From *C*-phosphanylated thiazole-2-thiones to phosphaalkenes and tricyclic 1,4-diphosphinines

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Education is not the learning of facts, it’s rather the training of the mind to think.

Albert Einstein

Some results of this PhD thesis were previously published.

(1) I. Begum, G. Schnakenburg, Z. Kelemen, L. Nyulászi, R. T. Boere´, R. Streubel, *Chem. Commun.* **2018**, DOI: 10.1039/c1038cc08158a.

Conference contributions

1. **I.Begum**, A. Koner, R. Streubel,11th European Workshop on Phosphorus Chemistry,Sofia/Bulgaria, 24.-26.03.2014; "Synthesis, structure and reactivity of novel backbone P-functionalised NHC-precursors" (Poster Presentation)

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3. SIPs Summer School 25. - 30. September 2014 (Small Angle Scattering methods) Chemistry Building of Graz University of Technology, Graz/Austria & Synchrotron facility Elettra, Trieste, Italy.

4. **I.Begum**, R. Streubel,13th European Workshop on Phosphorus Chemistry, Berlin/Germany, 07-09.03.2016; "Synthesis and reactivity studies on bis-NHC precursors based on new scaffolds containing P-linkers" (Poster Presentation)

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12. **I.Begum**, R. Streubel, 22nd International Conference on Phosphorus Chemistry, Budapest/Hungary, 08-13.07.2108. "tricyclic 1,4-diphosphinines: sequential and concerted reactions"
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Hiermit versichere ich, dass ich diese Arbeit selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

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Contents

Abbreviations

Xa,a'= Represent a mixture of two isomers (*cis*, *trans*); where **X**= compound number and **a,a'** are two isomers.

Å	Ångström	HMQC	Heteronuclear Multiple QuantumCorrelation
°	degree	IR	Infrared
ev	electron volt	ATR	Attenual Total Reflexion
g	gram	HMDS	Hexamethyldisilazide
k	Kelvin	KHMDS	Potassium hexamethyldisilazide
min	minutes	C_6D_6	deuerated benzene
h	hour	$CDCl_3$	deuterated chloroform
d	days	D_2O	deuterated water
au	Atomic unit	^{i}Pr	*iso*-propyl
°C	degree Celsius	^{n}Bu	*n*-butyl
br	broad signal	^{n}Pr	*n*-propyl
Hz	Hertz	$^{n}J_{X,Y}$	coupling constant (between the elements X,Y over n bonds) in Hz
cm	centimeter		
T	temperature	CSD	Cambridge Structural Database
Ar	aromatic substitution	$\Delta\delta$	chemical shift difference
ESI	electrospray ionization	DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
Et_2O	diethyl ether	tert	Tertiary
EA	elemental analysis	^{i}Pr	*iso*-propyl
eq.	equivalent	^{n}Pr	*n*-propyl
MLn	transition metal fragment bearing n ligands	^{n}Bu	*n*-butyl
mmol	millimol	$^{n}J_{X,Y}$	coupling constant (between the elements X,Y over n bonds) in Hz
MS	Mass spectrometery	THF	Tetrahydrofuran
m/z	mass to charge ratio	THFd_8	deuterated tetrahydrofuran
n	normal	TMEDA	Tetramethylethylenediamine
mm	nanometer	Toluene d_8	deuterated toluene
NMR	nuclear magnetic resonance	$\tilde{v}$	wave number
%	percent	vs	very strong
PE	Petroleum ether (40/60)	VT-NMR	variable temperature NMR
Ph	Phenyl	w	Weak
calc.	calculated	X	Halogen or leaving group

ppm	parts per mellion	quint	Quintet
q	quartet	R,R',R"	organic substituent
L	Ligand	r.t.	room temperature
m	medium	s	Singlet
m	multiplett	^{i}Pr	*iso*-propyl
DEPT	Distortionless Enhancement by Polarization	^{n}Pr	*n*-propyl
M	metal or molar weight in g/mol	^{n}Bu	*n*-butyl
LDA	lithium diisopropylamide	Me	Methyl
mg	milligram	$^{n}J_{X,Y}$	coupling constant (between the elements X,Y over n bonds) in Hz
mL	millilitter	CSD	Cambridge Structural Database

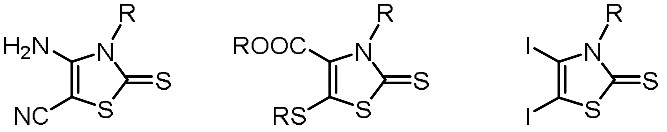
Chapter 1

Chapter 1: Introduction

1.1 1,3-Thiazole-2-thiones

The chemistry of 1,3-thiazoles started in thelate nineteenth century.[1]Since then, great interest emerged due to a broad spectrum of remarkable industrial, biological and pharmaceutical applications.[2]In particular, 1,3-thiazol-2-thiones have valuable applications in photography, radiochemistry, agrochemistry and polymer chemistry.[3]

Heteroatom substitution of the thiazole-2-thionebackbone (C^4/C^5) has been studied, and several examples can be found in literature (the numbering of the heterocycle atoms is according to the IUPAC conventions); some examples**I-III**are shown in Figure 1.1.

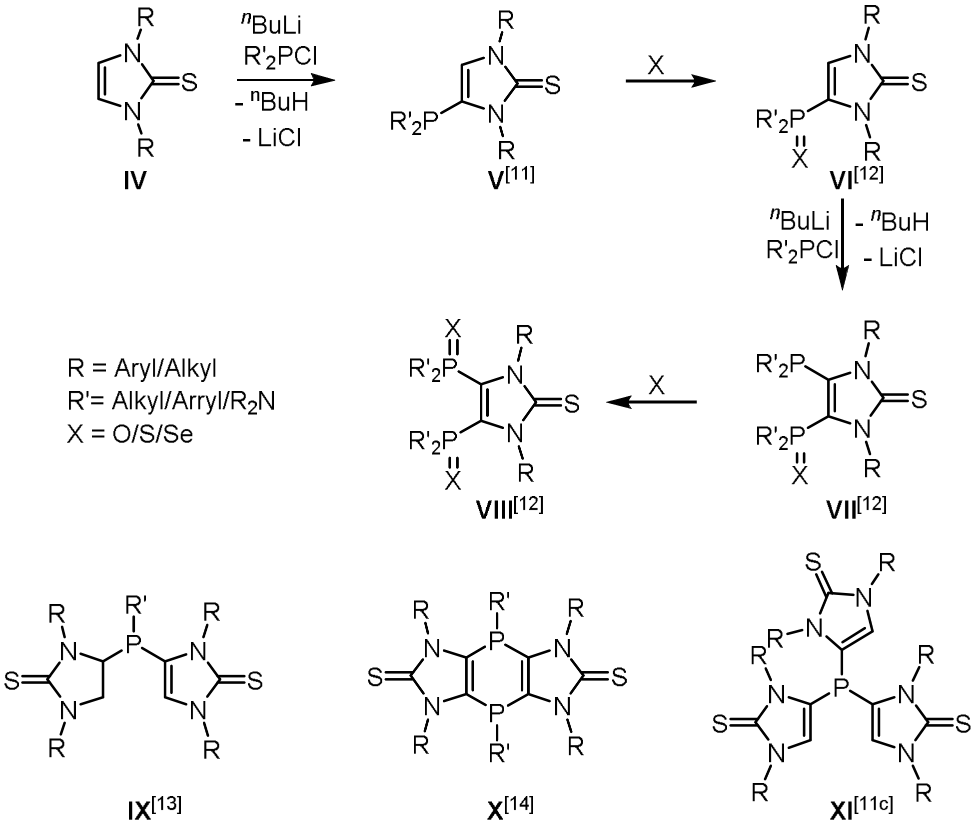


I **II** **III**

Figure 1.1. Backbone-substituted thiazole-2-thiones **I**,[4]**II**,[5]**III**[6] (R = alkyl or aryl groups).

Such substituted thiazole-2-thiones have profound effects on their performance in various applications. For example, commercially available4-amino-5-cyano-thiazole-2-thione **I**(and similar derivatives)has been used in several chemical transformations.[7].The remarkable aspect, however, is the application of **I** in the treatment of central nervous-disorders including Parkinson disease, Huntington's disease, etc.[8]Such compounds also show antitubercular[9] and other biological activities.[10]Beside this, several other heteroatom-substituted thiazole-2-thiones such asalkylthio-substituted thiazole-2-thiones **II**[5] and iodo-substituted thiazole-2-thione **III**[6]are known since long. However,backbone *P*-substituted thiazole-2-thiones are not known to date.

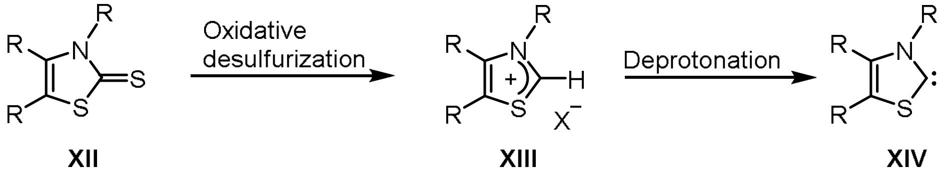
On the contrary, a library of *P*-substituted imidazole-2-thiones has been established by Streubel and co-workers.Treating imidazole-2-thiones with ^{n}BuLi *in situ* generates the lithiated salts in the first step, reacting it with chloro(diorgano)phosphanes gives access to a wide variety of phosphanylated imidazole-2-thiones**V**[11](Scheme 1.1). This experimental approach is very selective, high yielding and functional group tolerant and,therefore, permits a wide range of substitution pattern at *N*- and*P*-centers. The mono-phosphanylated imidazole-2-thionesthus obtained can be subjected to oxidation(**VI**), second-phosphanylation(**VII**), a second oxidation (**VIII**)and complexation.[12] Using the same lithiation-phosphanylation protocol, synthesis of bis-imidazolyl-phosphanes**IX**,[13]**X**[14]and also tris-imidazolyl-phosphanes **XI**[11c]wasachieved. All of them represent potential systems for a use as ligands in coordination chemistry.



Scheme 1.1. Phosphanylated imidazole-2-thiones.[11-14]

1.2 1,3-Thiazole-2-ylidenes

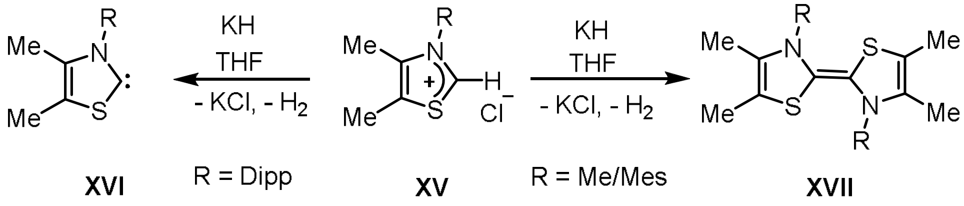
1,3-Thiazole-2-thiones are also potential precursors for thiazolium salts and, in turn, for*N*-heterocyclic carbenes (NHCs),[15]and thereby ofgreat interest in organometallic, coordinationand catalytic chemistry.[15b, 16]



Scheme 1.2. General synthetic route from 1,3-thiazole-2-thiones to thiazole-2-ylidenes (R = alkyl or aryl groups).

The quest of stable thiazole-2-ylidenes remained unsolved for a long time. In 1958, RonaldBreslow'sinvestigations about thiamine diphosphate (TDP) opened a gateway to thiazole-2-ylidene chemistry.[17] TDP is an essential cofactor and found to be involved in several biological processes. Breslow in his studies suggested that the essential intermediates in the thiamine catalyzed enzymatic pathways included the thiazole-based *N*-heterocyclic carbene and enaminol.[17]Despite this effective contribution and several other attempts, free thiazole-2-ylidene could not be isolated at that time.[18]

Although the synthesis of NHCcomplexes, wherein a sulfur atom is incorporated into the heterocyclic ring, was initiated by Lappert[19] and Stone,[20] independently, almost four decades ago.The first stable thiazole-2-ylidene**XVI**,however, was reported by Arduengo and co-workers in 1997.[15a]**XVI** was accessedvia deprotonation of 3-(2,6-diisopropylphenyl)-4,5-dimethylthiazolium chloride (**XV**) with potassium hydride as a colorless crystalline solid (Scheme 1.3). Attempts to isolate thiazole-2-ylidenes with sterically less demanding groups at the*N*-center, ended up in a dimerization via C^2-C^2 double bond formation (**XVII**), which was assignedto the lower kinetic stability (Scheme 1.3).



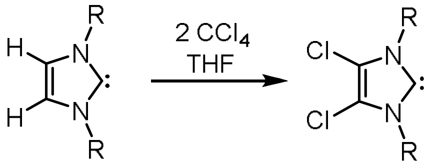
Scheme 1.3. Synthesis of the only known free thiazole-2-ylidene (**XVI**) and its dimer (**XVII**) according to Arduengo.[15a]

Today, it can be safely stated that the thiazole-based NHC chemistryis comparatively little developed, which is due to the ratherlower stability compared to imidazole-based NHCs; the latter results from the replacement of one nitrogen atom, being a far better π-donor to the carbene center than a sulfur atom.[21]

1.3 Backbone-functionalization of NHCs

The backbone (C^4/C^5) functionalization of NHCs with various groups,*e.g.,* halo,[22]cyano and nitro[23]has received considerable interest of chemists and the reason is mainly the impact of these moieties on the reactivity including the catalytic properties of NHC metal-complexes.[24]Due to these investigations, several studies on backbone-heteroatom substitution of NHCs have been reported recently.[25]However, such studies are mainly confined to the imidazole-based NHCs, and the thiazole-based NHCs possess (mostly) alkyl or aryl groups at C^4 and C^5 positions.[15a, 26]

Arduengo and co-workers reported the backbone functionalization of NHCs while keeping the carbene carbon (C^2) intact (Scheme 1.4). They presented the synthesis of 4,5-dichloro-imidazole-2-ylidene **XIX**,which showed stability towards moist air for a short exposure.The extraordinary stability of this compound was mainly attributed to the σ-electronegativity effect and π-electron releasing effect of the chlorine atoms positioned at the backbone of the heterocycle.[22a]



XVIII **XIX**

Scheme 1.4.Backbone halogenation of NHC **XVIII**(R= alkyl or aryl groups) according to Arduengo.[22a]

This findingwas followed by several other examples of NHC-backbone substitution; halogenations by Junk,[22b] deuteration by Rodenzo,[27] silylation by Cui,[25c] Stalke,[25e] and Roeskey,[28] phosphanylation by Gates[29] and substitution with various functional groups by Bertrand[30] (Figure 1.2).

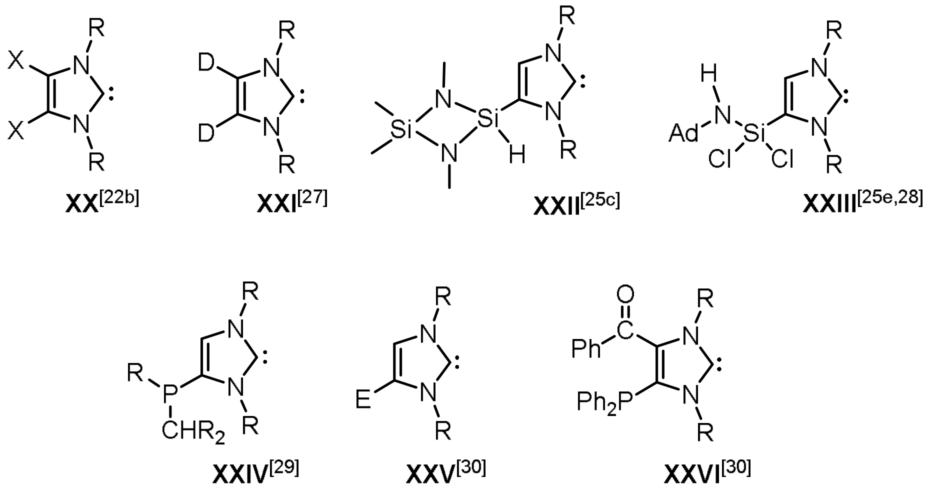
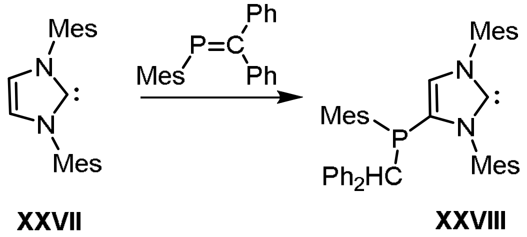


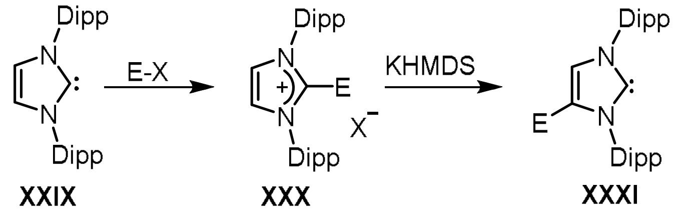
Figure 1.2. Backbone-functionalized imidazole-2-ylidenes (R = alkyl or aryl groups, X = Cl, Br).

Among these, the work of Gates and co-workers onthe synthesis of backbone P-functionalized imidazole-2-ylidenes can be regarded as prodigious breakthrough.They reported the first backbone phosphanylated imidazole-2-ylidene**XXVIII** by treating 1,3-dimesitylimidazole-2-ylidene with a phosphaalkene(Scheme 1.5). The C^4-substituted NHC derivative **XXVIII** holding the (almost) unprotected C^2-position intact was quite unexpected and is believed to be formed via intermediate formation of an abnormal NHC.[29]



Scheme 1.5. Backbone-phosphanylation of imidazole-2-ylideneaccording to Gates.[29]

Soon after this, Bertrand and co-workers also reported the synthesis of 4- and 4,5-functionalized imidazole-2-ylidenes from a single 4,5-unsubstituted imidazole-2-ylidene (Scheme 1.6). In the first step, an imidazolium salt was produced by reacting a sterically protected NHC (**XXIX**) with an electrophile. In the second step intramolecular transfer of the electrophile from C^2 to C^4 resulted in the backbone-functionalized NHC derivatives **XXXI**via the formation of formally abnormal carbene adduct.[30]



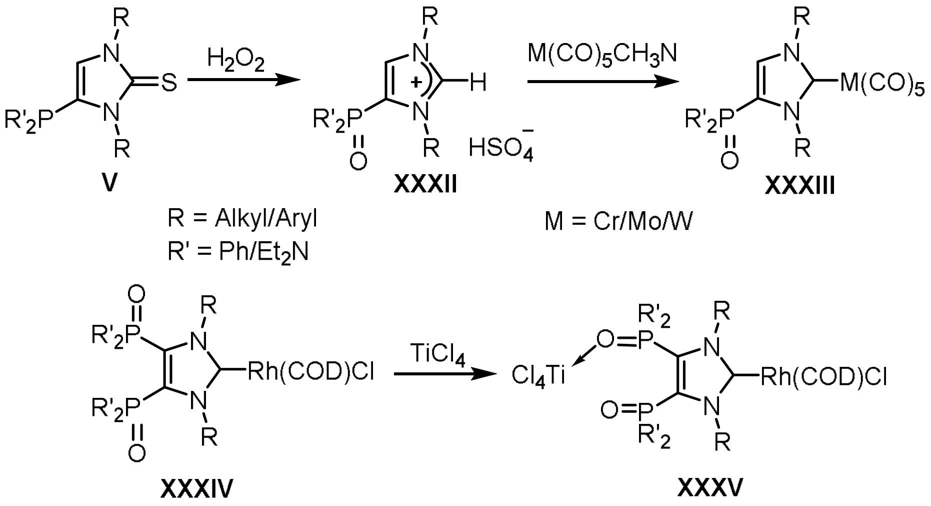
E = Cl, Br, PhC(O), CF_3SO_2, $SiMe_3$, PPh_2
X = Cl, Br

Scheme 1.6. Synthesis of backbone-phosphanylated imidazole-2-ylidene **XXXI** according to Bertrand.[30]

Ruiz devised another experimental approach to achieve the *P*-substituted imidazole-2-ylidenes starting from air and moisture stable imidazolium salts (rather than the NHC). Reaction of the imidazolium salt with LiHMDS gave access to P-functionalimidazole-2-ylidene; a less sterically demanding analogue of **XXVIII**,which also demonstrate that,back-bone-phosphanylation can be achieved without having sterically demanding group at the *N*-center of the heterocycle.[31]

This achievement of the NHCs bearing donor moieties positioned at the backbone of the heterocycle opened a new domain in the chemistry of *N*-heterocyclic carbenes with presumption of extra ordinary stability.[22] By using this strategy not only two chemically and electronically different environments werecombined in a single molecule,[32] but also the *P*(III)-functional ligand systemlead to multifunctional ligand systems to create homo- and heterobimetallic complexes.[31, 33]

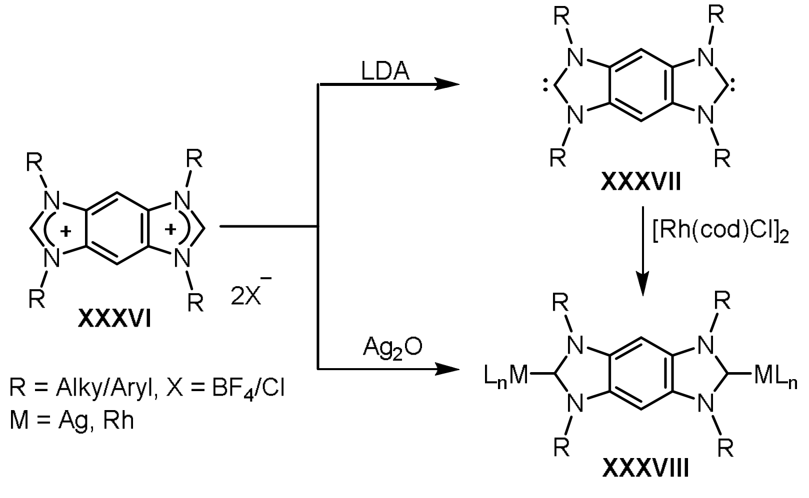
Streubel and co-workers contributed to the field by developing a high yieldsynthetic approach using easy to handle starting material,*i.e.*,backbone-phosphanylated imidazole-2-thiones (**V**, see section 1.1) to get access to P-functional imidazole-2-ylidenemetal complexes (Scheme1.7). They exploited both possible synthetic strategies:oxidative desulfurization (i) and reductive desulfurization (ii) of the P-functional thiones. In the first case, initially phosphanoyl-imidazolium saltswere produced by treating the imidazole-2-tiones **V** with H_2O_2. In the second step deprotonation with base, *in situ* generated NHC, which upon treatment with metal precursor lead to the NHC-metal complexes (**XXXIII**).[11b]The bis-phosphanoylNHC-complex **XXXIV** was accessed with same synthetic protocol and converted to heterobimetalliccomplex **XXXV**[34]. The reductive desulfurization will be discussed in thesection (1.5).



