109.5
H(15B)-C(15)-H(15A)	109.5
O(2)-C(16)-W	177.8(3)

O(3)-C(17)-W	176.6(3)
O(4)-C(18)-W	179.6(3)
O(5)-C(19)-W	178.5(3)
O(6)-C(20)-W	175.6(3)
C(8)-O(1)-P	119.79(15)
O(1)-P-C(1)	102.37(10)
O(1)-P-W	119.03(7)
C(1)-P-W	117.04(8)
O(1)-P-H(16)	97.2(16)
C(1)-P-H(16)	103.3(16)
W-P-H(16)	114.9(16)
C(4)-Si(1)-C(2)	110.52(13)
C(4)-Si(1)-C(3)	107.78(14)
C(2)-Si(1)-C(3)	106.57(14)
C(4)-Si(1)-C(1)	114.28(12)
C(2)-Si(1)-C(1)	108.84(12)
C(3)-Si(1)-C(1)	108.54(12)
C(7)-Si(2)-C(6)	112.36(14)
C(7)-Si(2)-C(5)	107.02(14)
C(6)-Si(2)-C(5)	106.55(15)
C(7)-Si(2)-C(1)	110.66(11)
C(6)-Si(2)-C(1)	107.65(13)
C(5)-Si(2)-C(1)	112.60(12)
C(18)-W-C(16)	89.22(12)
C(18)-W-C(17)	88.89(12)
C(16)-W-C(17)	89.30(11)
C(18)-W-C(20)	174.84(11)
C(16)-W-C(20)	90.55(12)
C(17)-W-C(20)	96.26(13)
C(18)-W-C(19)	88.30(13)
C(16)-W-C(19)	89.55(12)
C(17)-W-C(19)	176.98(11)
C(20)-W-C(19)	86.55(13)
C(18)-W-P	90.20(8)
C(16)-W-P	178.25(9)
C(17)-W-P	89.03(8)
C(20)-W-P	90.17(9)
C(19)-W-P	92.08(8)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **45d**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12

C(1)	14(1)	13(1)	17(1)	2(1)	6(1)	4(1)
C(2)	24(1)	30(2)	21(1)	8(1)	3(1)	11(1)
C(3)	28(1)	24(1)	32(1)	14(1)	14(1)	9(1)
C(4)	26(1)	31(2)	19(1)	5(1)	10(1)	15(1)
C(5)	27(1)	33(2)	17(1)	2(1)	3(1)	8(1)
C(6)	24(1)	18(1)	36(2)	-4(1)	8(1)	4(1)
C(7)	17(1)	26(1)	26(1)	0(1)	4(1)	7(1)
C(8)	19(1)	14(1)	15(1)	3(1)	8(1)	6(1)
C(9)	19(1)	19(1)	18(1)	4(1)	7(1)	8(1)
C(10)	29(1)	23(1)	30(1)	9(1)	11(1)	14(1)
C(11)	34(2)	15(1)	34(2)	5(1)	12(1)	7(1)
C(12)	20(1)	19(1)	24(1)	0(1)	9(1)	2(1)
C(13)	18(1)	18(1)	17(1)	1(1)	6(1)	6(1)
C(14)	18(1)	25(1)	26(1)	4(1)	4(1)	10(1)
C(15)	18(1)	26(1)	23(1)	4(1)	2(1)	6(1)
C(16)	25(1)	28(2)	20(1)	6(1)	8(1)	8(1)
C(17)	24(1)	27(2)	27(1)	6(1)	13(1)	11(1)
C(18)	23(1)	28(2)	23(1)	4(1)	12(1)	10(1)
C(19)	28(1)	29(2)	24(1)	9(1)	15(1)	10(1)
C(20)	28(1)	28(2)	29(1)	6(1)	19(1)	3(1)
O(1)	19(1)	14(1)	14(1)	3(1)	5(1)	6(1)
O(2)	27(1)	42(1)	33(1)	12(1)	18(1)	16(1)
O(3)	44(1)	51(2)	28(1)	8(1)	4(1)	31(1)
O(4)	41(1)	21(1)	44(1)	3(1)	19(1)	11(1)
O(5)	39(1)	56(2)	26(1)	18(1)	10(1)	20(1)
O(6)	64(2)	22(1)	50(2)	10(1)	37(1)	7(1)
P	13(1)	14(1)	13(1)	3(1)	4(1)	5(1)
Si(1)	17(1)	19(1)	16(1)	6(1)	7(1)	7(1)
Si(2)	15(1)	17(1)	19(1)	0(1)	4(1)	4(1)
W	17(1)	19(1)	16(1)	5(1)	9(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **45d**.

	x	y	z	U(eq)
H(1A)	10174	-3402	2483	18
H(2A)	12056	-1107	4624	38
H(2B)	11971	-2761	4414	38
H(2C)	11378	-2248	5256	38
H(3A)	8861	-5387	3745	40
H(3B)	7218	-5211	3437	40
H(3C)	8184	-4810	4522	40

H(4A)	7259	-2092	3772	36
H(4B)	8917	-655	4165	36
H(4C)	8317	-1761	4832	36
H(5A)	8506	-3316	262	42
H(5B)	7676	-2254	536	42
H(5C)	6607	-3933	-40	42
H(6A)	7261	-6300	1900	42
H(6B)	8187	-5968	1125	42
H(6C)	6298	-6504	835	42
H(7C)	4900	-4214	1396	36
H(7B)	6105	-2656	2093	36
H(7A)	5724	-4173	2459	36
H(10A)	10328	4121	2694	31
H(11A)	13008	5718	3339	34
H(12A)	14795	4796	4067	27
H(14A)	8500	335	2840	34
H(14B)	8399	1007	1918	34
H(14C)	8162	1801	2827	34
H(15C)	15213	2832	4771	36
H(15B)	14938	1817	3787	36
H(15A)	13861	1163	4450	36
H(16)	9590(40)	-710(40)	1840(20)	25(9)

Table 6. Torsion angles [deg] for **45d**.

O(1)-C(8)-C(9)-C(10)	-178.0(2)
C(13)-C(8)-C(9)-C(10)	6.9(4)
O(1)-C(8)-C(9)-C(14)	4.8(4)
C(13)-C(8)-C(9)-C(14)	-170.2(2)
C(8)-C(9)-C(10)-C(11)	-3.2(4)
C(14)-C(9)-C(10)-C(11)	174.1(3)
C(9)-C(10)-C(11)-C(12)	-1.6(4)
C(10)-C(11)-C(12)-C(13)	2.9(4)
C(11)-C(12)-C(13)-C(8)	0.6(4)
C(11)-C(12)-C(13)-C(15)	-179.3(3)
C(9)-C(8)-C(13)-C(12)	-5.7(4)
O(1)-C(8)-C(13)-C(12)	179.2(2)
C(9)-C(8)-C(13)-C(15)	174.3(2)
O(1)-C(8)-C(13)-C(15)	-0.9(3)
C(9)-C(8)-O(1)-P	74.6(3)
C(13)-C(8)-O(1)-P	-110.1(2)
C(8)-O(1)-P-C(1)	-161.76(18)
C(8)-O(1)-P-W	67.40(18)
Si(1)-C(1)-P-O(1)	-4.78(16)

Si(2)-C(1)-P-O(1)	131.70(12)
Si(1)-C(1)-P-W	127.27(11)
Si(2)-C(1)-P-W	-96.26(12)
P-C(1)-Si(1)-C(4)	63.41(17)
Si(2)-C(1)-Si(1)-C(4)	-71.20(17)
P-C(1)-Si(1)-C(2)	-60.66(18)
Si(2)-C(1)-Si(1)-C(2)	164.72(14)
P-C(1)-Si(1)-C(3)	-176.28(14)
Si(2)-C(1)-Si(1)-C(3)	49.11(18)
P-C(1)-Si(2)-C(7)	-100.03(15)
Si(1)-C(1)-Si(2)-C(7)	37.41(18)
P-C(1)-Si(2)-C(6)	136.84(14)
Si(1)-C(1)-Si(2)-C(6)	-85.73(16)
P-C(1)-Si(2)-C(5)	19.69(19)
Si(1)-C(1)-Si(2)-C(5)	157.12(15)
O(4)-C(18)-W-C(16)	-123(40)
O(4)-C(18)-W-C(17)	147(40)
O(4)-C(18)-W-C(20)	-36(40)
O(4)-C(18)-W-C(19)	-34(40)
O(4)-C(18)-W-P	58(40)
O(2)-C(16)-W-C(18)	-59(7)
O(2)-C(16)-W-C(17)	30(7)
O(2)-C(16)-W-C(20)	127(7)
O(2)-C(16)-W-C(19)	-147(7)
O(2)-C(16)-W-P	12(10)
O(3)-C(17)-W-C(18)	26(5)
O(3)-C(17)-W-C(16)	-63(5)
O(3)-C(17)-W-C(20)	-154(5)
O(3)-C(17)-W-C(19)	4(6)
O(3)-C(17)-W-P	116(5)
O(6)-C(20)-W-C(18)	-23(5)
O(6)-C(20)-W-C(16)	65(4)
O(6)-C(20)-W-C(17)	154(4)
O(6)-C(20)-W-C(19)	-25(4)
O(6)-C(20)-W-P	-117(4)
O(5)-C(19)-W-C(18)	-80(12)
O(5)-C(19)-W-C(16)	9(12)
O(5)-C(19)-W-C(17)	-59(12)
O(5)-C(19)-W-C(20)	99(12)
O(5)-C(19)-W-P	-171(12)
O(1)-P-W-C(18)	138.94(12)
C(1)-P-W-C(18)	15.00(12)
O(1)-P-W-C(16)	68(3)
C(1)-P-W-C(16)	-56(3)

O(1)-P-W-C(17)	50.06(12)
C(1)-P-W-C(17)	-73.89(12)
O(1)-P-W-C(20)	-46.20(12)
C(1)-P-W-C(20)	-170.15(13)
O(1)-P-W-C(19)	-132.75(12)
C(1)-P-W-C(19)	103.30(13)

6. Crystal data of molecule [{bis(trimethylsily)methyl}-*n*-butylphosphane] pentacarbonyl tungsten complex (**45e**) (joerg88)

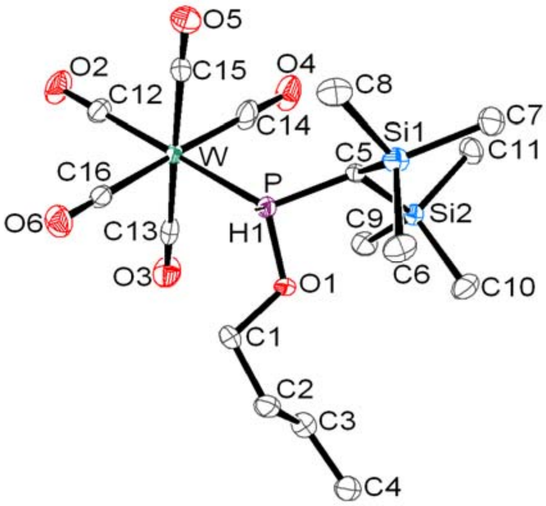

Table 1. Crystal data and structure refinement for **45e**.

Identification code	joerg88
Empirical formula	C16 H29 O6 P Si2 W
Formula weight	588.39
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P212121
Unit cell dimensions	a = 11.1201(3) A alpha = 90 deg. b = 11.9397(3) A beta = 90 deg. c = 17.9401(4) A gamma = 90 deg.

Volume	2381.92(10) A^3
Z, Calculated density	4, 1.641 Mg/m^3
Absorption coefficient	5.043 mm^-1
F(000)	1160
Crystal size	0.33 x 0.24 x 0.22 mm
Theta range for data collection	2.92 to 27.49 deg.
Limiting indices	-14<=h<=13, -15<=k<=13, -23<=l<=20
Reflections collected / unique	17207 / 5328 [R(int) = 0.0359]
Completeness to theta = 27.49	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4034 and 0.2869
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5328 / 0 / 351
Goodness-of-fit on F^2	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0214, wR2 = 0.0370
R indices (all data)	R1 = 0.0282, wR2 = 0.0385
Absolute structure parameter	-0.022(5)
Largest diff. peak and hole	1.217 and -0.962 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **45e**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W	1402(1)	916(1)	7511(1)	18(1)
P	2796(1)	784(1)	8583(1)	17(1)

Si(1)	4634(1)	2291(1)	9345(1)	21(1)
Si(2)	5497(1)	283(1)	8247(1)	18(1)
O(1)	3102(2)	-409(2)	8970(1)	23(1)
C(1)	2136(3)	-1043(3)	9308(2)	26(1)
C(2)	2705(3)	-1896(3)	9817(2)	25(1)
C(3)	3490(4)	-2749(3)	9418(2)	26(1)
C(4)	4176(4)	-3493(3)	9960(2)	32(1)
C(5)	4299(3)	1351(3)	8518(2)	16(1)
C(6)	4499(4)	1495(3)	10236(2)	29(1)
C(7)	6170(4)	2892(4)	9267(2)	29(1)
C(8)	3538(4)	3484(3)	9336(2)	31(1)
C(9)	4904(3)	-849(3)	7640(2)	26(1)
C(10)	6199(4)	-382(3)	9078(2)	29(1)
C(11)	6641(3)	1041(3)	7686(2)	28(1)
C(12)	181(3)	1086(3)	6680(2)	27(1)
C(13)	1412(3)	-786(3)	7344(2)	25(1)
C(14)	2820(3)	1087(3)	6813(2)	32(1)
C(15)	1425(3)	2608(3)	7648(2)	28(1)
C(16)	40(3)	763(3)	8265(2)	22(1)
O(2)	-509(3)	1191(2)	6213(1)	42(1)
O(3)	1412(2)	-1721(2)	7243(1)	37(1)
O(4)	3647(2)	1207(3)	6434(2)	47(1)
O(5)	1454(2)	3562(2)	7715(2)	49(1)
O(6)	-705(2)	695(2)	8701(1)	34(1)

Table 3. Bond lengths [A] and angles [deg] for **45e**.

W-C(14)	2.023(4)
W-C(12)	2.027(4)
W-C(15)	2.035(3)
W-C(16)	2.039(4)
W-C(13)	2.053(3)
W-P	2.4750(8)
P-O(1)	1.621(2)
P-C(5)	1.807(3)
P-H(1)	1.34(3)
Si(1)-C(7)	1.858(4)
Si(1)-C(6)	1.865(4)
Si(1)-C(8)	1.875(4)
Si(1)-C(5)	1.897(3)
Si(2)-C(9)	1.856(4)
Si(2)-C(11)	1.858(4)
Si(2)-C(10)	1.861(4)
Si(2)-C(5)	1.907(3)

O(1)-C(1)	1.448(4)
C(1)-C(2)	1.507(5)
C(1)-H(2A)	0.99(4)
C(1)-H(2B)	0.98(3)
C(2)-C(3)	1.521(5)
C(2)-H(3A)	1.12(3)
C(2)-H(3B)	0.95(4)
C(3)-C(4)	1.522(5)
C(3)-H(4A)	1.12(4)
C(3)-H(4B)	0.96(3)
C(4)-H(5A)	0.97(4)
C(4)-H(5B)	1.05(4)
C(4)-H(5C)	0.92(5)
C(5)-H(6)	1.01(3)
C(6)-H(7A)	0.99(5)
C(6)-H(7B)	0.93(4)
C(6)-H(7C)	1.00(5)
C(7)-H(8A)	0.94(4)
C(7)-H(8B)	1.03(4)
C(7)-H(8C)	0.93(4)
C(8)-H(9A)	1.03(5)
C(8)-H(9B)	0.93(4)
C(8)-H(9C)	0.96(4)
C(9)-H(10A)	0.96(4)
C(9)-H(10B)	0.87(4)
C(9)-H(10C)	0.94(4)
C(10)-H(11A)	0.96(3)
C(10)-H(11B)	0.92(5)
C(10)-H(11C)	0.95(5)
C(11)-H(12A)	0.94(4)
C(11)-H(12B)	1.02(3)
C(11)-H(12C)	0.87(4)
C(12)-O(2)	1.142(4)
C(13)-O(3)	1.131(4)
C(14)-O(4)	1.153(4)
C(15)-O(5)	1.146(4)
C(16)-O(6)	1.142(4)

C(14)-W-C(12)	93.27(14)
C(14)-W-C(15)	87.99(15)
C(12)-W-C(15)	89.91(15)
C(14)-W-C(16)	176.57(13)
C(12)-W-C(16)	90.01(13)
C(15)-W-C(16)	91.01(14)

C(14)-W-C(13)	90.33(15)
C(12)-W-C(13)	89.76(14)
C(15)-W-C(13)	178.27(12)
C(16)-W-C(13)	90.69(14)
C(14)-W-P	89.92(10)
C(12)-W-P	175.98(11)
C(15)-W-P	87.76(9)
C(16)-W-P	86.76(10)
C(13)-W-P	92.67(9)
O(1)-P-C(5)	99.33(13)
O(1)-P-W	121.39(9)
C(5)-P-W	120.38(11)
O(1)-P-H(1)	95.9(13)
C(5)-P-H(1)	105.2(13)
W-P-H(1)	111.0(12)
C(7)-Si(1)-C(6)	109.6(2)
C(7)-Si(1)-C(8)	107.7(2)
C(6)-Si(1)-C(8)	110.05(18)
C(7)-Si(1)-C(5)	110.46(16)
C(6)-Si(1)-C(5)	110.67(16)
C(8)-Si(1)-C(5)	108.38(17)
C(9)-Si(2)-C(11)	106.27(17)
C(9)-Si(2)-C(10)	107.93(18)
C(11)-Si(2)-C(10)	110.79(19)
C(9)-Si(2)-C(5)	112.85(16)
C(11)-Si(2)-C(5)	106.93(16)
C(10)-Si(2)-C(5)	111.95(16)
C(1)-O(1)-P	118.9(2)
O(1)-C(1)-C(2)	107.1(3)
O(1)-C(1)-H(2A)	106(2)
C(2)-C(1)-H(2A)	113(2)
O(1)-C(1)-H(2B)	105.6(18)
C(2)-C(1)-H(2B)	117.0(19)
H(2A)-C(1)-H(2B)	107(3)
C(1)-C(2)-C(3)	114.1(3)
C(1)-C(2)-H(3A)	110.2(17)
C(3)-C(2)-H(3A)	110.2(17)
C(1)-C(2)-H(3B)	105(2)
C(3)-C(2)-H(3B)	112(2)
H(3A)-C(2)-H(3B)	104(3)
C(2)-C(3)-C(4)	112.2(3)
C(2)-C(3)-H(4A)	112(2)
C(4)-C(3)-H(4A)	105(2)
C(2)-C(3)-H(4B)	107(2)

C(4)-C(3)-H(4B)	110(2)
H(4A)-C(3)-H(4B)	111(3)
C(3)-C(4)-H(5A)	106(2)
C(3)-C(4)-H(5B)	111(2)
H(5A)-C(4)-H(5B)	107(3)
C(3)-C(4)-H(5C)	113(3)
H(5A)-C(4)-H(5C)	109(4)
H(5B)-C(4)-H(5C)	109(3)
P-C(5)-Si(1)	110.66(17)
P-C(5)-Si(2)	114.32(16)
Si(1)-C(5)-Si(2)	117.28(17)
P-C(5)-H(6)	104.7(17)
Si(1)-C(5)-H(6)	106.3(16)
Si(2)-C(5)-H(6)	102.1(16)
Si(1)-C(6)-H(7A)	110(3)
Si(1)-C(6)-H(7B)	107(2)
H(7A)-C(6)-H(7B)	114(4)
Si(1)-C(6)-H(7C)	116(3)
H(7A)-C(6)-H(7C)	108(4)
H(7B)-C(6)-H(7C)	102(3)
Si(1)-C(7)-H(8A)	113(2)
Si(1)-C(7)-H(8B)	110(2)
H(8A)-C(7)-H(8B)	101(3)
Si(1)-C(7)-H(8C)	113(2)
H(8A)-C(7)-H(8C)	106(3)
H(8B)-C(7)-H(8C)	113(3)
Si(1)-C(8)-H(9A)	114(3)
Si(1)-C(8)-H(9B)	106(2)
H(9A)-C(8)-H(9B)	111(3)
Si(1)-C(8)-H(9C)	105(2)
H(9A)-C(8)-H(9C)	110(3)
H(9B)-C(8)-H(9C)	111(3)
Si(2)-C(9)-H(10A)	109(3)
Si(2)-C(9)-H(10B)	114(3)
H(10A)-C(9)-H(10B)	98(4)
Si(2)-C(9)-H(10C)	112(2)
H(10A)-C(9)-H(10C)	113(3)
H(10B)-C(9)-H(10C)	110(4)
Si(2)-C(10)-H(11A)	109.6(19)
Si(2)-C(10)-H(11B)	107(3)
H(11A)-C(10)-H(11B)	105(3)
Si(2)-C(10)-H(11C)	112(3)
H(11A)-C(10)-H(11C)	106(3)
H(11B)-C(10)-H(11C)	117(4)

Si(2)-C(11)-H(12A)	109(2)
Si(2)-C(11)-H(12B)	113.4(17)
H(12A)-C(11)-H(12B)	109(3)
Si(2)-C(11)-H(12C)	114(3)
H(12A)-C(11)-H(12C)	103(3)
H(12B)-C(11)-H(12C)	108(3)
O(2)-C(12)-W	179.4(4)
O(3)-C(13)-W	179.1(3)
O(4)-C(14)-W	177.7(4)
O(5)-C(15)-W	178.7(3)
O(6)-C(16)-W	178.2(3)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **45e**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
W	13(1)	21(1)	19(1)	2(1)	-2(1)	1(1)
P	14(1)	19(1)	18(1)	2(1)	1(1)	1(1)
Si(1)	26(1)	20(1)	17(1)	-2(1)	-3(1)	-2(1)
Si(2)	15(1)	18(1)	21(1)	1(1)	0(1)	1(1)
O(1)	16(1)	24(1)	28(1)	14(1)	1(1)	-1(1)
C(1)	16(2)	28(2)	32(2)	9(2)	4(2)	-3(2)
C(2)	24(2)	25(2)	26(2)	8(2)	5(2)	1(2)
C(3)	24(2)	27(2)	28(2)	1(2)	1(2)	-2(2)
C(4)	24(2)	31(2)	41(2)	10(2)	5(2)	4(2)
C(5)	15(2)	18(2)	15(2)	4(1)	0(1)	-2(1)
C(6)	38(3)	31(2)	19(2)	-1(2)	-4(2)	3(2)
C(7)	30(2)	30(2)	27(2)	1(2)	-11(2)	-8(2)
C(8)	41(3)	24(2)	26(2)	-4(2)	1(2)	2(2)
C(9)	28(2)	24(2)	27(2)	-2(2)	1(2)	0(2)
C(10)	29(2)	26(2)	32(2)	2(2)	-6(2)	7(2)
C(11)	18(2)	31(2)	36(2)	1(2)	8(1)	0(2)
C(12)	23(2)	31(2)	28(2)	6(2)	-1(2)	4(2)
C(13)	13(2)	37(2)	25(2)	-3(2)	-2(1)	4(1)
C(14)	23(2)	50(3)	24(2)	8(2)	-8(2)	2(2)
C(15)	16(2)	31(2)	36(2)	10(2)	-4(2)	-3(1)
C(16)	20(2)	18(2)	28(2)	2(2)	-7(2)	1(2)
O(2)	31(2)	61(2)	34(2)	6(1)	-14(1)	7(1)
O(3)	33(1)	25(1)	54(2)	-13(1)	-3(1)	6(1)
O(4)	24(2)	87(2)	31(1)	21(2)	8(1)	9(2)
O(5)	35(2)	23(1)	91(3)	8(1)	-11(2)	-5(1)
O(6)	24(1)	44(2)	34(1)	1(1)	8(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **45e**.

	x	y	z	U(eq)
H(2A)	1640(40)	-490(40)	9580(20)	51(13)
H(2B)	1650(30)	-1330(30)	8892(18)	19(9)
H(3A)	3230(30)	-1470(30)	10266(19)	27(9)
H(3B)	2060(30)	-2240(30)	10076(18)	24(9)
H(4A)	4200(40)	-2340(30)	9070(20)	48(12)
H(4B)	2960(30)	-3190(30)	9118(18)	26(10)
H(5A)	4700(40)	-3000(30)	10240(20)	46(12)
H(5B)	4720(30)	-4070(30)	9680(20)	35(10)
H(5C)	3690(40)	-3870(30)	10290(20)	59(14)
H(6)	4280(30)	1860(20)	8065(16)	9(7)
H(7A)	3740(50)	1070(40)	10250(30)	73(16)
H(7B)	4580(40)	2010(30)	10620(20)	53(13)
H(7C)	5170(40)	960(40)	10350(30)	66(14)
H(8A)	6780(30)	2360(30)	9330(20)	28(11)
H(8B)	6330(40)	3420(30)	9710(20)	49(12)
H(8C)	6310(30)	3230(30)	8810(20)	42(12)
H(9A)	3620(40)	4000(40)	8880(30)	63(15)
H(9B)	2780(40)	3160(30)	9360(20)	40(12)
H(9C)	3700(30)	3900(30)	9780(20)	39(11)
H(10A)	5550(40)	-1330(30)	7490(30)	57(11)
H(10B)	4690(40)	-620(30)	7200(20)	51(14)
H(10C)	4270(40)	-1250(30)	7870(20)	52(13)
H(11A)	5580(30)	-700(30)	9391(17)	17(9)
H(11B)	6640(40)	-990(40)	8910(20)	50(13)
H(11C)	6610(40)	150(40)	9380(30)	65(15)
H(12A)	7000(30)	1600(30)	7980(20)	38(11)
H(12B)	7290(30)	530(20)	7480(20)	25(7)
H(12C)	6340(30)	1420(30)	7310(20)	44(13)
H(1)	2320(30)	1260(20)	9192(16)	20(8)

Table 6. Torsion angles [deg] for **45e**.