Scheme 1.7. Synthesis of the backbone-phosphanoyl substituted NHC metal complexes **XXXIII** and heterobimetallic-complexes **XXXV** according to Streubel.[11b, 34]

1.4 Backbone-functionalized bis-NHCs

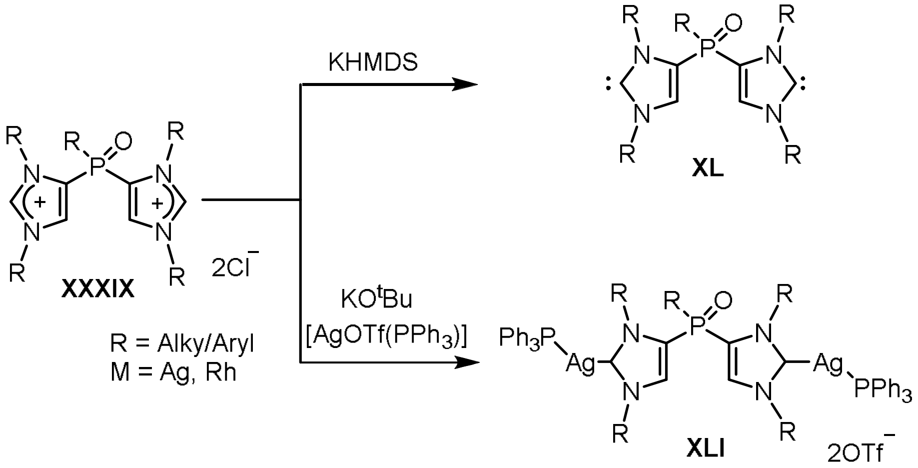
The design and construction of new organic-inorganic hybrid materials have been the subject of great interest for its considerable potential. However,rigid multitopic-NHCs, potential candidates having binding ability to different transition-metals, have not be studied in greater detail. Bielawski and co-workers introduced the design fornon-chelating, rigid bis-NHCs having a fused arene middle ring in 2006,representing a new type of Janus-bis-carbenes.[35] The benzobis(imidazolium)salt **XXXVI**was reacted with LDA to create the bis-NHC **XXXVII**, while its metalcomplexes**XXXVIII** were produced by reacting it with suitable metal precursors (Scheme 1.8).



Scheme 1.8. Synthesis of bis-NHCs and its complexes according to Bielawski.[35a]

Depending upon the steric bulk of the *N*-substituent, those bis-NHCs can be isolated as monomeric,[35a] dimeric[36] or polymeric[37] materials. Furthermore, when suitable metal precursors were reacted with the benzo-bis(imidazolium) salts, main chain-organometallic-polymeric materials were also accessed.[38]The same bis-NHCs were used by Hahn in 2014 to create, supramolecular materials including molecular squares and rectangles.[39]

A different synthetic approach was developed by Streubel and co-workers to establish a new design of bis-NHCs having a *P*(V)-center incorporated as linker (Scheme 1.9). The bis-imidazolium salt (**XXXIX**) was accessed via oxidative-desulfurization of the bis-imidazolyl phosphane **IX** (see section 1.1). Reacting **XXXIX**with two equivalents of potassium hexamethyldisilazide (KHMDS) gave access to the free bis-NHC derivative **XL**, while treating **XXXIX** with two equivalents of KO^{t}Bu and AgOTf(PPh$_3$) lead to the bis-NHCsilver complex**XLI**.[40]

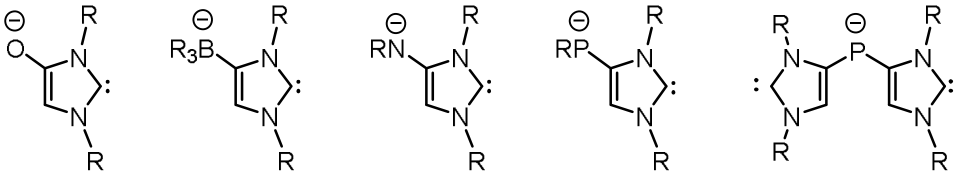


Scheme 1.9. Synthesis of bis-NHC having *P*(V) unit as linker**XL** and its silver-complex**XLI**according to Streubel.[40]

These studies have opened a new area in the design of discrete multitopic NHCs which potentially can bind to different (hard and soft) metal centers.

1.5 Backbone-functionalized anionic NHCs

Backbone-functionalized anionicNHCs represent the strategic approach to fine tune the electronic ligand properties by incorporating an anionic group to the NHCbackbone; Figure 1.3 displays selected examples according to their chronological appearance.



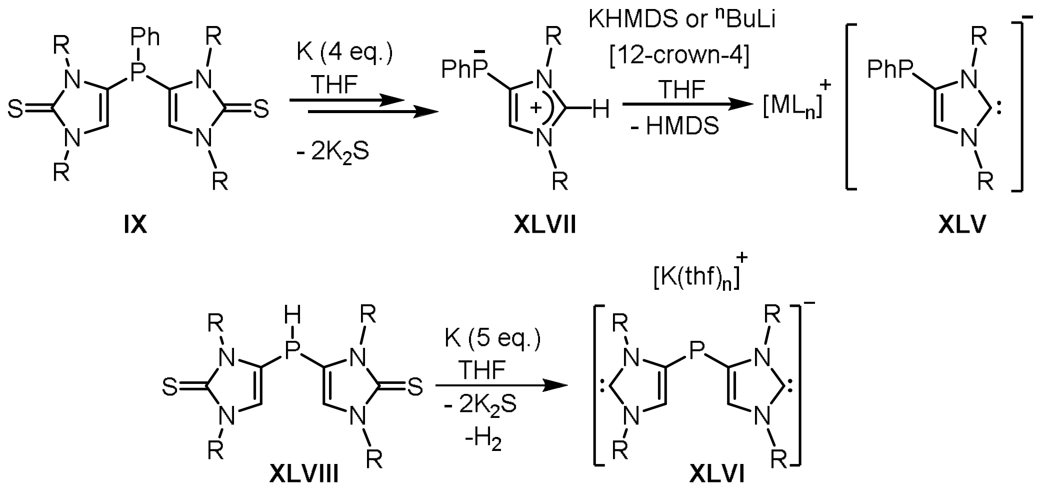
XLII[41] **XLIII**[25d] **XLIV**[25f] **XLV**[42] **XLVI**[11c]

Figure 1.3. Anionic NHCs (R = alkyl or aryl groups); the cationic parts are not shown.

Lavigne and co-workers[41] postulated the synthesis of anionic imidazol-2-ylidene-4-olate**XLII**, by reacting the starting material 4-hydroxyimidazolium chloride with LiHMDS (2 eq.) (Figure 1.3). The obtained anionic imiazole-2-ylidene was further reacted with sulfur to generate the C^2-thione and with a metal precursor to give the corresponding NHCmetal complex.Also,further functionalization at O- and C-centersof the coordinatedNHC was achieved upon reactions with electrophiles. In contrast to **XLII**, a weekly coordinating anionic functionality $B(C_6H_5)_3$ was introduced at the NHCbackbone by Tamm and co-workers (**XLIII**).[25d] An imidazole-2-ylidene was reacted with ^{n}BuLi at first to generate anionic dicarbene, which upon treatment with triaryl-borane produced the desired product. Zwitterionicgold complexes of the obtained NHC were obtained via reacting with suitable gold complexes and their catalytic studies towards skeletal rearrangement of enyne were undertaken.Another example of anionic NHC ligands was postulated by Braunstein and co-workers (**XLIV**).[25f] Backbone arylimino-substituted NHC ligands were accessed via reacting imidazolium precursors with LiHMDS and tmeda (N, N, N', N'-tetramethylethylenediamine).

In 2013,Streubel and co-workers[42] reported the synthesis and isolation of the novel zwitterionic compound **XLVII** via treatment of the imidazol-2-thion-4-yl-substituted phenyl phosphanes **IX** with four equivalents of potassium (Scheme 10). Reaction of **XLVII** with KHMDS or ^{n}Buli in the presence of two equivalents of [12-crown-4] resulted intoanionic-NHC derivative **XLV**.The reported ^{31}PNMR resonance was 66.1 ppm (t, $^{3}J_{P,H}$ = 5.4 Hz; M = Li) and 65.7 ppm (t, $^{3}J_{P,H}$ =5.1 Hz; M = K).

Synthesis of anionic bis-NHC **XLVI** was also reported by Streubel and co-workers (Scheme 1.10). This derivative was obtained via reaction of a *P*-H substituted imidazole-2-thione **XLVIII** with five-fold excess of potassium metal; the reported ^{31}PNMR resonance for this compound was reported to be at -116.0 ppm.[11c]

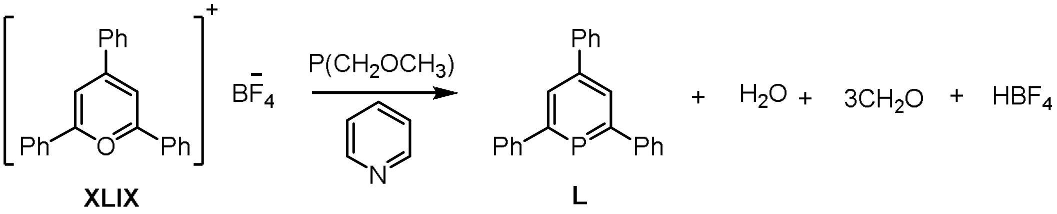


Scheme 1.10. Synthesis of anionic imidazole-2-ylidenes **XLV**[42] and **XLVI**[11c]according to Streubel.

1.6 Phosphinines

In the following a short overview on the chemistry of phosphinines will be given as they constitute an important part of this thesis.

In 1966, the successful synthesis of λ^3-phosphinine **L** by Märkl has opened a new area in the chemistry of low-coordinate phosphorus using $P(CH_2OH)_3$, acting formally as source of PH_3, and pyrylium salt **XLIX** in pyridine (Scheme 1.11).[43]



Scheme 1.11. Synthesis of 2,4,6-triphenylphosphinine **L**according to Märkl.[43]

Phosphinine, the heavy homologue of pyridine, possesses about 90 % of the aromaticity of benzene.[44] Interestingly, some of the chemical disparities of pyridines and phosphinines can be attributed to the lower lying LUMO energies, and consequently increased electron affinity of phosphinines. The lone pair at the phosphinine phosphorus resides in the more diffuse HOMO-2 orbital (Figure 1.4).[45] Altogether, this frontier orbital situation creates ligand properties of phosphinines as to be weaker sigma donors and stronger π–acceptors compared to pyridines.[46]

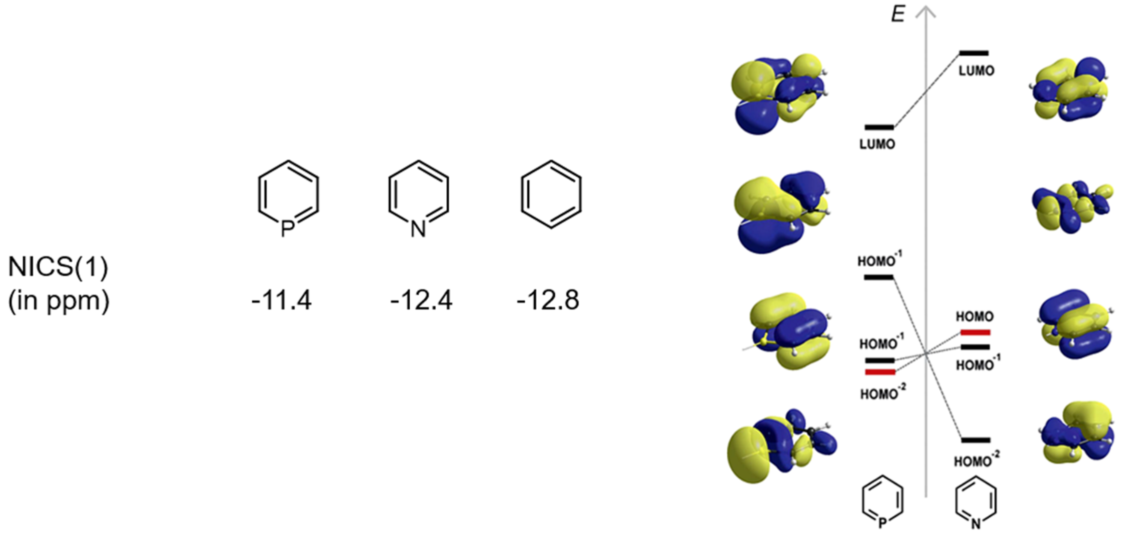
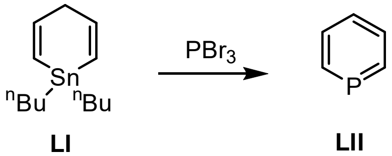


Figure 1.4. NICS(1) values of benzene and its hetero-analogs as well as frontier orbital energies of phosphinine and pyridine (taken from the literature, contribution of C. Müller)[45].

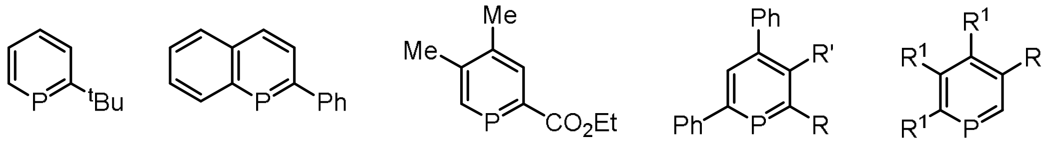
Since their first discovery, phosphinines have initiated intense research for more than five decades,[47] and, nowadays, the spectrum of applications ranges from luminescent materials, to polymer precursors and ligands in catalysis.[48]

A remarkable addition to this field of research was the synthesis of the parent compound, *i.e.,***LII** by Ashe in 1971. They treated the 1,4-dihydro-l,l-di-^{n}butylstannabenzene (**LI**) with phosphorus tribromide, which generated the hydrobromide initially; addition of 1,5-diaza-bicyclo[4.3.0]non-5-ene led to the final product **LII** (Scheme 1.12). In contrast to **L,** being a crystalline solid, **LII** was found to be a colorless, volatile liquid.[49]



Scheme 1.12. Synthesis of the parent phosphinine**LII**according to Ashe.[49]

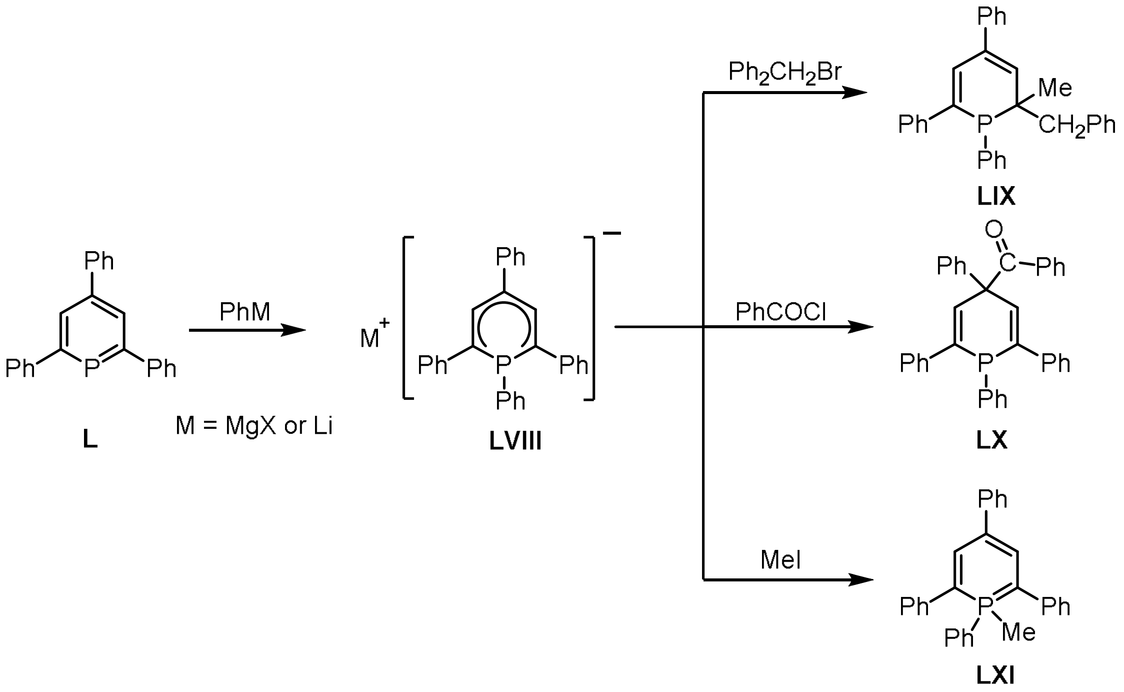
Later on, several new routes to λ^3-phosphinines were reported, including those derivatives listed in Figure1.5. For example: a [4+2]-cycloaddition reaction of 1,3-cyclopentadiene with ^{t}BuCP generated **LIII.**[50] 1-Benzyl-1,2-dihydro-phospha-naphthalene eliminatesa toluene unit upon heating at 260-300 °C to produce**LIV**, thus illustrating thatthermal elimination of a small molecule leading to aromatization can be used.[51]Compound **LV** was accessed via reaction of ethyldiazoacetate with a phosphole sulfide. During the course of reaction,the addition of a carbene at the C^2-C^3 bond of the phosphole initially generates a bicyclic derivative which thermally rearranged to produce **LV**.[52] Another route used a [4+2]-cycloaddition reaction between an 1,3-azaphosphinine and an alkyne, followed by elimination of a nitrile unit thus leading to phosphinine derivative **LVI**.[53]Recently, Hutner *et al.*reported a new route to synthesize λ^3-phosphinines: ring expansion of zirconacyclopentadienes by insertion of chloro(trimethylsilyl)methyllithium, followed by metathesis with phosphorusto produce phosphinine derivative**LVII**.[54]



LIII[50] **LIV**[51] **LV**[52] **LVI**[53] **LVII**[54]

Figure 1.5. Selected examples of phosphinines **LIII-LVII** to illustrate motifs accessible via different synthetic methodologies.

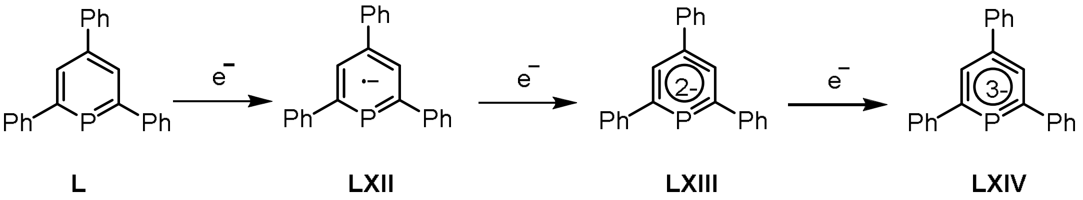
As mentioned beforehand, phosphinines have interesting π-ligand accepting properties, and a markedly electrophilic phosphorus center. Therefore, they readily react with Grignard and lithio compounds to furnish salts **LVIII**with dihydrophosphinine anions; the latter offer access to regiochemically different substitution products, *i.e.*, 1,1- or 1,2- or 1,4-regioisomers, depending on the nature of the electrophile used in the next step (Scheme 1.13).[55]



Scheme 1.13. Sequential reactions of phosphinine **L**with nucleophiles and electrophiles.[55]

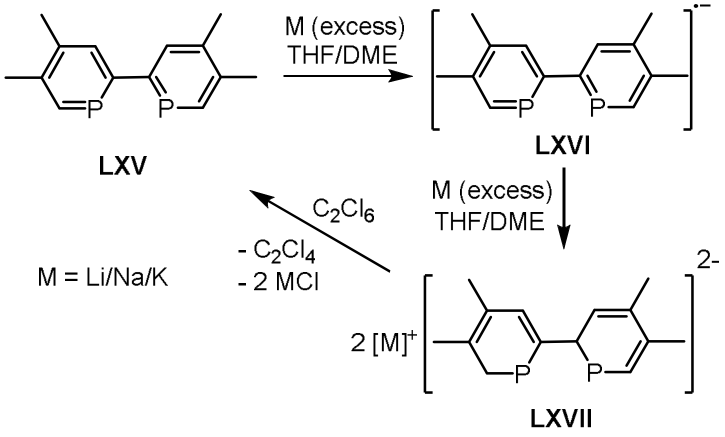
Besides, a broad spectrum of studies have shown complexation,[45, 56]*P*-alkylation,[57]*P*-oxidation,[58]*P*-reduction[59] and cycloaddition reactions[60] of phosphinines, the last two of the list are discussed below.

The reduction of phosphinines has been well established and several examples can be found in literature. In particular,λ^3-phosphinines are found to be easily reducible by alkali metals to generate paramagnetic anion radicals and diamagnetic dianions.[59, 61] Even paramagnetic trianion radicals have been established by Märkl (Scheme 1.14) for the 2,4,6-triphenyl phosphininevia combined CV and ESR studies.[61] Solutions of these species are found to be intensely colored and extremely sensitive towards oxygen.



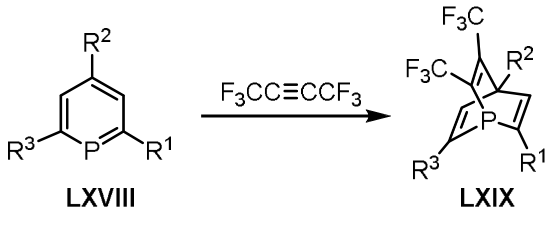
Scheme 1.14. Reduction of phosphinineL according to Märkl.[61]

In 1999, Mathey and LeFloch reported the synthesis and reactivity of a 2,2-bisphosphinine dianion, including their ^{31}PNMR features.[62] Upon reaction of 2,2-biphosphinine **LXV** with excess metal, initially an intense purple color of the reaction solution was observed, which was suggested to be associated with the formation of paramagnetic monoradical anion **LXVI**. This supposition was supported by the disappearance of the^{31}PNMR signal at that stage of reaction. Uponprolongedreaction time, a color change to dark green was observed which was associated with the appearance of (new) broad signals in the ^{31}PNMR spectra (between -5 and -15 ppm depending upon the metal used), and which were assigned to the diamagnetic dianions**LXVII**. **LXV** was regenerated by reacting it with stoichiometric equivalents of hexachloroethane thus represents a chemical evidence illustrating the formation of the dianion **LXVII** (Scheme 1.15).



Scheme 1.15. Synthesis of 2,2-biphosphinine dianions according to Mathey and LeFloch.[62]

Märkl and Lieb[60a] has demonstrated that the 2,4,6-trisubstituted phosphinines (**LXVIII**) show only a moderate dienic reactivity and,*e.g.,*2,4,6-triphenyl phosphinine, showed no reaction with diethyl acetylenedicarboxylate or with maleic anhydride.However, upon reacting **LXVIII** with highly reactive electron-poor dienophiles,*e.g.,* hexafluoro-2-butyne (at 100 °C), gave access to the corresponding phosphabarrelene **LXIX** (Scheme 1.16).



Scheme 1.16. Cycloaddition reaction of phosphinines (R = alkyl or aryl groups).[60a]

Later on, investigations were further extended by Märkl *et al.,*and [4+2] cycloaddition reactions of phosphinines and arynes to get phosphabarrelenes were established.[60c]

In contrast to efforts concerningheteroatom-substituted benzene derivatives, which had a great impact on the chemistry of arenes,[63] properties and reactivity of phosphinines are largely dominated by the presence of aryl substituents; this is illustrated by the examples **LXX** and **LXXI** (Figure 1.6).[64]In case of phosphinines, heteroatom per-substitution is unknown and only 2-hydroxy derivatives have been described, recently.[65]

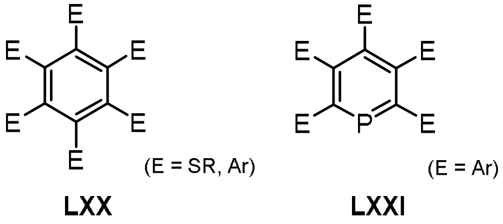
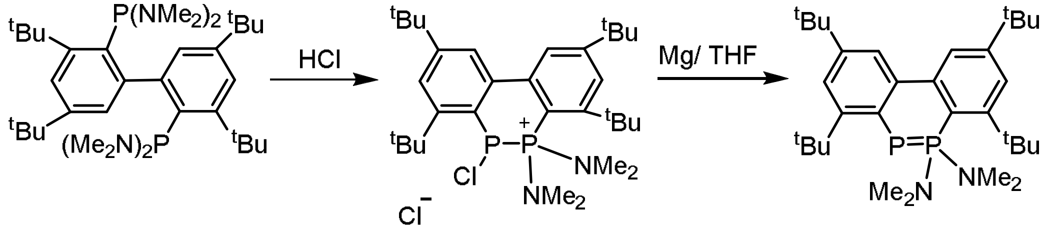


Figure 1.6. Benzenes **LXX** having a complete set of heteroatom substituents and phosphinines **LXXI**.

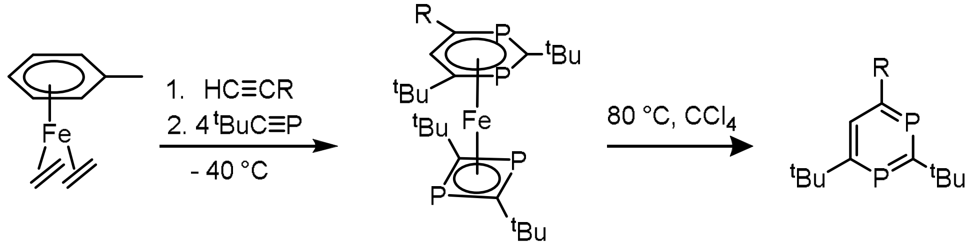
1.7 Diphosphinines

In contrast to phosphinines, the chemistry of diphosphinines has been scarcely investigated, and out of the three possible regioisomers, only a few reports on 1,2- and 1,3-diphosphinines are available. For example, Bickelhaupt and co-workers postulated the formation of λ^5,λ^3-diphosphaphenanthrene. When compound **LXXII**was treatedwith hydrogen chloride, initially a cyclic intermediate **LXXIII**was generated, rather than the originally targeted bis-dichlorophosphane derivative (Scheme 1.17). Reduction of the intermediate **LXXIII** with Mg yielded the λ^5,λ^3-diphosphinine **LXXIV**,which was found to be a ylide and, therefore, authors concluded no aromaticity. **LXXIV**was not isolable and was not purified, but was characterized via ^{31}PNMR spectroscopy,*i.e.,* two doublets at 94.5 and -129 ppm with a large $^1J_{P,P}$ coupling constant of 469 Hz strongly evidenced the proposed P=P motif in compound **LXXIV**.[66]


LXXII **LXXIII** **LXXIV**

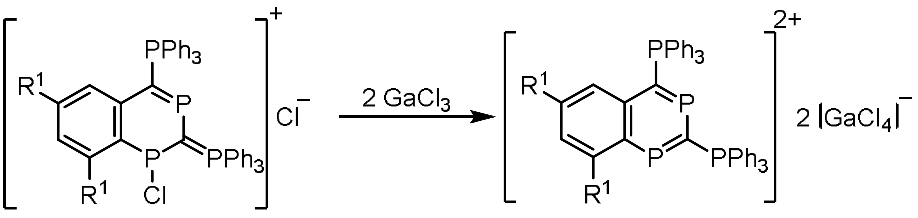
Scheme 1.17. Synthesis of 1,2-diphosphinine **LXXIV** according to Bickelhaupt.[66]

1,3-Diphosphinines are comparatively well investigated, and the first stable 1λ^3,3λ^3-diphosphinine **LXXVII** was reported by Zennek and co-workers (Scheme 1.18). They showed an efficient synthesis of**LXXVI** in the coordination sphere of iron(0) by [2+2+2]-cycloaddition of two phosphaalkynes and a terminal alkyne; subsequent decomplexationunder oxidative conditions led to unligated **LXXVII**(Scheme 1.18).[67]


LXXV **LXXVI** **LXXVII**

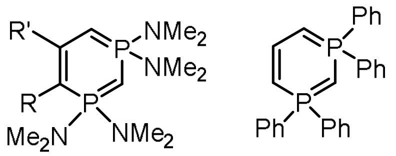
Scheme 1.18. Synthesis of 1,3-diphosphinine **LXXVII** according to Zenneck (R = H/CH$_2$OC(O)CH$_3$.[67]

A unique example of a 1λ^3,3λ^3-diphosphinine is represented by the bis-phosphonium substituted derivative **LXXIX** which was synthesized via dechlorination of 1,3-diphosphatetraline derivative **LXXVIII** using GaCl$_3$(Scheme 1.19).[68]


LXXVIII **LXXIX**

Scheme 1.19. Synthesis of bis-phosphonium substituted 1,3-diphosphinine **LXXIX**according to Schmidpeter.[68]

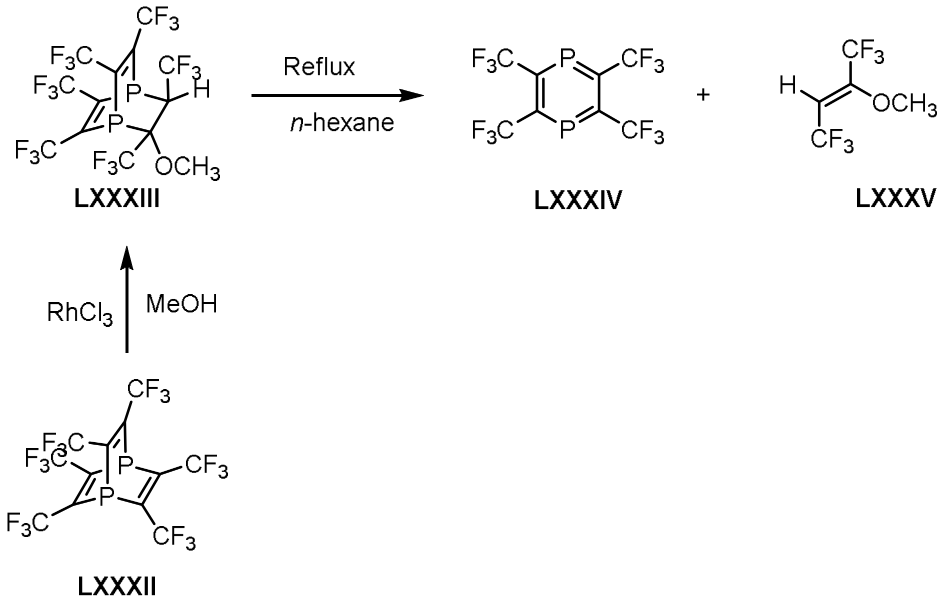
In comparison to 1λ^3,3λ^3-diphosphinines, 1λ^5,3λ^5-diphosphinines have studied in more detail, and a wide range of 1λ^5,3λ^5-diphosphinine derivatives can be found in literature. Especially interesting among these is **LXXX**(Figure 1.7),reported by Fluck and co-workers, obtained as the final product of the attempted synthesis of 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphete, which underwent a Diels-Alder reaction with an alkyne.[69] Compound **LXXXI** represents the most stable derivative of all known $1\lambda^5,3\lambda^5$-diphosphinines, which was reported first by Märkl in 1963, and was obtained by stepwise deprotonation of 1,1,3,3-tetraphenyl-1,3-diphosphoniocyclohex-4-ene (Figure 1.7).[70]



LXXX[69] **LXXXI**[70]

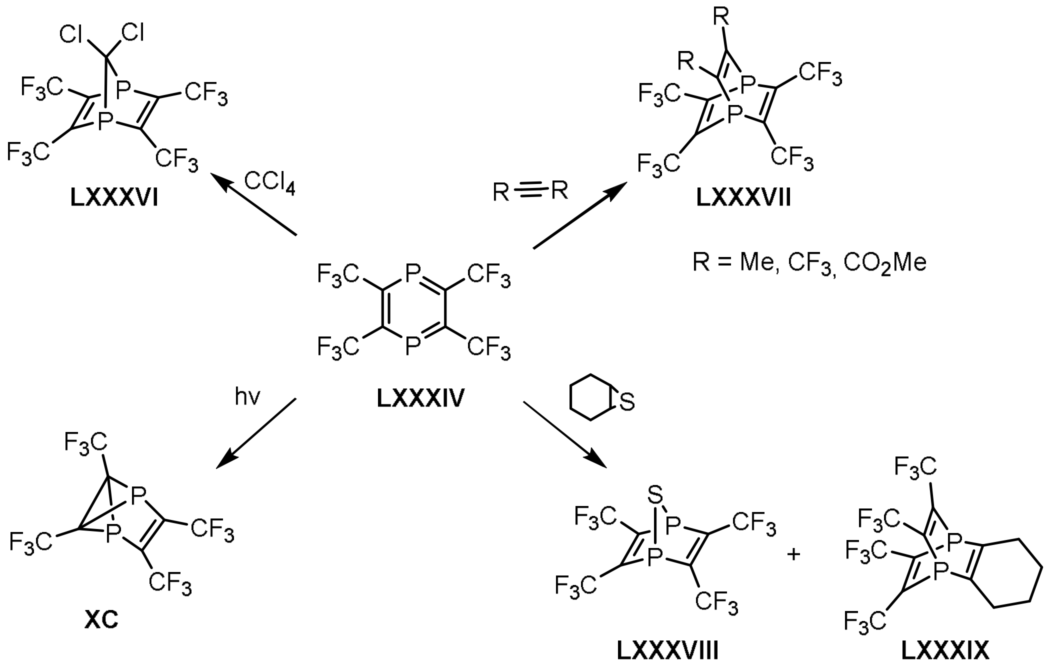
Figure 1.7. $1\lambda^5,3\lambda^5$–Diphosphinines according to Fluck**LXXX**[69] andMärkl**LXXXI**.[70]

By comparison, 1,4-diphosphinines are even less explored, and until recently only a single example of a monocyclic $1\lambda^3,4\lambda^3$-diphosphinine (**LXXXIV**)[71] was reported by Kobayashi and co-workers. They used a stepwise protocol, starting with a $RhCl_3$ catalyzedaddition of MeOH to the 1,4-diphosphabarrelene **LXXXII**to give **LXXXIII** which eliminates the alkene **LXXXV** under thermal conditions to provide the 1,4-diphosphinine **LXXXIV** having four electronwithdrawing CF_3 groups (Scheme 1.20). Owing to extreme air sensitivity, this compound could neither be isolated nor fully characterized and was only handled as hexane solution. Noteworthy is the reported ^{31}PNMR resonance of**LXXXIV**that was determined to be very much at low field (287.0 ppm).



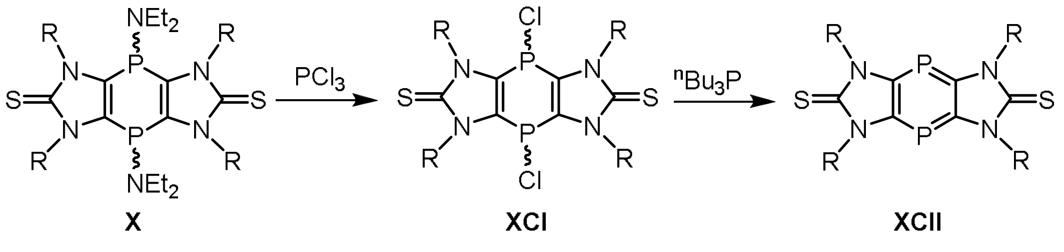
Scheme 1.20. First synthesis of a 1,4-diphosphinine according to Kobayashi (**LXXXIV**).[71]

The chemistry of **LXXXIV**remained largely unexplored due to the fact that its synthesis was very laborious and the compound was not isolable. Therefore, only few reactions were reported, resulting in formal [4+1]- and [4+2]-cycloaddition reaction products, and only one example of a photoisomerization to provide insight on valence bond isomerization (Scheme 1.21).[72]

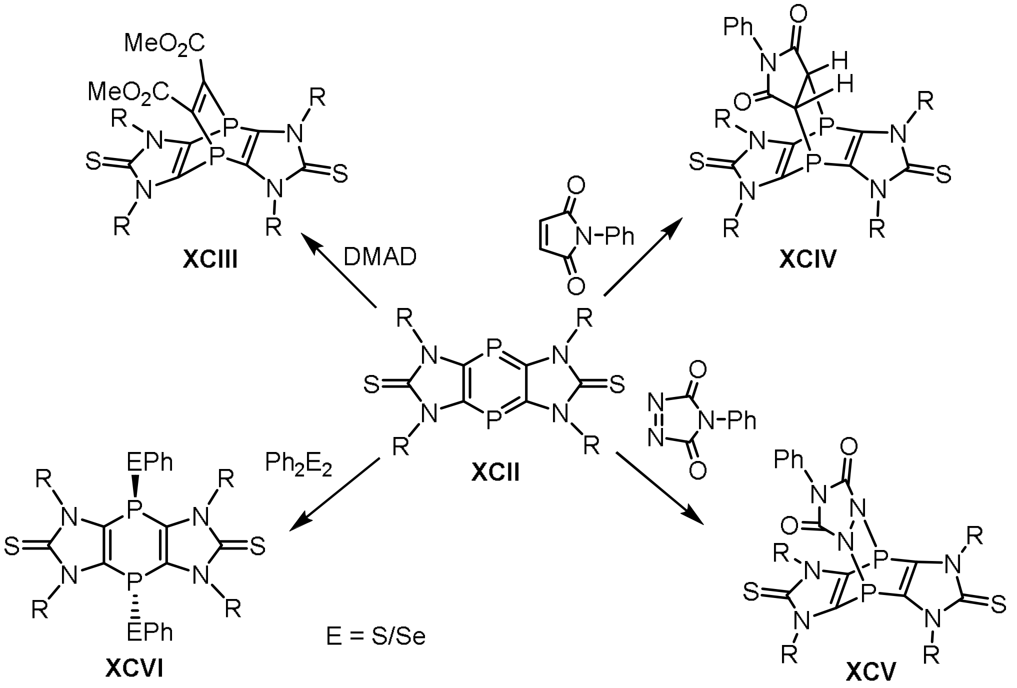


Scheme 1.21. Reactions of 1,4-diphosphinine**LXXXIV**.[72]

The easy access of imidazole-2-thione-based tricyclic 1,4-diphosphinines**XCII**[14a]by Streubel and co-workers has reopened this research area, recently (Scheme 1.22). They reported a multigram synthetic protocol to access 1,4-diphosphinines **XCII**via reduction of the 1,4-dihydro-1,4-dichloro-1,4-diphosphinines **XCI**with $^{n}Bu_3P$. Interestingly, derivatives **XCII**possess a high degree of aromaticity (NICS(1) value −9.5) and another very remarkable feature was revealed by cyclovoltammetric experiments: two reduction potentials (at −1.74 and −2.59 V) with a total and (!) reversible uptake of 3 electrons.[14a] First reactivity studies demonstrated that **XCII**can undergo [4+2]-cycloaddition reactions to give 1,4-diphosphabarellenes in high yields, but also reacted with dichalcogenides PhCh-ChPh (Ch = S, Se) in [4π+2σ]-cycloaddition reactions, followed by inversion at the phosphorus center (Scheme 1.23).[73]



Scheme 1.22. Imidazole-2-thione based 1,4-diphosphinine according to Streubel (R = alkyl groups).[14a]



Scheme 1.23. Reactivity studies of imidazole-2-thione-based 1,4-diphosphinine **XCII** (R = alkyl groups).[73]

Chapter 2

Chapter 2: Aims and objectives of the PhD thesis

The main aim of this PhD thesis was to synthesize first examples of C^5-phosphanyl substituted thiazole-2-thiones and to further extend their chemistry to the following fields of study:

- To employ the C^5-phosphanyl substituted thiazole-2-thiones as precursor to phosphaalkenes
- To investigate the formation of thiazole-2-thione-derived tricyclic 1,4-dihydro-1,4-diphosphinines
- To conduct reactivity studies of tricyclic 1,4-dihydro-1,4-diphosphinines
- To synthesize thiazole-2-thione-derived 1,4-diphosphinines, and to investigate its chemistry including reduction

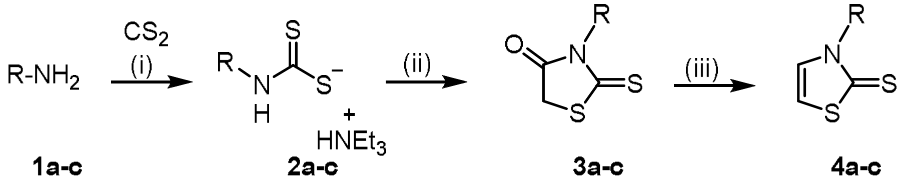
Chapter 3

Chapter 3: Synthesis and reactivity studies of P-functional thiazole-2-thiones

3.1 Synthesis of 1,3-thiazole-2-thiones

1,3-Thiazole-2-thiones were synthesized following literature known protocols (Scheme 3.1).[74] The *N*-methyl derivative was accessed via conventional cyclization reaction between the in situ formed *N*-alkyl dithiocarbamate nucleophile and chloroacetic acetic acid to create the rhodamine intermediate **3a**. Reduction of **3a** with sodium borohydride gave access to *N*-methyl thiazole-2-thione (**4a**). Crude **4a** was purified via sublimation.[74a]

Similar synthetic methodology was adopted (with slight modification) to achieve the *N*-^{i}Pr-derivative **4b**.[74b] The dithiocarbamate salt was obtained by adding carbon disulfide and triethylamine to a solution of the *iso*-propylamine in diethyl ether. The treatment of chloroacetaldehyde with the dithiocarbamate salt **2b,c**, led to cyclization followed by dehydration (one pot synthesis) delivered *N*-^{i}Pr-thiazole-2-thione **4b** in good yields after sublimation. The literature-known protocol for **4b** was extended successfully to **4c** and it was purified via column chromatography using silica as stationary phase and diethyl ether-petrolether (1:5) as eluent.[74b]



a) R = Me, (i) = NaOH (2 eq), Water, (ii) = aq. KO_2CCH_2Cl, H_2SO_4, (iii) = $NaBH_4$, EtOH, conc. HCl
b) R = ^{n}Pr, (i) = Et_3N, Et_2O, (ii) = CH_3CN, $ClCH_3CHO$, (iii) = H_2SO_4
c) R = ^{i}Pr, (i),(ii),(iii) = Same as b

Scheme 3.1. Synthesis of thiazole-2-thiones **4a,**[74a] **4b,c.**[74b]

3.2 Synthesis of P-functional thiazole-2-thiones

The chemistry of P-functional thiazoles can be traced back to 1964, when Dimroth and Hoffmann reported a new class of thiazole-based compounds: phosphacyanines, having a trivalent phosphorus moiety (**XCVII**).[75]Later, crystallographic characterization of such dicoordinated phosphorus compounds was reported by Allmann.[76] A recent report on phosphamethine cyanines (**XCVIII**),[77]and, other P-functional thiazoles[77-78] for example, 2-benzothiazolidinyl phosphonate (**XCIX**)[79]can also be found in the literature. However, in all the above mentioned examples the P-functional group is bound in the C^2-position of the heterocycle (Figure 3.1).

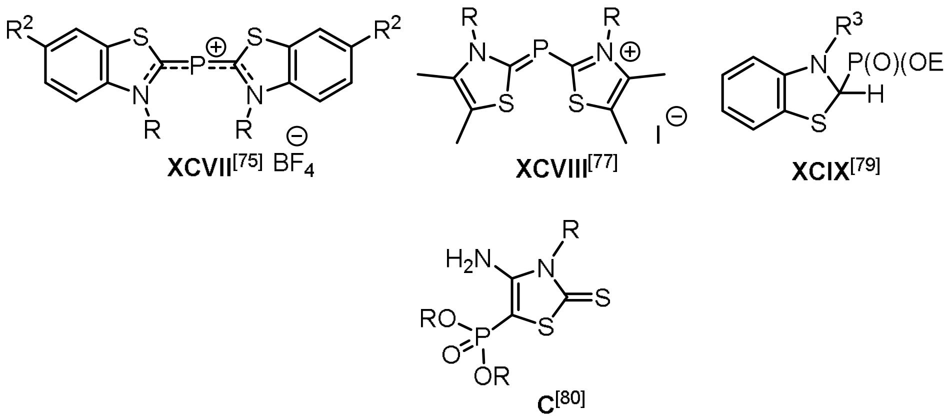
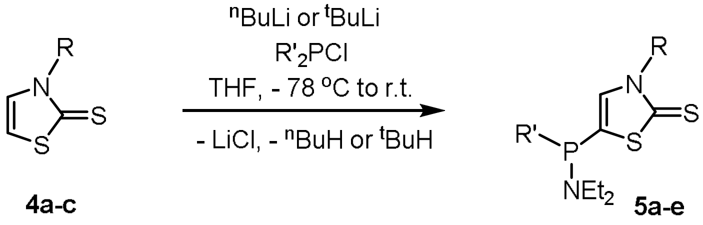


Figure 3.1. Literature known P-functional thiazoles (R/R^1/R^2/R^3 = alkyl/aryl group).