C(14)-W-P-O(1)	-102.92(16)
C(12)-W-P-O(1)	114.5(17)
C(15)-W-P-O(1)	169.09(13)
C(16)-W-P-O(1)	77.95(15)
C(13)-W-P-O(1)	-12.59(14)
C(14)-W-P-C(5)	22.40(16)
C(12)-W-P-C(5)	-120.2(16)

C(15)-W-P-C(5)	-65.60(15)
C(16)-W-P-C(5)	-156.74(17)
C(13)-W-P-C(5)	112.72(15)
C(5)-P-O(1)-C(1)	164.1(2)
W-P-O(1)-C(1)	-61.4(3)
P-O(1)-C(1)-C(2)	-162.8(2)
O(1)-C(1)-C(2)-C(3)	-63.2(4)
C(1)-C(2)-C(3)-C(4)	172.4(3)
O(1)-P-C(5)-Si(1)	-95.32(17)
W-P-C(5)-Si(1)	129.58(12)
O(1)-P-C(5)-Si(2)	39.74(19)
W-P-C(5)-Si(2)	-95.36(16)
C(7)-Si(1)-C(5)-P	-178.98(18)
C(6)-Si(1)-C(5)-P	59.5(2)
C(8)-Si(1)-C(5)-P	-61.3(2)
C(7)-Si(1)-C(5)-Si(2)	47.4(2)
C(6)-Si(1)-C(5)-Si(2)	-74.1(2)
C(8)-Si(1)-C(5)-Si(2)	165.13(19)
C(9)-Si(2)-C(5)-P	30.5(2)
C(11)-Si(2)-C(5)-P	146.96(18)
C(10)-Si(2)-C(5)-P	-91.5(2)
C(9)-Si(2)-C(5)-Si(1)	162.42(17)
C(11)-Si(2)-C(5)-Si(1)	-81.1(2)
C(10)-Si(2)-C(5)-Si(1)	40.4(2)
C(14)-W-C(12)-O(2)	-106(35)
C(15)-W-C(12)-O(2)	-18(35)
C(16)-W-C(12)-O(2)	73(35)
C(13)-W-C(12)-O(2)	164(100)
P-W-C(12)-O(2)	36(36)
C(14)-W-C(13)-O(3)	-71(19)
C(12)-W-C(13)-O(3)	22(19)
C(15)-W-C(13)-O(3)	-57(21)
C(16)-W-C(13)-O(3)	112(19)
P-W-C(13)-O(3)	-161(19)
C(12)-W-C(14)-O(4)	139(9)
C(15)-W-C(14)-O(4)	49(9)
C(16)-W-C(14)-O(4)	-24(11)
C(13)-W-C(14)-O(4)	-131(9)
P-W-C(14)-O(4)	-38(9)
C(14)-W-C(15)-O(5)	10(14)
C(12)-W-C(15)-O(5)	-83(14)
C(16)-W-C(15)-O(5)	-173(100)
C(13)-W-C(15)-O(5)	-4(17)
P-W-C(15)-O(5)	100(14)

C(14)-W-C(16)-O(6)	25(13)
C(12)-W-C(16)-O(6)	-138(11)
C(15)-W-C(16)-O(6)	-48(11)
C(13)-W-C(16)-O(6)	132(11)
P-W-C(16)-O(6)	40(11)

7. Crystal data of molecule [{bis(trimethylsily)methyl}phenoxyphosphane] pentacarbonyl tungsten complex (**45a**) (joerg153)

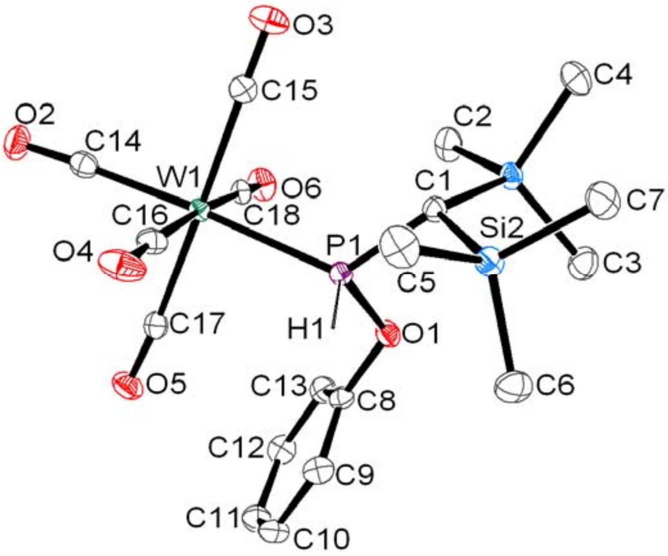

Table 1. Crystal data and structure refinement for **45a**.

Identification code	joerg153
Empirical formula	C18 H25 O6 P Si2 W
Formula weight	608.38
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.8195(2) A, α = 103.8230(10) deg.
	b = 13.38630(10) A, β = 92.7380(10) deg.
	c = 14.26660(10) A , γ = 90.3910(10) deg.

Volume	2374.19(4) A^3
Z, Calculated density	4, 1.702 Mg/m^3
Absorption coefficient	5.062 mm^-1
F(000)	1192
Crystal size	0.24 x 0.23 x 0.08 mm
Theta range for data collection	2.11 to 27.50 deg.
Limiting indices	-16<=h<=16, -17<=k<=17, -18<=l<=18
Reflections collected / unique	78053 / 10860 [R(int) = 0.0464]
Completeness to theta = 27.50	99.5 %
Absorption correction	Analytical
Max. and min. transmission	0.6875 and 0.3763
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10860 / 0 / 525
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0226, wR2 = 0.0521
R indices (all data)	R1 = 0.0270, wR2 = 0.0535
Largest diff. peak and hole	2.549 and -1.650 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **45a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W(1)	6678(1)	7597(1)	2251(1)	13(1)
W(2)	1694(1)	8551(1)	2298(1)	13(1)
P(1)	7143(1)	5957(1)	2671(1)	14(1)
P(2)	2226(1)	10399(1)	2725(1)	14(1)
Si(1)	8161(1)	4187(1)	1134(1)	16(1)

Si(2)	9034(1)	4934(1)	3373(1)	18(1)
Si(3)	3244(1)	11373(1)	1176(1)	17(1)
Si(4)	4156(1)	11760(1)	3408(1)	20(1)
O(1)	6269(1)	5005(1)	2427(1)	18(1)
O(2)	6081(2)	9779(1)	1930(1)	27(1)
O(3)	8803(2)	7528(2)	1167(1)	29(1)
O(4)	7672(2)	8707(2)	4328(1)	30(1)
O(5)	4538(2)	7741(2)	3303(1)	24(1)
O(6)	5440(1)	6435(1)	295(1)	24(1)
O(7)	1380(1)	11237(1)	2489(1)	18(1)
O(8)	1009(2)	6219(1)	1966(1)	27(1)
O(9)	2738(2)	8501(2)	4357(1)	34(1)
O(10)	3780(2)	8037(2)	1167(1)	28(1)
O(11)	449(2)	8743(1)	362(1)	26(1)
O(12)	-412(2)	8944(2)	3406(2)	31(1)
C(1)	8314(2)	5257(2)	2290(2)	15(1)
C(2)	7316(2)	4617(2)	208(2)	25(1)
C(3)	7593(2)	2989(2)	1362(2)	27(1)
C(4)	9492(2)	3944(2)	654(2)	25(1)
C(5)	9510(2)	6191(2)	4171(2)	28(1)
C(6)	8120(2)	4261(2)	4018(2)	27(1)
C(7)	10192(2)	4116(2)	3026(2)	27(1)
C(8)	5265(2)	5210(2)	2753(2)	17(1)
C(9)	5096(2)	5430(2)	3732(2)	21(1)
C(10)	4090(2)	5625(2)	4036(2)	23(1)
C(11)	3262(2)	5582(2)	3366(2)	24(1)
C(12)	3442(2)	5339(2)	2391(2)	22(1)
C(13)	4439(2)	5155(2)	2076(2)	20(1)
C(14)	6312(2)	8982(2)	2022(2)	18(1)
C(15)	8041(2)	7563(2)	1558(2)	19(1)
C(16)	7354(2)	8317(2)	3571(2)	19(1)
C(17)	5299(2)	7649(2)	2929(2)	17(1)
C(18)	5895(2)	6849(2)	988(2)	17(1)
C(19)	3404(2)	10890(2)	2329(2)	15(1)
C(20)	2382(2)	10475(2)	254(2)	25(1)
C(21)	2685(2)	12685(2)	1406(2)	29(1)
C(22)	4566(2)	11387(2)	680(2)	26(1)
C(23)	3278(2)	12783(2)	4056(2)	31(1)
C(24)	5326(2)	12400(2)	3054(2)	30(1)
C(25)	4637(2)	10926(2)	4213(2)	31(1)
C(26)	371(2)	11205(2)	2809(2)	18(1)
C(27)	-451(2)	10940(2)	2125(2)	21(1)
C(28)	-1459(2)	10928(2)	2437(2)	24(1)
C(29)	-1643(2)	11173(2)	3415(2)	25(1)

C(30)	-812(2)	11443(2)	4083(2)	27(1)
C(31)	195(2)	11464(2)	3787(2)	22(1)
C(32)	1274(2)	7056(2)	2060(2)	19(1)
C(33)	2400(2)	8502(2)	3603(2)	20(1)
C(34)	3033(2)	8211(2)	1574(2)	18(1)
C(35)	905(2)	8677(2)	1046(2)	18(1)
C(36)	340(2)	8855(2)	3009(2)	19(1)

Table 3. Bond lengths [A] and angles [deg] for **45a**.

W(1)-C(14)	2.012(3)
W(1)-C(15)	2.044(3)
W(1)-C(16)	2.048(2)
W(1)-C(17)	2.048(3)
W(1)-C(18)	2.051(2)
W(1)-P(1)	2.4791(6)
W(2)-C(32)	2.014(3)
W(2)-C(34)	2.043(3)
W(2)-C(33)	2.046(3)
W(2)-C(36)	2.047(3)
W(2)-C(35)	2.053(3)
W(2)-P(2)	2.4842(6)
P(1)-O(1)	1.6522(17)
P(1)-C(1)	1.811(2)
P(1)-H(1)	1.40(3)
P(2)-O(7)	1.6466(18)
P(2)-C(19)	1.810(2)
P(2)-H(2)	1.25(2)
Si(1)-C(3)	1.861(3)
Si(1)-C(2)	1.867(3)
Si(1)-C(4)	1.871(3)
Si(1)-C(1)	1.909(2)
Si(2)-C(7)	1.866(3)
Si(2)-C(5)	1.872(3)
Si(2)-C(6)	1.876(3)
Si(2)-C(1)	1.901(2)
Si(3)-C(21)	1.862(3)
Si(3)-C(20)	1.867(2)
Si(3)-C(22)	1.869(3)
Si(3)-C(19)	1.908(2)
Si(4)-C(24)	1.870(3)
Si(4)-C(25)	1.871(3)
Si(4)-C(23)	1.873(3)
Si(4)-C(19)	1.908(2)

O(1)-C(8)	1.396(3)
O(2)-C(14)	1.145(3)
O(3)-C(15)	1.143(3)
O(4)-C(16)	1.135(3)
O(5)-C(17)	1.129(3)
O(6)-C(18)	1.142(3)
O(7)-C(26)	1.396(3)
O(8)-C(32)	1.143(3)
O(9)-C(33)	1.141(3)
O(10)-C(34)	1.141(3)
O(11)-C(35)	1.136(3)
O(12)-C(36)	1.134(3)
C(1)-H(3)	1.0000
C(2)-H(4A)	0.9800
C(2)-H(4B)	0.9800
C(2)-H(4C)	0.9800
C(3)-H(5A)	0.9800
C(3)-H(5B)	0.9800
C(3)-H(5C)	0.9800
C(4)-H(6A)	0.9800
C(4)-H(6B)	0.9800
C(4)-H(6C)	0.9800
C(5)-H(7A)	0.9800
C(5)-H(7B)	0.9800
C(5)-H(7C)	0.9800
C(6)-H(8A)	0.9800
C(6)-H(8B)	0.9800
C(6)-H(8C)	0.9800
C(7)-H(9A)	0.9800
C(7)-H(9B)	0.9800
C(7)-H(9C)	0.9800
C(8)-C(9)	1.385(3)
C(8)-C(13)	1.388(3)
C(9)-C(10)	1.388(4)
C(9)-H(10)	0.9500
C(10)-C(11)	1.386(4)
C(10)-H(11)	0.9500
C(11)-C(12)	1.381(4)
C(11)-H(12)	0.9500
C(12)-C(13)	1.380(4)
C(12)-H(13)	0.9500
C(13)-H(14)	0.9500
C(19)-H(15)	1.0000
C(20)-H(16A)	0.9800

C(20)-H(16B)	0.9800
C(20)-H(16C)	0.9800
C(21)-H(17A)	0.9800
C(21)-H(17B)	0.9800
C(21)-H(17C)	0.9800
C(22)-H(18A)	0.9800
C(22)-H(18B)	0.9800
C(22)-H(18C)	0.9800
C(23)-H(19A)	0.9800
C(23)-H(19B)	0.9800
C(23)-H(19C)	0.9800
C(24)-H(20A)	0.9800
C(24)-H(20B)	0.9800
C(24)-H(20C)	0.9800
C(25)-H(21A)	0.9800
C(25)-H(21B)	0.9800
C(25)-H(21C)	0.9800
C(26)-C(31)	1.385(3)
C(26)-C(27)	1.386(3)
C(27)-C(28)	1.388(4)
C(27)-H(22)	0.9500
C(28)-C(29)	1.387(4)
C(28)-H(23)	0.9500
C(29)-C(30)	1.381(4)
C(29)-H(24)	0.9500
C(30)-C(31)	1.379(4)
C(30)-H(25)	0.9500
C(31)-H(26)	0.9500
C(14)-W(1)-C(15)	92.27(10)
C(14)-W(1)-C(16)	89.27(10)
C(15)-W(1)-C(16)	93.69(10)
C(14)-W(1)-C(17)	86.73(10)
C(15)-W(1)-C(17)	178.87(9)
C(16)-W(1)-C(17)	86.82(10)
C(14)-W(1)-C(18)	91.69(9)
C(15)-W(1)-C(18)	90.96(10)
C(16)-W(1)-C(18)	175.21(10)
C(17)-W(1)-C(18)	88.56(10)
C(14)-W(1)-P(1)	175.50(7)
C(15)-W(1)-P(1)	89.53(7)
C(16)-W(1)-P(1)	86.50(7)
C(17)-W(1)-P(1)	91.51(7)
C(18)-W(1)-P(1)	92.40(7)

C(32)-W(2)-C(34)	92.39(10)
C(32)-W(2)-C(33)	90.42(10)
C(34)-W(2)-C(33)	93.53(10)
C(32)-W(2)-C(36)	86.23(10)
C(34)-W(2)-C(36)	178.57(9)
C(33)-W(2)-C(36)	86.81(10)
C(32)-W(2)-C(35)	91.40(10)
C(34)-W(2)-C(35)	90.43(10)
C(33)-W(2)-C(35)	175.57(9)
C(36)-W(2)-C(35)	89.27(10)
C(32)-W(2)-P(2)	175.66(7)
C(34)-W(2)-P(2)	89.44(7)
C(33)-W(2)-P(2)	85.54(8)
C(36)-W(2)-P(2)	91.97(7)
C(35)-W(2)-P(2)	92.52(7)
O(1)-P(1)-C(1)	100.39(10)
O(1)-P(1)-W(1)	118.46(7)
C(1)-P(1)-W(1)	123.41(8)
O(1)-P(1)-H(1)	97.9(12)
C(1)-P(1)-H(1)	102.4(12)
W(1)-P(1)-H(1)	110.4(11)
O(7)-P(2)-C(19)	99.98(10)
O(7)-P(2)-W(2)	118.03(7)
C(19)-P(2)-W(2)	123.73(8)
O(7)-P(2)-H(2)	98.5(11)
C(19)-P(2)-H(2)	102.1(12)
W(2)-P(2)-H(2)	110.7(12)
C(3)-Si(1)-C(2)	109.35(13)
C(3)-Si(1)-C(4)	110.37(13)
C(2)-Si(1)-C(4)	107.99(13)
C(3)-Si(1)-C(1)	111.79(12)
C(2)-Si(1)-C(1)	110.27(11)
C(4)-Si(1)-C(1)	106.99(11)
C(7)-Si(2)-C(5)	108.03(13)
C(7)-Si(2)-C(6)	109.48(13)
C(5)-Si(2)-C(6)	110.89(13)
C(7)-Si(2)-C(1)	112.52(11)
C(5)-Si(2)-C(1)	106.12(12)
C(6)-Si(2)-C(1)	109.75(12)
C(21)-Si(3)-C(20)	108.87(13)
C(21)-Si(3)-C(22)	109.95(13)
C(20)-Si(3)-C(22)	108.00(13)
C(21)-Si(3)-C(19)	112.08(12)
C(20)-Si(3)-C(19)	110.50(11)

C(22)-Si(3)-C(19)	107.35(12)
C(24)-Si(4)-C(25)	107.26(14)
C(24)-Si(4)-C(23)	108.40(13)
C(25)-Si(4)-C(23)	111.19(14)
C(24)-Si(4)-C(19)	112.88(12)
C(25)-Si(4)-C(19)	107.25(12)
C(23)-Si(4)-C(19)	109.85(12)
C(8)-O(1)-P(1)	118.11(14)
C(26)-O(7)-P(2)	118.24(15)
P(1)-C(1)-Si(2)	109.77(12)
P(1)-C(1)-Si(1)	115.99(12)
Si(2)-C(1)-Si(1)	117.12(12)
P(1)-C(1)-H(3)	104.0
Si(2)-C(1)-H(3)	104.0
Si(1)-C(1)-H(3)	104.0
Si(1)-C(2)-H(4A)	109.5
Si(1)-C(2)-H(4B)	109.5
H(4A)-C(2)-H(4B)	109.5
Si(1)-C(2)-H(4C)	109.5
H(4A)-C(2)-H(4C)	109.5
H(4B)-C(2)-H(4C)	109.5
Si(1)-C(3)-H(5A)	109.5
Si(1)-C(3)-H(5B)	109.5
H(5A)-C(3)-H(5B)	109.5
Si(1)-C(3)-H(5C)	109.5
H(5A)-C(3)-H(5C)	109.5
H(5B)-C(3)-H(5C)	109.5
Si(1)-C(4)-H(6A)	109.5
Si(1)-C(4)-H(6B)	109.5
H(6A)-C(4)-H(6B)	109.5
Si(1)-C(4)-H(6C)	109.5
H(6A)-C(4)-H(6C)	109.5
H(6B)-C(4)-H(6C)	109.5
Si(2)-C(5)-H(7A)	109.5
Si(2)-C(5)-H(7B)	109.5
H(7A)-C(5)-H(7B)	109.5
Si(2)-C(5)-H(7C)	109.5
H(7A)-C(5)-H(7C)	109.5
H(7B)-C(5)-H(7C)	109.5
Si(2)-C(6)-H(8A)	109.5
Si(2)-C(6)-H(8B)	109.5
H(8A)-C(6)-H(8B)	109.5
Si(2)-C(6)-H(8C)	109.5
H(8A)-C(6)-H(8C)	109.5

H(8B)-C(6)-H(8C)	109.5
Si(2)-C(7)-H(9A)	109.5
Si(2)-C(7)-H(9B)	109.5
H(9A)-C(7)-H(9B)	109.5
Si(2)-C(7)-H(9C)	109.5
H(9A)-C(7)-H(9C)	109.5
H(9B)-C(7)-H(9C)	109.5
C(9)-C(8)-C(13)	120.9(2)
C(9)-C(8)-O(1)	120.4(2)
C(13)-C(8)-O(1)	118.7(2)
C(8)-C(9)-C(10)	119.2(2)
C(8)-C(9)-H(10)	120.4
C(10)-C(9)-H(10)	120.4
C(11)-C(10)-C(9)	120.2(2)
C(11)-C(10)-H(11)	119.9
C(9)-C(10)-H(11)	119.9
C(12)-C(11)-C(10)	119.7(2)
C(12)-C(11)-H(12)	120.1
C(10)-C(11)-H(12)	120.1
C(13)-C(12)-C(11)	120.8(2)
C(13)-C(12)-H(13)	119.6
C(11)-C(12)-H(13)	119.6
C(12)-C(13)-C(8)	119.1(2)
C(12)-C(13)-H(14)	120.4
C(8)-C(13)-H(14)	120.4
O(2)-C(14)-W(1)	176.8(2)
O(3)-C(15)-W(1)	179.0(2)
O(4)-C(16)-W(1)	175.7(2)
O(5)-C(17)-W(1)	175.7(2)
O(6)-C(18)-W(1)	178.6(2)
P(2)-C(19)-Si(3)	115.71(12)
P(2)-C(19)-Si(4)	109.72(12)
Si(3)-C(19)-Si(4)	117.25(13)
P(2)-C(19)-H(15)	104.1
Si(3)-C(19)-H(15)	104.1
Si(4)-C(19)-H(15)	104.1
Si(3)-C(20)-H(16A)	109.5
Si(3)-C(20)-H(16B)	109.5
H(16A)-C(20)-H(16B)	109.5
Si(3)-C(20)-H(16C)	109.5
H(16A)-C(20)-H(16C)	109.5
H(16B)-C(20)-H(16C)	109.5
Si(3)-C(21)-H(17A)	109.5
Si(3)-C(21)-H(17B)	109.5

H(17A)-C(21)-H(17B)	109.5
Si(3)-C(21)-H(17C)	109.5
H(17A)-C(21)-H(17C)	109.5
H(17B)-C(21)-H(17C)	109.5
Si(3)-C(22)-H(18A)	109.5
Si(3)-C(22)-H(18B)	109.5
H(18A)-C(22)-H(18B)	109.5
Si(3)-C(22)-H(18C)	109.5
H(18A)-C(22)-H(18C)	109.5
H(18B)-C(22)-H(18C)	109.5
Si(4)-C(23)-H(19A)	109.5
Si(4)-C(23)-H(19B)	109.5
H(19A)-C(23)-H(19B)	109.5
Si(4)-C(23)-H(19C)	109.5
H(19A)-C(23)-H(19C)	109.5
H(19B)-C(23)-H(19C)	109.5
Si(4)-C(24)-H(20A)	109.5
Si(4)-C(24)-H(20B)	109.5
H(20A)-C(24)-H(20B)	109.5
Si(4)-C(24)-H(20C)	109.5
H(20A)-C(24)-H(20C)	109.5
H(20B)-C(24)-H(20C)	109.5
Si(4)-C(25)-H(21A)	109.5
Si(4)-C(25)-H(21B)	109.5
H(21A)-C(25)-H(21B)	109.5
Si(4)-C(25)-H(21C)	109.5
H(21A)-C(25)-H(21C)	109.5
H(21B)-C(25)-H(21C)	109.5
C(31)-C(26)-C(27)	120.9(2)
C(31)-C(26)-O(7)	120.6(2)
C(27)-C(26)-O(7)	118.4(2)
C(26)-C(27)-C(28)	118.8(2)
C(26)-C(27)-H(22)	120.6
C(28)-C(27)-H(22)	120.6
C(29)-C(28)-C(27)	120.7(2)
C(29)-C(28)-H(23)	119.6
C(27)-C(28)-H(23)	119.6
C(30)-C(29)-C(28)	119.4(3)
C(30)-C(29)-H(24)	120.3
C(28)-C(29)-H(24)	120.3
C(31)-C(30)-C(29)	120.7(3)
C(31)-C(30)-H(25)	119.6
C(29)-C(30)-H(25)	119.6
C(30)-C(31)-C(26)	119.4(2)

C(30)-C(31)-H(26)	120.3
C(26)-C(31)-H(26)	120.3
O(8)-C(32)-W(2)	176.6(2)
O(9)-C(33)-W(2)	175.7(2)
O(10)-C(34)-W(2)	178.9(2)
O(11)-C(35)-W(2)	178.6(2)
O(12)-C(36)-W(2)	174.6(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **45a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
W(1)	12(1)	13(1)	12(1)	3(1)	1(1)	1(1)
W(2)	12(1)	14(1)	14(1)	4(1)	2(1)	0(1)
P(1)	14(1)	14(1)	13(1)	3(1)	1(1)	2(1)
P(2)	15(1)	15(1)	13(1)	2(1)	2(1)	0(1)
Si(1)	19(1)	14(1)	14(1)	2(1)	1(1)	2(1)
Si(2)	18(1)	22(1)	15(1)	6(1)	-1(1)	4(1)
Si(3)	19(1)	17(1)	15(1)	5(1)	2(1)	-2(1)
Si(4)	20(1)	22(1)	15(1)	0(1)	1(1)	-6(1)
O(1)	15(1)	17(1)	22(1)	3(1)	3(1)	2(1)
O(2)	35(1)	17(1)	29(1)	8(1)	1(1)	5(1)
O(3)	21(1)	39(1)	29(1)	8(1)	9(1)	-1(1)
O(4)	24(1)	46(1)	17(1)	0(1)	2(1)	-9(1)
O(5)	18(1)	28(1)	25(1)	5(1)	7(1)	5(1)
O(6)	25(1)	25(1)	18(1)	0(1)	-5(1)	2(1)
O(7)	17(1)	18(1)	20(1)	8(1)	7(1)	1(1)
O(8)	29(1)	17(1)	35(1)	7(1)	0(1)	-4(1)
O(9)	24(1)	62(2)	17(1)	13(1)	5(1)	12(1)
O(10)	20(1)	36(1)	25(1)	5(1)	7(1)	6(1)
O(11)	27(1)	30(1)	24(1)	10(1)	-6(1)	-5(1)
O(12)	21(1)	33(1)	40(1)	9(1)	13(1)	1(1)
C(1)	16(1)	14(1)	14(1)	4(1)	1(1)	1(1)
C(2)	34(2)	21(1)	16(1)	0(1)	-3(1)	4(1)
C(3)	32(2)	19(1)	27(1)	4(1)	1(1)	-1(1)
C(4)	25(1)	24(1)	21(1)	-2(1)	3(1)	4(1)
C(5)	27(2)	34(2)	20(1)	2(1)	-6(1)	2(1)
C(6)	25(2)	37(2)	25(1)	16(1)	1(1)	4(1)
C(7)	26(2)	35(2)	24(1)	12(1)	0(1)	11(1)
C(8)	15(1)	16(1)	22(1)	6(1)	4(1)	-2(1)
C(9)	20(1)	23(1)	19(1)	6(1)	-1(1)	-3(1)
C(10)	28(2)	25(1)	19(1)	7(1)	9(1)	0(1)
C(11)	17(1)	24(1)	30(1)	7(1)	6(1)	-1(1)

C(12)	20(1)	22(1)	24(1)	5(1)	-3(1)	-2(1)
C(13)	24(1)	18(1)	16(1)	1(1)	0(1)	-1(1)
C(14)	19(1)	21(1)	14(1)	1(1)	1(1)	0(1)
C(15)	18(1)	20(1)	18(1)	5(1)	0(1)	1(1)
C(16)	14(1)	23(1)	21(1)	6(1)	4(1)	0(1)
C(17)	17(1)	15(1)	18(1)	4(1)	-1(1)	2(1)
C(18)	18(1)	14(1)	20(1)	5(1)	4(1)	5(1)
C(19)	16(1)	13(1)	15(1)	2(1)	1(1)	0(1)
C(20)	31(2)	28(2)	17(1)	8(1)	-2(1)	-6(1)
C(21)	34(2)	22(1)	34(2)	12(1)	6(1)	3(1)
C(22)	26(2)	33(2)	22(1)	11(1)	4(1)	-1(1)
C(23)	35(2)	26(2)	27(2)	-4(1)	8(1)	-6(1)
C(24)	29(2)	29(2)	28(2)	0(1)	2(1)	-12(1)
C(25)	27(2)	46(2)	19(1)	7(1)	-6(1)	-4(1)
C(26)	17(1)	13(1)	23(1)	3(1)	5(1)	3(1)
C(27)	25(1)	19(1)	19(1)	5(1)	1(1)	2(1)
C(28)	20(1)	23(1)	31(1)	9(1)	-3(1)	4(1)
C(29)	18(1)	25(1)	32(2)	7(1)	7(1)	4(1)
C(30)	27(2)	30(2)	22(1)	-1(1)	8(1)	4(1)
C(31)	20(1)	23(1)	20(1)	-1(1)	2(1)	2(1)
C(32)	17(1)	21(1)	22(1)	7(1)	3(1)	2(1)
C(33)	15(1)	25(1)	22(1)	7(1)	8(1)	3(1)
C(34)	19(1)	20(1)	14(1)	4(1)	-2(1)	-1(1)
C(35)	18(1)	14(1)	19(1)	2(1)	3(1)	-3(1)
C(36)	20(1)	17(1)	22(1)	7(1)	1(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic isplacement parameters (A^2 x 10^3) for **45a**.

	X	y	z	U(eq)
H(1)	7230(20)	6090(20)	3676(19)	28(8)
H(2)	2320(20)	10731(19)	3620(17)	16(7)
H(3)	8778	5780	2114	17
H(4A)	7275	4076	-393	37
H(4B)	7615	5246	85	37
H(4C)	6614	4753	445	37
H(5A)	7518	2462	752	40
H(5B)	6906	3133	1632	40
H(5C)	8056	2741	1820	40
H(6A)	9869	3491	996	37
H(6B)	9878	4598	753	37
H(6C)	9427	3614	-38	37

H(7A)	9878	6068	4750	42
H(7B)	8914	6635	4361	42
H(7C)	9988	6527	3821	42
H(8A)	7758	3693	3551	41
H(8B)	7606	4749	4337	41
H(8C)	8517	3989	4503	41
H(9A)	10631	4431	2628	41
H(9B)	9958	3430	2659	41
H(9C)	10596	4058	3611	41
H(10)	5663	5446	4190	25
H(11)	3968	5789	4707	28
H(12)	2574	5718	3575	28
H(13)	2872	5298	1932	27
H(14)	4559	4993	1405	24
H(15)	3852	10272	2145	18
H(16A)	1671	10488	481	37
H(16B)	2650	9775	153	37
H(16C)	2372	10690	-357	37
H(17A)	3151	13169	1866	44
H(17B)	1997	12673	1675	44
H(17C)	2614	12902	797	44
H(18A)	4491	11373	-9	39
H(18B)	4950	10782	767	39
H(18C)	4950	12013	1024	39
H(19A)	3629	13153	4667	46
H(19B)	2629	12464	4189	46
H(19C)	3119	13265	3652	46
H(20A)	5747	12738	3636	45
H(20B)	5098	12914	2704	45
H(20C)	5745	11883	2637	45
H(21A)	5077	10388	3851	46
H(21B)	4040	10609	4443	46
H(21C)	5047	11346	4767	46
H(22)	-327	10771	1455	25
H(23)	-2030	10749	1975	29
H(24)	-2334	11156	3623	30
H(25)	-935	11617	4753	33
H(26)	763	11654	4250	27

Table 6. Torsion angles [deg] for **45a**.