Keeping in view to extend the chemistry later to low coordinate-phosphorus compounds and/or NHCs chemistry, we were more interested in backbone P-functional thiazole-2-thiones. However, upon literature survey it was concluded that only one report on 5-phosphoryl-4-amino-1,3-thiazoline-2-thiones (**C**) was present so far, which also lacked any structural characterization.[80]To explore and investigate the chemistry, a first study was initiated during my Qualification Thesis at University of Bonn[81] concerning synthesis and characterization of C^4/C^5-functional thiazole-2-thiones bearing only PPh_2 groups.

To accomplish the synthesis of C^5-aminophosphanyl-substituted thiazole-2-thiones, synthetic protocol already established by Sauerbrey[82] and Majhi[11c] was employed, but with required modifications.[81] Initial attempts to obtain the C^5-phosphanyl-thiazole-2-thiones via lithiation-phosphanylation reaction sequence for **4a** using ^{n}BuLi was met with limited success and led to unselective reactions. However, treating the THF solution of *N*-methyl-thiazole-2-thiones (**4a**) with one equivalent of ^{t}Buli at −78 °C, and stirring for three hours (between −78 °C and

−70 °C), followed by the addition of chloro(diorgano)phosphanes led to successful synthesis and isolation of C^5-phosphanylated thiazole-2-thione **5a,d** (Scheme 3.2).



5a) R = Me, R' = Et_2N
5b) R = ^iPr, R' = Et_2N
5c) R = ^nPr, R' = Et_2N
5d) R = Me, R' = Ph
5e) R = ^nPr, R' = Ph

Scheme 3.2. Synthesis of C^5-phosphanylated thiazole-2-thiones **5a-e**.

In contrast to the *N*-methyl derivative **4a,** successful lithiation was achieved using ^{n}BuLi for **4b,c** keeping other reaction conditions constant, and afforded C^5-phosphanylated thiazole-2-thione **5b,c,e.** The progress of each reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After the removal of the formed lithium chloride (via filtration over a frit with a pad of celite®), the products were purified via recrystallization from toluene and/or washing with *n*-pentane and obtained as white to yellow powder (**5c** as yellow sticky solid). The synthesis of selected derivatives of P-functional thiazole-2-thiones **5a-e** with different *N*- and *P*-substituents represents the strategic synthetic approach to extend the chemistry later using these compounds as potential building blocks.

The P-functional thiazole 2-thiones **5a-e** were characterized via ^1H, $^{13}C\{^1H\}$ and ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR analysis revealed that regioselective lithiation has occurred as only single signal was observed. Compounds **5a-c** resonate in the chemical shift range of $\delta\ ^{31}P = 79.2\text{-}79.7$ ppm depending on the substituent at the *N*-center, which are comparable with the related P-functional imidazole-2-thiones **V** (R' = R_2N, $\delta\ ^{31}P\{^1H\} = 72.0\text{-}75.0$ ppm),[11c] while compound **5d** and **5e** showed resonance signals in the ^{31}P NMR spectrum at 44.4 ppm and 44.3 ppm, respectively, which are also comparable with the reported P-functional imidazole-2-thiones ($\delta\ ^{31}P = 32.7\text{-}35.2$ ppm).[14c] Selected $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data of compounds **5a-e** are given in Table 3.1 (for details see experimental section). The assignment of the C^5, C^4 and C^2 carbon nuclei of **5a-e** was made upon comparison of the respective carbon nuclei of the parent thiazole compound (**4a**): $\delta\ ^{13}C = 110.9$ ppm, 132.3 ppm, 187.4 ppm), and with that of the related C^4-phosphanyl imidazole-2-thione (*N*-Me, *P*-Ph) (1.8185(18))[11a] or (N-^{i}Pr, P-(Ph)NEt$_2$) (1.8260(18) Å).[83]

Table 3.1.^{31}P{1H} and selected ^{13}C{1H} NMR data of **5a-e**.

	δ^{31}P{^{1}H} (ppm)	δ ^{13}C{^{1}H} of thiazole ring carbon (ppm)	Yield (%)
5a	79.6	128.9 (d, $^1J_{P,C}$ = 14.0 Hz, C^5), 132.1 (d, $^2J_{P,C}$ = 17.6 Hz, C^4), 189.5 (s, C^2)	88
5b	79.7	128.3 (d, $^2J_{P,C}$ = 18.2 Hz, C^4), 130.6 (d, $^1J_{P,C}$ = 13.6 Hz, C^5), 189.5 (s, C^2),	98
5c	79.2	129.9 (d, $^1J_{P,C}$ = 14.0 Hz, C^5), 132.4 (d, $^2J_{P,C}$ = 18.0 Hz, C^4), 190.2 (d, $^3J_{P,C}$ = 1.0 Hz, C^2)	88
5d	44.4	126.6 (d, $^1J_{P,C}$ = 55.6 Hz, C^5), 138.3 (d, $^2J_{P,C}$ = 46.9 Hz, C^4), 191.2 (d, $^4J_{P,C}$ = 1.6 Hz, C^2)	84
5e	44.3	126.6 (d, $^1J_{P,C}$ = 54.7 Hz, C^5), 137.8 (d, $^2J_{P,C}$ = 47.3 Hz, C^4), 190.9 (d, $^3J_{P,C}$ = 1.3 Hz, C^2)	80

X-ray diffraction study were performed on crystals, obtained via slow evaporation of dichloromethane solution of compounds **5a**,**d**. The structures with numbering scheme are given in Figure 3.2, and the selected structural parameters are given in Table 3.2. Complete crystallographic data of compounds **5a,d** are given in the appendix. Compound **5a** and **5d** crystallized in the monoclinic and triclinic system with space group P2$_1$/c and $P\overline{1}$, respectively. The molecular structures further confirm the regiochemistry, having the phosphanyl substituent in the C^5 position. The C1-P bond lengths of **5a** (1.8202(15) Å) and **5d** (1.826(6) Å) are comparable with that of the related C^4-phosphanyl imidazole-2-thione (*N*-Me, *P*-Ph) (1.8185(18))[11a] or (*N*-^{i}Pr, *P*-(Ph)Et$_2$N) (1.8260(18) Å).[83] Similarly the exocyclic C=S bond of **5a** (1.6676(15)) and **5d** (1.656(5)) are also comparable with those of the C^4-phosphanyl imidazole-2-thione (*N*-Me, *P*-Ph) (1.6821(18)).[11a]

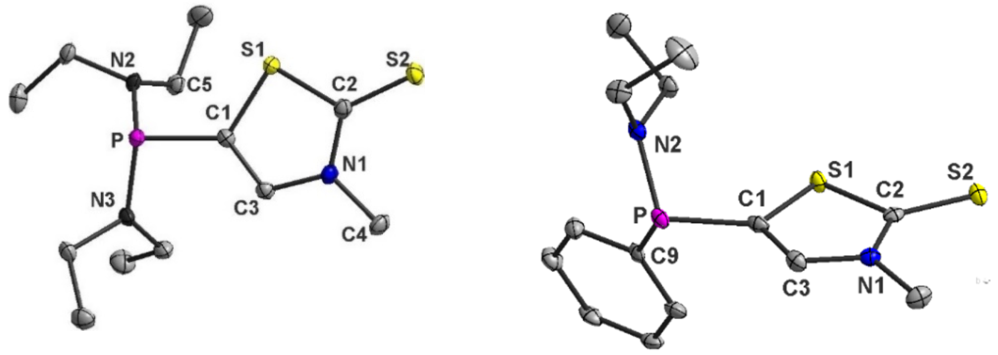


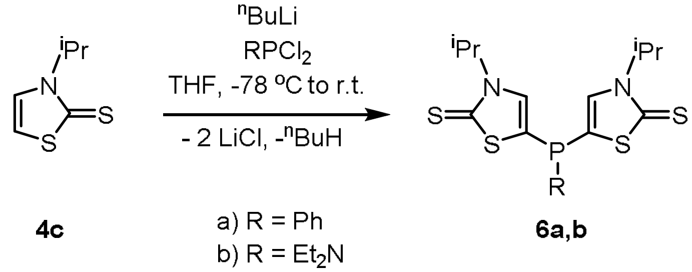
Figure 3.2. Displacement ellipsoids plot (50% probability) of molecular structure of **5a** (left), **5d** (right**)** in thecrystal. Hydrogen atoms have been omitted for clarity.

Table 3.2. Selected bond lengths (Å) and angles (°) of **5a,d.**

	5a	**5d**
C2-S2	1.6676(15)	1.656(5)
C1-P	1.8202(15)	1.826(6)
C9-P	-	1.831(6)
N2-P	1.6979(12)	1.697(5)
N1-C2-S1	108.16(11)	107.7(4)
S1-C1-P	122.63(8)	128.9(3)
C3-C1-P	127.66(11)	122.7(4)
C1-P-C9	-	101.0(2)
C1-P-N2	98.51(6)	107.8(2)

3.3 Synthesis of bis(thiazole-2-thione-5-yl)phosphanes

The synthesis of bis(thiazole-2-thione-5-yl)phosphanes were achieved by using the already discussed (Section 3.2) lithiation-phosphanylation protocol. Noteworthy is that using similar protocols to achieve the *N*-methyl derivative led to a mixture of products. However, lithiation of the *N*-^{i}Pr-substituted thiazole-2-thione **4c** with ^{n}Buli at low temperature (−78 °C), followed by the addition of dichloro(organo)phosphane, selectively afforded compounds **6a**,**b**(Scheme 3.3). After filtration through silica, recrystallization from toluene, and washing with *n*-pentane, **6a,b** were isolated in excellent yields (up to 95 %) as white powder. $^{31}P\{^{1}H\}$ NMR data of compounds **6a**,**b** and $^{13}C\{^{1}H\}$ NMR data of the heterocycle ring-carbon nuclei is given in Table 3.3. The ^{31}P NMR resonances of −42.0 ppm for **6a** and 28.3 ppm for **6b** are comparable with the reported values for the bis(imidazolyl)phosphanes **IX**{(R' = Ph, δ ^{31} = −54.7 ppm),[11c, 13] (R' = NMe$_2$, δ ^{31}P = 16.0 ppm)}.[84]



Scheme 3.3. Synthesis of bis(thiazolyl)phosphanes **6a,b**.

Table 3.3. ^{31}P{^{1}H}, selected ^{13}C{^{1}H} NMR data and yields of **6a,b**.

	δ P{^{1}H}(ppm)	δ ^{13}C{^{1}H} of thiazole ring carbon (ppm)	Yield (%)
6a	−42.0	120.6 (d, $^{1}J_{P,C}$ = 30.4 Hz, C^5), 136.2 (d, $^{2}J_{P,C}$ = 49.4 Hz, C^4), 191.1 (s, C^2),	88
6b	28.3	125.3 (d, $^{1}J_{P,C}$ = 34.9 Hz, C^5), 132.2 (d, $^{2}J_{P,C}$ = 37.9 Hz, C^4), 189.9 (s, C^2),	95

Interestingly no coupling to protons was observed in the ^{31}P NMR spectrum of **6a,**however, in case of **6b** coupling to both C^4-H and NEt$_2$ protons was observed {28.3 ppm (quint, $^{3}J_{P,H}$ = 11.4 Hz, $^{3}J_{P,H}$ = 3.4 Hz). Furthermore, **6a** and **6b** were characterized via IR, MS, elemental analysis and single crystal X-ray diffraction analysis. Single crystals for both **6a** and **6b** were obtained via slow evaporation of concentrated dichloromethane solution at low temperature (−35 C°). **6a** crystallized in orthorhombic crystal system with space group P2$_1$2$_1$2$_1$,while **6b** crystallized in monoclinic crystal system with space group P2$_1$/n. The structures having numbering scheme are given in Figure 3.3 and the selected structural parameters are given in Table 3.4. Complete crystallographic data having fully labeled structures are given in the appendix. The bond lengths and bond angles of both **6a** and **6b** are comparable with the bond lengths and bond angles of literature known bis(imidazolyl) phosphanes,[11c] for example the C1-P and C7-P bond lengths for **6a,b**; [C1-P =1.808(2), C7-P = 1.814(2)]**6a**,[C1-P = 1.8149(12), C7-P = 1.8213(12)]**6b** can be compared with the related bis(imidazolyl)phosphanes having –Ph group at *P*-center [C-P =1.817(2), C-P = 1.814(2)] and –NMe$_2$ at *P*-center [C-P =1.8314(19), C-P = 1.8038(18)]. Likewise the C1-P-C8 bond angle of **6a,b** [109.24(17)° **6a**, 108.73(8)° **6b**] is also quite comparable with same C-P-C bond angle of the related bis(imidazolyl) phosphanes **IX** having –Ph group at *P*-center [101.05(8)°] however relatively widened in comparison to bis(imidazolyl) phosphanes having the –NMe$_2$ group at *P*-center [98.97 (8)°]. [11c, 13, 84]

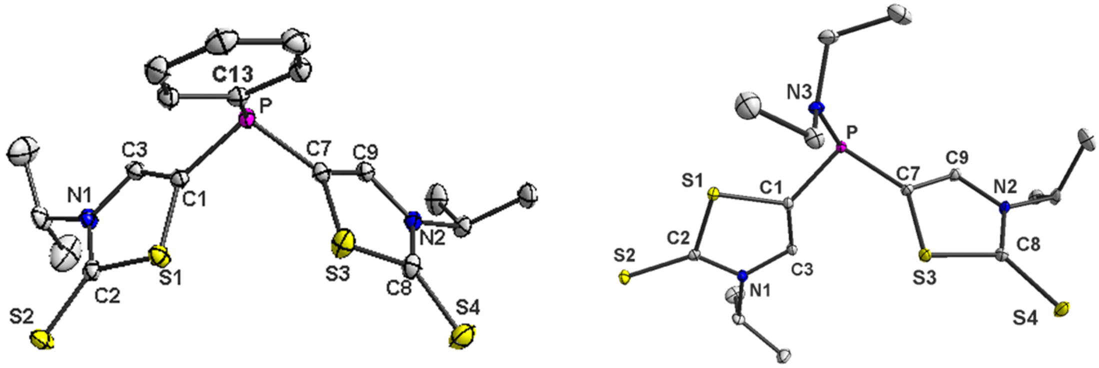


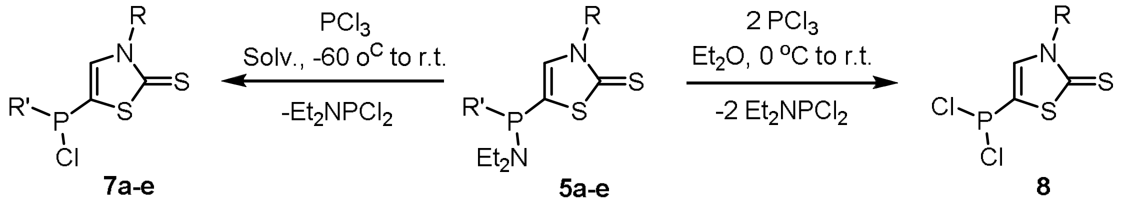
Figure 3.3. Displacement ellipsoids plot (50% probability) of molecular structure of **6a** (left), **6b** (right) in the crystal. Hydrogen atoms have been omitted for clarity.

Table 3.4. Selected bond lengths (Å) and angles (°) of **6a,b.**

	6a	**6b**
C2-S2	1.667(2)	1.6688(12)
C8-S4	1.663(2)	1.6762(12)
C1-P	1.808(2)	1.8149(12)
C7-P	1.814(2)	1.8213(12)
C13-P	1.838(2)	-
N3-P	-	1.6896(10)
N1-C2-S1	109.24(17)	108.73(8)
N2-C8-S3	108.51(17)	108.70(8)
S1-C1-P	128.51(15)	120.06(7)
S3-C7-P	126.84(13)	132.03(7)
C1-P-C7	101.84(11)	100.31(5)

3.4 Synthesis of C^5-chlorophosphanyl substituted thiazole-2-thiones

The chlorophosphanyl-substituted imidazole-2-thione derivatives have been synthesized and successfully employed as starting point for interesting low co-ordinate phosphorus chemistry by Streubel and co-workers recently.[14a, 84] Having had the aim to employ the chlorophosphanyl substituted thiazole-2-thiones in low coordinate phosphorus chemistry later, the synthesis of such derivatives was needed. Therefore,R'(Et$_2$N)P-substituted derivatives **5a-e** were subjected individually to a scrambling reaction using PCl_3 (1.05 eq.) in diethyl ether (or dichloromethane for **5d,e**) at −60 °C (Scheme 3.4).



a) R = Me, R' = Et_2N
b) R = ^iPr,R'= Et_2N
c) R = ^nPr, R' = Et_2N
d) R = Me, R' = Ph
e) R = ^nPr, R' = Ph

Scheme 3.4. Synthesis of *P*-chloro phosphanes (**7a-c** solv. = Et_2O, **7d,e** solv. = CH_2Cl_2).

The reaction progress was monitored by $^{31}P\{^1H\}$ NMR spectroscopy which revealed completion of reaction after one hour stirring as the the starting material had been completely consumed and two new signals were observed in the $^{31}P\{^1H\}$ NMR spectrum which wereassigned to products**7a-c** (114.3-115.1 ppm for **7a,c,d** or 55.3 for **7d/e**) and Et_2NPCl_2 (163.2 ppm).After work-up **7a-e** were isolated in excellent yields (up to 99 %). The ^{31}P NMR resonances of compounds **7a-c** (Table 3.5) are comparable with the related literature known *P*-chloro derivative **CI**.[14a] However, the signals appeared significantly downfield-shifted compared to **CIII** (δ ^{31}P = 168.7 ppm)[85] and **CIV**((δ ^{31}P = 166.8 ppm).[85] Likewise, the ^{31}P NMR resonances of **7d,e** follow the similar trend of difference with the ^{31}P NMR resonance of literature-known imidazole-based derivative**CII**(δ ^{31}P = 37.2 ppm)[14c](Figure 3.4, Table 3.5). Compounds **CI-CIV** were chosen for comparison mainly due to a related P-environment in the respective molecules and, secondly, also because these compounds were crystallographically established.

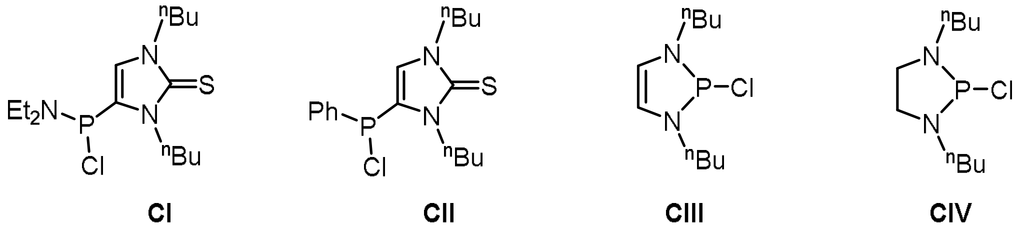


Figure 3.4. Literature reported *P*-chloro compounds **CI**,[14a]**CII**[14c]and **CIII,CIV**.[85]

Table 3.5. 31P NMR resonances of **7a-e** and **CI,CII** and yields of **7a-e.**

	R'	δ^{31}P (ppm)	Yield (%)
7a	Et$_2$N	114.5	96
7b	Et$_2$N	115.1	99
7c	Et$_2$N	114.4	96
7d	Ph	55.3	92
7e	Ph	55.3	96
CI	-	106.4	-
CII	-	37.2	-

Single crystal X-ray analysis was performed for derivatives **7a** and **7c**. Crystals of both compounds suitable for X-ray diffraction studies were obtained via slow evaporation ofconcentrated solutions in Et$_2$O and CH$_2$Cl$_2$ (2:1 ratio) at low temperature (−30 °C). The molecular structures of **7a** and **7c** are given in Figure 3.5 and selected metrical parameters are given in the table below (Table 3.6).

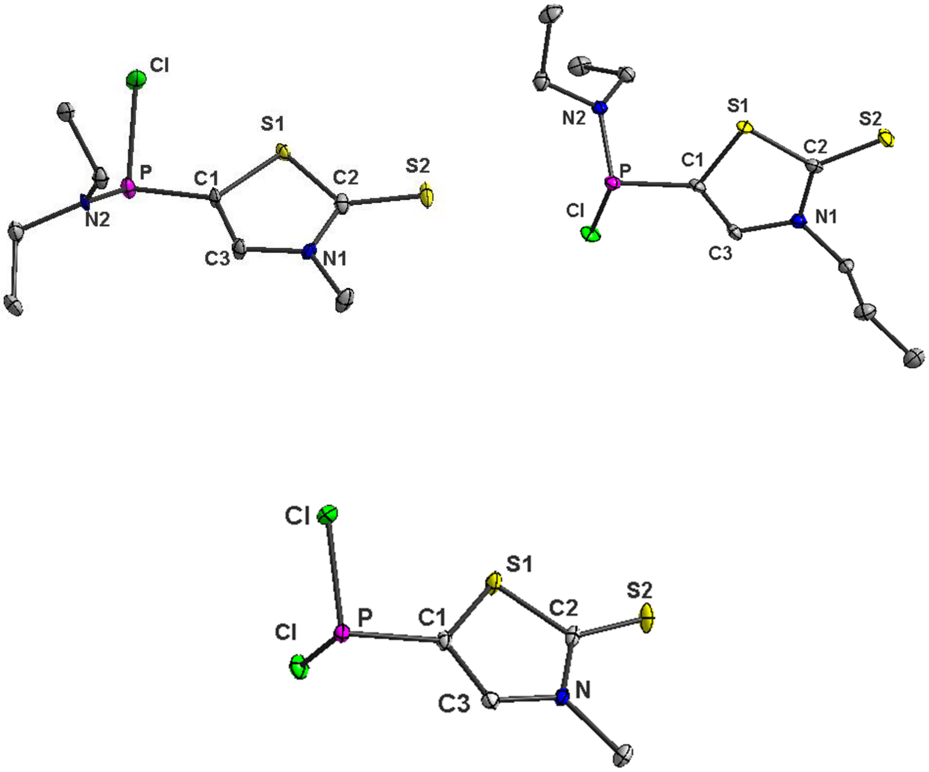


Figure 3.5. Displacement ellipsoids plot (50% probability) of molecular structure of **7a** (left), **7c** (right) and **8** (middle) in the crystal. Hydrogen atoms have been omitted for clarity.

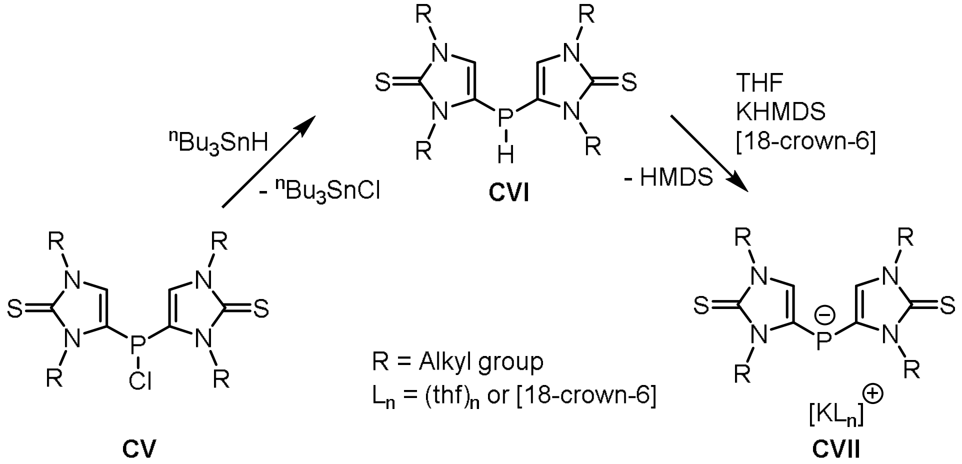
Table 3.6. Selected bond lengths (Å) and angles (°) of **7a,c** and **8a.**

	7a	**7c**	**8**
C2-S2	1.673(7)	1.670(3)	1.663(2)
C1-P	1.807(7)	1.817(3)	1.800(2)
N2-P	1.651(6)	1.655(2)	-
Cl-P	2.152(2)	2.1350(10)	2.0717(8)
-	-	-	2.0924(8)
C3-C1-P	126.4(5)	130.3(2)	122.04(15)
C1-P-N2	101.8(3)	100.05(11)	-
C1-P-Cl	94.7(2)	95.51(9)	99.12(7)

In contrast to **5a**, the bond lengths of the thiazole ring of **7a,c** showed some small variations. Specifically, a slight shortening was observed for C1-P: [1.807(7) Å in **7a**], [1.817(3)Å in **7c**], [1.8202(15) Å in **5a**]. The P-Cl bond distance of **7a,c**[2.152(2) Å **7a**, 2.1350(10) Å **7c**] is somewhat elongated but comparable with literature known values of related compounds, for example with **CI**[14a](dP-Cl = 2.1274(9) Å) and **CII**[14c](dP-Cl = 2.1056(1) Å), however it is significantly shorter when compared with heterocyclic chlorophosphanes **CIII**[85] (dP-Cl = 2.759(2) Å) and **CIV** (dP-Cl = 2.3136(7) Å).[85] However, the significantly long P-Cl bond in **CIII** was explained on the basis of high degree of aromatic stabilization of the cationic charge, thereby compound **CIII** was proposed to be ionic by Denk and co-workers.[85]

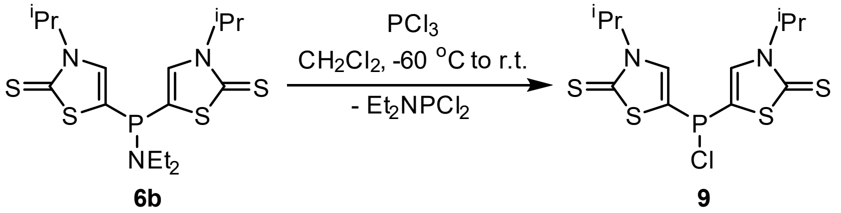
Interestingly, the methodology of „scrambling“ to replace the Et_2N group using PCl_3 was also successfully extended to replacement of both Et_2N groups by two Cl moieties. Upon treatment ofa diethyl ether solution of **5a** with two equivalents of PCl_3 at 0 °C afforded the dichlorophosphanyl thiazole-2-thione **8**. The reaction was slower and needed three days of stirring at ambient temperature to reach completion.However, it was selective as revealed by $^{31}P\{^1H\}$ NMR spectroscopic monitoring. The $^{31}P\{^1H\}$ NMR spectrum of an aliquot separated from the reaction mixture showed two signals at 133.4 and 163.2 ppm. The latter was assigned to the expected by-product (Et_2NPCl_2), while the former (133.2 ppm) was assigned to the dichloro-compound **8**. After *in vacuo* removal of volatiles, **8** was isolated as white powder by recrystallization from *n*-pentane and Et_2O mixture (3:1) at 0 °C in very good yield (82 %). **8** was fully characterized via NMR, IR, MS, and single crystal X-ray analysis. Single crystals suitable for measurement were obtained by slow evaporation of concentrated dichloromethane solution of **8** at −35 °C. The bond lengths and bond and bond angles of **8** are comparable with those of **7a** and **7c** however a noticeable bond contraction occurred in P-Cl bonds of **8** [2.0717(8), 2.0924(8) Å] was observed in comparison to that of **7a** and **7c**;[2.152(2) Å 7a, 2.1350(10) Å **7c**].

Recently, Streubel and co-workers synthesized the *P*-chloro substituted imidazole-2-thione **CV** and demonstrated its use as starting material to access low-coordinate phosphorus compounds (Scheme 3.5).[84] The *P*-chloro derivative **CV** was further converted to the *P*-H substituted imidazole-2-thione (**CVI**) by reacting it with $^{n}Bu_3SnH$. The obtained *P*-H was deprotonated with KHMDS to afford the phosphanido derivative **CVII**.[84]



Scheme 3.5. Literature-known *P*-cloro compound**CV** and some reactions.[84]

Motivated by the easy access and further chemistry of *P*-chloro substituted imidazole-2-thione derivatives**CV**, we were eager to explore if the the *bis*(thiazolyl)phosphane **6b** can also beconverted into the corresponding *P*-chloro derivative. The synthesis of bis(thiazolyl)chlorophosphane **9** was achieved using the protocol already employed for the synthesis of **8** using PCl_3 in dichloromethane (Scheme 3.6). The reaction was quite fast (completed in one hour) and selective as revealed by$^{31}P\{^{1}H\}$ NMR spectroscopic monitoring. The conversion of the *P*-NEt_2 derivative into the *P*-chloro was indicated by the expected shift and change in multiplicity of the^{31}P NMR resonance (s, 35.0 ppm) as the Δδ value (6.7 ppm) between starting material(**6b**) and product (**9**) is very similar to the Δδ value (5.8 ppm) in case of the imidazole-based system.[84]



Scheme 3.6. Synthesis of bis(thiazoly)chlorophosphane **9**.

Compound **9** was analyzed by NMR, IR, MS, elemental analysis and also single crystal X-ray diffraction techniques. Compound **9** crystallized in monoclinic crystal system with space group $P2_1/c$. The crystal structure of **9** is given in Figure 3.7 and selected structural parameters are given the figure caption. The P-Cl bond length of **9** (2.0796(4), Å) can be compared with the related literature known *P*-chloro derivatives (**CV**, **CVIII**, **CIX**). The P-Cl bond lengths of **9** [2.0796(4) Å] is somewhat shorter than that of **CV**[dP-Cl = 2.1029(6) Å],[84] however it was found to be quite comparable with compound **CVIII** [dP-Cl = 2.0982(2) Å][86] and **CIX**[dP-Cl = 2.061(1) Å].[87]

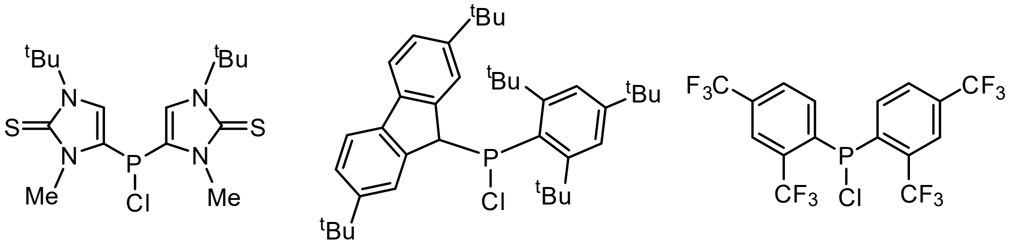

CV **CVIII** **CIX**

Figure 3.6. Literature-known*P*-chloro compounds **CV**,[84] **CVIII**,[86]**CIX**.[87]

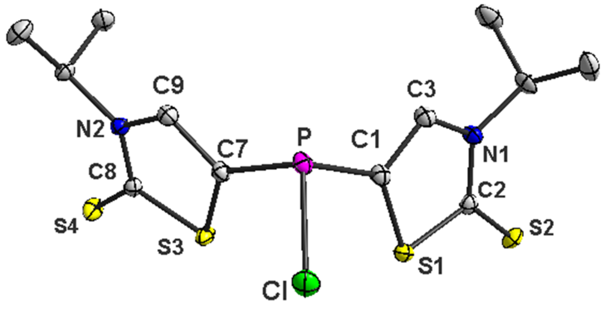


Figure 3.7. Displacement ellipsoids plot (50% probability) of molecular structure of **9** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) C2-S2 1.6658(13), C1-P 1.8030(13), C7-P 1.7909(13), P-Cl 2.0796(4), N1-C2-S1 108.80(9), S1-C1-P 129.52(7), C1-P-C7 101.95(6), C1-P-Cl 98.43(4), C7-P-Cl 101.47(4).

Chapter 4

Chapter 4: Attempted synthesis of C^5-thiazolyl substituted phosphaalkene

The prospect of using P=C bonds[43, 88] in polymer science[89] and catalysis[90] has attracted chemists to this growing field of low-coordinate main group element chemistry.[91]Although the first neutral isolated compound with a phosphorus-carbon π-bond was Märkl's phosphabenzene (2,4,6-triphenyl phosphinine) derivative **L**(Figure 4.1),[43] the first acyclic phosphaalkene **CX**was synthesized by Becker in 1976.[88a] The latter report coincided with a publication by Nixon and Kroto on the synthesis of unstable phosphaalkenes under pyrolysis conditions.[88b] These fascinating compounds **L**,**CX**, possessing a formal P=C bond with a (3p-2p)π-overlap, marked the beginning of what is now a highly active field of research that has had major impact on both fundamental and applied inorganic chemistry.

The strategy of electronic delocalization was key to providing the thermodynamic stabilization necessary for these early compounds featuring main group multiple bonds (**L**).[88c, 88d] Shortly thereafter, it was realized that large, sterically demanding substituents provide kinetic stability to P=C bonds,[88a, 88e] such as in **CX** and **CXI**.[88e]

The attempts of Bickelhaupt and his coworkers to achieve a phosphaalkene with „smaller" P-substituents than Mes, for example $PhP{=}CPh_2$, has led to polymeric materials.[88e] Later on, further attempts were made by Gates and co-workers to isolate the same compound, however, the monomer could only be detected by NMR spectroscopy and, finally, a 1,2-diphosphetane $(PhP\text{-}CPh_2)_2$, formed via head-to-head dimerization was obtained.[92] However, the *end*-on complex $[W(CO)_5(Ph_2C{=}PPh)]$ was isolated as such and, therefore, stabilization of phsophaalkenes with sterically less demanding („smaller") P-substituents via complexation was once more exemplified.[[92-93] This report, however, contrasts somehow with a head-to-head dimerization of $[W(CO)_5(Me_2C{=}PPh)]$, also leading to a 1,2-diphosphetane.[94]

Nowadays, a wide variety of synthetic methods are available to establish P=C bonds, including: (a)the Becker condensation reaction,[95] (b) phospha-variants of the Peterson olefination,[96] (c) 1,2-elimination reactions,[88e, 97](d) the phospha-Wittig reaction,[98]and several others.[99]

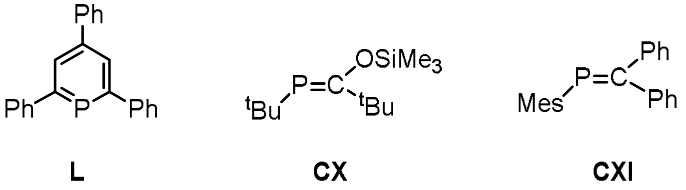
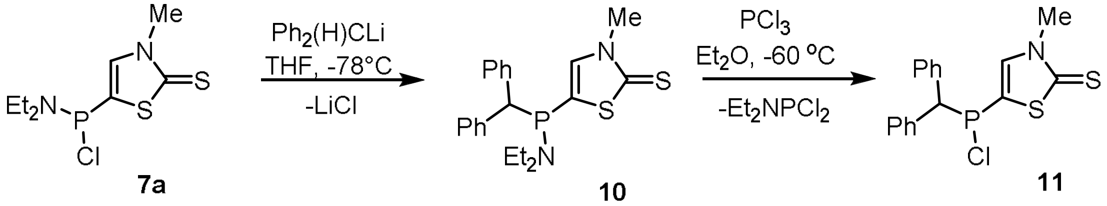


Figure 4.1. Literature-known phosphabenezene **L**[88c] and phosphaalkenes **CX**[88a] and **CXI**.[88e]

4.1 Substitution of *C*5-amino(chloro)phosphanyl thiazole-2-thiones leading to phosphaalkene precursors and a new phosphaalkene complex

As the generation of phosphaalkenes via 1,2-elimination reactions is well established,**7a** was used to introduce the CHPh2 group, using a freshly prepared solution of diphenyl-methyllithium,[100] added dropwise to a THF solution of **7a** at −78 °C. The $^{31}P\{^{1}H\}$ NMR spectroscopic monitoring revealed completion after 15 min (Scheme 4.1). Unexpectedly, the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture displayed two singlet resonances at 47.0 (80 %) and 119.1 ppm (20 %). The former was assigned to the phosphane derivative **10** while the latter could not be identified.



Scheme 4.1. Strategic synthesis of potential starting material for 1,2-elimination reaction.

Work-up provided**10** as crude product that was re-crystallized from a THF/*n*-hexane mixture at −40 °C and, finally, obtained in pure form as a white powder. The ^{1}H NMR spectrum of **10** (in $CDCl_3$) clearly supported the proposed formulation of the product (see experimental section). For example, the resonances at 7.13-7.50 (m, 10H) assigned to the C_6H_5 protons and, especially, at 4.65 (d, 1H) whichclearly indicated the Ph_2CH proton.

Single crystals of **10**, suitable for X-ray crystallographic analysis, were obtained by slow diffusion of *n*-hexane into a saturated dichloromethane solution at low temperature (−30 °C).

Compound **10** crystallized in the monoclinic space group $P2_1/n$; the molecular structure is shown in Figure 4.2 and selected bonding parameters are given in figure caption. Since the bond lengths are within the expected range and the differences from **5a** are negligible, they will not be discussed further. However, in contrast to **5a** some bond angles in **10** showed noticeable variation such as S1-C2-P1 130.36(6)° in **10** vs 122.63(8)° in **5a** and C3-C2-P1 121.46(8)° in **10**vs 127.66(11)° in **5a**.

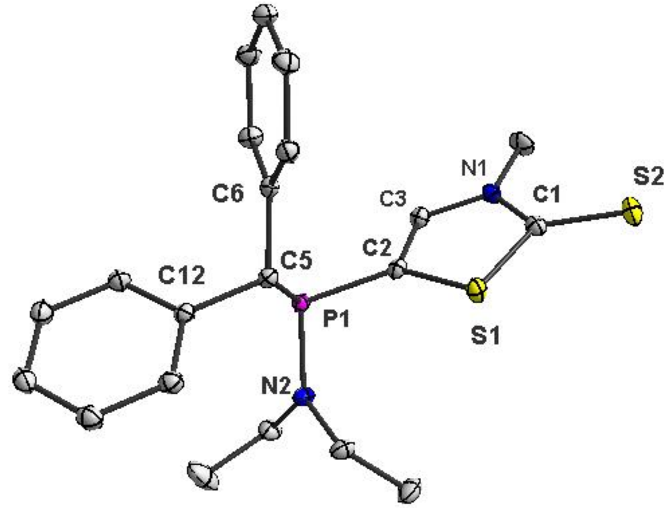


Figure 4.2 Displacement ellipsoids plot (50% probability) of molecular structure of**10** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): S1-C1 1.7460(11), S1-C2 1.7529(10), C3-C2 1.3489(15), P1-C2 1.8226(10), S2-C1 1.6649(10), P1-C5 1.8751(11), N1-C1-S1 107.82(7), S1-C2-P1 130.36(6), C3-C2-P1 121.46(8).

To substitute the remaining *P*-NEt_2 group in **10**, reaction with PCl_3 was performed in dichloromethane at –60 °C. The $^{31}P\{^1H\}$ NMR spectrum of an aliquot removed from the reaction solution after one h revealed that the resonance of **10** ($\delta^{31}P = 47.0$) had been replaced by a new signal at 57.9 ppm which was assigned to *P*-chloro derivative **11** (Scheme 4.1). After work-up (see Experimental Section), **11** was isolated in good yield (~ 62 %). Compound **11** was characterized via NMR, MS, IR, elemental analysis and single crystal X-ray diffraction analysis. Single crystals of **11** suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a concentrated dichloromethane solution at −30 °C. The molecular structure of **11** is given in Figure4.3, but as the bond lengths and bond angles are in a normal range, they will not be discussed further.

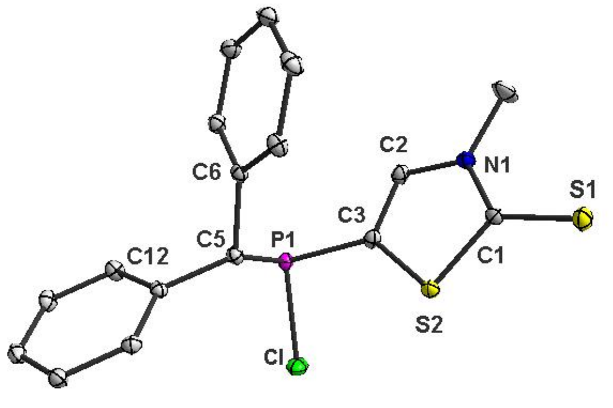
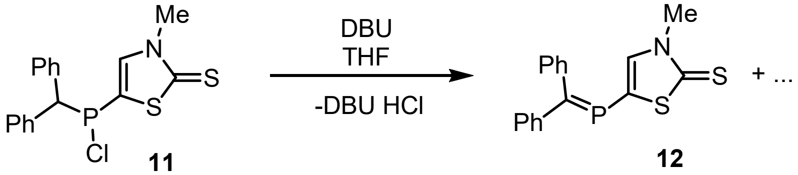


Figure 4.3. Displacement ellipsoids plot (50% probability) of molecular structure of compound **11** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): S2-C1 1.7380(10), S2-C3 1.7464(11), C2-C3 1.3542(14), P1-C3 1.8097(10), S1-C1 1.6661(11), P1-C5 1.8776(11), P1-Cl 2.0255(7), N1-C1-S2 108.60(7), P1-C3-S2 126.48(6), C2-C3-P1 123.27(8).

4.2 Attempted dehydrohalogenation reaction of 11

Having had the potential precursor **11** for 1,2-elemination reaction, its dehydrohalogenation reactions were attempted. Initial attempts using LDA, KtBuO$^-$, ^{t}BuLi or Et$_3$N(Table 4.1) with different solvents (THF, toluene, diethyl ether) did not meet any success and always led to unselective reactions. However, when a THF solution of **11** was treated with DBU (1.1 eq.) at ambient temperature (Scheme 4.2), reaction monitoring by ^{31}P{^{1}H} NMR spectroscopy showed that a selective reaction resulted, initially, showing **11** (57.9 ppm) and only one new resonance at 187.2 ppm.



Scheme 4.2. Dehydrohalogenation reaction of **11** with DBU.

Table 4.1. Percentage of **12** (based on ^{31}P NMR intigration) in the reaction mixture with different bases.

	Base	**12** (%)
I	DBU	23
Ii	Et$_3$N	17
Iii	^{t}BuLi	5
Iv	K^{t}BuO$^-$	0
V	LDA	0

As the downfield shift is characteristic of phosphaalkenes having aryl or alkyl substituents at the alkyledene carbon atom,[92, 101] it was tentatively assigned to phosphaalkene **12**. However, within 30 min, new signals of several other unidentified phosphorus-containing products (65% of the product mixture) emerged, while the starting material was not yet fully consumed. So we speculate that although the reaction itself was selective the formed phosphaalkene derivative **12** decomposed under the given reaction conditions, thus rendering **12** as inseparable part of a mixture. However, some support for the identity of **12** came from the EI-MS (70 eV) spectrum of this mixture which displayed a peak at *m/z* 328.1 that corresponds to the molecular ion of $[C_{17}H_{14}NPS_2]^+$.

4.3 Synthesis of tungsten complex 13

Due to the presence of alone pair at the phosphorus atom and a π-system in phosphaalkenes such ligands exhibit various metal-coordination modes (Figure 4.4),[90b, 102]and examples are known for all of those given in Figure 4.4; complexes having the η^1coordination mode have been reported the most.[92-93, 103]20]

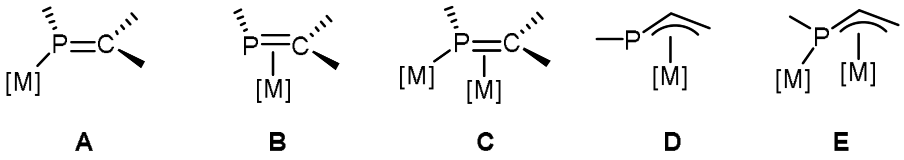
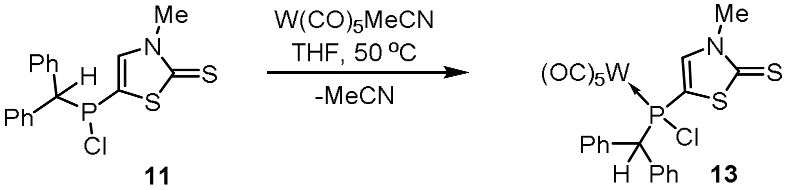


Figure 4.4. Possible metal-coordination modes of phosphaalkenes.[90b, 102]

In an effort to stabilize the proposed phosphaalkene **12**, we then turned to the well established concept of metal complex-stabilization due to *end*-on complexation of the P=C unit that had been used in the past with tremendous success, *e.g.* to synthesize $[W(CO)_5(ClP{=}CH_2)]$[104], having in mind that the free ligand is not stable in condensed phase. Therefore, the $W(CO)_5$ complex of **11** was prepared using a THF solution of **11** and $[W(CO)_5MeCN]$[105] (Scheme 4.3), surprisingly, the $^{31}P\{^1H\}$ NMR spectrum displayed two signals at 86.4 ($^1J_{W,P}$ = 295.2 Hz) and 88.2 ppm ($^1J_{W,P}$ = 291.6 Hz). The latter were assigned to two atropisomers of complex **13** due to a possible hindered rotation about the P-C bond.