C(14)-W(1)-P(1)-O(1)	117.1(9)
C(15)-W(1)-P(1)-O(1)	-129.34(10)
C(16)-W(1)-P(1)-O(1)	136.94(10)

C(17)-W(1)-P(1)-O(1)	50.23(10)
C(18)-W(1)-P(1)-O(1)	-38.39(10)
C(14)-W(1)-P(1)-C(1)	-115.8(9)
C(15)-W(1)-P(1)-C(1)	-2.21(11)
C(16)-W(1)-P(1)-C(1)	-95.94(11)
C(17)-W(1)-P(1)-C(1)	177.35(11)
C(18)-W(1)-P(1)-C(1)	88.73(11)
C(32)-W(2)-P(2)-O(7)	-116.7(10)
C(34)-W(2)-P(2)-O(7)	128.36(10)
C(33)-W(2)-P(2)-O(7)	-138.06(10)
C(36)-W(2)-P(2)-O(7)	-51.41(10)
C(35)-W(2)-P(2)-O(7)	37.95(10)
C(32)-W(2)-P(2)-C(19)	117.1(10)
C(34)-W(2)-P(2)-C(19)	2.10(12)
C(33)-W(2)-P(2)-C(19)	95.68(12)
C(36)-W(2)-P(2)-C(19)	-177.67(12)
C(35)-W(2)-P(2)-C(19)	-88.31(12)
C(1)-P(1)-O(1)-C(8)	170.83(17)
W(1)-P(1)-O(1)-C(8)	-51.75(18)
C(19)-P(2)-O(7)-C(26)	-172.03(16)
W(2)-P(2)-O(7)-C(26)	50.89(17)
O(1)-P(1)-C(1)-Si(2)	-95.76(12)
W(1)-P(1)-C(1)-Si(2)	129.69(9)
O(1)-P(1)-C(1)-Si(1)	39.82(15)
W(1)-P(1)-C(1)-Si(1)	-94.73(13)
C(7)-Si(2)-C(1)-P(1)	175.17(13)
C(5)-Si(2)-C(1)-P(1)	-66.89(16)
C(6)-Si(2)-C(1)-P(1)	52.99(16)
C(7)-Si(2)-C(1)-Si(1)	40.15(19)
C(5)-Si(2)-C(1)-Si(1)	158.10(14)
C(6)-Si(2)-C(1)-Si(1)	-82.02(16)
C(3)-Si(1)-C(1)-P(1)	-80.14(16)
C(2)-Si(1)-C(1)-P(1)	41.73(18)
C(4)-Si(1)-C(1)-P(1)	158.93(14)
C(3)-Si(1)-C(1)-Si(2)	52.13(18)
C(2)-Si(1)-C(1)-Si(2)	174.00(14)
C(4)-Si(1)-C(1)-Si(2)	-68.80(17)
P(1)-O(1)-C(8)-C(9)	-68.3(3)
P(1)-O(1)-C(8)-C(13)	113.9(2)
C(13)-C(8)-C(9)-C(10)	-1.9(4)
O(1)-C(8)-C(9)-C(10)	-179.6(2)
C(8)-C(9)-C(10)-C(11)	1.2(4)
C(9)-C(10)-C(11)-C(12)	0.2(4)
C(10)-C(11)-C(12)-C(13)	-1.1(4)

C(11)-C(12)-C(13)-C(8)	0.4(4)
C(9)-C(8)-C(13)-C(12)	1.1(4)
O(1)-C(8)-C(13)-C(12)	178.9(2)
C(15)-W(1)-C(14)-O(2)	-149(4)
C(16)-W(1)-C(14)-O(2)	-56(4)
C(17)-W(1)-C(14)-O(2)	31(4)
C(18)-W(1)-C(14)-O(2)	120(4)
P(1)-W(1)-C(14)-O(2)	-36(5)
C(14)-W(1)-C(15)-O(3)	-151(13)
C(16)-W(1)-C(15)-O(3)	120(13)
C(17)-W(1)-C(15)-O(3)	-124(12)
C(18)-W(1)-C(15)-O(3)	-59(13)
P(1)-W(1)-C(15)-O(3)	33(13)
C(14)-W(1)-C(16)-O(4)	95(3)
C(15)-W(1)-C(16)-O(4)	-173(3)
C(17)-W(1)-C(16)-O(4)	8(3)
C(18)-W(1)-C(16)-O(4)	-7(4)
P(1)-W(1)-C(16)-O(4)	-84(3)
C(14)-W(1)-C(17)-O(5)	-14(3)
C(15)-W(1)-C(17)-O(5)	-41(7)
C(16)-W(1)-C(17)-O(5)	75(3)
C(18)-W(1)-C(17)-O(5)	-106(3)
P(1)-W(1)-C(17)-O(5)	162(3)
C(14)-W(1)-C(18)-O(6)	-84(9)
C(15)-W(1)-C(18)-O(6)	-176(100)
C(16)-W(1)-C(18)-O(6)	18(9)
C(17)-W(1)-C(18)-O(6)	3(9)
P(1)-W(1)-C(18)-O(6)	94(9)
O(7)-P(2)-C(19)-Si(3)	-39.62(14)
W(2)-P(2)-C(19)-Si(3)	94.10(13)
O(7)-P(2)-C(19)-Si(4)	95.81(12)
W(2)-P(2)-C(19)-Si(4)	-130.47(9)
C(21)-Si(3)-C(19)-P(2)	79.09(16)
C(20)-Si(3)-C(19)-P(2)	-42.53(17)
C(22)-Si(3)-C(19)-P(2)	-160.08(13)
C(21)-Si(3)-C(19)-Si(4)	-52.92(18)
C(20)-Si(3)-C(19)-Si(4)	-174.54(13)
C(22)-Si(3)-C(19)-Si(4)	67.91(16)
C(24)-Si(4)-C(19)-P(2)	-174.86(14)
C(25)-Si(4)-C(19)-P(2)	67.21(16)
C(23)-Si(4)-C(19)-P(2)	-53.76(16)
C(24)-Si(4)-C(19)-Si(3)	-40.19(19)
C(25)-Si(4)-C(19)-Si(3)	-158.12(14)
C(23)-Si(4)-C(19)-Si(3)	80.91(17)

P(2)-O(7)-C(26)-C(31)	67.6(3)
P(2)-O(7)-C(26)-C(27)	-114.4(2)
C(31)-C(26)-C(27)-C(28)	-0.7(4)
O(7)-C(26)-C(27)-C(28)	-178.6(2)
C(26)-C(27)-C(28)-C(29)	-0.1(4)
C(27)-C(28)-C(29)-C(30)	0.7(4)
C(28)-C(29)-C(30)-C(31)	-0.5(4)
C(29)-C(30)-C(31)-C(26)	-0.4(4)
C(27)-C(26)-C(31)-C(30)	1.0(4)
O(7)-C(26)-C(31)-C(30)	178.8(2)
C(34)-W(2)-C(32)-O(8)	151(4)
C(33)-W(2)-C(32)-O(8)	57(4)
C(36)-W(2)-C(32)-O(8)	-29(4)
C(35)-W(2)-C(32)-O(8)	-119(4)
P(2)-W(2)-C(32)-O(8)	36(5)
C(32)-W(2)-C(33)-O(9)	-99(3)
C(34)-W(2)-C(33)-O(9)	169(3)
C(36)-W(2)-C(33)-O(9)	-13(3)
C(35)-W(2)-C(33)-O(9)	15(4)
P(2)-W(2)-C(33)-O(9)	79(3)
C(32)-W(2)-C(34)-O(10)	156(11)
C(33)-W(2)-C(34)-O(10)	-113(11)
C(36)-W(2)-C(34)-O(10)	143(11)
C(35)-W(2)-C(34)-O(10)	65(11)
P(2)-W(2)-C(34)-O(10)	-28(11)
C(32)-W(2)-C(35)-O(11)	64(9)
C(34)-W(2)-C(35)-O(11)	156(9)
C(33)-W(2)-C(35)-O(11)	-50(10)
C(36)-W(2)-C(35)-O(11)	-22(9)
P(2)-W(2)-C(35)-O(11)	-114(9)
C(32)-W(2)-C(36)-O(12)	17(2)
C(34)-W(2)-C(36)-O(12)	30(6)
C(33)-W(2)-C(36)-O(12)	-74(2)
C(35)-W(2)-C(36)-O(12)	108(2)
P(2)-W(2)-C(36)-O(12)	-159(2)

8. Crystal data of molecule [{bis(trimethylsily)methyl}phenoxyphosphane]pentacarbonyl chromium complex (**47**) (GSTR092, Greg885)

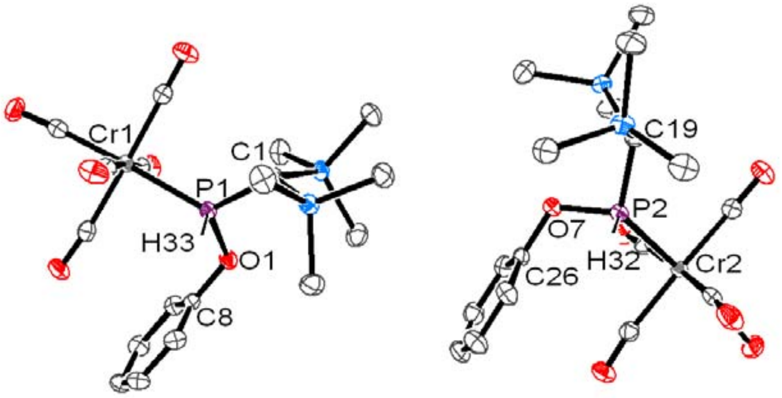

Table 1. Crystal data and structure refinement for **47**.

Identification code	GSTR092, Greg885
Device Type	Nonius KappaCCD
Empirical formula	C18 H25 Cr O6 P Si2
Formula weight	476.53
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 12.5841(2) A alpha = 103.9080(10) deg. b = 13.3203(2) A beta = 92.8557(10) deg. c = 14.2790(2) A gamma = 90.2843(10) deg.
Volume	2320.09(6) A^3
Z, Calculated density	4, 1.364 Mg/m^3
Absorption coefficient	0.694 mm^-1

F(000)	992
Crystal size	0.46 x 0.18 x 0.16 mm
Theta range for data collection	1.62 to 28.00 deg.
Limiting indices	-16<=h<=16, -17<=k<=17, -18<=l<=17
Reflections collected / unique	60034 / 11184 [R(int) = 0.0716]
Completeness to theta = 28.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.89290 and 0.74155
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11184 / 0 / 523
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0783
R indices (all data)	R1 = 0.0523, wR2 = 0.0839
Largest diff. peak and hole	0.333 and -0.488 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **47**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3337(1)	301(1)	2273(1)	16(1)
C(2)	4533(2)	1231(2)	4173(1)	33(1)
C(3)	5233(2)	-848(2)	3037(1)	31(1)
C(4)	3108(2)	-699(2)	3998(1)	31(1)
C(5)	4560(2)	-1045(2)	668(1)	29(1)
C(6)	2609(2)	-1982(2)	1350(2)	32(1)
C(7)	2356(2)	-366(2)	182(1)	29(1)
C(8)	240(1)	219(1)	2731(1)	19(1)
C(9)	-613(1)	151(1)	2070(1)	22(1)
C(10)	-1627(2)	326(1)	2405(1)	26(1)

C(11)	-1783(2)	569(1)	3389(1)	26(1)
C(12)	-921(2)	625(2)	4040(1)	27(1)
C(13)	97(2)	438(1)	3715(1)	24(1)
C(14)	1310(1)	3855(2)	2048(1)	22(1)
C(15)	2334(1)	3232(1)	3477(1)	22(1)
C(16)	2966(2)	2559(1)	1610(1)	22(1)
C(17)	936(1)	1865(1)	1082(1)	21(1)
C(18)	387(2)	2610(1)	2893(1)	21(1)
C(19)	8400(1)	-4145(1)	2326(1)	17(1)
C(20)	9633(2)	-4080(2)	4229(1)	35(1)
C(21)	8233(2)	-2235(2)	4041(1)	33(1)
C(22)	10331(2)	-2611(2)	3062(2)	34(1)
C(23)	7662(2)	-2355(2)	1393(2)	34(1)
C(24)	9603(2)	-3622(2)	702(1)	30(1)
C(25)	7398(2)	-4567(2)	230(1)	30(1)
C(26)	5313(1)	-3819(1)	2799(1)	20(1)
C(27)	5167(2)	-3550(2)	3776(1)	26(1)
C(28)	4140(2)	-3558(2)	4094(1)	31(1)
C(29)	3281(2)	-3817(2)	3438(2)	30(1)
C(30)	3443(2)	-4060(2)	2461(1)	28(1)
C(31)	4462(2)	-4061(1)	2132(1)	24(1)
C(32)	6296(1)	-7802(2)	2085(1)	22(1)
C(33)	7385(2)	-6462(1)	3505(1)	24(1)
C(34)	7957(2)	-6741(1)	1626(1)	21(1)
C(35)	5934(2)	-6290(1)	1149(1)	22(1)
C(36)	5427(2)	-6129(1)	2978(1)	23(1)
Cr(1)	1679(1)	2562(1)	2257(1)	16(1)
Cr(2)	6697(1)	-6407(1)	2306(1)	17(1)
O(1)	1262(1)	42(1)	2385(1)	20(1)
O(2)	1052(1)	4650(1)	1948(1)	31(1)
O(3)	2668(1)	3633(1)	4235(1)	33(1)
O(4)	3731(1)	2543(1)	1209(1)	34(1)
O(5)	470(1)	1468(1)	385(1)	29(1)
O(6)	-395(1)	2729(1)	3274(1)	29(1)
O(7)	6336(1)	-3816(1)	2455(1)	21(1)
O(8)	6011(1)	-8641(1)	1979(1)	31(1)
O(9)	7736(1)	-6476(1)	4257(1)	38(1)
O(10)	8707(1)	-6938(1)	1208(1)	31(1)
O(11)	5461(1)	-6239(1)	458(1)	31(1)
O(12)	4660(1)	-6066(1)	3384(1)	35(1)
P(1)	2138(1)	1006(1)	2642(1)	16(1)
P(2)	7199(1)	-4655(1)	2706(1)	17(1)
Si(1)	4052(1)	-25(1)	3367(1)	21(1)
Si(2)	3197(1)	-783(1)	1123(1)	19(1)

Si(3)	9142(1)	-3260(1)	3408(1)	22(1)
Si(4)	8247(1)	-3661(1)	1171(1)	20(1)

Table 3. Bond lengths [A] and angles [deg] for **47**.

C(1)-P(1)	1.8149(17)
C(1)-Si(1)	1.9042(17)
C(1)-Si(2)	1.9080(16)
C(1)-H(1A)	1.0000
C(2)-Si(1)	1.867(2)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-Si(1)	1.8626(19)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-Si(1)	1.874(2)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-Si(2)	1.8691(19)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-Si(2)	1.861(2)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-Si(2)	1.8599(19)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.381(2)
C(8)-C(13)	1.387(2)
C(8)-O(1)	1.401(2)
C(9)-C(10)	1.385(3)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.388(3)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.384(3)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.387(3)
C(12)-H(12A)	0.9500

C(13)-H(13A)	0.9500
C(14)-O(2)	1.148(2)
C(14)-Cr(1)	1.873(2)
C(15)-O(3)	1.145(2)
C(15)-Cr(1)	1.9003(19)
C(16)-O(4)	1.142(2)
C(16)-Cr(1)	1.9024(19)
C(17)-O(5)	1.139(2)
C(17)-Cr(1)	1.9076(19)
C(18)-O(6)	1.141(2)
C(18)-Cr(1)	1.8960(19)
C(19)-P(2)	1.8131(17)
C(19)-Si(3)	1.9023(17)
C(19)-Si(4)	1.9110(17)
C(19)-H(19A)	1.0000
C(20)-Si(3)	1.871(2)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-Si(3)	1.874(2)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-Si(3)	1.870(2)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-Si(4)	1.855(2)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-Si(4)	1.8680(19)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-Si(4)	1.8634(19)
C(25)-H(25C)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25A)	0.9800
C(26)-C(27)	1.376(2)
C(26)-C(31)	1.380(2)
C(26)-O(7)	1.401(2)
C(27)-C(28)	1.391(3)
C(27)-H(27A)	0.9500

C(28)-C(29)	1.380(3)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.380(3)
C(29)-H(29A)	0.9500
C(30)-C(31)	1.387(3)
C(30)-H(30A)	0.9500
C(31)-H(31A)	0.9500
C(32)-O(8)	1.145(2)
C(32)-Cr(2)	1.8705(19)
C(33)-O(9)	1.145(2)
C(33)-Cr(2)	1.897(2)
C(34)-O(10)	1.140(2)
C(34)-Cr(2)	1.8998(19)
C(35)-O(11)	1.143(2)
C(35)-Cr(2)	1.909(2)
C(36)-O(12)	1.144(2)
C(36)-Cr(2)	1.8973(19)
Cr(1)-P(1)	2.3368(5)
Cr(2)-P(2)	2.3408(5)
O(1)-P(1)	1.6488(12)
O(7)-P(2)	1.6498(13)
P(1)-H(33)	1.369(18)
P(2)-H(32)	1.364(18)

P(1)-C(1)-Si(1)	109.48(8)
P(1)-C(1)-Si(2)	116.27(9)
Si(1)-C(1)-Si(2)	116.70(9)
P(1)-C(1)-H(1A)	104.2
Si(1)-C(1)-H(1A)	104.2
Si(2)-C(1)-H(1A)	104.2
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
Si(1)-C(3)-H(3A)	109.5
Si(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
Si(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
Si(1)-C(4)-H(4A)	109.5
Si(1)-C(4)-H(4B)	109.5

H(4A)-C(4)-H(4B)	109.5
Si(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
Si(2)-C(5)-H(5A)	109.5
Si(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Si(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
Si(2)-C(6)-H(6A)	109.5
Si(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
Si(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
Si(2)-C(7)-H(7A)	109.5
Si(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	121.22(17)
C(9)-C(8)-O(1)	118.59(15)
C(13)-C(8)-O(1)	120.18(16)
C(8)-C(9)-C(10)	118.97(17)
C(8)-C(9)-H(9A)	120.5
C(10)-C(9)-H(9A)	120.5
C(9)-C(10)-C(11)	120.64(18)
C(9)-C(10)-H(10A)	119.7
C(11)-C(10)-H(10A)	119.7
C(12)-C(11)-C(10)	119.64(18)
C(12)-C(11)-H(11A)	120.2
C(10)-C(11)-H(11A)	120.2
C(11)-C(12)-C(13)	120.38(18)
C(11)-C(12)-H(12A)	119.8
C(13)-C(12)-H(12A)	119.8
C(8)-C(13)-C(12)	119.11(17)
C(8)-C(13)-H(13A)	120.4
C(12)-C(13)-H(13A)	120.4
O(2)-C(14)-Cr(1)	177.14(16)
O(3)-C(15)-Cr(1)	175.79(15)
O(4)-C(16)-Cr(1)	178.80(17)
O(5)-C(17)-Cr(1)	178.13(16)

O(6)-C(18)-Cr(1)	173.96(16)
P(2)-C(19)-Si(3)	109.85(8)
P(2)-C(19)-Si(4)	115.85(9)
Si(3)-C(19)-Si(4)	116.95(9)
P(2)-C(19)-H(19A)	104.1
Si(3)-C(19)-H(19A)	104.1
Si(4)-C(19)-H(19A)	104.1
Si(3)-C(20)-H(20A)	109.5
Si(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
Si(3)-C(21)-H(21A)	109.5
Si(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Si(3)-C(22)-H(22A)	109.5
Si(3)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
Si(3)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
Si(4)-C(23)-H(23A)	109.5
Si(4)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(4)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Si(4)-C(24)-H(24A)	109.5
Si(4)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(4)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Si(4)-C(25)-H(25C)	109.5
Si(4)-C(25)-H(25B)	109.5
H(25C)-C(25)-H(25B)	109.5
Si(4)-C(25)-H(25A)	109.5
H(25C)-C(25)-H(25A)	109.5
H(25B)-C(25)-H(25A)	109.5
C(27)-C(26)-C(31)	121.39(17)

C(27)-C(26)-O(7)	120.36(16)
C(31)-C(26)-O(7)	118.20(16)
C(26)-C(27)-C(28)	119.01(18)
C(26)-C(27)-H(27A)	120.5
C(28)-C(27)-H(27A)	120.5
C(29)-C(28)-C(27)	120.37(18)
C(29)-C(28)-H(28A)	119.8
C(27)-C(28)-H(28A)	119.8
C(28)-C(29)-C(30)	119.66(18)
C(28)-C(29)-H(29A)	120.2
C(30)-C(29)-H(29A)	120.2
C(29)-C(30)-C(31)	120.67(18)
C(29)-C(30)-H(30A)	119.7
C(31)-C(30)-H(30A)	119.7
C(26)-C(31)-C(30)	118.85(18)
C(26)-C(31)-H(31A)	120.6
C(30)-C(31)-H(31A)	120.6
O(8)-C(32)-Cr(2)	176.67(16)
O(9)-C(33)-Cr(2)	175.35(16)
O(10)-C(34)-Cr(2)	179.10(17)
O(11)-C(35)-Cr(2)	178.29(16)
O(12)-C(36)-Cr(2)	172.99(16)
C(14)-Cr(1)-C(18)	86.21(8)
C(14)-Cr(1)-C(15)	89.61(8)
C(18)-Cr(1)-C(15)	86.97(7)
C(14)-Cr(1)-C(16)	91.86(8)
C(18)-Cr(1)-C(16)	178.07(8)
C(15)-Cr(1)-C(16)	93.00(8)
C(14)-Cr(1)-C(17)	91.34(8)
C(18)-Cr(1)-C(17)	88.97(7)
C(15)-Cr(1)-C(17)	175.76(8)
C(16)-Cr(1)-C(17)	91.10(8)
C(14)-Cr(1)-P(1)	175.65(6)
C(18)-Cr(1)-P(1)	91.61(6)
C(15)-Cr(1)-P(1)	86.51(6)
C(16)-Cr(1)-P(1)	90.32(6)
C(17)-Cr(1)-P(1)	92.38(5)
C(32)-Cr(2)-C(33)	90.29(8)
C(32)-Cr(2)-C(36)	85.85(8)
C(33)-Cr(2)-C(36)	87.01(8)
C(32)-Cr(2)-C(34)	91.90(8)
C(33)-Cr(2)-C(34)	92.89(8)
C(36)-Cr(2)-C(34)	177.75(8)
C(32)-Cr(2)-C(35)	91.18(8)

C(33)-Cr(2)-C(35)	176.05(8)
C(36)-Cr(2)-C(35)	89.43(8)
C(34)-Cr(2)-C(35)	90.72(8)
C(32)-Cr(2)-P(2)	175.76(6)
C(33)-Cr(2)-P(2)	85.95(6)
C(36)-Cr(2)-P(2)	91.99(6)
C(34)-Cr(2)-P(2)	90.24(5)
C(35)-Cr(2)-P(2)	92.45(5)
C(8)-O(1)-P(1)	118.53(10)
C(26)-O(7)-P(2)	118.29(11)
O(1)-P(1)-C(1)	99.71(7)
O(1)-P(1)-Cr(1)	118.61(5)
C(1)-P(1)-Cr(1)	124.17(6)
O(1)-P(1)-H(33)	100.7(8)
C(1)-P(1)-H(33)	101.9(8)
Cr(1)-P(1)-H(33)	108.3(8)
O(7)-P(2)-C(19)	99.44(7)
O(7)-P(2)-Cr(2)	118.07(5)
C(19)-P(2)-Cr(2)	124.35(6)
O(7)-P(2)-H(32)	99.5(8)
C(19)-P(2)-H(32)	102.6(8)
Cr(2)-P(2)-H(32)	109.2(8)
C(3)-Si(1)-C(2)	107.81(9)
C(3)-Si(1)-C(4)	109.47(9)
C(2)-Si(1)-C(4)	110.83(10)
C(3)-Si(1)-C(1)	112.41(8)
C(2)-Si(1)-C(1)	106.39(8)
C(4)-Si(1)-C(1)	109.89(8)
C(7)-Si(2)-C(6)	109.19(10)
C(7)-Si(2)-C(5)	108.22(9)
C(6)-Si(2)-C(5)	109.92(9)
C(7)-Si(2)-C(1)	110.43(8)
C(6)-Si(2)-C(1)	111.83(8)
C(5)-Si(2)-C(1)	107.17(8)
C(22)-Si(3)-C(20)	107.24(10)
C(22)-Si(3)-C(21)	108.35(10)
C(20)-Si(3)-C(21)	111.00(10)
C(22)-Si(3)-C(19)	112.63(8)
C(20)-Si(3)-C(19)	107.56(9)
C(21)-Si(3)-C(19)	110.05(9)
C(23)-Si(4)-C(25)	108.77(10)
C(23)-Si(4)-C(24)	109.70(10)
C(25)-Si(4)-C(24)	107.98(9)
C(23)-Si(4)-C(19)	112.01(8)

C(25)-Si(4)-C(19)	110.96(8)
C(24)-Si(4)-C(19)	107.32(8)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **47**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	14(1)	18(1)	16(1)	5(1)	0(1)	2(1)
C(2)	30(1)	41(1)	24(1)	3(1)	-9(1)	1(1)
C(3)	26(1)	39(1)	29(1)	13(1)	-1(1)	9(1)
C(4)	29(1)	41(1)	30(1)	19(1)	1(1)	4(1)
C(5)	29(1)	31(1)	25(1)	-1(1)	6(1)	5(1)
C(6)	37(1)	23(1)	34(1)	3(1)	1(1)	-2(1)
C(7)	36(1)	30(1)	19(1)	1(1)	-4(1)	6(1)
C(8)	18(1)	15(1)	23(1)	5(1)	3(1)	-1(1)
C(9)	23(1)	22(1)	20(1)	3(1)	-1(1)	-2(1)
C(10)	19(1)	27(1)	31(1)	6(1)	-5(1)	-4(1)
C(11)	18(1)	28(1)	35(1)	8(1)	7(1)	-1(1)
C(12)	28(1)	33(1)	24(1)	10(1)	7(1)	-2(1)
C(13)	24(1)	28(1)	22(1)	8(1)	-3(1)	-4(1)
C(14)	20(1)	26(1)	20(1)	3(1)	3(1)	-1(1)
C(15)	17(1)	24(1)	28(1)	8(1)	6(1)	1(1)
C(16)	24(1)	20(1)	22(1)	6(1)	-1(1)	0(1)
C(17)	19(1)	19(1)	27(1)	9(1)	6(1)	5(1)
C(18)	23(1)	19(1)	20(1)	4(1)	-3(1)	2(1)
C(19)	16(1)	17(1)	17(1)	3(1)	2(1)	-1(1)
C(20)	31(1)	49(1)	24(1)	9(1)	-7(1)	-5(1)
C(21)	38(1)	26(1)	29(1)	-4(1)	5(1)	-5(1)
C(22)	28(1)	36(1)	35(1)	0(1)	1(1)	-13(1)
C(23)	39(1)	27(1)	38(1)	14(1)	5(1)	4(1)
C(24)	29(1)	39(1)	25(1)	12(1)	7(1)	-2(1)
C(25)	35(1)	36(1)	20(1)	8(1)	-1(1)	-8(1)
C(26)	17(1)	14(1)	27(1)	4(1)	4(1)	1(1)
C(27)	21(1)	28(1)	26(1)	0(1)	1(1)	1(1)
C(28)	28(1)	35(1)	27(1)	1(1)	8(1)	3(1)
C(29)	19(1)	29(1)	42(1)	8(1)	9(1)	4(1)
C(30)	21(1)	28(1)	37(1)	10(1)	-5(1)	1(1)
C(31)	24(1)	23(1)	25(1)	8(1)	0(1)	3(1)
C(32)	19(1)	25(1)	25(1)	8(1)	4(1)	3(1)
C(33)	17(1)	28(1)	28(1)	8(1)	9(1)	4(1)
C(34)	21(1)	20(1)	21(1)	3(1)	-2(1)	-2(1)
C(35)	20(1)	17(1)	29(1)	3(1)	5(1)	-2(1)
C(36)	21(1)	21(1)	28(1)	7(1)	-1(1)	-2(1)

Cr(1)	15(1)	17(1)	17(1)	4(1)	1(1)	1(1)
Cr(2)	15(1)	17(1)	20(1)	4(1)	2(1)	0(1)
O(1)	16(1)	20(1)	24(1)	2(1)	2(1)	-1(1)
O(2)	34(1)	22(1)	37(1)	11(1)	1(1)	4(1)
O(3)	29(1)	46(1)	21(1)	0(1)	0(1)	-10(1)
O(4)	24(1)	44(1)	36(1)	11(1)	10(1)	0(1)
O(5)	30(1)	30(1)	24(1)	1(1)	-7(1)	3(1)
O(6)	21(1)	33(1)	33(1)	6(1)	9(1)	4(1)
O(7)	17(1)	21(1)	26(1)	7(1)	5(1)	2(1)
O(8)	33(1)	21(1)	40(1)	8(1)	3(1)	-3(1)
O(9)	28(1)	65(1)	24(1)	17(1)	5(1)	13(1)
O(10)	24(1)	37(1)	31(1)	4(1)	8(1)	5(1)
O(11)	31(1)	34(1)	27(1)	10(1)	-7(1)	-6(1)
O(12)	23(1)	36(1)	48(1)	12(1)	15(1)	1(1)
P(1)	15(1)	18(1)	16(1)	4(1)	0(1)	1(1)
P(2)	16(1)	18(1)	16(1)	3(1)	2(1)	-1(1)
Si(1)	18(1)	26(1)	19(1)	7(1)	-2(1)	3(1)
Si(2)	22(1)	18(1)	17(1)	2(1)	0(1)	2(1)
Si(3)	21(1)	24(1)	19(1)	1(1)	-1(1)	-6(1)
Si(4)	21(1)	21(1)	19(1)	6(1)	1(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **47**.

	x	y	z	U(eq)
H(1A)	3815	824	2102	19
H(2A)	3928	1689	4338	49
H(2B)	5046	1557	3839	49
H(2C)	4877	1107	4765	49
H(3A)	5693	-527	2653	46
H(3B)	4997	-1534	2658	46
H(3C)	5629	-915	3626	46
H(4A)	2642	-1172	3518	47
H(4B)	2676	-185	4417	47
H(4C)	3513	-1091	4390	47
H(5A)	4923	-1517	1005	44
H(5B)	4967	-393	788	44
H(5C)	4505	-1362	-28	44
H(6A)	1883	-1848	1559	48
H(6B)	3041	-2196	1856	48
H(6C)	2594	-2533	755	48
H(7A)	2637	289	89	44
H(7B)	1624	-271	388	44

H(7C)	2363	-895	-428	44
H(9A)	-507	-13	1397	27
H(10A)	-2220	279	1958	31
H(11A)	-2480	696	3614	31
H(12A)	-1026	792	4714	33
H(13A)	687	460	4161	29
H(19A)	8867	-4760	2149	20
H(20A)	10092	-4618	3878	52
H(20B)	9025	-4403	4454	52
H(20C)	10039	-3647	4785	52
H(21A)	7592	-2562	4206	49
H(21B)	8033	-1782	3615	49
H(21C)	8600	-1826	4632	49
H(22A)	10097	-2124	2680	51
H(22B)	10784	-3133	2679	51
H(22C)	10734	-2235	3647	51
H(23A)	8092	-1876	1901	50
H(23B)	6934	-2388	1597	50
H(23C)	7653	-2111	797	50
H(24A)	9999	-4229	786	45
H(24B)	9983	-2992	1060	45
H(24C)	9538	-3625	15	45
H(25C)	7427	-4367	-386	45
H(25B)	6661	-4538	426	45
H(25A)	7658	-5273	154	45
H(27A)	5758	-3362	4226	31
H(28A)	4030	-3384	4767	37
H(29A)	2582	-3829	3658	36
H(30A)	2851	-4227	2009	34
H(31A)	4572	-4225	1459	29
H(33)	2243(15)	1178(14)	3627(13)	24
H(32)	7294(15)	-4309(14)	3687(13)	25

Table 6. Torsion angles [deg] for **47**.

C(13)-C(8)-C(9)-C(10)	1.3(3)
O(1)-C(8)-C(9)-C(10)	-179.92(15)
C(8)-C(9)-C(10)-C(11)	0.2(3)
C(9)-C(10)-C(11)-C(12)	-0.8(3)
C(10)-C(11)-C(12)-C(13)	-0.1(3)
C(9)-C(8)-C(13)-C(12)	-2.1(3)
O(1)-C(8)-C(13)-C(12)	179.09(16)
C(11)-C(12)-C(13)-C(8)	1.5(3)
C(31)-C(26)-C(27)-C(28)	2.3(3)

O(7)-C(26)-C(27)-C(28)	179.79(17)
C(26)-C(27)-C(28)-C(29)	-1.0(3)
C(27)-C(28)-C(29)-C(30)	-0.6(3)
C(28)-C(29)-C(30)-C(31)	1.0(3)
C(27)-C(26)-C(31)-C(30)	-1.9(3)
O(7)-C(26)-C(31)-C(30)	-179.48(16)
C(29)-C(30)-C(31)-C(26)	0.2(3)
O(2)-C(14)-Cr(1)-C(18)	14(3)
O(2)-C(14)-Cr(1)-C(15)	-73(3)
O(2)-C(14)-Cr(1)-C(16)	-166(3)
O(2)-C(14)-Cr(1)-C(17)	103(3)
O(2)-C(14)-Cr(1)-P(1)	-46(4)
O(6)-C(18)-Cr(1)-C(14)	-11.8(15)
O(6)-C(18)-Cr(1)-C(15)	78.0(15)
O(6)-C(18)-Cr(1)-C(16)	-11(3)
O(6)-C(18)-Cr(1)-C(17)	-103.2(15)
O(6)-C(18)-Cr(1)-P(1)	164.4(15)
O(3)-C(15)-Cr(1)-C(14)	87(2)
O(3)-C(15)-Cr(1)-C(18)	1(2)
O(3)-C(15)-Cr(1)-C(16)	179(100)
O(3)-C(15)-Cr(1)-C(17)	-16(3)
O(3)-C(15)-Cr(1)-P(1)	-91(2)
O(4)-C(16)-Cr(1)-C(14)	-110(9)
O(4)-C(16)-Cr(1)-C(18)	-110(9)
O(4)-C(16)-Cr(1)-C(15)	160(9)
O(4)-C(16)-Cr(1)-C(17)	-18(9)
O(4)-C(16)-Cr(1)-P(1)	74(9)
O(5)-C(17)-Cr(1)-C(14)	-39(5)
O(5)-C(17)-Cr(1)-C(18)	47(5)
O(5)-C(17)-Cr(1)-C(15)	64(6)
O(5)-C(17)-Cr(1)-C(16)	-131(5)
O(5)-C(17)-Cr(1)-P(1)	138(5)
O(8)-C(32)-Cr(2)-C(33)	80(3)
O(8)-C(32)-Cr(2)-C(36)	-7(3)
O(8)-C(32)-Cr(2)-C(34)	173(3)
O(8)-C(32)-Cr(2)-C(35)	-97(3)
O(8)-C(32)-Cr(2)-P(2)	52(3)
O(9)-C(33)-Cr(2)-C(32)	-90(2)
O(9)-C(33)-Cr(2)-C(36)	-5(2)
O(9)-C(33)-Cr(2)-C(34)	178(100)
O(9)-C(33)-Cr(2)-C(35)	21(3)
O(9)-C(33)-Cr(2)-P(2)	88(2)
O(12)-C(36)-Cr(2)-C(32)	16.3(14)
O(12)-C(36)-Cr(2)-C(33)	-74.2(14)

O(12)-C(36)-Cr(2)-C(34)	14(3)
O(12)-C(36)-Cr(2)-C(35)	107.5(14)
O(12)-C(36)-Cr(2)-P(2)	-160.0(14)
O(10)-C(34)-Cr(2)-C(32)	106(11)
O(10)-C(34)-Cr(2)-C(33)	-163(11)
O(10)-C(34)-Cr(2)-C(36)	109(11)
O(10)-C(34)-Cr(2)-C(35)	15(11)
O(10)-C(34)-Cr(2)-P(2)	-77(11)
O(11)-C(35)-Cr(2)-C(32)	29(6)
O(11)-C(35)-Cr(2)-C(33)	-83(6)
O(11)-C(35)-Cr(2)-C(36)	-57(6)
O(11)-C(35)-Cr(2)-C(34)	121(6)
O(11)-C(35)-Cr(2)-P(2)	-149(6)
C(9)-C(8)-O(1)-P(1)	115.19(15)
C(13)-C(8)-O(1)-P(1)	-65.99(19)
C(27)-C(26)-O(7)-P(2)	65.66(19)
C(31)-C(26)-O(7)-P(2)	-116.75(15)
C(8)-O(1)-P(1)-C(1)	168.12(12)
C(8)-O(1)-P(1)-Cr(1)	-53.95(13)
Si(1)-C(1)-P(1)-O(1)	-95.52(9)
Si(2)-C(1)-P(1)-O(1)	39.40(10)
Si(1)-C(1)-P(1)-Cr(1)	129.79(6)
Si(2)-C(1)-P(1)-Cr(1)	-95.29(9)
C(14)-Cr(1)-P(1)-O(1)	111.2(8)
C(18)-Cr(1)-P(1)-O(1)	51.31(7)
C(15)-Cr(1)-P(1)-O(1)	138.18(7)
C(16)-Cr(1)-P(1)-O(1)	-128.84(7)
C(17)-Cr(1)-P(1)-O(1)	-37.72(7)
C(14)-Cr(1)-P(1)-C(1)	-121.8(8)
C(18)-Cr(1)-P(1)-C(1)	178.35(8)
C(15)-Cr(1)-P(1)-C(1)	-94.79(8)
C(16)-Cr(1)-P(1)-C(1)	-1.80(9)
C(17)-Cr(1)-P(1)-C(1)	89.31(8)
C(26)-O(7)-P(2)-C(19)	-169.02(12)
C(26)-O(7)-P(2)-Cr(2)	53.51(13)
Si(3)-C(19)-P(2)-O(7)	95.62(9)
Si(4)-C(19)-P(2)-O(7)	-39.66(10)
Si(3)-C(19)-P(2)-Cr(2)	-130.64(6)
Si(4)-C(19)-P(2)-Cr(2)	94.08(9)
C(32)-Cr(2)-P(2)-O(7)	-112.2(8)
C(33)-Cr(2)-P(2)-O(7)	-139.73(7)
C(36)-Cr(2)-P(2)-O(7)	-52.87(8)
C(34)-Cr(2)-P(2)-O(7)	127.39(7)
C(35)-Cr(2)-P(2)-O(7)	36.65(7)

C(32)-Cr(2)-P(2)-C(19)	121.6(8)
C(33)-Cr(2)-P(2)-C(19)	94.14(9)
C(36)-Cr(2)-P(2)-C(19)	-178.99(9)
C(34)-Cr(2)-P(2)-C(19)	1.26(9)
C(35)-Cr(2)-P(2)-C(19)	-89.47(9)
P(1)-C(1)-Si(1)-C(3)	175.14(9)
Si(2)-C(1)-Si(1)-C(3)	40.44(13)
P(1)-C(1)-Si(1)-C(2)	-67.09(11)
Si(2)-C(1)-Si(1)-C(2)	158.21(10)
P(1)-C(1)-Si(1)-C(4)	52.95(11)
Si(2)-C(1)-Si(1)-C(4)	-81.75(11)
P(1)-C(1)-Si(2)-C(7)	42.20(13)
Si(1)-C(1)-Si(2)-C(7)	173.85(10)
P(1)-C(1)-Si(2)-C(6)	-79.61(12)
Si(1)-C(1)-Si(2)-C(6)	52.04(13)
P(1)-C(1)-Si(2)-C(5)	159.87(10)
Si(1)-C(1)-Si(2)-C(5)	-68.48(12)
P(2)-C(19)-Si(3)-C(22)	-175.08(10)
Si(4)-C(19)-Si(3)-C(22)	-40.35(13)
P(2)-C(19)-Si(3)-C(20)	66.97(11)
Si(4)-C(19)-Si(3)-C(20)	-158.30(10)
P(2)-C(19)-Si(3)-C(21)	-54.07(12)
Si(4)-C(19)-Si(3)-C(21)	80.66(11)
P(2)-C(19)-Si(4)-C(23)	79.07(12)
Si(3)-C(19)-Si(4)-C(23)	-52.98(12)
P(2)-C(19)-Si(4)-C(25)	-42.71(12)
Si(3)-C(19)-Si(4)-C(25)	-174.76(10)
P(2)-C(19)-Si(4)-C(24)	-160.47(10)
Si(3)-C(19)-Si(4)-C(24)	67.48(11)

9. Crystal data of molecule [{bis(trimethylsily)methyl}isocyanatephosphane] pentacarbonyl tungsten complex (**48**) (GSTR186, Greg1493nx)

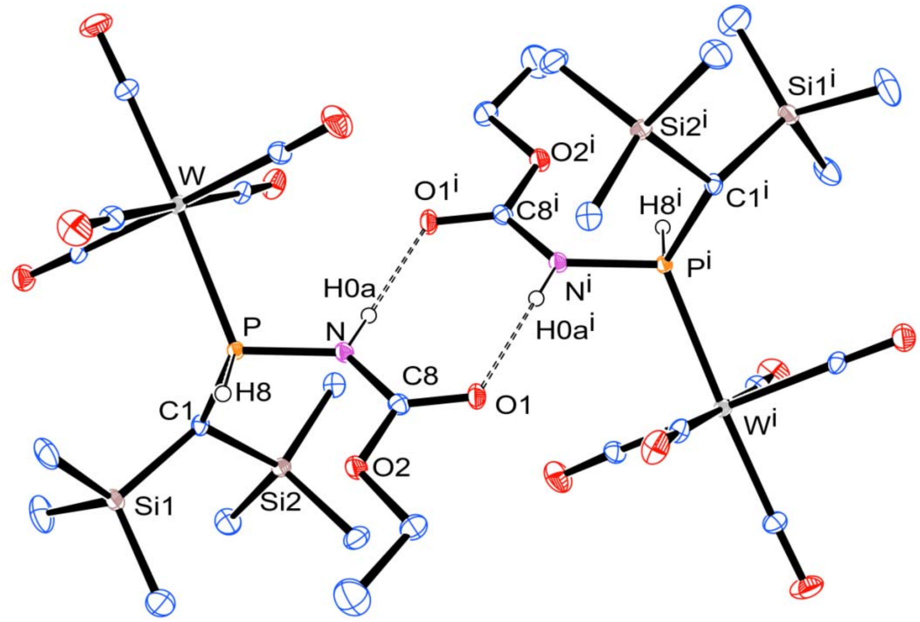

Table 1. Crystal data and structure refinement for **48**.

Identification code	GSTR186, Greg1493nx
Device Type	Nonius KappaCCD
Empirical formula	C15 H26 N O7 P Si2 W
Moiety formula	C15 H26 N O7 P Si2 W
Formula weight	603.37
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.5433(8) A alpha = 95.534(5) deg. b = 10.7743(10) A beta = 90.628(5) deg. c = 11.5207(7) A gamma = 99.482(4) deg.
Volume	1162.52(16) A^3
Z, Calculated density	2, 1.724 Mg/m^3
Absorption coefficient	5.173 mm^-1

F(000)	592
Crystal size	0.16 x 0.12 x 0.03 mm
Theta range for data collection	2.75 to 28.00 deg.
Limiting indices	-12<=h<=12, -14<=k<=14, -15<=l<=15
Reflections collected / unique	39191 / 5609 [R(int) = 0.0862]
Completeness to theta = 28.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8478 and 0.4879
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5609 / 17 / 254
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0455
R indices (all data)	R1 = 0.0344, wR2 = 0.0471
Largest diff. peak and hole	0.722 and -0.983 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **48**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8251(3)	7600(3)	2639(2)	16(1)
C(2)	5016(3)	7307(4)	2008(3)	34(1)
C(3)	7082(4)	9181(4)	908(3)	44(1)
C(4)	6985(5)	6320(4)	238(3)	53(1)
C(5)	10647(4)	8710(4)	1134(3)	33(1)
C(6)	10409(4)	5936(3)	1468(3)	31(1)
C(7)	11373(3)	7937(3)	3478(3)	23(1)
C(8)	8720(3)	4454(3)	3573(2)	18(1)
C(9)	7729(4)	2855(3)	2114(3)	31(1)

C(10)	6630(5)	2685(4)	1147(3)	49(1)
C(11)	6318(3)	8885(3)	7055(3)	24(1)
C(12)	4859(3)	7056(3)	5273(3)	23(1)
C(13)	6646(3)	9347(3)	4694(3)	18(1)
C(14)	9004(3)	8662(3)	6004(3)	19(1)
C(15)	7129(3)	6420(3)	6587(3)	22(1)
N	8680(3)	5642(2)	4093(2)	17(1)
O(1)	9505(2)	3767(2)	3886(2)	24(1)
O(2)	7784(2)	4137(2)	2668(2)	24(1)
O(3)	5968(3)	9472(2)	7850(2)	39(1)
O(4)	3731(3)	6556(3)	5055(2)	39(1)
O(5)	6468(2)	10161(2)	4180(2)	28(1)
O(6)	10143(2)	9120(2)	6239(2)	31(1)
O(7)	7208(3)	5601(2)	7126(2)	41(1)
P	7567(1)	6677(1)	3824(1)	13(1)
Si(1)	6851(1)	7574(1)	1437(1)	21(1)
Si(2)	10145(1)	7502(1)	2186(1)	18(1)
W	6916(1)	7890(1)	5635(1)	15(1)

Table 3. Bond lengths [A] and angles [deg] for **48**.

C(1)-P	1.829(3)
C(1)-Si(2)	1.904(3)
C(1)-Si(1)	1.909(3)
C(1)-H(1A)	1.0000
C(2)-Si(1)	1.865(3)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-Si(1)	1.871(4)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-Si(1)	1.858(4)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-Si(2)	1.872(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-Si(2)	1.863(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800

C(6)-H(6C)	0.9800
C(7)-Si(2)	1.858(3)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-O(1)	1.211(4)
C(8)-O(2)	1.346(3)
C(8)-N	1.367(4)
C(9)-O(2)	1.457(4)
C(9)-C(10)	1.499(5)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10C)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10A)	0.9800
C(11)-O(3)	1.147(4)
C(11)-W	2.009(3)
C(12)-O(4)	1.136(4)
C(12)-W	2.041(3)
C(13)-O(5)	1.139(3)
C(13)-W	2.040(3)
C(14)-O(6)	1.135(4)
C(14)-W	2.052(3)
C(15)-O(7)	1.139(4)
C(15)-W	2.046(3)
N-P	1.708(2)
N-H(0A)	0.8800
P-W	2.4932(8)
P-H(8)	1.41(3)

P-C(1)-Si(2)	116.80(15)
P-C(1)-Si(1)	112.40(15)
Si(2)-C(1)-Si(1)	117.89(15)
P-C(1)-H(1A)	102.1
Si(2)-C(1)-H(1A)	102.1
Si(1)-C(1)-H(1A)	102.1
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
Si(1)-C(3)-H(3A)	109.5
Si(1)-C(3)-H(3B)	109.5

H(3A)-C(3)-H(3B)	109.5
Si(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
Si(1)-C(4)-H(4A)	109.5
Si(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
Si(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
Si(2)-C(5)-H(5A)	109.5
Si(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Si(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
Si(2)-C(6)-H(6A)	109.5
Si(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
Si(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
Si(2)-C(7)-H(7A)	109.5
Si(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
O(1)-C(8)-O(2)	123.9(3)
O(1)-C(8)-N	124.1(3)
O(2)-C(8)-N	112.0(3)
O(2)-C(9)-C(10)	106.3(3)
O(2)-C(9)-H(9A)	110.5
C(10)-C(9)-H(9A)	110.5
O(2)-C(9)-H(9B)	110.5
C(10)-C(9)-H(9B)	110.5
H(9A)-C(9)-H(9B)	108.7
C(9)-C(10)-H(10C)	109.5
C(9)-C(10)-H(10B)	109.5
H(10C)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10A)	109.5
H(10C)-C(10)-H(10A)	109.5
H(10B)-C(10)-H(10A)	109.5
O(3)-C(11)-W	178.5(3)

O(4)-C(12)-W	177.6(3)
O(5)-C(13)-W	178.6(3)
O(6)-C(14)-W	177.5(3)
O(7)-C(15)-W	178.0(3)
C(8)-N-P	129.8(2)
C(8)-N-H(0A)	115.1
P-N-H(0A)	115.1
C(8)-O(2)-C(9)	114.5(2)
N-P-C(1)	109.73(13)
N-P-W	112.82(8)
C(1)-P-W	116.64(10)
N-P-H(8)	94.3(12)
C(1)-P-H(8)	103.9(11)
W-P-H(8)	117.0(11)
C(4)-Si(1)-C(2)	108.69(19)
C(4)-Si(1)-C(3)	112.0(2)
C(2)-Si(1)-C(3)	105.20(17)
C(4)-Si(1)-C(1)	111.16(16)
C(2)-Si(1)-C(1)	111.62(14)
C(3)-Si(1)-C(1)	108.02(16)
C(7)-Si(2)-C(6)	109.12(15)
C(7)-Si(2)-C(5)	107.50(16)
C(6)-Si(2)-C(5)	108.03(16)
C(7)-Si(2)-C(1)	109.62(14)
C(6)-Si(2)-C(1)	114.97(15)
C(5)-Si(2)-C(1)	107.33(14)
C(11)-W-C(13)	88.41(12)
C(11)-W-C(12)	90.62(13)
C(13)-W-C(12)	90.52(13)
C(11)-W-C(15)	90.91(13)
C(13)-W-C(15)	178.43(12)
C(12)-W-C(15)	88.06(13)
C(11)-W-C(14)	90.44(13)
C(13)-W-C(14)	91.38(12)
C(12)-W-C(14)	177.85(13)
C(15)-W-C(14)	90.05(13)
C(11)-W-P	177.46(9)
C(13)-W-P	89.85(8)
C(12)-W-P	87.55(9)
C(15)-W-P	90.78(9)
C(14)-W-P	91.45(8)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **48**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	16(2)	14(2)	19(2)	5(1)	2(1)	3(1)
C(2)	19(2)	51(2)	33(2)	14(2)	-6(1)	6(2)
C(3)	36(2)	49(3)	53(2)	33(2)	3(2)	12(2)
C(4)	47(3)	75(3)	38(2)	-21(2)	-20(2)	30(2)
C(5)	25(2)	44(2)	32(2)	12(2)	8(2)	5(2)
C(6)	30(2)	36(2)	28(2)	-4(2)	5(2)	11(2)
C(7)	14(2)	23(2)	30(2)	5(1)	2(1)	-1(1)
C(8)	19(2)	19(2)	17(2)	5(1)	2(1)	2(1)
C(9)	44(2)	19(2)	29(2)	-8(1)	-7(2)	8(2)
C(10)	56(3)	38(2)	50(3)	2(2)	-14(2)	2(2)
C(11)	23(2)	29(2)	22(1)	1(1)	6(1)	8(1)
C(12)	16(1)	29(2)	23(2)	6(1)	5(1)	1(1)
C(13)	17(2)	18(1)	22(1)	2(1)	4(1)	6(1)
C(14)	17(1)	18(2)	24(2)	0(1)	1(1)	4(1)
C(15)	24(2)	24(1)	20(2)	8(1)	5(1)	4(1)
N	20(2)	15(1)	17(1)	0(1)	-4(1)	4(1)
O(1)	28(1)	19(1)	27(1)	2(1)	-6(1)	11(1)
O(2)	30(1)	19(1)	22(1)	-2(1)	-9(1)	7(1)
O(3)	40(2)	48(2)	28(1)	-10(1)	9(1)	13(1)
O(4)	21(1)	49(2)	45(2)	11(1)	2(1)	-6(1)
O(5)	29(1)	26(1)	31(1)	7(1)	2(1)	9(1)
O(6)	18(1)	27(1)	48(2)	-5(1)	-3(1)	1(1)
O(7)	50(2)	39(2)	38(2)	22(1)	3(1)	7(1)
P	14(1)	14(1)	14(1)	3(1)	1(1)	4(1)
Si(1)	21(1)	28(1)	17(1)	7(1)	0(1)	8(1)
Si(2)	16(1)	21(1)	17(1)	3(1)	4(1)	4(1)
W	14(1)	16(1)	15(1)	2(1)	2(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **48**.

	x	y	z	U(eq)
H(1A)	8347	8487	3015	19
H(2A)	4959	7910	2693	40
H(2B)	4788	6443	2229	40
H(2C)	4337	7430	1403	40
H(3A)	7995	9348	523	53
H(3B)	7065	9819	1572	53
H(3C)	6309	9219	353	53
H(4A)	6938	5505	560	64

H(4B)	7891	6523	-151	64
H(4C)	6198	6270	-327	64
H(5A)	10436	9529	1467	40
H(5B)	10103	8447	400	40
H(5C)	11665	8786	985	40
H(6A)	9599	5588	938	37
H(6B)	10483	5357	2064	37
H(6C)	11284	6039	1024	37
H(7A)	11236	7254	3991	28
H(7B)	11173	8717	3904	28
H(7C)	12357	8067	3221	28
H(9A)	7460	2231	2683	37
H(9B)	8666	2742	1800	37
H(10C)	6944	3268	563	59
H(10B)	5727	2864	1463	59
H(10A)	6501	1813	781	59
H(0A)	9326	5915	4650	21
H(8)	6500(30)	5730(30)	3270(20)	20

Table 6. Torsion angles [deg] for **48**.