Scheme 4.3. Synthesis of complex **13.**

The resonances and the $^{1}J_{\mathrm{W,P}}$ coupling constants support the constitution of complex **13**, especially when compared with the complex [W(CO)$_5${PPh$_2$Cl}] (95.4 ppm, $^{1}J_{\mathrm{W,P}}$ = 282.8 Hz).[106] Complex **13** was isolated via column chromatography at low temperature and finally obtained as bright yellow powder. The ^{1}H NMR spectrum displayed two sets of resonances for the two isomers, *e.g.,* at 6.7 ppm (d, 1H, $^{2}J_{\mathrm{P,H}}$ = 5.2 Hz) and 6.9 (d, 1H, $^{2}J_{\mathrm{P,H}}$ = 4.3 Hz) for the C^4-H protons and at 4.8 ppm (d, 1H, $^{2}J_{\mathrm{P,H}}$ = 3.3 Hz) and 4.9 ppm (d, 1H, $^{2}J_{\mathrm{P,H}}$ = 3.7 Hz) for the C*H*Ph$_2$ protons. In the ^{13}C{^{1}H} NMR spectrum the resonances at 65.9 ppm (d, $^{1}J_{\mathrm{P,C}}$ = 7.5 Hz) and 66.5 ppm (d, $^{1}J_{\mathrm{P,C}}$ = 6.2 Hz) were assigned to the *C*HPh$_2$ carbon nuclei of the two isomers. Single crystals of **13** suitable for X-ray diffraction studies were obtained by slow evaporation of a concentrated solution in diethyl ether.

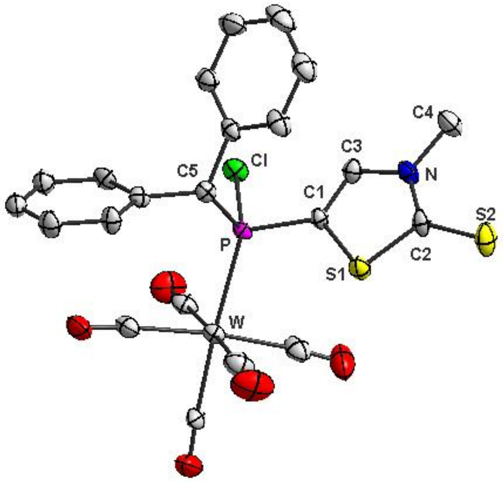
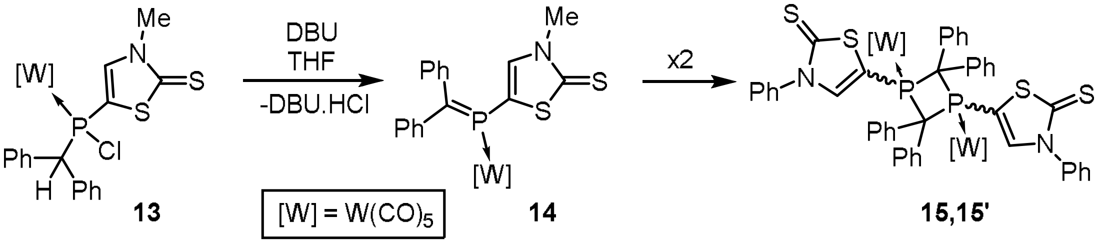


Figure 4.5. Displacement ellipsoids plot (50% probability) of molecular structure of compound **13** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): S1-C2 1.735(7), S1-C1 1.747(6), C1-C3 1.331(9), P1-C1 1.807(6), S2-C2 1.747(6), P1-C5 1.875(6), P1-Cl 2.069(2), P1-W 2.4671(15), N1-C2-S1 108.5(4), P1-C1-S1 121.5(3), C3-C1-P1 128.6(5).

Compound **13** crystallized in the triclinic system with space group $P\overline{1}$. The molecular structure is shown in Figure 4.5 and selected bond lengths and bond angles are given in the caption The bond lengths in **13** showed only one mentionable deviation from **11**: the (exocyclic) bond C2–S2 was significantly elongated [1.747(6) in **13** and 1.6661(11) in **11**]. As the latter value was almost invariant within the set of unligated derivatives described beforehand, it clearly reflects the effect of P-complexation. The bond angles in **13** follow those of the unligated compound **11**, except for P1-C1-S(1) in **13** which was more acute than in **11** [126.48(6)° vs (121.5(3)° in **13**]. This was accompanied by a widening of the C3-C1-P1 angle [128.6(5)° in **13** vs (123.27(8)° in **11**], thus pointing to a somewhat surprising distortion of the metrics of the thiazole ring, thereby enabling a position of the *N*-Me group that minimizes steric repulsion. This ring distortion may also affect the C2-S2 bond.

4.4 Dehydrohalogenation reaction of 13

With complex **13** in hand, attempts were then made to achieve a selective 1,2-elimination using DBU as base (Scheme 4.4). Treatment of a THF solution of **13** with DBU at -78 °C resulted in an immediate color change from yellow to bright red. Importantly, the $^{31}P\{^1H\}$ NMR spectrum of an aliquot, taken from the reaction mixture shortly after the addition of DBU, revealed the formation of one major product at 141.1 ppm ($^1J_{W,P}$ = 281.7 Hz) and two minor products at 74.9 ppm ($^1J_{W,P}$ = 270.2 Hz) and 73.2 ppm ($^1J_{W,P}$ = 269.2 Hz) (ratio 72:8:20) (Figure 4.6).



Scheme 4.4. 1,2-Elimination reaction of 13 to give **14,** and its dimerization to **15,15'**

Using the data of the known *end*-on complexes [W(CO)$_5$(PhP=CPh$_2$)] (δ = 188.1 ppm, $^1J_{W,P}$ = 270.8 Hz),[92-93] and [W(CO)$_5$(PhP=CMe$_2$)] (δ = 176.0 ppm, $^1J_{W,P}$ = 261.0 Hz),[94] and taking into account that the thiazole-2-thione substituent exerts a shielding effect on the phosphorus nucleus compared to the phenyl group in all previous cases, the resonance at 141.1 ppm was tentatively assigned to the *end*-on phosphaalkene tungsten complex **14**. In order to gain further support for this assignment of **14**, the solvent was removed *in vacuo* at -30 °C (shortly after having added DBU (≃ 5 min)). The thus obtained solid was used for an EI-MS experiment that showed *m/z* 651, clearly assignable to the molecular ion peak of **14**, and the base peak at *m/z* 327 representing the fragment ion after loss of the W(CO)$_5$ group.

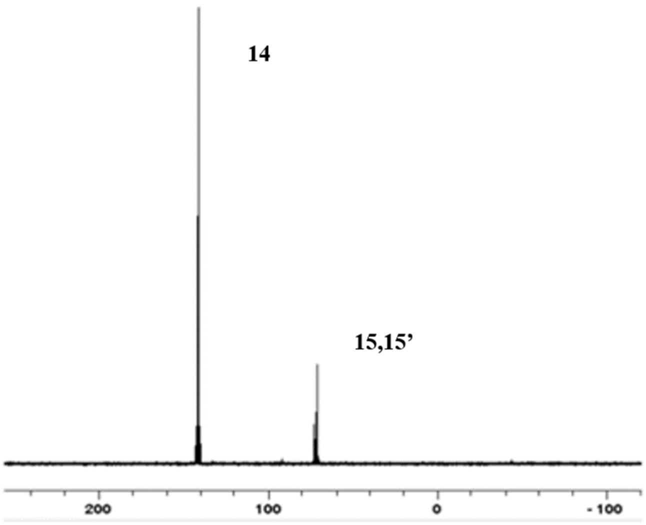


Figure 4.6. $^{31}P\{^1H\}$ NMR spectrum (THF, 121.5 MHz, -50 °C, ≃ 5 min) of an aliquot from the reaction mixture of the synthesis of **14**.

Interestingly, if the same reaction mixture was kept at −30 °C for 12 h, the $^{31}P\{^1H\}$ NMR spectrum showed that the resonance at 141.1 ppm was no longer present, and the color had changed from red to pale yellow, and only signals at 74.9 ppm (major) and 73.2 ppm (minor) had remained (ratio 97:3) (Figure 4.7 It should be noted that the two products (at 74.9 and 73.2 ppm) grew at the expense of product **14** (at 141.1 ppm).

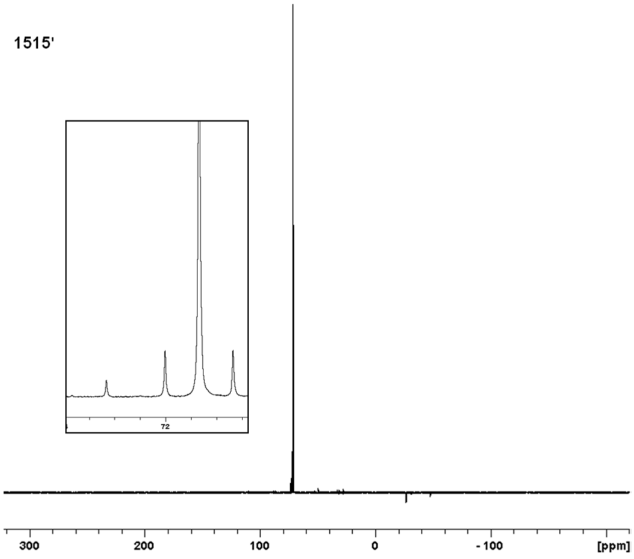
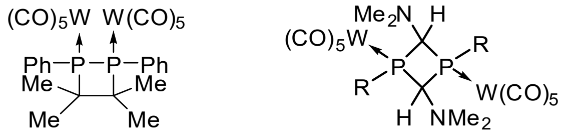


Figure 4.7.$^{31}P\{^1H\}$ NMR spectrum (THF, 121.5 MHz, -30 °C, 12 h) of an aliquot from the reaction mixture of the synthesis of **14**.

The experimental observations and the analytical data suggested the assignment of resonances at 74.9 and 73.2 ppm to two isomeric dimers of the intermediately formed phosphaalkene complex **14**. Filtration at -30 °C and subsequent drying under reduced pressure at -30 °C led to **15,15'** as a yellow powder, containing only little amounts of impurities. To obtain a better quality NMR spectroscopic data, complexes **15,15'** were characterized *in situ.* The^{1}H NMR spectrum of a THF-d_8 solution of **15,15'** (−30 °C) revealed a singlet at 3.5 ppm (6H) assigned to NCH_3 and a multiplet at 6.9-7.8 (22H) assigned to C^4-H and C_6H_5-H protons (only the major isomer *i.e.* 97 %). The $^{13}C\{^1H\}$ NMR spectrum exhibited all signals attributable to the expected carbon nuclei of **15** (only the major isomer *i.e.* 97 %) including two sets of four signals for the phenyl carbon atoms, which suggests the inequivalence of the two phenyl groups. This assignment of **15,15'** as dimers is further supported by the neg. ESI-MS spectrum (salt), *i.e.,* m/z 1336.888 found for $[C_{44}H_{28}N_2O_{10}P_2S_4W_2]Cl$ (calc. 1336.880). At this point it should be also noted that a selective dimerization was observed only in small scale reactions (up to 100 mg of **13**).

Our assignment of complexes **15,15'** as to be head-to-tail dimers of **14**, *i.e.*, diastereomeric, dinuclear 1,3-diphosphetane complexes, is based on the characteristic $^{13}C\{^1H\}$ NMR resonance of the CPh_2 carbon nuclei found to be a triplet at 68.0 ppm with a $^1J_{P,C}$ coupling of 7.0 Hz. Furthermore, the absence of the $^3J_{P,C}$ coupling, expected for the head-to-head-dimer (phosphorus and the CO nuclei) should be noted and which supports the proposed head-to-tail dimerization of **14**.

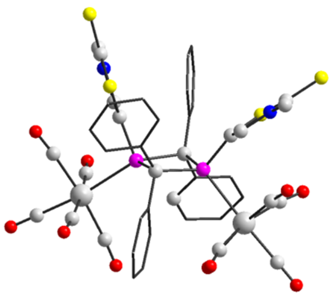
This assignment is further supported by a comparison with NMR data of the head-to-head dimer of $W(CO)_5(PhP{=}CMe_2)$ (**CXII**) (Figure 4.8)[94] showing a doublet for the CMe_2 nuclei (36.9 ppm, d, $^1J_{P,C}$ = 28.2 Hz). So far, there is only one report on dinuclear 1,3-diphosphetane tungsten(0) complexes having *P*-alkyl substituents, complexes **CXIII** (Figure 4.8).[107] The ^{31}P resonances of **CXIII** were in the range of 8.9 to 51.1 ppm ($^1J_{W,P}$ =188.2 and 218.1 Hz, respectively), but most importantly derivatives **CXIII** possess $^{13}C\{^1H\}$ NMR features of the NMe_2-substituted ring carbon nucleiat 60.5 (R = Me) and 62.7 (R = Et) ppm, displaying both a triplet splitting pattern ($^1J_{P,C}$ = 29.7 Hz and 28.7 Hz, respectively) that lend further strong support for **15,15'** to be head-to-tail dimers.



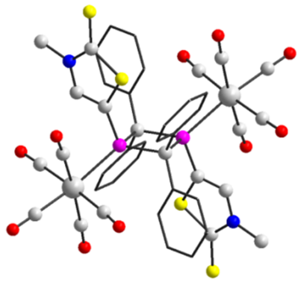
CXII R = Me/Et **CXIII**

Figure 4.8. Literature known dinuclear tungsten(0) complexes of 1,2- and 1,3-diphephetanes **CXII**[94] and **CXIII**.[107]

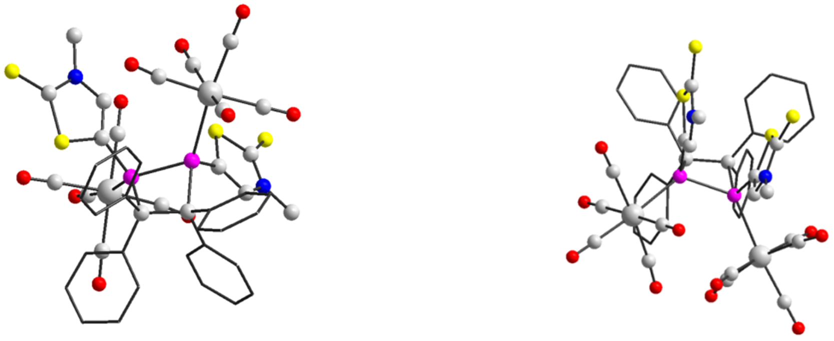
In order to get more insight into the dimerization product **15,15'**,theoretical calculations were performed by Frontera at BP86-D3/def2-TZVPP level of theory.[108] Solvent effects were taken into consideration using the COSMO method[109] and calculated the relative energies of the four possible (calculated) structures given in Figure 4.9. The comparison of the relative energies (Table 4.2) suggested that for both possible dimerization products, head-to-head and head-to-tail, the Gibbs free energies are very similar for both regioisomeric species in *trans* conformation. Furthermore, the dimer formation energy was found to be favorable for both solvents: −23.5 kcal/mol in CH_2Cl_2 and −23.9 kcal/mol in THF. Therefore, it has been concluded that despite the interesting observation of solvent dependent dimerization of the formed phosphaalkene (**14**), the stability of reactants/products could not be differentiated via DFT analysis using the standard solvation methods.



1,3 diphosphetane *trans*



1,3 diphosphetane *cis*



1,2 diphosphetane *trans*

1,2 diphosphetane *cis*

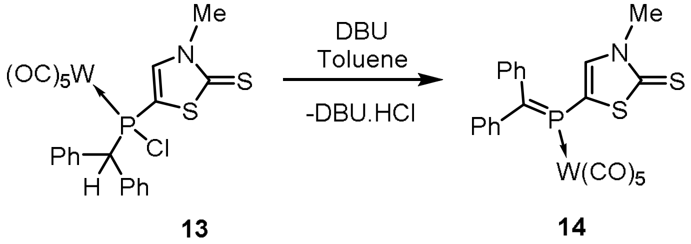
Figure 4.9. Optimized structures for the proposed dinuclear tungsten(0) complexes of 1,3- and 1,2-diphosphetanes (by Frontera).

Table 4.2. Calculated relative energies of various dimers **15,15'** (by Frontera).

	Relative Energies (kcal/mol)		
	Gas phase	CH_2Cl_2	THF
Head-to-tail *cis*	14.1	12.6	13.1
Head-to-tail *trans*	1.7	1.3	1.5
Head-to-head *cis*	10.6	11.1	11.2
Head-to-head *trans*	0.0	0.0	0.0

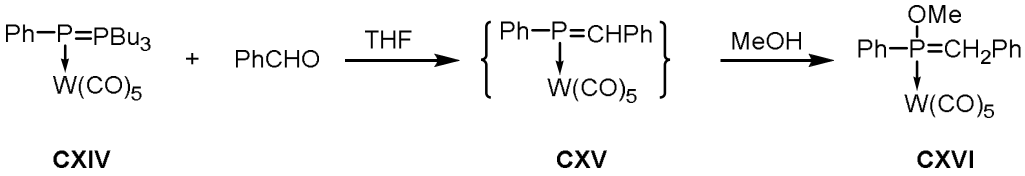
4.5 Optimization of reaction conditions

Further efforts were undertaken to find improved conditions for the formation and isolation of phosphaalkene complex **14** using toluene as solvent. Upon addition of DBU to **13** in toluene under ambient conditions, an orange precipitate was formed immediately which, after filtration, formed a red solution in dichloromethane (Scheme 4.5). The $^{31}P\{^{1}H\}$ NMR spectrum of this solution showed only one signal at 140.7 ppm ($^{1}J_{W,P}$ = 283.4 Hz). The isolated complex **14** was firmly established via NMR and IR spectroscopy and mass spectrometry. For example, the $^{13}C\{^{1}H\}$ NMR spectrum of **14** showed a resonance at 184.7 ppm ($^{1}J_{P,C}$ = 51.5 Hz) for the P=C carbon nucleus which is very close to that of $[W(CO)_5(PhP{=}CPh_2)]$ (δ ^{13}C = 186.7 ppm, $^{1}J_{P,C}$ = 43.2 Hz).[93]



Scheme 4.5. Synthesis of phosphaalkene complex **14.**

Attempts were made to crystallize the phosphaalkene complex **14** using different solvents and/or solvent mixtures, however every time it was only the DBU•HCl which crystallized and those attempts were never met with success. In one of the crystallization efforts, *n*-pentane was slowly diffused into dichloromethane solution of **14**at −35 °C, thus yielding a few crystals that were used for single crystal X-ray analysis, which showed that during the process of crystallization, hydrolysis of compound **14** has occurred and only the hydrolyzed product had crystallized (triclinic,$P\bar{1}$). The crystal structure of the hydrolysis product **15** is given in Figure 4.10 and selected bond lengths and bond angles are given in figure caption. The instability of P=C bonds despite transition-metal complexation has been previously observed and studied.[103a, 110] For example, Mathey reported a study where **CXIV** was found to react with benzaldehyde at room temperature to generate the phosphaalkene complex **CXV**, which was prone to decomposition under thermal conditions and trapped by MeOH or benzoic acid (Scheme 4.6).[103a]



Scheme 4.6. Literature-known synthesis of phosphaalkene tungsten complex and its trapping reaction with MeOH.[103a]

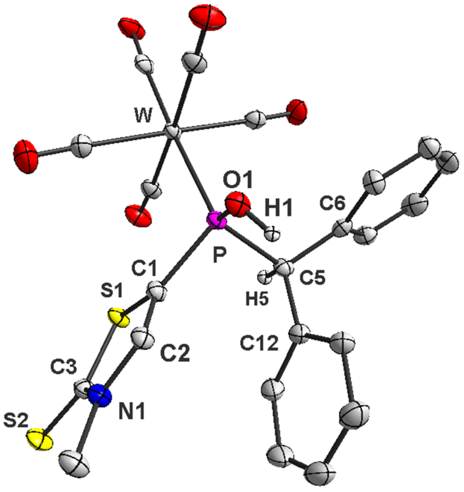


Figure 4.10. Displacement ellipsoids plot (50% probability) of molecular structure of hydrolysis product **14** in the crystal. Hydrogen atoms have been omitted for clarity (Except H1 and H5). Selected bond distances (Å) and angles (°): S1-C3 1.736(4), S1-C1 1.731(4), C1-C2 1.343(5), P-C1 1.831(4), S2-C3 1.666(4), P-C5 1.892(4), P-W 2.5095(10), P-O1 1.521(3), N1-C3-S1 108.7(3), P1-C1-S1 124.9(2), C2-C1-P1 125.5(3).