O(1)-C(8)-N-P	-175.1(2)
O(2)-C(8)-N-P	5.1(4)
O(1)-C(8)-O(2)-C(9)	3.0(4)
N-C(8)-O(2)-C(9)	-177.2(3)
C(10)-C(9)-O(2)-C(8)	179.6(3)
C(8)-N-P-C(1)	-85.7(3)
C(8)-N-P-W	142.4(2)
Si(2)-C(1)-P-N	-12.3(2)
Si(1)-C(1)-P-N	128.46(15)
Si(2)-C(1)-P-W	117.51(14)
Si(1)-C(1)-P-W	-101.69(14)
P-C(1)-Si(1)-C(4)	-94.9(2)
Si(2)-C(1)-Si(1)-C(4)	45.5(2)
P-C(1)-Si(1)-C(2)	26.7(2)
Si(2)-C(1)-Si(1)-C(2)	167.01(18)
P-C(1)-Si(1)-C(3)	141.86(18)
Si(2)-C(1)-Si(1)-C(3)	-77.8(2)
P-C(1)-Si(2)-C(7)	-55.2(2)
Si(1)-C(1)-Si(2)-C(7)	166.21(16)
P-C(1)-Si(2)-C(6)	68.2(2)
Si(1)-C(1)-Si(2)-C(6)	-70.5(2)
P-C(1)-Si(2)-C(5)	-171.65(18)
Si(1)-C(1)-Si(2)-C(5)	49.7(2)

O(3)-C(11)-W-C(13)	8(11)
O(3)-C(11)-W-C(12)	-82(11)
O(3)-C(11)-W-C(15)	-171(11)
O(3)-C(11)-W-C(14)	99(11)
O(3)-C(11)-W-P	-39(13)
O(5)-C(13)-W-C(11)	-48(12)
O(5)-C(13)-W-C(12)	43(12)
O(5)-C(13)-W-C(15)	17(15)
O(5)-C(13)-W-C(14)	-138(12)
O(5)-C(13)-W-P	131(12)
O(4)-C(12)-W-C(11)	-149(7)
O(4)-C(12)-W-C(13)	122(7)
O(4)-C(12)-W-C(15)	-59(7)
O(4)-C(12)-W-C(14)	-30(9)
O(4)-C(12)-W-P	32(7)
O(7)-C(15)-W-C(11)	55(9)
O(7)-C(15)-W-C(13)	-10(12)
O(7)-C(15)-W-C(12)	-36(9)
O(7)-C(15)-W-C(14)	145(9)
O(7)-C(15)-W-P	-123(9)
O(6)-C(14)-W-C(11)	-10(6)
O(6)-C(14)-W-C(13)	79(6)
O(6)-C(14)-W-C(12)	-129(6)
O(6)-C(14)-W-C(15)	-100(6)
O(6)-C(14)-W-P	169(6)
N-P-W-C(11)	-161(2)
C(1)-P-W-C(11)	70(2)
N-P-W-C(13)	152.01(13)
C(1)-P-W-C(13)	23.64(14)
N-P-W-C(12)	-117.46(13)
C(1)-P-W-C(12)	114.16(14)
N-P-W-C(15)	-29.43(13)
C(1)-P-W-C(15)	-157.81(14)
N-P-W-C(14)	60.63(13)
C(1)-P-W-C(14)	-67.74(14)

10. Crystal data of molecule [lithium(12-crown-4)][{bis(trimethylsily)methyl}-oxanido-phosphane] pentacarbonyl tungsten complex (**58**) (GSTR076, Greg729)

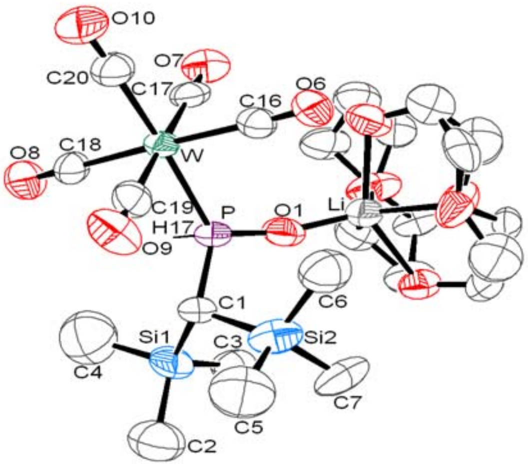

Table 1. Crystal data and structure refinement for **58**.

Identification code	GSTR076, Greg729
Device Type	Nonius KappaCCD
Empirical formula	C20 H36 Li O10 P Si2 W
Formula weight	714.43
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 10.2454(4) A alpha = 90 deg.
	b = 16.2432(7) A beta = 93.788(2) deg.
	c = 17.7500(6) A gamma = 90 deg.
Volume	2947.5(2) A^3
Z, Calculated density	4, 1.610 Mg/m^3
Absorption coefficient	4.100 mm^-1
F(000)	1424
Crystal size	0.68 x 0.17 x 0.16 mm
Theta range for data collection	2.62 to 27.87 deg.

Limiting indices	-11<=h<=13, -21<=k<=19, -21<=l<=23
Reflections collected / unique	27067 / 6838 [R(int) = 0.0577]
Completeness to theta = 27.87	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.43427 and 0.26964
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6838 / 54 / 363
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1216
R indices (all data)	R1 = 0.0808, wR2 = 0.1319
Largest diff. peak and hole	1.972 and -1.909 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **58**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3210(7)	1883(5)	10159(4)	61(2)
C(2)	1749(12)	1483(8)	11568(7)	114(4)
C(3)	2323(8)	3276(5)	11195(5)	73(2)
C(4)	4537(16)	2104(10)	11743(9)	155(6)
C(5)	1030(13)	684(8)	9691(8)	131(4)
C(6)	1920(10)	1761(6)	8487(6)	94(3)
C(7)	377(8)	2504(7)	9692(7)	101(3)
C(8)	1635(9)	5426(6)	9639(6)	84(3)
C(9S)	2573(14)	5920(10)	9272(10)	61(5)
C(9)	3170(20)	5327(14)	9692(12)	92(6)
C(10S)	4337(19)	5732(12)	8493(11)	81(6)
C(10)	5011(16)	5114(13)	9048(10)	89(7)
C(11)	5139(10)	4989(6)	8240(6)	90(3)
C(12)	3701(11)	4367(8)	7294(6)	101(3)
C(13S)	2520(30)	4573(19)	7274(15)	111(8)

C(13)	2446(19)	3985(12)	7248(8)	71(5)
C(14S)	919(14)	4868(10)	7876(7)	54(4)
C(14)	430(30)	4320(20)	8051(17)	121(9)
C(15)	269(8)	4784(7)	8623(5)	82(3)
C(16)	5026(7)	2006(5)	7960(4)	56(2)
C(17)	6901(7)	2933(5)	8833(4)	57(2)
C(18)	7042(7)	1680(5)	9992(4)	58(2)
C(19)	5182(8)	721(6)	9078(4)	63(2)
C(20)	7505(8)	1280(6)	8451(4)	68(2)
Li	2969(12)	4127(8)	8822(7)	61(3)
O(1)	3604(6)	3288(3)	9375(3)	75(2)
O(2)	1192(5)	4707(3)	9240(3)	64(1)
O(3)	3596(6)	5288(4)	9066(4)	97(2)
O(4)	4369(6)	4305(4)	8001(3)	79(2)
O(5)	1746(6)	4174(6)	7858(3)	110(3)
O(6)	4468(6)	2106(4)	7378(3)	72(2)
O(7)	7395(6)	3559(4)	8738(3)	77(2)
O(8)	7576(6)	1618(4)	10551(3)	86(2)
O(9)	4686(7)	89(4)	9136(3)	85(2)
O(10)	8349(6)	954(4)	8170(4)	97(2)
P	4338(2)	2550(1)	9693(1)	56(1)
Si(1)	2938(3)	2212(2)	11148(1)	90(1)
Si(2)	1665(3)	1726(2)	9523(2)	84(1)
W	6056(1)	1824(1)	8957(1)	48(1)

Table 3. Bond lengths [A] and angles [deg] for **58**.

C(1)-P	1.822(7)
C(1)-Si(1)	1.874(8)
C(1)-Si(2)	1.900(9)
C(1)-H(1)	1.0000
C(2)-Si(1)	1.888(11)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-Si(1)	1.842(9)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-Si(1)	1.898(16)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-Si(2)	1.844(13)

C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-Si(2)	1.874(11)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-Si(2)	1.866(10)
C(7)-H(7C)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7A)	0.9800
C(8)-O(2)	1.424(10)
C(8)-C(9S)	1.442(17)
C(8)-C(9)	1.57(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9S)-O(3)	1.529(15)
C(9S)-H(9C)	0.9900
C(9S)-H(9D)	0.9900
C(9)-O(3)	1.22(2)
C(9)-Li	2.49(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10S)-O(3)	1.493(18)
C(10S)-C(11)	1.54(2)
C(10S)-H(10C)	0.9900
C(10S)-H(10D)	0.9900
C(10)-C(11)	1.462(19)
C(10)-O(3)	1.479(18)
C(10)-Li	2.64(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-O(4)	1.412(11)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13S)	1.25(3)
C(12)-O(4)	1.393(12)
C(12)-C(13)	1.43(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13S)-O(5)	1.49(3)
C(13S)-H(13C)	0.9900
C(13S)-H(13D)	0.9900
C(13)-O(5)	1.373(16)

C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14S)-O(5)	1.412(15)
C(14S)-C(15)	1.529(16)
C(14S)-H(14C)	0.9900
C(14S)-H(14D)	0.9900
C(14)-C(15)	1.28(3)
C(14)-O(5)	1.43(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-O(2)	1.405(10)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-O(6)	1.158(9)
C(16)-W	2.022(8)
C(17)-O(7)	1.153(9)
C(17)-W	2.017(9)
C(18)-O(8)	1.106(9)
C(18)-W	2.050(8)
C(19)-O(9)	1.153(10)
C(19)-W	2.020(9)
C(20)-O(10)	1.156(9)
C(20)-W	1.992(8)
Li-O(1)	1.777(14)
Li-O(3)	2.029(15)
Li-O(5)	2.055(14)
Li-O(4)	2.131(12)
Li-O(2)	2.221(13)
O(1)-P	1.505(6)
P-W	2.5483(17)
P-H(17)	1.50(8)

P-C(1)-Si(1)	113.2(4)
P-C(1)-Si(2)	109.8(4)
Si(1)-C(1)-Si(2)	115.2(4)
P-C(1)-H(1)	106.0
Si(1)-C(1)-H(1)	106.0
Si(2)-C(1)-H(1)	106.0
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5

Si(1)-C(3)-H(3A)	109.5
Si(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
Si(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
Si(1)-C(4)-H(4A)	109.5
Si(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
Si(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
Si(2)-C(5)-H(5A)	109.5
Si(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Si(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
Si(2)-C(6)-H(6A)	109.5
Si(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
Si(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
Si(2)-C(7)-H(7C)	109.5
Si(2)-C(7)-H(7B)	109.5
H(7C)-C(7)-H(7B)	109.5
Si(2)-C(7)-H(7A)	109.5
H(7C)-C(7)-H(7A)	109.5
H(7B)-C(7)-H(7A)	109.5
O(2)-C(8)-C(9S)	115.6(8)
O(2)-C(8)-C(9)	103.3(10)
C(9S)-C(8)-C(9)	52.5(10)
O(2)-C(8)-H(8A)	111.1
C(9S)-C(8)-H(8A)	132.9
C(9)-C(8)-H(8A)	111.1
O(2)-C(8)-H(8B)	111.1
C(9S)-C(8)-H(8B)	58.9
C(9)-C(8)-H(8B)	111.1
H(8A)-C(8)-H(8B)	109.1
C(8)-C(9S)-O(3)	102.8(11)
C(8)-C(9S)-H(9C)	111.2
O(3)-C(9S)-H(9C)	111.2
C(8)-C(9S)-H(9D)	111.2

O(3)-C(9S)-H(9D)	111.2
H(9C)-C(9S)-H(9D)	109.1
O(3)-C(9)-C(8)	111.5(16)
O(3)-C(9)-Li	54.2(9)
C(8)-C(9)-Li	90.1(10)
O(3)-C(9)-H(9A)	109.3
C(8)-C(9)-H(9A)	109.3
Li-C(9)-H(9A)	159.1
O(3)-C(9)-H(9B)	109.3
C(8)-C(9)-H(9B)	109.3
Li-C(9)-H(9B)	71.1
H(9A)-C(9)-H(9B)	108.0
O(3)-C(10S)-C(11)	97.2(12)
O(3)-C(10S)-H(10C)	112.3
C(11)-C(10S)-H(10C)	112.3
O(3)-C(10S)-H(10D)	112.3
C(11)-C(10S)-H(10D)	112.3
H(10C)-C(10S)-H(10D)	109.9
C(11)-C(10)-O(3)	101.5(13)
C(11)-C(10)-Li	83.6(8)
O(3)-C(10)-Li	49.7(6)
C(11)-C(10)-H(10A)	111.5
O(3)-C(10)-H(10A)	111.5
Li-C(10)-H(10A)	159.3
C(11)-C(10)-H(10B)	111.5
O(3)-C(10)-H(10B)	111.5
Li-C(10)-H(10B)	76.0
H(10A)-C(10)-H(10B)	109.3
O(4)-C(11)-C(10)	108.7(9)
O(4)-C(11)-C(10S)	113.9(10)
C(10)-C(11)-C(10S)	61.4(12)
O(4)-C(11)-H(11A)	110.0
C(10)-C(11)-H(11A)	110.0
C(10S)-C(11)-H(11A)	50.1
O(4)-C(11)-H(11B)	110.0
C(10)-C(11)-H(11B)	110.0
C(10S)-C(11)-H(11B)	135.7
H(11A)-C(11)-H(11B)	108.3
C(13S)-C(12)-O(4)	117.3(15)
C(13S)-C(12)-C(13)	41.3(13)
O(4)-C(12)-C(13)	114.0(10)
C(13S)-C(12)-H(12A)	132.3
O(4)-C(12)-H(12A)	108.8
C(13)-C(12)-H(12A)	108.8

C(13S)-C(12)-H(12B)	69.0
O(4)-C(12)-H(12B)	108.8
C(13)-C(12)-H(12B)	108.8
H(12A)-C(12)-H(12B)	107.7
C(12)-C(13S)-O(5)	115(2)
C(12)-C(13S)-H(13C)	108.5
O(5)-C(13S)-H(13C)	108.5
C(12)-C(13S)-H(13D)	108.5
O(5)-C(13S)-H(13D)	108.5
H(13C)-C(13S)-H(13D)	107.5
O(5)-C(13)-C(12)	112.0(12)
O(5)-C(13)-H(13A)	109.2
C(12)-C(13)-H(13A)	109.2
O(5)-C(13)-H(13B)	109.2
C(12)-C(13)-H(13B)	109.2
H(13A)-C(13)-H(13B)	107.9
O(5)-C(14S)-C(15)	104.2(11)
O(5)-C(14S)-H(14C)	110.9
C(15)-C(14S)-H(14C)	110.9
O(5)-C(14S)-H(14D)	110.9
C(15)-C(14S)-H(14D)	110.9
H(14C)-C(14S)-H(14D)	108.9
C(15)-C(14)-O(5)	118(2)
C(15)-C(14)-H(14A)	107.9
O(5)-C(14)-H(14A)	107.9
C(15)-C(14)-H(14B)	107.9
O(5)-C(14)-H(14B)	107.9
H(14A)-C(14)-H(14B)	107.2
C(14)-C(15)-O(2)	116.7(14)
C(14)-C(15)-C(14S)	43.7(14)
O(2)-C(15)-C(14S)	112.0(8)
C(14)-C(15)-H(15A)	108.1
O(2)-C(15)-H(15A)	108.1
C(14S)-C(15)-H(15A)	138.7
C(14)-C(15)-H(15B)	108.1
O(2)-C(15)-H(15B)	108.1
C(14S)-C(15)-H(15B)	69.0
H(15A)-C(15)-H(15B)	107.3
O(6)-C(16)-W	178.1(6)
O(7)-C(17)-W	177.6(6)
O(8)-C(18)-W	178.6(8)
O(9)-C(19)-W	179.0(7)
O(10)-C(20)-W	178.5(8)
O(1)-Li-O(3)	119.8(7)

O(1)-Li-O(5)	131.9(8)
O(3)-Li-O(5)	108.1(7)
O(1)-Li-O(4)	104.1(6)
O(3)-Li-O(4)	78.6(5)
O(5)-Li-O(4)	80.0(5)
O(1)-Li-O(2)	114.8(6)
O(3)-Li-O(2)	77.9(5)
O(5)-Li-O(2)	78.1(5)
O(4)-Li-O(2)	140.8(7)
O(1)-Li-C(9)	104.3(8)
O(3)-Li-C(9)	29.3(5)
O(5)-Li-C(9)	120.6(8)
O(4)-Li-C(9)	106.7(7)
O(2)-Li-C(9)	59.7(6)
O(1)-Li-C(10)	97.2(8)
O(3)-Li-C(10)	33.8(5)
O(5)-Li-C(10)	122.5(8)
O(4)-Li-C(10)	57.3(5)
O(2)-Li-C(10)	110.5(7)
C(9)-Li-C(10)	53.1(7)
P-O(1)-Li	166.7(5)
C(15)-O(2)-C(8)	119.4(7)
C(15)-O(2)-Li	107.6(5)
C(8)-O(2)-Li	105.8(6)
C(9)-O(3)-C(10)	116.2(14)
C(9)-O(3)-C(10S)	145.3(14)
C(10)-O(3)-C(10S)	62.3(11)
C(9)-O(3)-C(9S)	57.0(12)
C(10)-O(3)-C(9S)	145.3(10)
C(10S)-O(3)-C(9S)	103.0(11)
C(9)-O(3)-Li	96.5(12)
C(10)-O(3)-Li	96.6(9)
C(10S)-O(3)-Li	118.1(9)
C(9S)-O(3)-Li	117.6(7)
C(12)-O(4)-C(11)	116.4(8)
C(12)-O(4)-Li	108.3(7)
C(11)-O(4)-Li	106.8(6)
C(13)-O(5)-C(14S)	122.8(11)
C(13)-O(5)-C(14)	140.8(15)
C(14S)-O(5)-C(14)	44.2(12)
C(13)-O(5)-C(13S)	38.8(11)
C(14S)-O(5)-C(13S)	90.9(14)
C(14)-O(5)-C(13S)	129.9(17)
C(13)-O(5)-Li	109.1(9)

C(14S)-O(5)-Li	110.2(8)
C(14)-O(5)-Li	109.8(13)
C(13S)-O(5)-Li	105.7(12)
O(1)-P-C(1)	109.1(3)
O(1)-P-W	121.4(2)
C(1)-P-W	115.9(3)
O(1)-P-H(17)	104(3)
C(1)-P-H(17)	99(3)
W-P-H(17)	103(3)
C(3)-Si(1)-C(1)	112.5(4)
C(3)-Si(1)-C(2)	109.8(5)
C(1)-Si(1)-C(2)	109.3(5)
C(3)-Si(1)-C(4)	110.3(6)
C(1)-Si(1)-C(4)	108.6(6)
C(2)-Si(1)-C(4)	106.1(7)
C(5)-Si(2)-C(7)	109.6(5)
C(5)-Si(2)-C(6)	105.1(5)
C(7)-Si(2)-C(6)	106.4(5)
C(5)-Si(2)-C(1)	108.4(5)
C(7)-Si(2)-C(1)	112.6(4)
C(6)-Si(2)-C(1)	114.4(4)
C(20)-W-C(17)	90.5(3)
C(20)-W-C(19)	90.2(3)
C(17)-W-C(19)	179.2(3)
C(20)-W-C(16)	91.8(3)
C(17)-W-C(16)	88.7(3)
C(19)-W-C(16)	90.8(3)
C(20)-W-C(18)	90.9(3)
C(17)-W-C(18)	90.6(3)
C(19)-W-C(18)	89.9(3)
C(16)-W-C(18)	177.2(3)
C(20)-W-P	175.3(2)
C(17)-W-P	87.63(19)
C(19)-W-P	91.7(2)
C(16)-W-P	92.4(2)
C(18)-W-P	84.9(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **58**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	50(4)	78(5)	57(4)	15(4)	21(3)	7(4)
C(2)	124(5)	116(5)	106(5)	12(4)	40(4)	0(4)

C(3)	60(5)	99(7)	61(5)	-11(4)	15(4)	-6(4)
C(4)	157(7)	166(7)	143(7)	5(5)	7(5)	12(5)
C(5)	135(6)	128(6)	133(6)	-1(4)	19(4)	-15(4)
C(6)	80(6)	112(9)	89(7)	-9(6)	6(5)	-9(5)
C(7)	41(4)	138(10)	125(8)	-24(7)	11(5)	-11(5)
C(8)	86(6)	73(6)	95(7)	-24(5)	32(5)	-12(5)
C(9S)	58(9)	50(9)	78(11)	-38(8)	25(8)	-9(7)
C(9)	95(7)	97(7)	85(7)	0(5)	6(5)	-10(5)
C(10S)	80(7)	82(7)	83(7)	2(5)	13(5)	-7(5)
C(10)	65(10)	123(16)	81(12)	-15(11)	9(9)	-48(11)
C(11)	84(4)	92(5)	94(5)	5(4)	15(4)	-16(4)
C(12)	103(5)	113(5)	87(5)	7(4)	15(4)	3(4)
C(13S)	114(9)	113(9)	106(9)	-1(5)	0(5)	7(5)
C(13)	114(14)	66(12)	32(7)	-12(7)	-9(8)	23(10)
C(14S)	50(8)	71(10)	42(7)	2(7)	-3(6)	15(7)
C(14)	118(10)	124(10)	121(10)	-3(5)	5(5)	4(5)
C(15)	53(5)	126(8)	68(5)	4(5)	8(4)	17(5)
C(16)	53(4)	69(5)	46(4)	0(3)	9(3)	-1(3)
C(17)	43(4)	81(6)	50(4)	-7(4)	16(3)	0(4)
C(18)	43(4)	84(6)	46(4)	0(4)	-3(3)	4(3)
C(19)	67(5)	76(6)	44(4)	1(4)	1(3)	9(4)
C(20)	58(5)	95(6)	52(4)	-4(4)	9(4)	7(4)
Li	55(7)	75(8)	53(7)	1(6)	11(6)	3(6)
O(1)	75(4)	79(4)	73(4)	20(3)	35(3)	14(3)
O(2)	56(3)	76(4)	62(3)	-11(3)	15(2)	-7(3)
O(3)	67(4)	126(6)	101(5)	-29(4)	28(4)	-34(4)
O(4)	82(4)	97(5)	59(3)	10(3)	12(3)	-20(3)
O(5)	67(4)	196(8)	66(4)	-46(4)	-12(3)	44(4)
O(6)	68(3)	103(4)	44(3)	7(3)	1(3)	2(3)
O(7)	71(4)	81(4)	80(4)	-6(3)	19(3)	-12(3)
O(8)	71(4)	135(6)	49(3)	12(3)	-11(3)	1(4)
O(9)	115(5)	75(4)	63(4)	6(3)	-1(3)	-25(4)
O(10)	92(4)	123(5)	79(4)	-10(4)	34(4)	34(4)
P	48(1)	76(1)	47(1)	8(1)	9(1)	7(1)
Si(1)	95(2)	120(2)	58(1)	23(2)	36(1)	23(2)
Si(2)	66(2)	90(2)	100(2)	-5(2)	23(1)	-19(1)
W	43(1)	67(1)	34(1)	2(1)	9(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **58**.

	x	y	z	U(eq)
H(1)	3644	1332	10203	73

H(2A)	2168	947	11656	171
H(2B)	975	1419	11219	171
H(2C)	1487	1706	12048	171
H(3A)	1368	3268	11199	109
H(3B)	2580	3585	10754	109
H(3C)	2696	3540	11657	109
H(4A)	5179	2494	11565	233
H(4B)	4869	1542	11699	233
H(4C)	4390	2221	12272	233
H(5A)	694	660	10195	197
H(5B)	1736	281	9658	197
H(5C)	323	557	9310	197
H(6A)	2507	1314	8359	140
H(6B)	2309	2291	8363	140
H(6C)	1077	1697	8199	140
H(7C)	-381	2414	9335	152
H(7B)	726	3058	9620	152
H(7A)	110	2449	10210	152
H(8A)	1293	5446	10148	100
H(8B)	1364	5931	9359	100
H(9C)	2963	6345	9618	74
H(9D)	2167	6192	8815	74
H(9A)	3569	5802	9970	111
H(9B)	3410	4821	9979	111
H(10C)	4899	6174	8721	97
H(10D)	3755	5959	8077	97
H(10A)	5547	5585	9242	107
H(10B)	5262	4614	9342	107
H(11A)	4841	5486	7956	107
H(11B)	6066	4888	8144	107
H(12A)	4240	4114	6913	121
H(12B)	3592	4957	7164	121
H(13C)	2108	4438	6769	134
H(13D)	2470	5178	7338	134
H(13A)	1949	4166	6780	86
H(13B)	2557	3380	7220	86
H(14C)	257	4863	7443	65
H(14D)	1430	5384	7862	65
H(14A)	-51	4574	7606	146
H(14B)	17	3785	8141	146
H(15A)	-607	4668	8802	99
H(15B)	268	5365	8452	99
H(17)	5110(80)	2870(50)	10380(50)	90(30)

Table 6. Torsion angles [deg] for **58**.

O(2)-C(8)-C(9S)-O(3)	-50.1(14)
C(9)-C(8)-C(9S)-O(3)	37.3(11)
O(2)-C(8)-C(9)-O(3)	59.7(18)
C(9S)-C(8)-C(9)-O(3)	-52.5(14)
O(2)-C(8)-C(9)-Li	8.6(10)
C(9S)-C(8)-C(9)-Li	-103.6(11)
O(3)-C(10)-C(11)-O(4)	-62.0(15)
Li-C(10)-C(11)-O(4)	-15.4(10)
O(3)-C(10)-C(11)-C(10S)	45.6(12)
Li-C(10)-C(11)-C(10S)	92.2(10)
O(3)-C(10S)-C(11)-O(4)	54.7(14)
O(3)-C(10S)-C(11)-C(10)	-44.4(10)
O(4)-C(12)-C(13S)-O(5)	-42(3)
C(13)-C(12)-C(13S)-O(5)	54.0(19)
C(13S)-C(12)-C(13)-O(5)	-59(2)
O(4)-C(12)-C(13)-O(5)	45.3(18)
O(5)-C(14)-C(15)-O(2)	-37(3)
O(5)-C(14)-C(15)-C(14S)	58(2)
O(5)-C(14S)-C(15)-C(14)	-52(2)
O(5)-C(14S)-C(15)-O(2)	54.6(14)
O(3)-C(9)-Li-O(1)	126.4(12)
C(8)-C(9)-Li-O(1)	-116.8(10)
C(8)-C(9)-Li-O(3)	116.8(17)
O(3)-C(9)-Li-O(5)	-71.6(13)
C(8)-C(9)-Li-O(5)	45.3(12)
O(3)-C(9)-Li-O(4)	16.6(12)
C(8)-C(9)-Li-O(4)	133.4(9)
O(3)-C(9)-Li-O(2)	-123.0(13)
C(8)-C(9)-Li-O(2)	-6.2(7)
O(3)-C(9)-Li-C(10)	38.1(10)
C(8)-C(9)-Li-C(10)	154.9(14)
C(11)-C(10)-Li-O(1)	113.6(11)
O(3)-C(10)-Li-O(1)	-135.4(9)
C(11)-C(10)-Li-O(3)	-111.0(14)
C(11)-C(10)-Li-O(5)	-37.8(14)
O(3)-C(10)-Li-O(5)	73.2(10)
C(11)-C(10)-Li-O(4)	11.4(8)
O(3)-C(10)-Li-O(4)	122.4(10)
C(11)-C(10)-Li-O(2)	-126.5(10)
O(3)-C(10)-Li-O(2)	-15.5(9)
C(11)-C(10)-Li-C(9)	-143.9(14)
O(3)-C(10)-Li-C(9)	-32.9(8)

O(3)-Li-O(1)-P	-100(3)
O(5)-Li-O(1)-P	74(3)
O(4)-Li-O(1)-P	-15(3)
O(2)-Li-O(1)-P	170(2)
C(9)-Li-O(1)-P	-127(3)
C(10)-Li-O(1)-P	-73(3)
C(14)-C(15)-O(2)-C(8)	140.3(19)
C(14S)-C(15)-O(2)-C(8)	92.3(10)
C(14)-C(15)-O(2)-Li	20(2)
C(14S)-C(15)-O(2)-Li	-28.1(11)
C(9S)-C(8)-O(2)-C(15)	-76.8(12)
C(9)-C(8)-O(2)-C(15)	-131.3(10)
C(9S)-C(8)-O(2)-Li	44.5(12)
C(9)-C(8)-O(2)-Li	-10.0(11)
O(1)-Li-O(2)-C(15)	-131.6(8)
O(3)-Li-O(2)-C(15)	111.0(6)
O(5)-Li-O(2)-C(15)	-0.7(7)
O(4)-Li-O(2)-C(15)	56.6(12)
C(9)-Li-O(2)-C(15)	135.8(8)
C(10)-Li-O(2)-C(15)	119.7(8)
O(1)-Li-O(2)-C(8)	99.7(9)
O(3)-Li-O(2)-C(8)	-17.7(7)
O(5)-Li-O(2)-C(8)	-129.4(7)
O(4)-Li-O(2)-C(8)	-72.0(12)
C(9)-Li-O(2)-C(8)	7.1(8)
C(10)-Li-O(2)-C(8)	-8.9(9)
C(8)-C(9)-O(3)-C(10)	-174.3(13)
Li-C(9)-O(3)-C(10)	-100.6(13)
C(8)-C(9)-O(3)-C(10S)	107(2)
Li-C(9)-O(3)-C(10S)	-179(3)
C(8)-C(9)-O(3)-C(9S)	45.1(13)
Li-C(9)-O(3)-C(9S)	118.7(10)
C(8)-C(9)-O(3)-Li	-73.6(15)
C(11)-C(10)-O(3)-C(9)	171.9(15)
Li-C(10)-O(3)-C(9)	100.6(15)
C(11)-C(10)-O(3)-C(10S)	-47.2(12)
Li-C(10)-O(3)-C(10S)	-118.4(11)
C(11)-C(10)-O(3)-C(9S)	-119.1(18)
Li-C(10)-O(3)-C(9S)	170(2)
C(11)-C(10)-O(3)-Li	71.2(12)
C(11)-C(10S)-O(3)-C(9)	140(2)
C(11)-C(10S)-O(3)-C(10)	43.3(11)
C(11)-C(10S)-O(3)-C(9S)	-170.4(10)
C(11)-C(10S)-O(3)-Li	-39.0(14)

C(8)-C(9S)-O(3)-C(9)	-47.6(14)
C(8)-C(9S)-O(3)-C(10)	-136.8(17)
C(8)-C(9S)-O(3)-C(10S)	163.5(12)
C(8)-C(9S)-O(3)-Li	31.7(14)
O(1)-Li-O(3)-C(9)	-64.0(13)
O(5)-Li-O(3)-C(9)	120.8(12)
O(4)-Li-O(3)-C(9)	-163.8(12)
O(2)-Li-O(3)-C(9)	47.8(12)
C(10)-Li-O(3)-C(9)	-117.4(15)
O(1)-Li-O(3)-C(10)	53.4(10)
O(5)-Li-O(3)-C(10)	-121.8(9)
O(4)-Li-O(3)-C(10)	-46.5(9)
O(2)-Li-O(3)-C(10)	165.1(9)
C(9)-Li-O(3)-C(10)	117.4(15)
O(1)-Li-O(3)-C(10S)	115.4(12)
O(5)-Li-O(3)-C(10S)	-59.8(12)
O(4)-Li-O(3)-C(10S)	15.5(11)
O(2)-Li-O(3)-C(10S)	-132.9(10)
C(9)-Li-O(3)-C(10S)	179.4(17)
C(10)-Li-O(3)-C(10S)	62.0(11)
O(1)-Li-O(3)-C(9S)	-120.0(10)
O(5)-Li-O(3)-C(9S)	64.8(11)
O(4)-Li-O(3)-C(9S)	140.1(10)
O(2)-Li-O(3)-C(9S)	-8.3(10)
C(9)-Li-O(3)-C(9S)	-56.0(12)
C(10)-Li-O(3)-C(9S)	-173.4(13)
C(13S)-C(12)-O(4)-C(11)	-98(2)
C(13)-C(12)-O(4)-C(11)	-144.2(11)
C(13S)-C(12)-O(4)-Li	22(2)
C(13)-C(12)-O(4)-Li	-23.9(14)
C(10)-C(11)-O(4)-C(12)	141.1(12)
C(10S)-C(11)-O(4)-C(12)	74.8(12)
C(10)-C(11)-O(4)-Li	20.0(13)
C(10S)-C(11)-O(4)-Li	-46.2(12)
O(1)-Li-O(4)-C(12)	132.0(8)
O(3)-Li-O(4)-C(12)	-109.8(7)
O(5)-Li-O(4)-C(12)	1.1(8)
O(2)-Li-O(4)-C(12)	-55.7(13)
C(9)-Li-O(4)-C(12)	-118.0(9)
C(10)-Li-O(4)-C(12)	-138.4(9)
O(1)-Li-O(4)-C(11)	-101.9(8)
O(3)-Li-O(4)-C(11)	16.3(7)
O(5)-Li-O(4)-C(11)	127.2(7)
O(2)-Li-O(4)-C(11)	70.4(12)

C(9)-Li-O(4)-C(11)	8.1(10)
C(10)-Li-O(4)-C(11)	-12.3(8)
C(12)-C(13)-O(5)-C(14S)	89.1(17)
C(12)-C(13)-O(5)-C(14)	145(2)
C(12)-C(13)-O(5)-C(13S)	50(2)
C(12)-C(13)-O(5)-Li	-42.0(16)
C(15)-C(14S)-O(5)-C(13)	175.3(12)
C(15)-C(14S)-O(5)-C(14)	44.0(17)
C(15)-C(14S)-O(5)-C(13S)	-161.2(15)
C(15)-C(14S)-O(5)-Li	-54.1(12)
C(15)-C(14)-O(5)-C(13)	-153(2)
C(15)-C(14)-O(5)-C(14S)	-65(2)
C(15)-C(14)-O(5)-C(13S)	-99(3)
C(15)-C(14)-O(5)-Li	34(3)
C(12)-C(13S)-O(5)-C(13)	-62(2)
C(12)-C(13S)-O(5)-C(14S)	150(2)
C(12)-C(13S)-O(5)-C(14)	173(2)
C(12)-C(13S)-O(5)-Li	39(3)
O(1)-Li-O(5)-C(13)	-78.0(13)
O(3)-Li-O(5)-C(13)	96.4(11)
O(4)-Li-O(5)-C(13)	22.0(11)
O(2)-Li-O(5)-C(13)	169.2(11)
C(9)-Li-O(5)-C(13)	125.6(12)
C(10)-Li-O(5)-C(13)	62.3(13)
O(1)-Li-O(5)-C(14S)	144.5(11)
O(3)-Li-O(5)-C(14S)	-41.1(10)
O(4)-Li-O(5)-C(14S)	-115.5(9)
O(2)-Li-O(5)-C(14S)	31.7(9)
C(9)-Li-O(5)-C(14S)	-11.9(13)
C(10)-Li-O(5)-C(14S)	-75.2(11)
O(1)-Li-O(5)-C(14)	97.2(17)
O(3)-Li-O(5)-C(14)	-88.4(16)
O(4)-Li-O(5)-C(14)	-162.8(15)
O(2)-Li-O(5)-C(14)	-15.5(15)
C(9)-Li-O(5)-C(14)	-59.2(17)
C(10)-Li-O(5)-C(14)	-122.4(16)
O(1)-Li-O(5)-C(13S)	-118.7(15)
O(3)-Li-O(5)-C(13S)	55.7(14)
O(4)-Li-O(5)-C(13S)	-18.7(13)
O(2)-Li-O(5)-C(13S)	128.6(13)
C(9)-Li-O(5)-C(13S)	85.0(15)
C(10)-Li-O(5)-C(13S)	21.7(15)
Li-O(1)-P-C(1)	-141(3)
Li-O(1)-P-W	-2(3)

Si(1)-C(1)-P-O(1)	-82.9(5)
Si(2)-C(1)-P-O(1)	47.3(5)
Si(1)-C(1)-P-W	135.6(3)
Si(2)-C(1)-P-W	-94.2(4)
P-C(1)-Si(1)-C(3)	57.3(5)
Si(2)-C(1)-Si(1)-C(3)	-70.2(5)
P-C(1)-Si(1)-C(2)	179.6(5)
Si(2)-C(1)-Si(1)-C(2)	52.1(6)
P-C(1)-Si(1)-C(4)	-65.0(7)
Si(2)-C(1)-Si(1)-C(4)	167.5(6)
P-C(1)-Si(2)-C(5)	147.5(5)
Si(1)-C(1)-Si(2)-C(5)	-83.3(6)
P-C(1)-Si(2)-C(7)	-91.1(5)
Si(1)-C(1)-Si(2)-C(7)	38.0(6)
P-C(1)-Si(2)-C(6)	30.6(6)
Si(1)-C(1)-Si(2)-C(6)	159.7(5)
O(10)-C(20)-W-C(17)	128(33)
O(10)-C(20)-W-C(19)	-53(33)
O(10)-C(20)-W-C(16)	-144(33)
O(10)-C(20)-W-C(18)	37(33)
O(10)-C(20)-W-P	62(35)
O(7)-C(17)-W-C(20)	41(17)
O(7)-C(17)-W-C(19)	-101(23)
O(7)-C(17)-W-C(16)	-51(17)
O(7)-C(17)-W-C(18)	132(17)
O(7)-C(17)-W-P	-143(17)
O(9)-C(19)-W-C(20)	-52(43)
O(9)-C(19)-W-C(17)	90(47)
O(9)-C(19)-W-C(16)	40(43)
O(9)-C(19)-W-C(18)	-143(43)
O(9)-C(19)-W-P	132(43)
O(6)-C(16)-W-C(20)	-15(21)
O(6)-C(16)-W-C(17)	75(21)
O(6)-C(16)-W-C(19)	-106(21)
O(6)-C(16)-W-C(18)	149(18)
O(6)-C(16)-W-P	163(21)
O(8)-C(18)-W-C(20)	114(28)
O(8)-C(18)-W-C(17)	24(28)
O(8)-C(18)-W-C(19)	-156(28)
O(8)-C(18)-W-C(16)	-50(30)
O(8)-C(18)-W-P	-64(28)
O(1)-P-W-C(20)	118(3)
C(1)-P-W-C(20)	-105(3)
O(1)-P-W-C(17)	52.2(4)

C(1)-P-W-C(17)	-171.4(4)
O(1)-P-W-C(19)	-127.3(4)
C(1)-P-W-C(19)	9.1(4)
O(1)-P-W-C(16)	-36.4(4)
C(1)-P-W-C(16)	100.0(4)
O(1)-P-W-C(18)	143.0(4)
C(1)-P-W-C(18)	-80.6(4)

11. Crystal data of molecule of [*N,N*-di-*tert*-butyl-imidazolium][{bis(trimethylsilyl) methyl}phenoxyphosphinidenoid] tungsten complex (**68a**) (GSTR184, Greg1468)

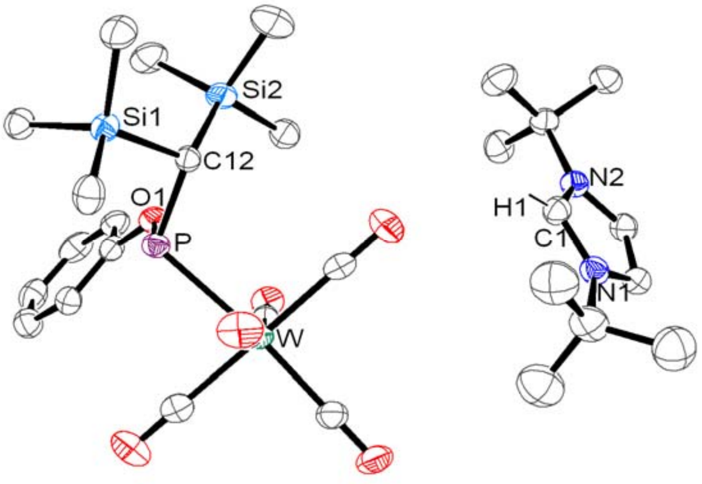

Table 1. Crystal data and structure refinement for **68a**.

Identification code	GSTR184, Greg1468
Device Type	Nonius KappaCCD
Empirical formula	C29 H45 N2 O6 P Si2 W
Moiety formula	C18 H24 O6 P Si2 W, C11 H21 N2
Formula weight	788.67
Temperature	123(2) K
Wavelength	0.71073 A

Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 18.4241(6) A alpha = 90 deg. b = 19.4516(5) A beta = 90 deg. c = 19.8408(4) A gamma = 90 deg.
Volume	7110.5(3) A^3
Z, Calculated density	8, 1.473 Mg/m^3
Absorption coefficient	3.401 mm^-1
F(000)	3184
Crystal size	0.48 x 0.32 x 0.12 mm
Theta range for data collection	2.33 to 28.00 deg.
Limiting indices	-19<=h<=24, -25<=k<=25, -26<=l<=22
Reflections collected / unique	51159 / 8550 [R(int) = 0.0872]
Completeness to theta = 28.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6857 and 0.2921
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8550 / 43 / 383
Goodness-of-fit on F^2	0.911
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0699
R indices (all data)	R1 = 0.0729, wR2 = 0.0780
Extinction coefficient	0.00014(3)
Largest diff. peak and hole	1.638 and -1.496 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **68a**. U(eq) is defined as one third of the trace of the orthogonalized Uij

tensor.

	x	y	z	U(eq)
C(1)	7918(2)	1899(2)	6309(2)	29(1)
C(2)	8259(2)	2974(2)	6412(2)	31(1)
C(3)	7532(2)	2957(2)	6419(2)	28(1)
C(4)	9282(3)	2072(2)	6296(2)	44(1)
C(5)	9314(3)	1317(3)	6443(3)	62(1)
C(6)	9545(3)	2248(3)	5608(3)	64(1)
C(7)	9702(3)	2448(3)	6843(3)	61(1)
C(8)	6543(2)	2034(2)	6305(2)	29(1)
C(9)	6245(2)	2287(2)	5634(2)	40(1)
C(10)	6538(3)	1252(2)	6341(2)	41(1)
C(11)	6131(2)	2330(2)	6894(2)	35(1)
C(12)	7201(2)	-493(2)	3974(2)	24(1)
C(13)	8355(2)	-1620(2)	3827(2)	38(1)
C(14)	6913(2)	-1726(2)	3044(2)	33(1)
C(15)	6990(3)	-1991(2)	4554(2)	41(1)
C(16)	5547(3)	-621(2)	3639(2)	45(1)
C(17)	6036(3)	-489(3)	5076(2)	54(1)
C(18)	6102(3)	732(2)	4174(2)	39(1)
C(19)	6742(2)	323(2)	2204(2)	29(1)
C(20)	6070(2)	576(2)	2007(2)	33(1)
C(21)	5922(3)	687(2)	1329(3)	42(1)
C(22)	6435(3)	545(2)	848(2)	42(1)
C(23)	7110(3)	302(2)	1041(2)	38(1)
C(24)	7269(2)	200(2)	1726(2)	30(1)
C(25)	9134(2)	1691(2)	3702(2)	33(1)
C(26)	8021(2)	1015(2)	4459(2)	30(1)
C(27)	7639(2)	1482(2)	3166(2)	28(1)
C(28)	8939(2)	749(2)	2622(2)	33(1)
C(29)	9111(2)	186(2)	3973(2)	31(1)
N(1)	8497(2)	2297(2)	6348(2)	29(1)
N(2)	7317(2)	2278(2)	6352(2)	26(1)
O(1)	6839(2)	220(1)	2877(1)	30(1)
O(2)	9512(2)	2157(2)	3793(2)	43(1)
O(3)	7784(2)	1072(2)	4994(2)	44(1)
O(4)	7132(2)	1766(2)	2982(2)	38(1)
O(5)	9217(2)	659(2)	2107(2)	50(1)
O(6)	9445(2)	-228(2)	4242(2)	44(1)
P	7633(1)	-118(1)	3204(1)	25(1)
Si(1)	7354(1)	-1448(1)	3851(1)	28(1)
Si(2)	6243(1)	-217(1)	4187(1)	32(1)

W	8467(1)	905(1)	3536(1)	25(1)

Table 3. Bond lengths [A] and angles [deg] for **68a**.

C(1)-N(1)	1.320(5)
C(1)-N(2)	1.334(5)
C(1)-H(1)	0.9500
C(2)-C(3)	1.340(6)
C(2)-N(1)	1.394(5)
C(2)-H(2)	0.9500
C(3)-N(2)	1.386(5)
C(3)-H(3)	0.9500
C(4)-C(6)	1.488(7)
C(4)-C(5)	1.498(6)
C(4)-N(1)	1.516(6)
C(4)-C(7)	1.522(7)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-N(2)	1.505(5)
C(8)-C(11)	1.510(5)
C(8)-C(10)	1.522(6)
C(8)-C(9)	1.522(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-P	1.870(4)
C(12)-Si(2)	1.893(4)
C(12)-Si(1)	1.895(4)
C(12)-H(12)	1.0000
C(13)-Si(1)	1.876(4)
C(13)-H(13A)	0.9800

C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-Si(1)	1.874(4)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-Si(1)	1.873(4)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-Si(2)	1.857(5)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-Si(2)	1.881(5)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-Si(2)	1.865(4)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-O(1)	1.362(5)
C(19)-C(24)	1.381(6)
C(19)-C(20)	1.388(6)
C(20)-C(21)	1.389(6)
C(20)-H(20)	0.9500
C(21)-C(22)	1.370(7)
C(21)-H(21)	0.9500
C(22)-C(23)	1.384(6)
C(22)-H(22)	0.9500
C(23)-C(24)	1.403(6)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-O(2)	1.157(5)
C(25)-W	1.990(5)
C(26)-O(3)	1.153(5)
C(26)-W	2.018(5)
C(27)-O(4)	1.143(5)
C(27)-W	2.032(4)
C(28)-O(5)	1.157(5)
C(28)-W	2.034(5)
C(29)-O(6)	1.147(5)
C(29)-W	2.028(5)

O(1)-P	1.730(3)
P-W	2.5980(11)

N(1)-C(1)-N(2)	110.0(4)
N(1)-C(1)-H(1)	125.0
N(2)-C(1)-H(1)	125.0
C(3)-C(2)-N(1)	107.0(4)
C(3)-C(2)-H(2)	126.5
N(1)-C(2)-H(2)	126.5
C(2)-C(3)-N(2)	107.9(4)
C(2)-C(3)-H(3)	126.0
N(2)-C(3)-H(3)	126.0
C(6)-C(4)-C(5)	113.1(4)
C(6)-C(4)-N(1)	107.8(4)
C(5)-C(4)-N(1)	107.9(4)
C(6)-C(4)-C(7)	112.3(4)
C(5)-C(4)-C(7)	108.2(4)
N(1)-C(4)-C(7)	107.3(4)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
N(2)-C(8)-C(11)	107.9(3)
N(2)-C(8)-C(10)	108.6(3)
C(11)-C(8)-C(10)	110.0(4)
N(2)-C(8)-C(9)	107.1(3)
C(11)-C(8)-C(9)	111.9(4)
C(10)-C(8)-C(9)	111.2(4)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5

H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P-C(12)-Si(2)	118.0(2)
P-C(12)-Si(1)	102.36(18)
Si(2)-C(12)-Si(1)	116.4(2)
P-C(12)-H(12)	106.4
Si(2)-C(12)-H(12)	106.4
Si(1)-C(12)-H(12)	106.4
Si(1)-C(13)-H(13A)	109.5
Si(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
Si(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
Si(2)-C(16)-H(16A)	109.5
Si(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
Si(2)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(1)-C(19)-C(24)	123.8(4)
O(1)-C(19)-C(20)	116.5(4)
C(24)-C(19)-C(20)	119.7(4)
C(19)-C(20)-C(21)	120.2(4)
C(19)-C(20)-H(20)	119.9
C(21)-C(20)-H(20)	119.9
C(22)-C(21)-C(20)	120.5(4)
C(22)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
C(21)-C(22)-C(23)	119.7(4)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(22)-C(23)-C(24)	120.3(4)
C(22)-C(23)-H(23)	119.9
C(24)-C(23)-H(23)	119.9
C(19)-C(24)-C(23)	119.6(4)
C(19)-C(24)-H(24)	120.2
C(23)-C(24)-H(24)	120.2
O(2)-C(25)-W	178.7(4)
O(3)-C(26)-W	178.2(4)
O(4)-C(27)-W	174.0(4)
O(5)-C(28)-W	179.1(4)
O(6)-C(29)-W	176.4(4)
C(1)-N(1)-C(2)	107.8(4)
C(1)-N(1)-C(4)	126.6(4)
C(2)-N(1)-C(4)	125.5(4)
C(1)-N(2)-C(3)	107.2(3)
C(1)-N(2)-C(8)	127.5(3)
C(3)-N(2)-C(8)	125.3(3)
C(19)-O(1)-P	122.3(3)

O(1)-P-C(12)	95.39(16)
O(1)-P-W	107.70(10)
C(12)-P-W	110.08(13)
C(15)-Si(1)-C(14)	108.6(2)
C(15)-Si(1)-C(13)	105.6(2)
C(14)-Si(1)-C(13)	110.7(2)
C(15)-Si(1)-C(12)	113.79(19)
C(14)-Si(1)-C(12)	109.18(18)
C(13)-Si(1)-C(12)	108.90(19)
C(16)-Si(2)-C(18)	108.4(2)
C(16)-Si(2)-C(17)	106.9(2)
C(18)-Si(2)-C(17)	105.2(2)
C(16)-Si(2)-C(12)	113.2(2)
C(18)-Si(2)-C(12)	114.09(19)
C(17)-Si(2)-C(12)	108.6(2)
C(25)-W-C(26)	91.13(17)
C(25)-W-C(29)	95.64(17)
C(26)-W-C(29)	85.61(16)
C(25)-W-C(27)	95.66(17)
C(26)-W-C(27)	87.96(16)
C(29)-W-C(27)	167.10(16)
C(25)-W-C(28)	89.84(17)
C(26)-W-C(28)	177.10(16)
C(29)-W-C(28)	91.58(16)
C(27)-W-C(28)	94.67(16)
C(25)-W-P	174.70(12)
C(26)-W-P	94.07(11)
C(29)-W-P	85.74(12)
C(27)-W-P	83.57(11)
C(28)-W-P	85.01(12)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **68a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	26(2)	32(2)	30(2)	-4(2)	-1(2)	-1(2)
C(2)	33(3)	31(2)	28(2)	-1(2)	2(2)	-3(2)
C(3)	28(2)	25(2)	29(2)	-2(2)	1(2)	4(2)
C(4)	36(1)	51(2)	45(2)	-1(1)	1(1)	6(1)
C(5)	54(2)	62(2)	69(2)	1(2)	2(2)	7(2)
C(6)	56(2)	75(2)	61(2)	5(2)	2(2)	6(2)
C(7)	54(2)	68(2)	61(2)	-6(2)	-6(2)	3(2)
C(8)	20(2)	33(2)	33(2)	-2(2)	0(2)	1(2)

C(9)	30(3)	55(3)	36(3)	-6(2)	-9(2)	2(2)
C(10)	28(3)	36(3)	59(3)	-6(2)	1(2)	-3(2)
C(11)	23(2)	46(3)	35(3)	0(2)	2(2)	2(2)
C(12)	23(2)	25(2)	25(2)	-4(2)	0(2)	0(2)
C(13)	38(3)	34(2)	42(3)	-7(2)	-7(2)	8(2)
C(14)	36(3)	32(2)	30(2)	0(2)	-3(2)	-2(2)
C(15)	53(3)	36(3)	36(3)	6(2)	-2(2)	-6(2)
C(16)	26(3)	45(3)	64(3)	-1(2)	0(2)	-3(2)
C(17)	38(3)	70(4)	53(3)	5(3)	13(2)	4(3)
C(18)	29(3)	40(3)	47(3)	-9(2)	6(2)	3(2)
C(19)	32(3)	25(2)	30(2)	-1(2)	-3(2)	-4(2)
C(20)	25(3)	30(2)	44(3)	-1(2)	-2(2)	-1(2)
C(21)	30(3)	38(3)	57(3)	4(2)	-19(2)	-3(2)
C(22)	51(4)	39(3)	35(3)	-2(2)	-13(2)	-6(2)
C(23)	44(3)	36(3)	34(3)	-1(2)	1(2)	0(2)
C(24)	28(3)	28(2)	33(2)	-2(2)	-3(2)	3(2)
C(25)	29(3)	34(2)	36(3)	0(2)	3(2)	-1(2)
C(26)	25(2)	25(2)	39(3)	5(2)	-4(2)	-3(2)
C(27)	34(3)	26(2)	25(2)	0(2)	2(2)	-4(2)
C(28)	29(3)	31(2)	39(3)	4(2)	-3(2)	1(2)
C(29)	26(3)	36(2)	31(2)	-2(2)	4(2)	-5(2)
N(1)	25(2)	35(2)	26(2)	-2(2)	0(2)	2(2)
N(2)	21(2)	30(2)	28(2)	-2(2)	0(1)	3(2)
O(1)	19(2)	37(2)	33(2)	0(1)	-3(1)	1(1)
O(2)	31(2)	39(2)	58(2)	-2(2)	2(2)	-10(2)
O(3)	51(2)	52(2)	31(2)	0(2)	8(2)	3(2)
O(4)	34(2)	36(2)	43(2)	4(1)	-4(2)	5(2)
O(5)	45(2)	66(2)	39(2)	1(2)	11(2)	12(2)
O(6)	36(2)	42(2)	54(2)	14(2)	-2(2)	6(2)
P	22(1)	26(1)	28(1)	0(1)	2(1)	0(1)
Si(1)	29(1)	26(1)	28(1)	-1(1)	-3(1)	-2(1)
Si(2)	22(1)	37(1)	38(1)	-2(1)	6(1)	-1(1)
W	20(1)	24(1)	30(1)	2(1)	1(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **68a**.

	x	y	z	U(eq)
H(1)	7929	1413	6259	35
H(2)	8555	3372	6445	37
H(3)	7219	3343	6462	33
H(5A)	9040	1066	6099	92

H(5B)	9103	1228	6887	92
H(5C)	9821	1164	6438	92
H(6A)	10056	2115	5564	96
H(6B)	9497	2744	5535	96
H(6C)	9255	2001	5272	96
H(7A)	10213	2309	6829	92
H(7B)	9497	2334	7285	92
H(7C)	9666	2945	6769	92
H(9A)	6259	2790	5623	60
H(9B)	5743	2130	5581	60
H(9C)	6542	2103	5265	60
H(10A)	6817	1064	5962	61
H(10B)	6037	1086	6317	61
H(10C)	6758	1103	6766	61
H(11A)	6358	2180	7316	52
H(11B)	5627	2170	6880	52
H(11C)	6141	2833	6869	52
H(12)	7511	-353	4364	29
H(13A)	8440	-2115	3773	57
H(13B)	8577	-1463	4248	57
H(13C)	8573	-1373	3447	57
H(14A)	6802	-1321	2769	49
H(14B)	6463	-1973	3146	49
H(14C)	7243	-2029	2796	49
H(15A)	6459	-1967	4556	62
H(15B)	7178	-1820	4985	62
H(15C)	7144	-2468	4489	62
H(16A)	5075	-403	3720	67
H(16B)	5514	-1113	3742	67
H(16C)	5684	-561	3165	67
H(17A)	5524	-399	5175	80
H(17B)	6341	-227	5390	80
H(17C)	6136	-981	5127	80
H(18A)	6184	907	3718	58
H(18B)	6443	952	4486	58
H(18C)	5603	837	4313	58
H(20)	5710	674	2336	40
H(21)	5462	862	1197	50
H(22)	6328	613	385	50
H(23)	7467	205	709	46
H(24)	7737	46	1858	35

Table 6. Torsion angles [deg] for **68a**.