Chapter 5

Chapter 5: Investigations on synthesis of tricyclic 1,4-dihydro-1,4-diphosphinines

In 1964, Mann and co-workers reported the first example of 1,4-dihydro-1,4-diphosphinines (**CXVIII**) by a stepwise ring closure using dichloro(organo)phosphanes.[111] The reported synthetic protocol suffered, however, from an unselective reaction, which was later improved by Uchida and co-workers. The structural and electron donor properties of **CXVIII** were investigated by Uchida.[112] The synthesis of the parent compound (**CXVII**) was reported by Märkl via reaction of diethinylphosphanes with primary phosphane leading to 1,4-dihydro-1,4-diphosphinine derivatives with different substituents at the *P*-center.[113] The tricyclic system was not only limited to the unsubstituted benzene annulated units but also tetrafluoro-benzene[114] and xylene[115] based systems were reported by Wu and Mazaki, respectively.[114-115]

Compounds **CXIX**-**CXXI** (Figure 5.1) represent the examples having sulfur rich heterocycles, incorporated into the 1,4-dihydro-1,4-diphosphinine framework; thiophene (**CXIX**),[116] TTF (**CXX**)[117] and 2,5-thiophenedione (**CXXI** E = S).[118] The synthesis of compound **CXIX** and **CXX** represent the synthetic strategy of lithiation of the heterocycle, followed by reaction with dichloro(organo)phosphanes (resulting in lithium halide elimination), while **CXXI** (E = O/S) was a unique example obtained via an elimination of chlorotrimethylsilane.[116-118]

Compounds **CXXII** and **X** having the *N*-heterocycles incorporated into the tricyclic framework illustrates the possible synthetic diversity of this class of compounds. Kostyuk and co-workers reported the synthesis of **CXXII** via reaction of the corresponding 1,4-dichloro-1,4-diphosphinine with dimethyamine.[119]**X** was reported recently by Streubel and co-workers via *in situ* backbone lithiation of the C^4-amino(chloro)phosphanyl-substituted imidazole-2-thione followed by salt metathesis and lithium chloride elimination.[14]

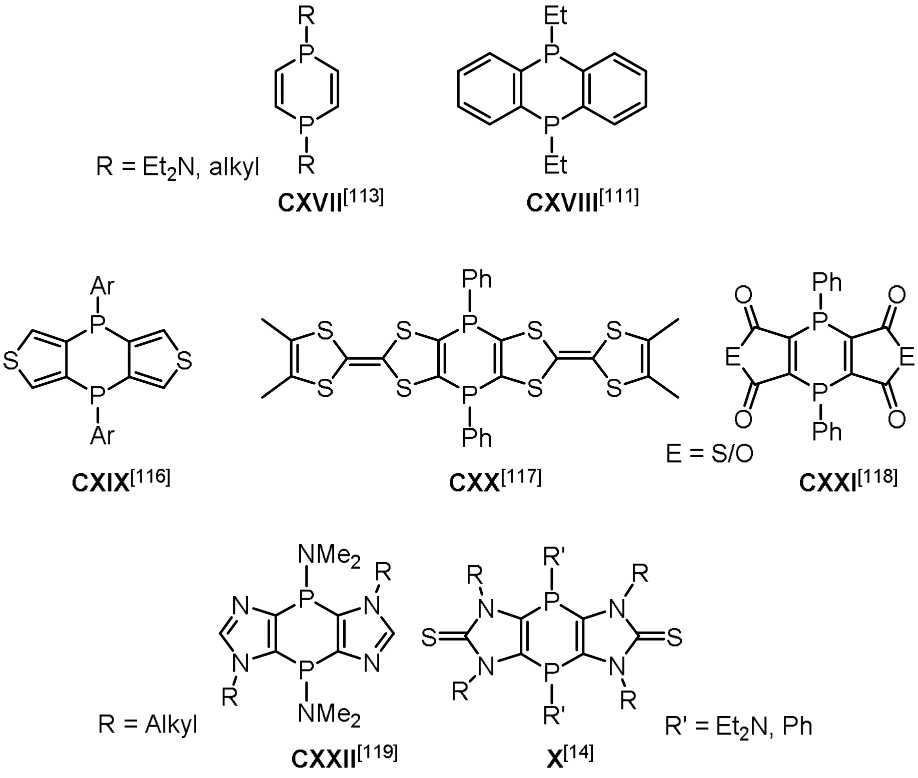


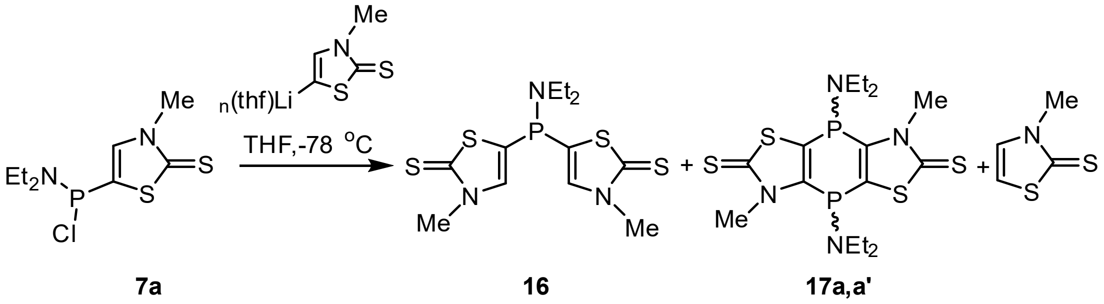
Figure 5.1. Literature-known 1,4-dihydro-1,4-diphosphinines.

5.1 Synthesis of thiazole-2-thione-derived tricyclic 1,4-dihydro-1,4-diphosphinines

Regarding the above mentioned background of 1,4-dihydro-1,4-diphosphinine chemistry, we were eager to extend this chemistry to a thiazole-based tricyclic system and explore its properties and reactivities.

5.1.1 Reaction of amino(chloro)thioazole-2-thione with a *C*5-lithiated thiazole-2-thione

Having the amino(chloro)phosphanyl thiazole-2-thiones **7a-e** in hand, initial attempts were made to synthesize the acyclic *bis*(thiazolyl)phosphanes. Upon reaction of *N*-methyl derivative **7a** with the *in situ* prepared lithiated thiazole-2-thione (Scheme 5.1), a mixture of products was obtained as revealed by $^{31}P\{^1H\}$ NMR spectroscopic monitoring. The major signal in the $^{31}P\{^1H\}$ NMR spectrum at 28.9 ppm (45 %) was accompanied by two closely spaced signals at 18.8 ppm (22 %) and 19.5 ppm (33 %) (Figure 5.2). The major signal was assigned to the corresponding acyclic compound **16** as the ^{31}P NMR resonance was in close accordance with the literature known bis(imidazolyl)phosphane (R = NMe_2, $\delta\,^{31}P$ = 16.0 ppm)},[84] while the two minor resonances at 18.8 ppm and 19.5 ppm were proposed to be the *cis*/*trans* isomers of the tricyclic 1,4-dihydro-1,4-diphosphinine **17a**,**a'** as the said NMR chemical shifts are similar to the ^{31}P NMR resonances of the literature known tricyclic compound **CXXII** (δ ^{31}P = 16.5 ppm);[119] the latter is downfield-shifted compared to **X** (R = Et_2N, δ ^{31}P = 3.3 and 3.9 ppm).[14b]



Scheme 5.1. Reaction of lithiated thiazole-2-thione with **7a**

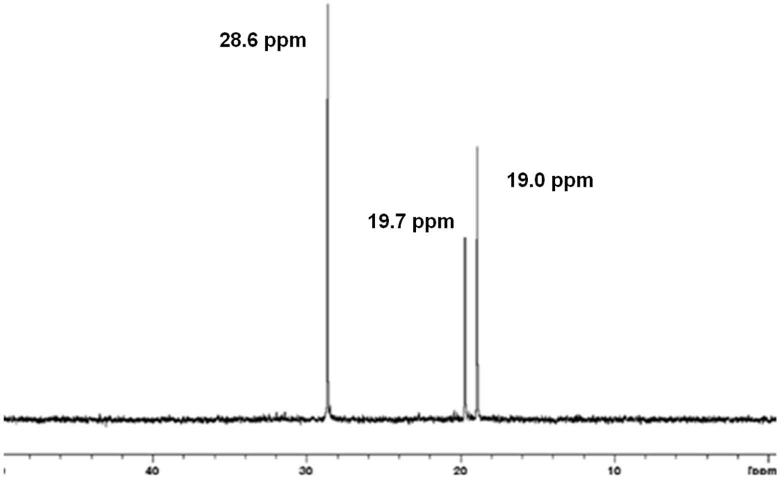


Figure 5.2. ^{31}P{^{1}H} NMR spectrum (THF, 25 °C) of the reaction mixture of **16**.

This mixture of products was subjected to column chromatography at −20 °C using silica gel as stationary phase and a mixture of petrol ether and diethyl ether (50:50) as eluent. **17a**,**a'**could be separated and was isolated in low yield (19 %). In ^{1}H and ^{13}C NMR spectra of **17a**,**a'** two sets of signals were observed for each isomer, the experimentally found EI-HRMS m/z value of 464.0514 was in good agreement with the calculated one (464.0515). Owing to a similar solubility of **17a**,**a'** towards common organic solvents, the *cis/trans* isomers could not be separated by column chromatography. However, based on comparison with the literature known imidazole-based tricycle **X**,[14b] the assignment of the ^{31}P NMR resonances to the *cis*

(18.8 ppm) *trans* (19.5 ppm) isomers of **17** was made tentatively.Besides NMR and MS, **17a**,**a'** was established via, IR, elemental analysis and also single crystal X-ray diffraction analysis. Single crystals of **17a**,**a'** were obtained via slow evaporation of its dichloromethane solution at −35 °C. However, **16** could only be purified up to 95 % and it contained 5% of **17a**,**a'** as impurity, nevertheless it was also crystallized from this mixture (at −35 °C) and analyzed via single crystal X-ray diffraction technique. The molecular structure of both **16** and **17**(*cis* isomer) are given in Figure 5.3 and selected bond lengths and bond angles are given in Table 5.1. Both **16** and **17** crystallized in triclinic crystal system with space group $P\overline{1}$ In contrast to the C1-P (1.818(4)) and C5-P (1.824(4)) bond lengths of **16** the C1-P1 (1.8344(12)) and C5-P5 (1.8326(12)) bond lengths in **17** were closer in magnitude. The six-membered ring in **17** was not completely planar and P1 and P2 were found to deviate from the plane C1-C2-C5-C6 (P1 by 0.25 Å and P2 by 0.11 Å).

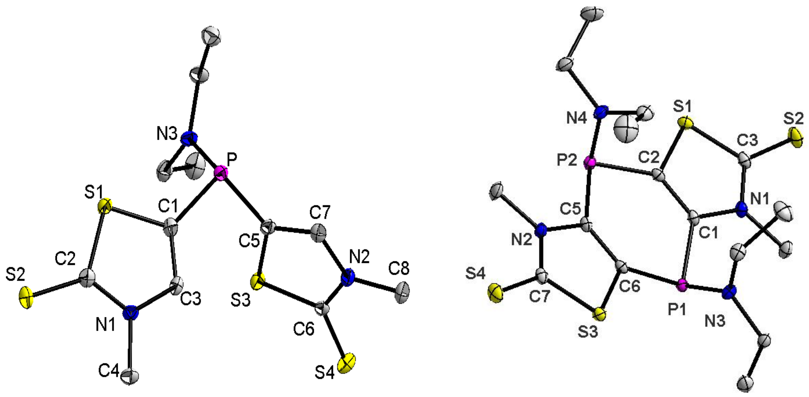


Figure 5.3. Displacement ellipsoids plot (50% probability) of molecular structure of **16** (left) and **17** (right) in crystal. Hydrogen atoms have been omitted for clarity.

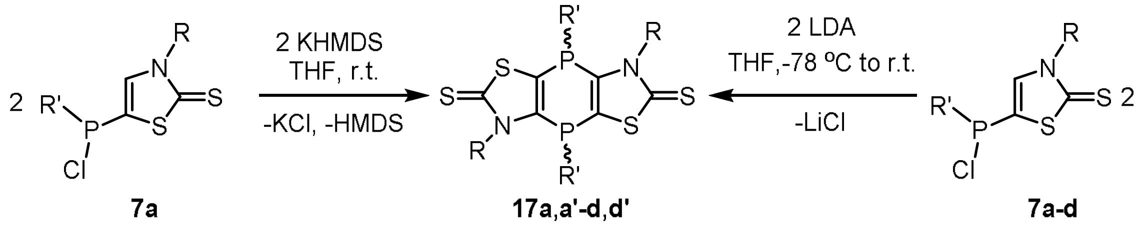
Table 5.1. Selected bond lengths (Å) and angles (°) of **16** and **17**.

	16	**17**
C2(3)-S2	1.672(3)	1.6659(12)
C6(7)-S4	1.667(4)	1.6706(12)
C1-P(1)	1.818(4)	1.8344(12)
C5-P(2)	1.824(4)	1.8326(12)
N3(4)-P(2)	1.682(3)	1.6729(11)
N1-C2(3)-S1	108.2(2)	108.94(8)
N2-C6(7)-S3	108.8(2)	108.75(8)
S1-C1(2)-P(2)	121.8(2)	115.83(7)
S3-C5(6)-P(1)	128.4(2)	116.40(6)

C1-P-C5(6)	96.77(16)	96.60(5)

5.2 Studies on the optimization of the reaction conditions and yields

Having shed light on the mechanism of the tricycle formation, *i.e.* deprotonation of the amino(chloro)phosphanyl thiazole-2-thione followed by intermolecular nucleophilic substitution reaction with **7a**, further attempts were made to optimize the reaction using other bases. Initially, potassium hexamethyldisilazide (KHMDS) was chosen as a sterically demanding and weakly nucleophilic base. The *N*-methyl derivative **7a** was chosen as start for the investigations and which was subjected to reaction with KHMDS under different reaction conditions. After several attempts, THF turned out as solvent of choice and ambient temperature worked best for a deprotonation, thus leading cleanly to the formation of tricycles **17a-d** (Scheme 5.2).



a) R = Me, R' = Et_2N c) R = Me, R' = Ph
b) R = ^nPr, R' = Et_2N d) R = ^nPr, R' = Ph

Scheme 5.2. Deprotonation of the amino(chloro)phosphanyl thiazole-2-thiones **7a-d** to form **17a**,**a'**-**d**,**d'**

Compounds**17a**,**a'** were isolated in 50 % yield using the above mentioned reaction conditions. However further attempts were also undertaken using LDA as base (Scheme 5.2). Upon addition of a pre-cooled (−78 °C) THF solution of LDA to the solution of**7a,b** (THF at −78 °C), a clean conversion to *cis*/*trans* mixture of **17a,a'b,b'**was achieved after two hours stirring. Products **17a,a'b,b'**were isolated in excellent yields (up to 97 %) after removal of LiCl as white powder (**17a**,**a'**) or sticky oily solid (**17b**,**b'**).

The synthetic protocol for **17a**,**a'b**,**b'** (R' = NEt_2) could be further extended to **17c**,**c'd**,**d'** having a phenyl group at the *P*-center (R' = Ph) starting from the phenyl(chloro)phosphanes **7c**,**d**. The ^{31}P NMR revealed clean conversion into the corresponding *cis*/*trans* tricyclic compounds with resonances: **17c**,**c'** (−40.1 and −37.9 ppm) and **17d**,**d'** (−39.8, −40.0 ppm), which are comparable with those of the literature known imidazole-derived tricyclic compound **X** (R = Me, R' = Phδ ^{31}P = −55.9, −57.1 ppm)[14c] and also the TTF based tricyclic system **CXX** (−21.5, −25.6 ppm).[117] All compounds were isolated in pretty good yields (up to 90 %) as white powders and obtained as mixtures of *cis*/*trans* isomers. ^{31}P NMR data, yields and isomer ratios (calculated from ^{31}P{^{1}H} NMR of reaction mixture) of **17a**,**a-d**,**d'**are given in Table 5.**2**.

Table 5.2.^{31}P NMR data and yields of **17a,a'-d,d'.**

	δ^{31}P{^{1}H}(ppm)	Isomer ratio	Yield (%)
17a,**a'**	18.8, 19.5	1:1	80
17b,**b'**	16.5, 19.3	1:1.2	97
17c,**c'**	-40.1, -37.9	1:2	89
17d,**d'**	-39.8, -39.0	1:1	90

Besides NMR spectroscopy, **17b**,**b'-d**,**d'** were characterized via MS, IR, elemental analysis (mostly) and also by single crystal X-ray diffraction studies in case of **17a-c**. Molecular structure of **17a** was discussed in section 5.1, while molecular structures of **17b** and **17c** are given the Figure 5.4, and selected structural parameters are given in Table 5.3. In case of **17b** the *trans* isomer crystallized in the triclinic crystal system with space group $P\bar{1}$. In contrast to **17a** (*cis*), the six membered ring in **17b** (*trans*) is close to planarity and the distance of P-centers from the ring plane is only −0.12 Å and 0.12 Å below and above the ring plane (C3-C1-C1-C3) respectively. **17c** crystallized in the monoclinic crystal system with space group $P2_1/n$. Though the phenyl groups of **17c** were found to be somewhat distorted*i.e.,*having split sites (0.621 and 0.387 for one Ph 0.533 and 0.466 for the other Ph), however the stereochemistry could be concluded to be *cis*. The packing pattern in *cis***17b** illustrate that the molecules are arranged in the form where the phenyl rings of the two parallel lyres are packed opposite to each other, as depicted in diamond plot of **17c** in Figure 5.4. The bond lengths and bond angles of both **17b** and **17c** are comparable with the those of literature known similar compounds,[14b, 14c] thereby will not be discussed further.

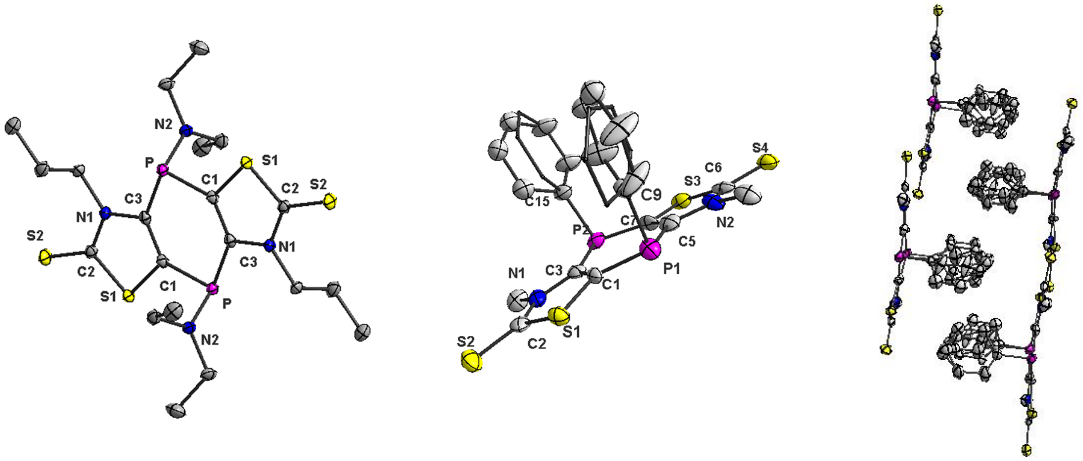


Figure 5.4 Displacement ellipsoids plot (50% probability) of molecular structure ofof **17b** (left) **17c** (middle) and its arrangement (right) in the crystal. Hydrogen atoms have been omitted for clarity.

Table 5.3. Selected bond lengths (Å) and angles (°) of **17b** and **17c**.

	17b	**17c**
C2-S2	1.6632(18)	1.679(8)
C6-S4	-	1.687(8)
C1-P(1)	1.8105(17)	1.827(7)
C3-P(2)	1.8339(17)	1.820(8)
N2-P	1.6684(15)	-
C9-P1	-	1.940(7)
C15-P2	-	1.861(7)
N1-C2-S1	108.55(12)	109.0(5)
N2-C6-S3	-	108.8(6)
S1-C1-P(1)	115.46(9)	118.0(4)
S3-C7-P2	-	117.0(5)

Chapter 6

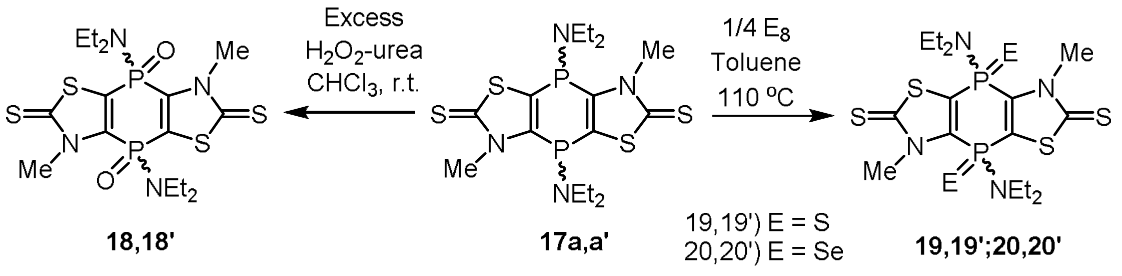
Chapter 6: Reactivity studies of tricyclic 1,4-dihydro-1,4-diphosphinines

The chemistry of 1,4-dihydro-1,4-diphosphinines has not been well explored in terms of reactivity studies so far and mostly remained limited to P-centered coordination chemistry[120] or oxidative studies.[111, 113, 119] For most of the examples discussed in the chapter 5 (**CXVII-CXVI-CXXII** and **X**)[14b, 111-113, 116-119] the functionalization of the *P*-center is limited to only alkyl or aryl groups (except for **CXXII** and **X**).[14b, 119] The incorporation of heterocycles into the tricyclic framework of 1,4-dihydro-1,4-diphosphinine, and introduction of reactive groups at *P*-center might bring further diversity to this class of compound. Recently, Streubel and co-workers established the chemistry of imidazole-2-thione-based tricyclic 1,4-dihydro-1,4-diphosphinines, thus offering a unique building block with more than one potential reactive sites and explored various aspects of this class of compounds.[14]

Inspired by the successfully established imidazole-2-thione-based system, it should be of great interest to explore the unique thiazole-2-thione-based 1,4-dihydro-1,4-diphosphinines and investigate their reactivity.

6.1 Oxidation of the *P*-centers in tricyclic 1,4-dihydro-1,4-diphosphinines

In order to study the oxidation of the *P*-centers of 1,4-dihydro-1,4-diphosphinines, while keeping the thione moieties intact, a mild oxidant such as the H_2O_2-urea adduct was chosen. A chloroform solution of an isomeric mixture (1:1) of **17a**,**a'**was treated with excess of H_2O_2-urea adduct at room temperature. A slow but clean reaction resulted in the complete consumption of the starting material and the formation of the P(V/V) 1,4-dihydro-1,4-diphosphinine **18**,**18'** was observed (Scheme 6.1).



Scheme 6.1. Oxidation reactions of **17a,a'** with H_2O_2-urea, elemental sulfur and selenium.

The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which displayed two signals at −4.2 and −3.3 (1:1) assigned to the *cis*/*trans* isomers of **18**,**18'**. The conversion of P(III) centers to the corresponding P(V) centers was evident from the $^{31}P\{^1H\}$ shift as it was in the expected range for the literature known, similar compound **CXXIII** (−4.6, −5.2 ppm),[14b] however upfield-shifted in comparison to **CXXIV**(9.1 and 10.3 ppm).[115] After filtration of the unreacted urea and removal of the volatiles *in vacuo,* **18**,**18'** were isolated as white solid. Compounds **18**,**18'** were established via $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy which showed two sets of all signals corresponding to the two (*cis*/*trans*) isomers. Due to the similar solubility of both isomers of **18**,**18'** further separation and, hence, assignment of the isomers could not be achieved. Besides NMR, the composition of **18**,**18'** was confirmed by the EI-HRMS as the experimentally found m/z value (496.0416) was in close agreement to the calculated one (496.0413).

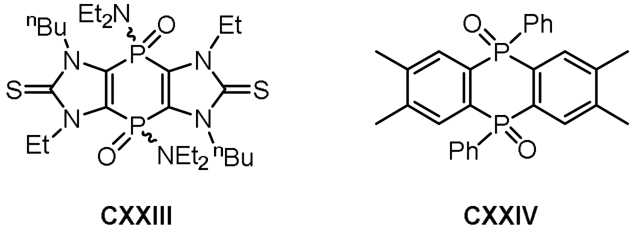


Figure 6.1. Literature known P,P'-oxides of 1,4-dihydro-1,4-diphosphinines **CXXIII**[14b] and **CXXIV.**[115]

Besides NMR spectroscopy and MS spectrometry, **18**,**18'** was characterized via IR spectroscopy, elemental analysis and also by single crystal X-ray diffraction technique. Preferentially, the *trans* isomer crystallized from a concentrated dichloromethane solution of **18**,**18'** at ambient temperature in monoclinic crystal system with space group C2/c. The molecular structure of **18** is given in Figure 6.2, while the selected structural parameters are given in the figure caption. Upon comparison of bonding parameters with similar P(V)-oxide derivative **CXXIII**,[14b] it was evident that the bond lengths and bond angles of **18** falls in the expected range for such compounds and, therefore, will not be discussed further.