N(1)-C(2)-C(3)-N(2)	-0.6(4)
O(1)-C(19)-C(20)-C(21)	-179.0(4)
C(24)-C(19)-C(20)-C(21)	1.7(6)
C(19)-C(20)-C(21)-C(22)	0.3(7)
C(20)-C(21)-C(22)-C(23)	-1.2(7)
C(21)-C(22)-C(23)-C(24)	0.2(7)
O(1)-C(19)-C(24)-C(23)	178.1(4)
C(20)-C(19)-C(24)-C(23)	-2.8(6)
C(22)-C(23)-C(24)-C(19)	1.8(6)
N(2)-C(1)-N(1)-C(2)	-0.6(4)
N(2)-C(1)-N(1)-C(4)	-177.7(3)
C(3)-C(2)-N(1)-C(1)	0.8(4)
C(3)-C(2)-N(1)-C(4)	178.0(4)
C(6)-C(4)-N(1)-C(1)	102.3(5)
C(5)-C(4)-N(1)-C(1)	-20.2(6)
C(7)-C(4)-N(1)-C(1)	-136.6(4)
C(6)-C(4)-N(1)-C(2)	-74.4(5)
C(5)-C(4)-N(1)-C(2)	163.2(4)
C(7)-C(4)-N(1)-C(2)	46.7(5)
N(1)-C(1)-N(2)-C(3)	0.2(4)
N(1)-C(1)-N(2)-C(8)	177.5(3)
C(2)-C(3)-N(2)-C(1)	0.3(4)
C(2)-C(3)-N(2)-C(8)	-177.1(3)
C(11)-C(8)-N(2)-C(1)	130.6(4)
C(10)-C(8)-N(2)-C(1)	11.4(5)
C(9)-C(8)-N(2)-C(1)	-108.8(4)
C(11)-C(8)-N(2)-C(3)	-52.5(5)
C(10)-C(8)-N(2)-C(3)	-171.7(4)
C(9)-C(8)-N(2)-C(3)	68.1(5)
C(24)-C(19)-O(1)-P	-2.9(5)
C(20)-C(19)-O(1)-P	177.9(3)
C(19)-O(1)-P-C(12)	-153.3(3)
C(19)-O(1)-P-W	93.6(3)
Si(2)-C(12)-P-O(1)	-13.0(2)
Si(1)-C(12)-P-O(1)	116.20(18)
Si(2)-C(12)-P-W	98.1(2)
Si(1)-C(12)-P-W	-132.72(13)
P-C(12)-Si(1)-C(15)	179.2(2)
Si(2)-C(12)-Si(1)-C(15)	-50.6(3)
P-C(12)-Si(1)-C(14)	-59.4(2)
Si(2)-C(12)-Si(1)-C(14)	70.8(3)
P-C(12)-Si(1)-C(13)	61.6(2)
Si(2)-C(12)-Si(1)-C(13)	-168.2(2)
P-C(12)-Si(2)-C(16)	75.5(3)

Si(1)-C(12)-Si(2)-C(16)	-46.8(3)
P-C(12)-Si(2)-C(18)	-49.0(3)
Si(1)-C(12)-Si(2)-C(18)	-171.3(2)
P-C(12)-Si(2)-C(17)	-166.0(2)
Si(1)-C(12)-Si(2)-C(17)	71.7(3)
O(2)-C(25)-W-C(26)	-88(17)
O(2)-C(25)-W-C(29)	-174(100)
O(2)-C(25)-W-C(27)	0(17)
O(2)-C(25)-W-C(28)	95(17)
O(2)-C(25)-W-P	81(18)
O(3)-C(26)-W-C(25)	-69(12)
O(3)-C(26)-W-C(29)	27(12)
O(3)-C(26)-W-C(27)	-164(12)
O(3)-C(26)-W-C(28)	41(14)
O(3)-C(26)-W-P	112(12)
O(6)-C(29)-W-C(25)	121(6)
O(6)-C(29)-W-C(26)	31(6)
O(6)-C(29)-W-C(27)	-30(7)
O(6)-C(29)-W-C(28)	-149(6)
O(6)-C(29)-W-P	-64(6)
O(4)-C(27)-W-C(25)	-147(3)
O(4)-C(27)-W-C(26)	-56(3)
O(4)-C(27)-W-C(29)	4(4)
O(4)-C(27)-W-C(28)	123(3)
O(4)-C(27)-W-P	38(3)
O(5)-C(28)-W-C(25)	64(25)
O(5)-C(28)-W-C(26)	-45(27)
O(5)-C(28)-W-C(29)	-31(25)
O(5)-C(28)-W-C(27)	160(25)
O(5)-C(28)-W-P	-117(25)
O(1)-P-W-C(25)	-83.3(14)
C(12)-P-W-C(25)	173.9(14)
O(1)-P-W-C(26)	86.05(15)
C(12)-P-W-C(26)	-16.76(18)
O(1)-P-W-C(29)	171.33(16)
C(12)-P-W-C(29)	68.52(18)
O(1)-P-W-C(27)	-1.43(15)
C(12)-P-W-C(27)	-104.24(17)
O(1)-P-W-C(28)	-96.71(16)
C(12)-P-W-C(28)	160.48(18)

12. Crystal data of molecule [{bis(trimethylsilyl)methyl}methylphenoxyphosphane] pentacarbonyl tungsten complex (**73a**) (GSTR095, Greg909f)

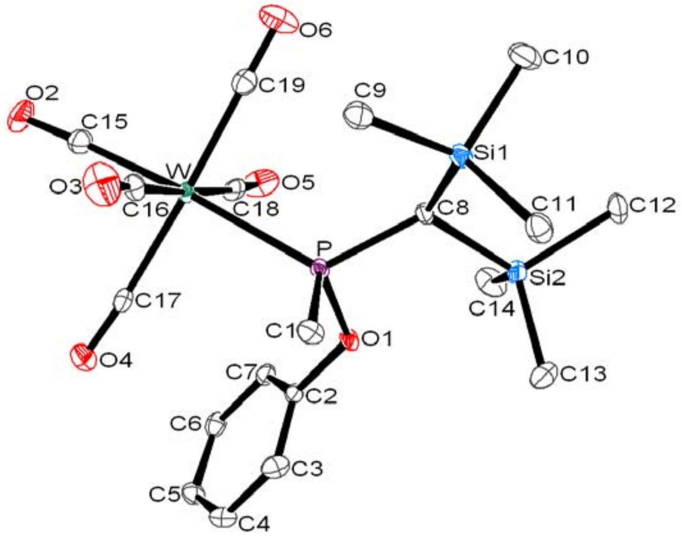

Table 1. Crystal data and structure refinement for **73a**.

Identification code	GSTR095, Greg909f
Device Type	X8-KappaApexII
Empirical formula	C19 H27 O6 P Si2 W
Formula weight	622.41
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 9.7329(6) A alpha = 90 deg. b = 12.5170(7) A beta = 115.163(2) deg. c = 11.2360(7) A gamma = 90 deg.
Volume	1238.94(13) A^3
Z, Calculated density	2, 1.668 Mg/m^3
Absorption coefficient	4.853 mm^-1
F(000)	612

Crystal size	0.60 x 0.40 x 0.12 mm
Theta range for data collection	2.83 to 28.00 deg.
Limiting indices	-12<=h<=11, -16<=k<=11, -14<=l<=14
Reflections collected / unique	11600 / 5293 [R(int) = 0.0337]
Completeness to theta = 28.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5936 and 0.1588
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5293 / 1 / 270
Goodness-of-fit on F^2	0.940
Final R indices [I>2sigma(I)]	R1 = 0.0162, wR2 = 0.0413
R indices (all data)	R1 = 0.0165, wR2 = 0.0414
Absolute structure parameter	0.139(5)
Largest diff. peak and hole	0.965 and -1.511 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **73a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	1079(3)	3217(2)	1435(3)	14(1)
C(2)	766(3)	1010(2)	-381(3)	11(1)
C(3)	-543(3)	1528(2)	-1232(3)	17(1)
C(4)	-1056(3)	1352(2)	-2567(3)	18(1)
C(5)	-281(3)	664(2)	-3045(3)	17(1)
C(6)	987(3)	134(2)	-2175(3)	15(1)
C(7)	1510(3)	295(2)	-837(3)	14(1)
C(8)	2797(3)	1660(2)	3455(3)	12(1)
C(9)	3968(3)	3993(2)	4507(3)	19(1)

C(10)	4527(3)	2196(3)	6385(3)	23(1)
C(11)	1308(3)	3090(2)	4884(3)	18(1)
C(12)	2032(3)	119(2)	5209(3)	19(1)
C(13)	-554(3)	841(3)	2683(3)	23(1)
C(14)	1865(4)	-727(2)	2689(3)	24(1)
C(15)	6302(3)	2701(2)	680(3)	17(1)
C(16)	4392(4)	4080(3)	1392(3)	18(1)
C(17)	3165(3)	2584(4)	-686(3)	15(1)
C(18)	5004(4)	873(3)	1262(3)	17(1)
C(19)	6145(3)	2416(5)	3186(3)	18(1)
O(1)	1302(2)	1154(2)	977(2)	13(1)
O(2)	7208(2)	2811(2)	297(2)	26(1)
O(3)	4251(3)	4988(2)	1452(2)	32(1)
O(4)	2408(3)	2696(2)	-1777(2)	27(1)
O(5)	5294(3)	-23(2)	1336(2)	28(1)
O(6)	7005(2)	2349(3)	4267(2)	30(1)
Si(1)	3117(1)	2724(1)	4772(1)	13(1)
Si(2)	1508(1)	500(1)	3459(1)	14(1)
P	2435(1)	2132(1)	1817(1)	10(1)
W	4637(1)	2472(1)	1270(1)	11(1)

Table 3. Bond lengths [A] and angles [deg] for **73a**.

C(1)-P	1.814(3)
C(1)-H(1C)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1A)	0.9800
C(2)-C(7)	1.380(4)
C(2)-C(3)	1.386(4)
C(2)-O(1)	1.398(3)
C(3)-C(4)	1.382(4)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.394(4)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.376(4)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.381(4)
C(6)-H(6A)	0.9500
C(7)-H(7A)	0.9500
C(8)-P	1.819(3)
C(8)-Si(1)	1.916(3)
C(8)-Si(2)	1.921(3)
C(8)-H(8A)	1.0000
C(9)-Si(1)	1.873(3)

C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-Si(1)	1.868(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-Si(1)	1.875(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-Si(2)	1.870(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-Si(2)	1.866(3)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-Si(2)	1.867(3)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-O(2)	1.143(4)
C(15)-W	2.015(3)
C(16)-O(3)	1.150(4)
C(16)-W	2.038(4)
C(17)-O(4)	1.139(3)
C(17)-W	2.055(3)
C(18)-O(5)	1.150(4)
C(18)-W	2.035(3)
C(19)-O(6)	1.148(3)
C(19)-W	2.026(3)
O(1)-P	1.649(2)
P-W	2.5045(7)

P-C(1)-H(1C)	109.5
P-C(1)-H(1B)	109.5
H(1C)-C(1)-H(1B)	109.5
P-C(1)-H(1A)	109.5
H(1C)-C(1)-H(1A)	109.5
H(1B)-C(1)-H(1A)	109.5
C(7)-C(2)-C(3)	121.4(3)
C(7)-C(2)-O(1)	118.5(2)

C(3)-C(2)-O(1)	120.0(3)
C(4)-C(3)-C(2)	118.4(3)
C(4)-C(3)-H(3A)	120.8
C(2)-C(3)-H(3A)	120.8
C(3)-C(4)-C(5)	120.8(3)
C(3)-C(4)-H(4A)	119.6
C(5)-C(4)-H(4A)	119.6
C(6)-C(5)-C(4)	119.5(3)
C(6)-C(5)-H(5A)	120.2
C(4)-C(5)-H(5A)	120.2
C(5)-C(6)-C(7)	120.5(3)
C(5)-C(6)-H(6A)	119.8
C(7)-C(6)-H(6A)	119.8
C(2)-C(7)-C(6)	119.4(3)
C(2)-C(7)-H(7A)	120.3
C(6)-C(7)-H(7A)	120.3
P-C(8)-Si(1)	117.00(14)
P-C(8)-Si(2)	113.72(15)
Si(1)-C(8)-Si(2)	114.57(14)
P-C(8)-H(8A)	103.0
Si(1)-C(8)-H(8A)	103.0
Si(2)-C(8)-H(8A)	103.0
Si(1)-C(9)-H(9A)	109.5
Si(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
Si(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
Si(1)-C(10)-H(10A)	109.5
Si(1)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
Si(1)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
Si(1)-C(11)-H(11A)	109.5
Si(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
Si(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
Si(2)-C(12)-H(12A)	109.5
Si(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
Si(2)-C(12)-H(12C)	109.5

H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
Si(2)-C(13)-H(13A)	109.5
Si(2)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
Si(2)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
Si(2)-C(14)-H(14A)	109.5
Si(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
Si(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(2)-C(15)-W	177.1(3)
O(3)-C(16)-W	179.6(3)
O(4)-C(17)-W	175.6(3)
O(5)-C(18)-W	175.4(3)
O(6)-C(19)-W	177.7(5)
C(2)-O(1)-P	124.68(17)
C(10)-Si(1)-C(9)	105.24(14)
C(10)-Si(1)-C(11)	110.15(14)
C(9)-Si(1)-C(11)	107.17(14)
C(10)-Si(1)-C(8)	108.34(14)
C(9)-Si(1)-C(8)	113.85(13)
C(11)-Si(1)-C(8)	111.86(13)
C(13)-Si(2)-C(14)	110.30(15)
C(13)-Si(2)-C(12)	107.95(14)
C(14)-Si(2)-C(12)	104.86(14)
C(13)-Si(2)-C(8)	113.52(14)
C(14)-Si(2)-C(8)	111.75(14)
C(12)-Si(2)-C(8)	107.99(13)
O(1)-P-C(1)	100.28(12)
O(1)-P-C(8)	97.66(12)
C(1)-P-C(8)	106.89(13)
O(1)-P-W	114.80(8)
C(1)-P-W	115.28(10)
C(8)-P-W	119.05(9)
C(15)-W-C(19)	91.91(11)
C(15)-W-C(18)	88.33(12)
C(19)-W-C(18)	85.5(2)
C(15)-W-C(16)	90.87(13)
C(19)-W-C(16)	90.9(2)
C(18)-W-C(16)	176.26(12)

C(15)-W-C(17)	86.06(11)
C(19)-W-C(17)	177.4(2)
C(18)-W-C(17)	96.08(16)
C(16)-W-C(17)	87.51(16)
C(15)-W-P	175.29(8)
C(19)-W-P	92.44(8)
C(18)-W-P	90.22(10)
C(16)-W-P	90.86(10)
C(17)-W-P	89.64(8)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **73a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	16(1)	15(1)	13(1)	-1(1)	6(1)	3(1)
C(2)	12(1)	14(1)	9(1)	-3(1)	5(1)	-4(1)
C(3)	14(1)	17(1)	19(2)	-4(1)	7(1)	-1(1)
C(4)	13(1)	21(2)	15(1)	0(1)	2(1)	0(1)
C(5)	19(1)	20(2)	9(1)	-2(1)	4(1)	-6(1)
C(6)	19(1)	14(1)	17(1)	-4(1)	11(1)	-4(1)
C(7)	13(1)	14(1)	14(1)	0(1)	7(1)	-3(1)
C(8)	12(1)	16(1)	9(1)	3(1)	6(1)	3(1)
C(9)	22(2)	20(2)	14(1)	-4(1)	7(1)	-5(1)
C(10)	21(2)	31(3)	13(1)	-1(1)	4(1)	3(1)
C(11)	21(1)	21(2)	16(2)	2(1)	10(1)	5(1)
C(12)	24(2)	21(2)	18(2)	7(1)	14(1)	2(1)
C(13)	15(1)	29(2)	26(2)	5(1)	10(1)	-3(1)
C(14)	33(2)	18(2)	19(2)	-1(1)	9(1)	0(1)
C(15)	16(1)	18(2)	17(1)	0(1)	8(1)	0(1)
C(16)	19(1)	24(2)	12(1)	1(1)	9(1)	-3(1)
C(17)	16(1)	13(2)	18(1)	0(1)	10(1)	-4(1)
C(18)	11(1)	26(2)	16(2)	-4(1)	10(1)	-1(1)
C(19)	17(1)	19(1)	20(1)	-1(2)	10(1)	-1(2)
O(1)	17(1)	17(1)	6(1)	-2(1)	6(1)	-5(1)
O(2)	21(1)	30(1)	35(1)	2(1)	20(1)	-3(1)
O(3)	50(2)	17(1)	31(1)	-3(1)	20(1)	-2(1)
O(4)	27(1)	37(2)	15(1)	5(1)	5(1)	-9(1)
O(5)	22(1)	20(1)	37(1)	-5(1)	10(1)	1(1)
O(6)	28(1)	37(2)	17(1)	0(1)	2(1)	6(1)
Si(1)	14(1)	16(1)	10(1)	0(1)	6(1)	1(1)
Si(2)	14(1)	15(1)	14(1)	3(1)	7(1)	0(1)
P	11(1)	11(1)	9(1)	0(1)	5(1)	0(1)
W	11(1)	13(1)	10(1)	0(1)	7(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **73a**.

	x	y	z	U(eq)
H(1C)	680	3389	497	21
H(1B)	1582	3848	1955	21
H(1A)	241	3002	1648	21
H(3A)	-1075	1993	-906	20
H(4A)	-1947	1704	-3166	21
H(5A)	-625	563	-3965	20
H(6A)	1507	-347	-2496	18
H(7A)	2373	-83	-237	16
H(8A)	3816	1314	3760	14
H(9A)	3226	4362	3730	28
H(9B)	4876	3827	4372	28
H(9C)	4247	4455	5280	28
H(10A)	5425	1936	6291	34
H(10B)	4070	1607	6667	34
H(10C)	4823	2767	7044	34
H(11A)	890	2457	5126	27
H(11B)	573	3359	4031	27
H(11C)	1513	3644	5554	27
H(12A)	1836	722	5671	29
H(12B)	3111	-68	5637	29
H(12C)	1423	-497	5234	29
H(13A)	-870	1002	1749	35
H(13B)	-732	1467	3122	35
H(13C)	-1142	235	2769	35
H(14A)	2915	-723	2788	36
H(14B)	1169	-742	1752	36
H(14C)	1697	-1362	3121	36

Table 6. Torsion angles [deg] for **73a**.

C(7)-C(2)-C(3)-C(4)	-3.1(4)
O(1)-C(2)-C(3)-C(4)	-178.8(2)
C(2)-C(3)-C(4)-C(5)	0.4(4)
C(3)-C(4)-C(5)-C(6)	1.7(4)
C(4)-C(5)-C(6)-C(7)	-1.3(4)
C(3)-C(2)-C(7)-C(6)	3.5(4)
O(1)-C(2)-C(7)-C(6)	179.4(2)
C(5)-C(6)-C(7)-C(2)	-1.3(4)

C(7)-C(2)-O(1)-P	97.5(3)
C(3)-C(2)-O(1)-P	-86.6(3)
P-C(8)-Si(1)-C(10)	-145.89(16)
Si(2)-C(8)-Si(1)-C(10)	77.28(18)
P-C(8)-Si(1)-C(9)	-29.2(2)
Si(2)-C(8)-Si(1)-C(9)	-166.01(14)
P-C(8)-Si(1)-C(11)	92.50(18)
Si(2)-C(8)-Si(1)-C(11)	-44.33(19)
P-C(8)-Si(2)-C(13)	-60.4(2)
Si(1)-C(8)-Si(2)-C(13)	77.90(18)
P-C(8)-Si(2)-C(14)	65.17(18)
Si(1)-C(8)-Si(2)-C(14)	-156.58(15)
P-C(8)-Si(2)-C(12)	179.99(14)
Si(1)-C(8)-Si(2)-C(12)	-41.75(18)
C(2)-O(1)-P-C(1)	78.7(2)
C(2)-O(1)-P-C(8)	-172.5(2)
C(2)-O(1)-P-W	-45.5(2)
Si(1)-C(8)-P-O(1)	-147.82(15)
Si(2)-C(8)-P-O(1)	-10.64(16)
Si(1)-C(8)-P-C(1)	-44.59(19)
Si(2)-C(8)-P-C(1)	92.60(16)
Si(1)-C(8)-P-W	88.21(15)
Si(2)-C(8)-P-W	-134.61(10)
O(2)-C(15)-W-C(19)	153(5)
O(2)-C(15)-W-C(18)	68(5)
O(2)-C(15)-W-C(16)	-116(5)
O(2)-C(15)-W-C(17)	-29(5)
O(2)-C(15)-W-P	-4(6)
O(6)-C(19)-W-C(15)	-89(6)
O(6)-C(19)-W-C(18)	-1(6)
O(6)-C(19)-W-C(16)	-180(100)
O(6)-C(19)-W-C(17)	-128(9)
O(6)-C(19)-W-P	89(6)
O(5)-C(18)-W-C(15)	79(4)
O(5)-C(18)-W-C(19)	-13(4)
O(5)-C(18)-W-C(16)	1(6)
O(5)-C(18)-W-C(17)	165(4)
O(5)-C(18)-W-P	-106(4)
O(3)-C(16)-W-C(15)	69(44)
O(3)-C(16)-W-C(19)	161(100)
O(3)-C(16)-W-C(18)	147(42)
O(3)-C(16)-W-C(17)	-17(44)
O(3)-C(16)-W-P	-106(44)
O(4)-C(17)-W-C(15)	-38(5)

O(4)-C(17)-W-C(19)	1(9)
O(4)-C(17)-W-C(18)	-126(5)
O(4)-C(17)-W-C(16)	53(5)
O(4)-C(17)-W-P	144(5)
O(1)-P-W-C(15)	28.5(10)
C(1)-P-W-C(15)	-87.3(10)
C(8)-P-W-C(15)	143.6(10)
O(1)-P-W-C(19)	-129.0(2)
C(1)-P-W-C(19)	115.2(2)
C(8)-P-W-C(19)	-13.9(2)
O(1)-P-W-C(18)	-43.49(12)
C(1)-P-W-C(18)	-159.32(13)
C(8)-P-W-C(18)	71.63(13)
O(1)-P-W-C(16)	140.09(12)
C(1)-P-W-C(16)	24.27(13)
C(8)-P-W-C(16)	-104.79(13)
O(1)-P-W-C(17)	52.59(16)
C(1)-P-W-C(17)	-63.23(18)
C(8)-P-W-C(17)	167.71(16)

13. Crystal data of molecule [{bis(trimethylsilyl)methyl}chlorophenoxyphosphane] pentacarbonyl tungsten complex (**75a**) (GSTR185, Greg1470)

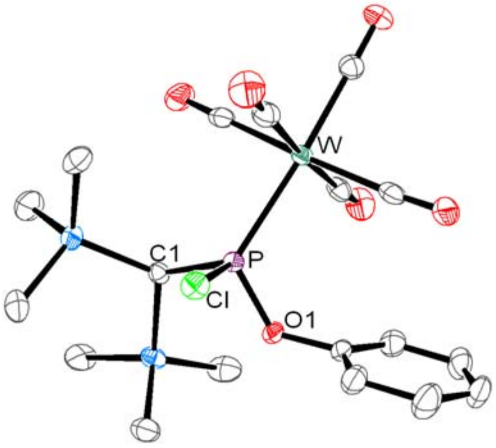

Table 1. Crystal data and structure refinement for **75a**.

Identification code	GSTR185, Greg1470
Device Type	Nonius KappaCCD

Empirical formula	C18 H24 Cl O6 P Si2 W
Moiety formula	C18 H24 Cl O6 P Si2 W
Formula weight	642.82
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 14.9583(2) A alpha = 90 deg. b = 14.2798(4) A beta = 97.233(2) deg. c = 11.6683(3) A gamma = 90 deg.
Volume	2472.53(10) A^3
Z, Calculated density	4, 1.727 Mg/m^3
Absorption coefficient	4.971 mm^-1
F(000)	1256
Crystal size	0.56 x 0.40 x 0.32 mm
Theta range for data collection	2.53 to 28.00 deg.
Limiting indices	-19<=h<=19, -18<=k<=18, -15<=l<=15
Reflections collected / unique	34586 / 5961 [R(int) = 0.0587]
Completeness to theta = 28.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.2992 and 0.1673
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5961 / 0 / 269
Goodness-of-fit on F^2	0.985

Final R indices [I>2sigma(I)]	R1 = 0.0221, wR2 = 0.0467
R indices (all data)	R1 = 0.0301, wR2 = 0.0486
Extinction coefficient	0.00057(8)
Largest diff. peak and hole	1.593 and -0.995 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **75a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2921(2)	238(2)	1759(2)	19(1)
C(2)	1338(2)	1321(2)	316(3)	31(1)
C(3)	1683(2)	-723(2)	-263(2)	38(1)
C(4)	2975(2)	758(3)	-795(2)	38(1)
C(5)	3367(2)	2372(2)	1775(3)	37(1)
C(6)	4302(2)	1202(2)	3719(2)	32(1)
C(7)	4803(2)	908(2)	1361(3)	39(1)
C(8)	557(2)	-658(2)	2603(2)	24(1)
C(9)	34(2)	-81(2)	3185(2)	32(1)
C(10)	-738(2)	-461(2)	3575(3)	41(1)
C(11)	-960(2)	-1378(2)	3367(3)	37(1)
C(12)	-432(2)	-1940(2)	2756(2)	35(1)
C(13)	335(2)	-1580(2)	2371(2)	29(1)
C(14)	3437(2)	-2389(2)	5304(2)	24(1)
C(15)	1659(2)	-1603(2)	4857(2)	24(1)
C(16)	2536(2)	-2376(2)	3038(2)	25(1)
C(17)	4089(2)	-1234(2)	3649(2)	25(1)
C(18)	3197(2)	-409(2)	5556(2)	26(1)
Cl	2019(1)	1137(1)	3696(1)	25(1)
O(1)	1315(1)	-292(1)	2149(1)	22(1)
O(2)	3770(1)	-2968(1)	5889(2)	34(1)
O(3)	1013(1)	-1768(2)	5233(2)	32(1)
O(4)	2360(1)	-2969(2)	2400(2)	39(1)
O(5)	4768(1)	-1185(1)	3296(2)	36(1)
O(6)	3359(1)	103(2)	6294(2)	41(1)
P	2290(1)	-124(1)	2896(1)	18(1)
Si(1)	2214(1)	403(1)	272(1)	23(1)
Si(2)	3826(1)	1183(1)	2156(1)	24(1)
W	2877(1)	-1373(1)	4254(1)	18(1)

Table 3. Bond lengths [A] and angles [deg] for **75a**.

C(1)-P	1.799(2)
C(1)-Si(2)	1.926(2)
C(1)-Si(1)	1.930(2)
C(1)-H(1)	1.0000
C(2)-Si(1)	1.857(3)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-Si(1)	1.866(3)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-Si(1)	1.860(3)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-Si(2)	1.864(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-Si(2)	1.873(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-Si(2)	1.868(3)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.374(4)
C(8)-C(13)	1.377(4)
C(8)-O(1)	1.411(3)
C(9)-C(10)	1.403(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.366(4)
C(10)-H(10)	0.9500
C(11)-C(12)	1.384(4)
C(11)-H(11)	0.9500
C(12)-C(13)	1.382(4)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-O(2)	1.145(3)
C(14)-W	2.012(3)

C(15)-O(3)	1.136(3)
C(15)-W	2.060(3)
C(16)-O(4)	1.136(3)
C(16)-W	2.035(3)
C(17)-O(5)	1.146(3)
C(17)-W	2.035(3)
C(18)-O(6)	1.132(3)
C(18)-W	2.062(3)
Cl-P	2.0918(9)
O(1)-P	1.6187(16)
P-W	2.4731(6)

P-C(1)-Si(2)	116.28(13)
P-C(1)-Si(1)	114.76(12)
Si(2)-C(1)-Si(1)	114.83(12)
P-C(1)-H(1)	102.7
Si(2)-C(1)-H(1)	102.7
Si(1)-C(1)-H(1)	102.7
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
Si(1)-C(3)-H(3A)	109.5
Si(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
Si(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
Si(1)-C(4)-H(4A)	109.5
Si(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
Si(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
Si(2)-C(5)-H(5A)	109.5
Si(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Si(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
Si(2)-C(6)-H(6A)	109.5
Si(2)-C(6)-H(6B)	109.5

H(6A)-C(6)-H(6B)	109.5
Si(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
Si(2)-C(7)-H(7A)	109.5
Si(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	122.2(2)
C(9)-C(8)-O(1)	119.9(2)
C(13)-C(8)-O(1)	117.8(2)
C(8)-C(9)-C(10)	118.2(3)
C(8)-C(9)-H(9)	120.9
C(10)-C(9)-H(9)	120.9
C(11)-C(10)-C(9)	120.3(3)
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8
C(10)-C(11)-C(12)	120.4(3)
C(10)-C(11)-H(11)	119.8
C(12)-C(11)-H(11)	119.8
C(13)-C(12)-C(11)	120.2(3)
C(13)-C(12)-H(12)	119.9
C(11)-C(12)-H(12)	119.9
C(8)-C(13)-C(12)	118.8(3)
C(8)-C(13)-H(13)	120.6
C(12)-C(13)-H(13)	120.6
O(2)-C(14)-W	178.7(2)
O(3)-C(15)-W	175.9(2)
O(4)-C(16)-W	176.5(2)
O(5)-C(17)-W	177.8(2)
O(6)-C(18)-W	177.8(2)
C(8)-O(1)-P	124.36(15)
O(1)-P-C(1)	99.58(10)
O(1)-P-Cl	99.00(7)
C(1)-P-Cl	103.34(9)
O(1)-P-W	117.48(7)
C(1)-P-W	120.18(8)
Cl-P-W	114.08(3)
C(2)-Si(1)-C(4)	108.65(14)
C(2)-Si(1)-C(3)	110.21(13)
C(4)-Si(1)-C(3)	106.39(15)
C(2)-Si(1)-C(1)	111.70(12)

C(4)-Si(1)-C(1)	108.78(11)
C(3)-Si(1)-C(1)	110.93(12)
C(5)-Si(2)-C(7)	111.16(14)
C(5)-Si(2)-C(6)	107.63(14)
C(7)-Si(2)-C(6)	105.12(13)
C(5)-Si(2)-C(1)	110.71(12)
C(7)-Si(2)-C(1)	107.67(13)
C(6)-Si(2)-C(1)	114.45(12)
C(14)-W-C(16)	88.08(11)
C(14)-W-C(17)	87.75(10)
C(16)-W-C(17)	89.04(10)
C(14)-W-C(15)	89.74(10)
C(16)-W-C(15)	88.30(10)
C(17)-W-C(15)	176.40(10)
C(14)-W-C(18)	89.55(11)
C(16)-W-C(18)	176.65(10)
C(17)-W-C(18)	93.24(10)
C(15)-W-C(18)	89.32(10)
C(14)-W-P	175.86(7)
C(16)-W-P	91.29(8)
C(17)-W-P	88.15(7)
C(15)-W-P	94.33(7)
C(18)-W-P	91.24(7)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **75a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	20(1)	17(1)	20(1)	1(1)	4(1)	2(1)
C(2)	31(2)	28(2)	31(2)	4(1)	-1(1)	5(1)
C(3)	43(2)	36(2)	32(2)	-10(1)	-6(1)	6(1)
C(4)	36(2)	63(2)	14(1)	10(1)	6(1)	1(1)
C(5)	36(2)	26(2)	48(2)	6(1)	5(1)	-8(1)
C(6)	25(2)	33(2)	35(2)	-6(1)	-2(1)	-5(1)
C(7)	25(2)	50(2)	45(2)	5(2)	13(1)	0(1)
C(8)	17(1)	32(2)	21(1)	8(1)	-3(1)	-6(1)
C(9)	23(1)	26(2)	48(2)	3(1)	7(1)	-1(1)
C(10)	27(2)	42(2)	57(2)	-1(2)	16(1)	-1(1)
C(11)	23(2)	46(2)	41(2)	5(2)	5(1)	-14(1)
C(12)	37(2)	36(2)	31(2)	0(1)	-1(1)	-19(1)
C(13)	30(2)	35(2)	22(1)	-1(1)	-2(1)	-8(1)
C(14)	26(1)	24(2)	22(1)	0(1)	2(1)	-1(1)
C(15)	31(2)	23(2)	17(1)	4(1)	-3(1)	1(1)

C(16)	33(2)	26(2)	17(1)	3(1)	4(1)	0(1)
C(17)	26(2)	23(2)	23(1)	3(1)	-4(1)	4(1)
C(18)	29(1)	28(2)	21(1)	1(1)	1(1)	0(1)
Cl	24(1)	24(1)	27(1)	-3(1)	5(1)	3(1)
O(1)	18(1)	29(1)	19(1)	5(1)	-1(1)	-5(1)
O(2)	37(1)	32(1)	33(1)	13(1)	-2(1)	4(1)
O(3)	29(1)	41(1)	28(1)	9(1)	7(1)	0(1)
O(4)	54(1)	38(1)	26(1)	-8(1)	6(1)	-10(1)
O(5)	23(1)	44(1)	41(1)	1(1)	7(1)	4(1)
O(6)	51(1)	42(1)	28(1)	-10(1)	3(1)	-7(1)
P	17(1)	19(1)	16(1)	2(1)	1(1)	-1(1)
Si(1)	27(1)	26(1)	17(1)	2(1)	2(1)	4(1)
Si(2)	20(1)	25(1)	28(1)	2(1)	5(1)	-3(1)
W	21(1)	19(1)	15(1)	2(1)	0(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **75a**.

	x	y	z	U(eq)
H(1)	3288	-330	1637	22
H(2A)	970	1360	-439	46
H(2B)	1629	1926	503	46
H(2C)	953	1160	907	46
H(3A)	1499	-681	-1097	57
H(3B)	1153	-846	130	57
H(3C)	2118	-1234	-101	57
H(4A)	3284	1341	-539	56
H(4B)	2621	856	-1550	56
H(4C)	3422	265	-856	56
H(5A)	3155	2398	946	55
H(5B)	3841	2841	1966	55
H(5C)	2863	2502	2212	55
H(6A)	4759	1695	3849	47
H(6B)	4579	594	3934	47
H(6C)	3818	1325	4192	47
H(7A)	5305	1328	1623	59
H(7B)	4626	994	531	59
H(7C)	4991	258	1514	59
H(9)	191	558	3320	38
H(10)	-1108	-78	3987	49
H(11)	-1480	-1632	3642	44
H(12)	-597	-2574	2601	42
H(13)	701	-1963	1954	35

Table 6. Torsion angles [deg] for **75a**.

C(13)-C(8)-C(9)-C(10)	1.6(4)
O(1)-C(8)-C(9)-C(10)	177.0(2)
C(8)-C(9)-C(10)-C(11)	-0.6(4)
C(9)-C(10)-C(11)-C(12)	-0.8(5)
C(10)-C(11)-C(12)-C(13)	1.2(5)
C(9)-C(8)-C(13)-C(12)	-1.2(4)
O(1)-C(8)-C(13)-C(12)	-176.7(2)
C(11)-C(12)-C(13)-C(8)	-0.3(4)
C(9)-C(8)-O(1)-P	81.4(3)
C(13)-C(8)-O(1)-P	-102.9(2)
C(8)-O(1)-P-C(1)	175.1(2)
C(8)-O(1)-P-Cl	-79.6(2)
C(8)-O(1)-P-W	43.6(2)
Si(2)-C(1)-P-O(1)	144.24(13)
Si(1)-C(1)-P-O(1)	6.21(15)
Si(2)-C(1)-P-Cl	42.52(14)
Si(1)-C(1)-P-Cl	-95.51(12)
Si(2)-C(1)-P-W	-86.01(14)
Si(1)-C(1)-P-W	135.96(9)
P-C(1)-Si(1)-C(2)	60.92(17)
Si(2)-C(1)-Si(1)-C(2)	-77.72(16)
P-C(1)-Si(1)-C(4)	-179.15(16)
Si(2)-C(1)-Si(1)-C(4)	42.20(18)
P-C(1)-Si(1)-C(3)	-62.46(17)
Si(2)-C(1)-Si(1)-C(3)	158.90(13)
P-C(1)-Si(2)-C(5)	-94.74(16)
Si(1)-C(1)-Si(2)-C(5)	43.27(17)
P-C(1)-Si(2)-C(7)	143.56(15)
Si(1)-C(1)-Si(2)-C(7)	-78.44(16)
P-C(1)-Si(2)-C(6)	27.11(18)
Si(1)-C(1)-Si(2)-C(6)	165.11(13)
O(2)-C(14)-W-C(16)	73(11)
O(2)-C(14)-W-C(17)	-16(11)
O(2)-C(14)-W-C(15)	161(11)
O(2)-C(14)-W-C(18)	-109(11)
O(2)-C(14)-W-P	-8(11)
O(4)-C(16)-W-C(14)	6(4)
O(4)-C(16)-W-C(17)	94(4)
O(4)-C(16)-W-C(15)	-83(4)
O(4)-C(16)-W-C(18)	-39(5)
O(4)-C(16)-W-P	-178(100)

O(5)-C(17)-W-C(14)	62(6)
O(5)-C(17)-W-C(16)	-26(6)
O(5)-C(17)-W-C(15)	16(7)
O(5)-C(17)-W-C(18)	151(6)
O(5)-C(17)-W-P	-117(6)
O(3)-C(15)-W-C(14)	4(3)
O(3)-C(15)-W-C(16)	92(3)
O(3)-C(15)-W-C(17)	50(4)
O(3)-C(15)-W-C(18)	-85(3)
O(3)-C(15)-W-P	-177(3)
O(6)-C(18)-W-C(14)	-54(6)
O(6)-C(18)-W-C(16)	-9(8)
O(6)-C(18)-W-C(17)	-142(6)
O(6)-C(18)-W-C(15)	36(6)
O(6)-C(18)-W-P	130(6)
O(1)-P-W-C(14)	126.9(10)
C(1)-P-W-C(14)	5.6(10)
Cl-P-W-C(14)	-117.9(10)
O(1)-P-W-C(16)	45.64(10)
C(1)-P-W-C(16)	-75.67(12)
Cl-P-W-C(16)	160.82(8)
O(1)-P-W-C(17)	134.64(10)
C(1)-P-W-C(17)	13.33(12)
Cl-P-W-C(17)	-110.18(8)
O(1)-P-W-C(15)	-42.75(11)
C(1)-P-W-C(15)	-164.06(12)
Cl-P-W-C(15)	72.43(8)
O(1)-P-W-C(18)	-132.16(10)
C(1)-P-W-C(18)	106.53(12)
Cl-P-W-C(18)	-16.98(8)

14. Crystal data of molecule **85** (GSTR116, Greg1070)

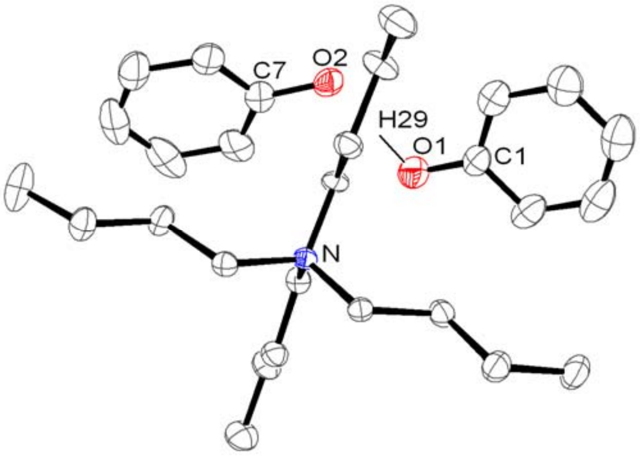

Table 1.   Crystal data and structure refinement for **85**.

Identification code	GSTR116, Greg1070
Device Type	Bruker X8-KappaApexII
Empirical formula	C28 H47 N O2
Formula weight	429.67
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C c
Unit cell dimensions	a = 13.718(4) A alpha = 90 deg. b = 13.442(4) A beta = 114.619(5) deg. c = 16.163(3) A gamma = 90 deg.
Volume	2709.5(12) A^3
Z, Calculated density	4, 1.053 Mg/m^3
Absorption coefficient	0.064 mm^-1
F(000)	952
Crystal size	0.40 x 0.24 x 0.22 mm

Theta range for data collection	3.03 to 28.00 deg.
Limiting indices	-18<=h<=17, -17<=k<=8, -20<=l<=11
Reflections collected / unique	4938 / 3173 [R(int) = 0.0299]
Completeness to theta = 28.00	96.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9860 and 0.9747
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3173 / 2 / 285
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0631, wR2 = 0.1506
R indices (all data)	R1 = 0.0816, wR2 = 0.1622
Extinction coefficient	0.0135(15)
Largest diff. peak and hole	0.299 and -0.269 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **85**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N	6810(2)	3985(2)	5028(2)	18(1)
C(13)	5691(3)	4351(3)	4424(2)	23(1)
C(14)	4996(3)	4606(3)	4916(3)	25(1)
C(15)	3925(3)	5023(3)	4265(3)	31(1)
C(16)	3223(4)	5311(4)	4762(3)	38(1)
C(17)	6757(3)	3098(3)	5587(2)	20(1)
C(18)	6116(3)	2215(3)	5030(2)	25(1)
C(19)	6130(3)	1368(3)	5644(3)	31(1)
C(20)	5463(4)	491(3)	5106(3)	38(1)
C(21)	7355(3)	3708(3)	4410(2)	21(1)
C(22)	8488(3)	3316(3)	4899(2)	24(1)
C(23)	8961(3)	3043(3)	4228(3)	32(1)

C(24)	10093(3)	2636(4)	4714(3)	39(1)
C(25)	7439(3)	4791(3)	5706(2)	20(1)
C(26)	7543(3)	5774(3)	5289(3)	27(1)
C(27)	8250(3)	6487(3)	6008(3)	31(1)
C(28)	8279(4)	7509(3)	5622(4)	47(1)
O(1)	5112(3)	3325(2)	2231(2)	43(1)
O(2)	6509(2)	4478(2)	2214(2)	36(1)
C(1)	5473(3)	2386(3)	2301(3)	34(1)
C(2)	4897(4)	1621(4)	2497(3)	44(1)
C(3)	5242(5)	650(4)	2563(3)	53(2)
C(4)	6151(5)	395(4)	2430(3)	56(2)
C(5)	6729(4)	1139(4)	2252(3)	50(1)
C(6)	6398(4)	2129(3)	2191(3)	38(1)
C(7)	6503(4)	5396(3)	2493(2)	34(1)
C(8)	7463(4)	5939(4)	2865(3)	44(1)
C(9)	7494(6)	6921(4)	3144(3)	57(2)
C(10)	6550(6)	7371(4)	3066(3)	62(2)
C(11)	5597(6)	6853(4)	2710(3)	59(2)
C(12)	5573(4)	5871(4)	2423(3)	44(1)

Table 3. Bond lengths [A] and angles [deg] for **85**.

N-C(17)	1.515(4)
N-C(13)	1.519(4)
N-C(21)	1.522(4)
N-C(25)	1.526(4)
C(13)-C(14)	1.513(5)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.514(5)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.540(6)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.527(5)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.504(5)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900

C(19)-C(20)	1.524(6)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.515(5)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.522(5)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.521(6)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(26)	1.517(5)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(27)	1.506(5)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-C(28)	1.516(6)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
O(1)-C(1)	1.344(6)
O(1)-H(29)	1.1944
O(2)-C(7)	1.316(5)
O(2)-H(29)	1.2861
C(1)-C(6)	1.395(7)
C(1)-C(2)	1.411(6)
C(2)-C(3)	1.378(8)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.393(9)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.379(8)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.397(7)
C(5)-H(5A)	0.9500

C(6)-H(6A)	0.9500
C(7)-C(12)	1.388(7)
C(7)-C(8)	1.403(7)
C(8)-C(9)	1.389(7)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.386(10)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.378(9)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.395(7)
C(11)-H(11A)	0.9500
C(12)-H(12A)	0.9500
C(17)-N-C(13)	110.5(3)
C(17)-N-C(21)	111.0(3)
C(13)-N-C(21)	107.3(3)
C(17)-N-C(25)	106.5(2)
C(13)-N-C(25)	110.5(3)
C(21)-N-C(25)	111.1(3)
C(14)-C(13)-N	115.1(3)
C(14)-C(13)-H(13A)	108.5
N-C(13)-H(13A)	108.5
C(14)-C(13)-H(13B)	108.5
N-C(13)-H(13B)	108.5
H(13A)-C(13)-H(13B)	107.5
C(13)-C(14)-C(15)	111.1(3)
C(13)-C(14)-H(14A)	109.4
C(15)-C(14)-H(14A)	109.4
C(13)-C(14)-H(14B)	109.4
C(15)-C(14)-H(14B)	109.4
H(14A)-C(14)-H(14B)	108.0
C(14)-C(15)-C(16)	111.5(3)
C(14)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15A)	109.3
C(14)-C(15)-H(15B)	109.3
C(16)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N-C(17)-C(18)	114.8(3)

N-C(17)-H(17A)	108.6
C(18)-C(17)-H(17A)	108.6
N-C(17)-H(17B)	108.6
C(18)-C(17)-H(17B)	108.6
H(17A)-C(17)-H(17B)	107.5
C(19)-C(18)-C(17)	110.7(3)
C(19)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18A)	109.5
C(19)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	108.1
C(18)-C(19)-C(20)	111.7(3)
C(18)-C(19)-H(19A)	109.3
C(20)-C(19)-H(19A)	109.3
C(18)-C(19)-H(19B)	109.3
C(20)-C(19)-H(19B)	109.3
H(19A)-C(19)-H(19B)	107.9
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-N	114.8(3)
C(22)-C(21)-H(21A)	108.6
N-C(21)-H(21A)	108.6
C(22)-C(21)-H(21B)	108.6
N-C(21)-H(21B)	108.6
H(21A)-C(21)-H(21B)	107.6
C(21)-C(22)-C(23)	111.1(3)
C(21)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22A)	109.4
C(21)-C(22)-H(22B)	109.4
C(23)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0
C(24)-C(23)-C(22)	111.5(3)
C(24)-C(23)-H(23A)	109.3
C(22)-C(23)-H(23A)	109.3
C(24)-C(23)-H(23B)	109.3
C(22)-C(23)-H(23B)	109.3
H(23A)-C(23)-H(23B)	108.0
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5

C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-N	115.5(3)
C(26)-C(25)-H(25A)	108.4
N-C(25)-H(25A)	108.4
C(26)-C(25)-H(25B)	108.4
N-C(25)-H(25B)	108.4
H(25A)-C(25)-H(25B)	107.5
C(27)-C(26)-C(25)	111.2(3)
C(27)-C(26)-H(26A)	109.4
C(25)-C(26)-H(26A)	109.4
C(27)-C(26)-H(26B)	109.4
C(25)-C(26)-H(26B)	109.4
H(26A)-C(26)-H(26B)	108.0
C(26)-C(27)-C(28)	112.2(3)
C(26)-C(27)-H(27A)	109.2
C(28)-C(27)-H(27A)	109.2
C(26)-C(27)-H(27B)	109.2
C(28)-C(27)-H(27B)	109.2
H(27A)-C(27)-H(27B)	107.9
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(1)-O(1)-H(29)	105.6
C(7)-O(2)-H(29)	119.7
O(1)-C(1)-C(6)	123.0(4)
O(1)-C(1)-C(2)	118.8(4)
C(6)-C(1)-C(2)	118.2(4)
C(3)-C(2)-C(1)	120.1(5)
C(3)-C(2)-H(2A)	120.0
C(1)-C(2)-H(2A)	120.0
C(2)-C(3)-C(4)	121.4(5)
C(2)-C(3)-H(3A)	119.3
C(4)-C(3)-H(3A)	119.3
C(5)-C(4)-C(3)	118.9(5)
C(5)-C(4)-H(4A)	120.5
C(3)-C(4)-H(4A)	120.5
C(4)-C(5)-C(6)	120.5(6)
C(4)-C(5)-H(5A)	119.8
C(6)-C(5)-H(5A)	119.8

C(1)-C(6)-C(5)	120.9(4)
C(1)-C(6)-H(6A)	119.6
C(5)-C(6)-H(6A)	119.6
O(2)-C(7)-C(12)	122.7(4)
O(2)-C(7)-C(8)	119.7(5)
C(12)-C(7)-C(8)	117.6(4)
C(9)-C(8)-C(7)	121.9(6)
C(9)-C(8)-H(8A)	119.0
C(7)-C(8)-H(8A)	119.0
C(10)-C(9)-C(8)	119.0(6)
C(10)-C(9)-H(9A)	120.5
C(8)-C(9)-H(9A)	120.5
C(11)-C(10)-C(9)	120.3(5)
C(11)-C(10)-H(10A)	119.8
C(9)-C(10)-H(10A)	119.8
C(10)-C(11)-C(12)	120.3(6)
C(10)-C(11)-H(11A)	119.9
C(12)-C(11)-H(11A)	119.9
C(7)-C(12)-C(11)	120.9(5)
C(7)-C(12)-H(12A)	119.5
C(11)-C(12)-H(12A)	119.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **85**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N	22(1)	19(1)	16(1)	1(1)	8(1)	0(1)
C(13)	26(2)	22(2)	18(2)	1(1)	4(1)	1(1)
C(14)	27(2)	23(2)	27(2)	1(2)	13(2)	3(2)
C(15)	28(2)	32(2)	30(2)	-2(2)	9(2)	5(2)
C(16)	32(2)	38(3)	43(2)	0(2)	17(2)	7(2)
C(17)	26(2)	19(2)	16(2)	2(1)	8(1)	1(1)
C(18)	29(2)	21(2)	24(2)	-3(1)	11(2)	0(2)
C(19)	42(2)	25(2)	27(2)	1(2)	15(2)	-6(2)
C(20)	48(3)	26(2)	41(2)	-2(2)	20(2)	-12(2)
C(21)	27(2)	24(2)	14(1)	-1(1)	11(1)	-2(1)
C(22)	29(2)	24(2)	22(2)	0(2)	12(2)	3(2)
C(23)	34(2)	40(2)	23(2)	-6(2)	13(2)	6(2)
C(24)	30(2)	46(3)	42(2)	-13(2)	16(2)	1(2)
C(25)	22(2)	21(2)	15(1)	0(1)	6(1)	-1(1)
C(26)	31(2)	21(2)	27(2)	2(2)	9(2)	-6(2)
C(27)	35(2)	25(2)	29(2)	-1(2)	9(2)	-6(2)
C(28)	43(3)	25(2)	51(3)	1(2)	-3(2)	-10(2)

O(1)	46(2)	40(2)	44(2)	-7(2)	20(2)	-9(2)
O(2)	50(2)	31(2)	30(2)	3(1)	21(1)	-5(1)
C(1)	40(2)	35(2)	20(2)	-8(2)	6(2)	-13(2)
C(2)	49(3)	49(3)	26(2)	-5(2)	8(2)	-24(2)
C(3)	68(4)	44(3)	27(2)	-1(2)	1(2)	-26(3)
C(4)	80(4)	37(3)	33(2)	-2(2)	7(3)	-8(3)
C(5)	56(3)	48(3)	36(2)	-7(2)	10(2)	-6(2)
C(6)	41(2)	40(2)	25(2)	1(2)	6(2)	-8(2)
C(7)	61(3)	29(2)	14(2)	8(2)	16(2)	-2(2)
C(8)	69(3)	42(3)	28(2)	0(2)	28(2)	-13(2)
C(9)	104(5)	40(3)	35(3)	-5(2)	37(3)	-24(3)
C(10)	126(6)	30(3)	25(2)	2(2)	27(3)	-2(3)
C(11)	94(5)	53(3)	26(2)	8(2)	22(3)	29(3)
C(12)	61(3)	49(3)	20(2)	4(2)	15(2)	6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **85**.

	x	y	z	U(eq)
H(13A)	5755	4949	4093	28
H(13B)	5323	3831	3965	28
H(14A)	5370	5102	5397	30
H(14B)	4877	4001	5211	30
H(15A)	3545	4520	3792	37
H(15B)	4046	5617	3957	37
H(16A)	3035	4712	5009	56
H(16B)	2567	5636	4334	56
H(16C)	3621	5769	5261	56
H(17A)	6433	3316	6002	24
H(17B)	7497	2874	5968	24
H(18A)	5366	2422	4662	30
H(18B)	6428	1991	4609	30
H(19A)	5844	1602	6081	38
H(19B)	6879	1149	5997	38
H(20A)	4716	700	4772	57
H(20B)	5498	-49	5525	57
H(20C)	5746	256	4675	57
H(21A)	6915	3196	3973	25
H(21B)	7370	4303	4054	25
H(22A)	8484	2721	5259	29
H(22B)	8941	3829	5326	29
H(23A)	8500	2538	3797	38
H(23B)	8973	3641	3875	38

H(24A)	10573	3165	5076	58
H(24B)	10341	2391	4263	58
H(24C)	10096	2088	5115	58
H(25A)	7087	4915	6120	24
H(25B)	8168	4535	6079	24
H(26A)	7850	5657	4842	33
H(26B)	6823	6073	4963	33
H(27A)	8987	6215	6292	37
H(27B)	7983	6548	6488	37
H(28A)	8505	7448	5124	71
H(28B)	8787	7933	6102	71
H(28C)	7562	7808	5392	71
H(29)	5839	3840	2269	65
H(2A)	4270	1776	2584	52
H(3A)	4851	142	2701	63
H(4A)	6369	-280	2462	67
H(5A)	7358	976	2171	59
H(6A)	6807	2634	2073	46
H(8A)	8111	5626	2928	53
H(9A)	8151	7277	3385	69
H(10A)	6561	8040	3258	74
H(11A)	4954	7165	2661	71
H(12A)	4911	5522	2175	53

Table 6. Torsion angles [deg] for **85**.

C(17)-N-C(13)-C(14)	55.4(4)
C(21)-N-C(13)-C(14)	176.6(3)
C(25)-N-C(13)-C(14)	-62.3(4)
N-C(13)-C(14)-C(15)	176.4(3)
C(13)-C(14)-C(15)-C(16)	-178.5(3)
C(13)-N-C(17)-C(18)	57.7(4)
C(21)-N-C(17)-C(18)	-61.2(4)
C(25)-N-C(17)-C(18)	177.8(3)
N-C(17)-C(18)-C(19)	178.8(3)
C(17)-C(18)-C(19)-C(20)	178.0(3)
C(17)-N-C(21)-C(22)	-58.7(4)
C(13)-N-C(21)-C(22)	-179.6(3)
C(25)-N-C(21)-C(22)	59.6(4)
N-C(21)-C(22)-C(23)	179.1(3)
C(21)-C(22)-C(23)-C(24)	-179.2(4)
C(17)-N-C(25)-C(26)	-177.0(3)
C(13)-N-C(25)-C(26)	-56.9(4)
C(21)-N-C(25)-C(26)	62.0(4)

N-C(25)-C(26)-C(27)	-175.4(3)
C(25)-C(26)-C(27)-C(28)	-174.4(4)
O(1)-C(1)-C(2)-C(3)	179.3(4)
C(6)-C(1)-C(2)-C(3)	-0.9(6)
C(1)-C(2)-C(3)-C(4)	-0.7(7)
C(2)-C(3)-C(4)-C(5)	1.6(7)
C(3)-C(4)-C(5)-C(6)	-1.1(7)
O(1)-C(1)-C(6)-C(5)	-178.7(4)
C(2)-C(1)-C(6)-C(5)	1.5(6)
C(4)-C(5)-C(6)-C(1)	-0.5(7)
O(2)-C(7)-C(8)-C(9)	178.0(4)
C(12)-C(7)-C(8)-C(9)	-0.9(6)
C(7)-C(8)-C(9)-C(10)	1.1(7)
C(8)-C(9)-C(10)-C(11)	-0.5(7)
C(9)-C(10)-C(11)-C(12)	-0.3(7)
O(2)-C(7)-C(12)-C(11)	-178.7(4)
C(8)-C(7)-C(12)-C(11)	0.2(6)
C(10)-C(11)-C(12)-C(7)	0.4(7)