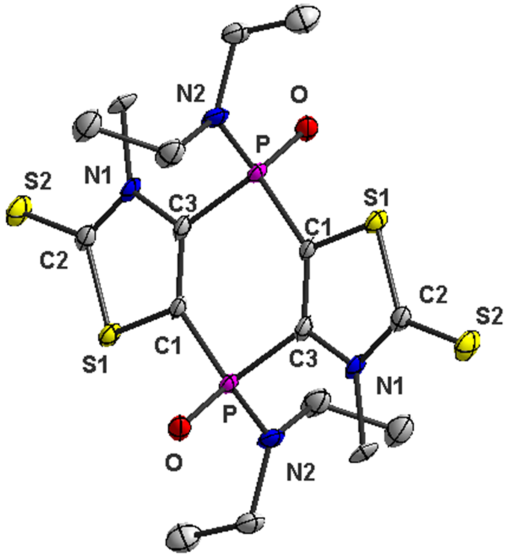


Figure 6.2. Displacement ellipsoids plot (50% probability) of molecular structure of **18** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C2-S2 1.652(3), C1-P 1.795(3), C3-P 1.811(3), P-N2 1.633(3), P-O 1.479(2) N1-C2-S1 108.7(2), S1-C1-P 118.36(18), C1-P-C3 102.10(14), N2-P-O 113.49(14).

Once having achieved the *P*-oxide derivative **18**,**18'** it was of interest to explore the oxidation of the two P-centers with chalcogenes. Oxidation of 1,4-dihydro-1,4-diphosphinine with sulfur has been previously investigated (Figure 6.3, **CXXV**-**CXXVII**).[14b, 119-120] However, for oxidation with selenium, only one example (**CXXVI**, X = Se)[119] is known so far, for the class of compounds under discussion. In order to achieve the P,P'-disulfide and P,P'-diselenide, a toluene solution of the *cis*/*trans* isomer mixture (1:1) of **17a**,**a'** was treated with 2.1 molar equivalents of sulfur or selenium at ambient temperature (Scheme 6.1), and thenheated to 100 °C for 5 days; both reactions were monitored via $^{31}P\{^{1}H\}$ spectroscopy.

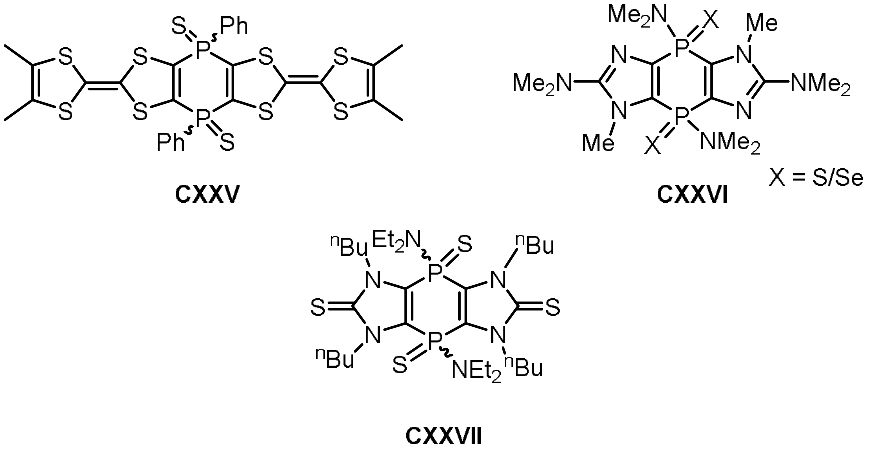


Figure 6.3. Literature known P,P′-sulfides and selenides of 1,4-dihydro-1,4-diphosphphosphinines. [14b, 119-120]

In case of sulfurafter 5 days the starting material was completely consumed, and two new signals had appeared in the $^{31}P\{^{1}H\}$ NMR spectrum at 22.8 ppm and 23.7 ppm (*cis*/*trans* ratio 1:1). Similarly for the reaction with selenium two new signals were observed at 13.4 ppm ($S_{sat}{}^{1}J_{Se,P}$ = 812.0 Hz) and 14.3 ppm ($S_{sat}{}^{1}J_{Se,P}$ = 830.0 Hz) corresponding to the *cis*/*trans* (1.2:1) isomers. Upon comparison with the literature known similar P,P'-disulfide derivatives **CXXV** ($\delta^{31}P$ = 11.6, 12.0 ppm),[120]**CXXVI**($\delta^{31}P$ = 31.9 ppm)[119] and **CXXVII** ($\delta^{31}P$ = 13.1, 13.3 ppm)[14b] the signals at 22.8 ppm and 23.7 ppm were easy to assign to the *cis*/*trans* isomers of **19**,**19'**.There is only one example of P,P'-diselenide known for 1,4-dihydro-1,4-diphosphinine (**CXXVI**),[119] the observed ^{31}P NMR resonance for the reaction of **17a**,**a'** with selenium (13.4 ppm and 14.3 ppm) is close to the observed values for **CXXVI** (21.1 ppm, 21.4 ppm) which were assigned to **20**,**20'**.

Both **19**,**19'** and **20**,**20'** were isolated in excellent yields (88 % and 76 %) by crystallization from their reaction solutions at −35 °C. The ratio of the *cis*/*trans* isomers of both products *i.e.***19**,**19'** (1:1) and **20**,**20'** (1:1) remained unchanged if compared to the reactant **17a**,**a'** (1:1). Compounds **19**,**19'** and **20**,**20'** were analyzed via $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopic techniques. The $^{31}P\{^{1}H\}$ NMR data of **19**,**19'** and **20**,**20'** together with yields and isomer ratios are given in Table 6.1.

Table 6.1. $^{31}P\{1H\}$ NMR data and yields of **19**,**19' and 20**,**20'**.

	$\delta^{31}P\{^{1}H\}$(ppm)	Isomer ratio	Yield (%)
19,19'	22.8, 23.7	1:1	88.8
20, 20'	13.4, 14.3	1.2:1	76.5

Besides NMR spectroscopy, **19**,**19'** and **20**,**20'** were characterized via IR, MS, elemental analysis and also by single crystal X-ray diffraction studies. Single crystals were obtained via cooling (−35 °C) the concentrated toluene (reaction) solution of **19**,**19'** and **20**,**20'**. The *cis* isomer of **19** crystallized in the orthorhombic crystal system with space group Pca2_1. The molecular structure and numbering scheme of **19** is given in Figure 6.4 while selected bonding parameters are given in the figure caption. Complete crystallographic data and picture with full labeling is given in the appendix. The structural parameters of **19** will not be discussed further as the bond lengths and angles falls in the range of related P,P'-sulfide derivative **CXXVII**.[14b]

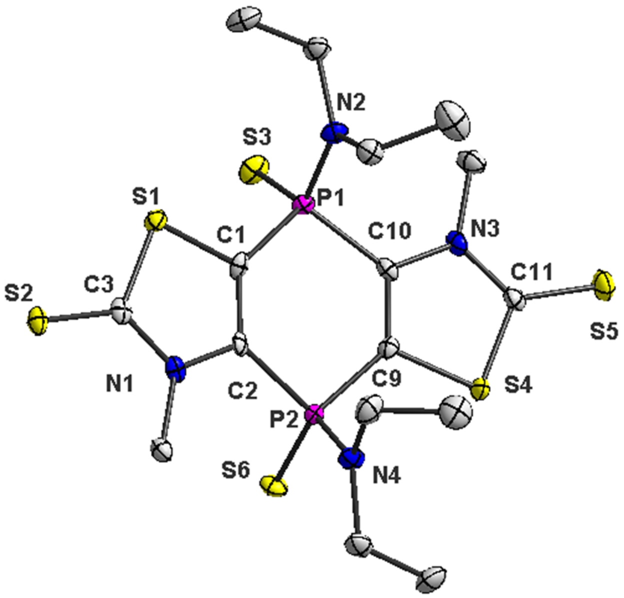


Figure 6.4. Displacement ellipsoids plot (50% probability) of molecular structure of **19** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C3-S2 1.651(7), C1-P1 1.800(7), C2-P2 1.820(6), P1-N2 1.635(6), P2-N4 1.636(5), P1-S3 1.935(2), P2-S6 1.938(2) N1-C3-S1 108.5(5) N3-C11 -S4 108.8(5), S1-C1-P1 117.4(4), C1-P-C10 101.7(3), N2-P1-S3 114.6(2).

In case of **20**,**20'**, preferably the *trans* isomers crystallized in triclinic crystal system with space group $P\overline{1}$ the unit cell contained one independent molecule along with a toluene molecule.The molecular structure and numbering scheme of **20** is given in the Figure 6.5 and selected bonding parameters are given in the figure caption. Complete crystallographic data and picture with full labeling is given in the appendix. Although a crystal structure of the only known P,P'-diselenide derivative of a 1,4-dihydro-1,4-diphosphinine (**CXXVI**)[119] was not reported, upon comparison of bonding parameters with other heterocyclic P(V)-selenide derivatives, namely 3-methyl-5-diphenylselenophosphanoyl-thiazol-2-thione[121] and 1-

isopropyl-3-methyl-4-diphenylselenophosphoryl-imidazole-2-thione,[11a] it was evident that the bond lengths and bond angles of **20** falls in the expected range.

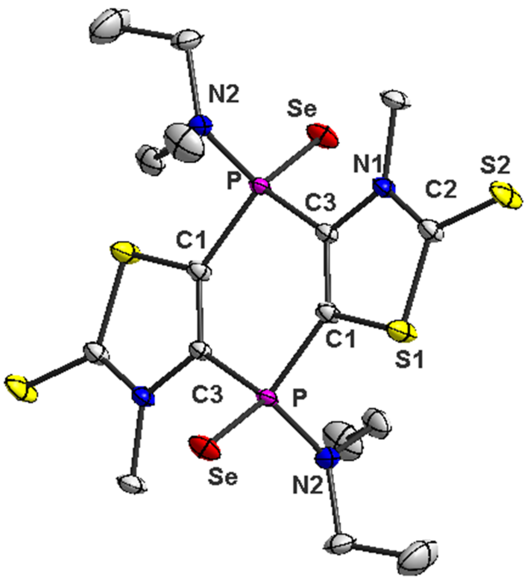
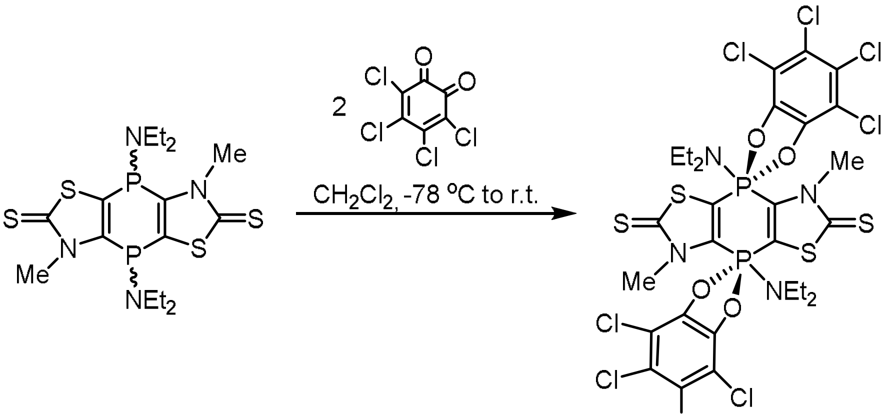


Figure 6.5. Displacement ellipsoids plot (50% probability) of molecular structure of **20** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C2-S2 1.669(2), C1-P 1.795(2), C3-P 1.813(2), P-N2 1.638(2), P-Se 2.0850(6) N1-C2-S1 109.57(17), S1-C1-P 116.83(13), C1-P-C3 101.34(10), N2-P-Se 117.25(8).

6.2 Oxidation reaction of tricyclic 1,4-dihydro-1,4-diphosphinine 17a with *ortho*-chloranil

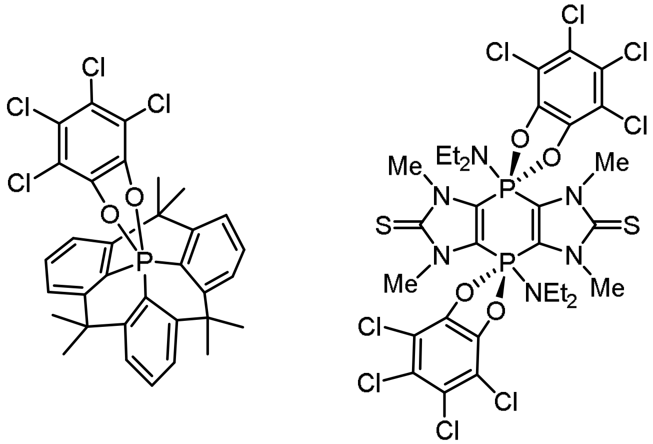
Investigations of oxidation reactions of 1,4-dihydro-1,4-diphosphinines was further extended to the use of *ortho*-chloranil, a potential reagent that may provide access to the interesting class of spirocyclic phosphorane derivatives.[14b, 122] Upon treatment of a dichloromethane solution of **17a**,**a'** withtwo equivalents of *ortho*-chloranil at −80 °C, light brown color reaction solution was formed (Scheme 6.2). After stirring of the reaction mixture for 16 hours at ambient temperature, an off-white precipitate had formed which was separated via filtration.



17a,a'

21,21'

Scheme 6.2. Reaction of **17a,a'** with *o*-chloranil.


CXXVIII

CXXIX

Figure 6.6. Literature known spirocyclic phosphoranes **CXXVIII**[123] and**CXXIX.**[14b]

The ^{31}P{^{1}H} NMR spectrum of the brown reaction solution showed significantly upfield-shifted signals compared to **17a,a'** (δ^{31}P = 18.8, 19.5 ppm, ratio = 1:1) at −60.1 ppm and −59.2 ppm (ratio 3:1) which were assigned to the *cis*/*trans* isomers **21,21'**. Upon re-dissolving the off-white precipitate in dichloromethane and measurement of the ^{31}P{^{1}H} NMR spectrum one major signal at −59.2 ppm and another minor signal at −60.1ppm (15:1) appeared, thus revealing that one of the isomers has a significantly lower solubility and, therefore, had precipitated (Figure 6.7). The assignment of the ^{31}P NMR resonances at −60.1 ppm and −59.2 ppm were supported by comparison with literature known similar compounds:**CXXVIII**−63.3 ppm[123], **CXXIX**−53.2, −54.9 (Figure 6.6).[14b]

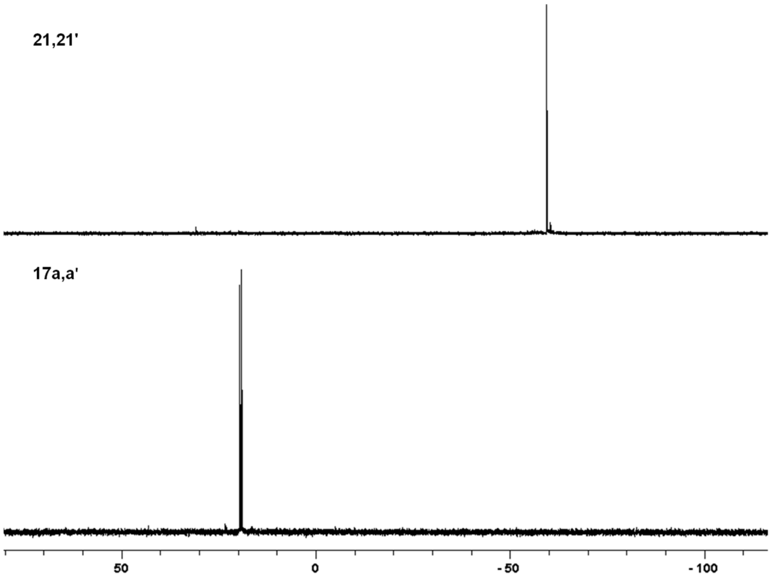


Figure 6.7. ^{31}P{^{1}H} NMR comparison of **17a,a'** (THF, 25 °C) and **21,21'** (CD_2Cl_2,25 °C).

21,21' was(almost) isolated (yield = 70 %, isomer ratio 15:1) after removing the solvent and washing several times with *n*-pentane (see experimental section). **21,21'** was established via ^{31}P{^{1}H}, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy**.** The ^{31}P{^{1}H} and selected ^{13}C{^{1}H} NMR data of **21,21'** are given in Table**6.2.** The proposed composition of **21,21'** was further supported by FTMS (pos. ESI) with the experimentally found m/z value of 956.7840 for [$C_{28}H_{26}Cl_8N_4O_4P_2S_4$]H, being in good agreement with the calculated m/z value of 956.7840.

Table 6.2. Selected NMR data of **21,21'.**

	δ^{31}P{^{1}H}(ppm)	Isomer ratio	δ ^{13}C{^{1}H} of thiazole ring carbon (ppm)
21,21'	-59.2, -60.	15:1	115.6 (t, $J_{P,C}$ = 7.4 Hz, *o-chloranil ringC*)122.0 (dd,$^1J_{P,C}$ = 194.1 Hz, $^2J_{P,C}$ = 9.3 Hz, $C^{5/4}$), 125.8 (s, *o-chloranil ringC*), 140.2 (s, *o-chloranil ringC*),158.3 (dd, $^1J_{P,C}$ = 120.0 Hz, $^2J_{P,C}$ = 24.2 Hz, $C^{4/5}$), 193.2 (t, $J_{P,C}$ = 7.6 Hz, *C*=S).

Single crystal X-ray diffraction studies were performed on crystals grown from a concentracted dichloromethane solution of **21**, which showed that the *cis* isomer of **21** got prefentially crystallized (Figure 6.8). However, the quality of the result was only moderate and therefore, structural parameters will not be discussed.

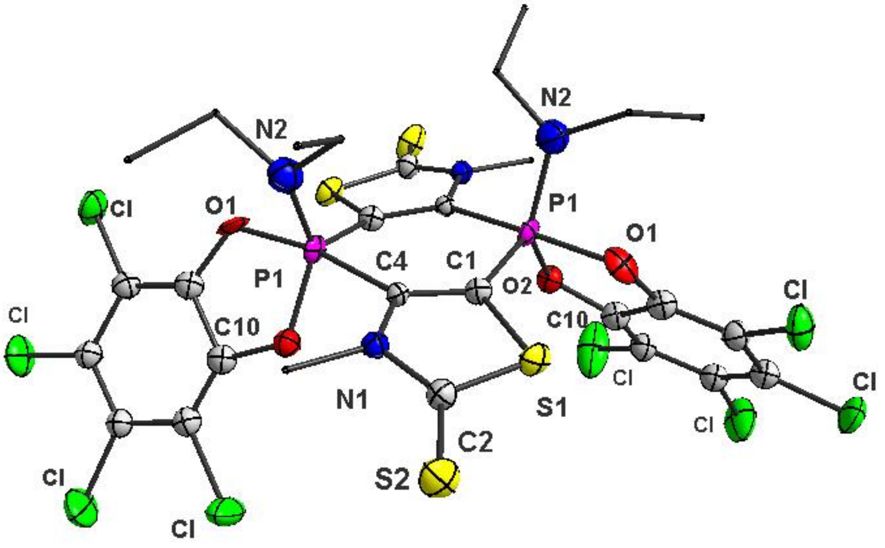


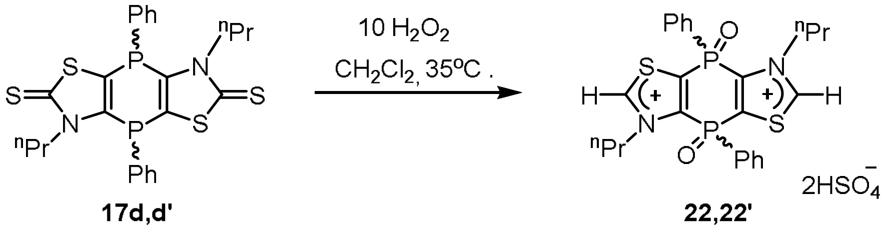
Figure 6.8. Displacement ellipsoids plot (50% probability) of molecular structure (reduced) of **21** in the crystal. Hydrogen atoms have been omitted for clarity.

6.3 Attempted oxidative desulfurization of 1,4-dihydro-1,4-diphosphinines

It is well established that oxidative desulfurization of imidazole-2-thiones and thiazole-2-thiones thiones can lead to corresponding hetazolium salts,[11b, 40, 81a] which in turn are known precursors to *N*-heterocyclic carbenes (NHCs).[34][11b, 15, 40, 81a] With this background the tricyclic thiazole-based 1,4-dihydro-1,4-diphosphinines (**17a**,**a'**-**d**,**d'**) represent potential systems to access Bielawski-type bis-carbenes and/or their metal complexes.[35-37]

In order to execute the idea, initially **17a**,**a'b**,**b'** (R = Et_2N) were reacted with 10 molar equivalents of H_2O_2 in dichloromethane at 0 °C, thus using the established protocol for oxidative desulfurization of bis(imidazolyl)phosphanes.[40] Although initially a clean reaction was observed which was the oxidation of the P-centers, however, the desulfurization step was found to be very unselective.

In an attempt to solve this issue, and motivated by the anticipation that a P-C bond would be more stable than a P-N bond under such harsh oxidative conditions, a reaction was tried using **17c**,**c'd**,**d'** (R = Ph). But initial attempts using the *N*-methyl derivative **17c**,**c'** were met with limited success. However, a selective conversion of the P(III) into P(V), resulting in a P,P'-dioxide, was evident from the upfield shift in $^{31}P\{^1H\}$ NMR spectrum (−3.1 ppm and −3.8 ppm,) in comparison to that of **17d,d'** (−39.8 ppm, −39.0 ppm) but further analysis of the ^1H and $^{13}C\{^1H\}$ NMR spectra revealed that the desulfurization has not occurred as no C^2-*H* resonance was observed in the range between 9 and 10 ppm.[11b, 81a] Similarly, the resonance of the C^2 carbon atom at 190.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum confirmed the presence of a *C*=S moiety; the expected C^2-H carbon resonance of a thiazolium derivative would be expected within 140 and144 ppm.[11b, 40, 81a] Upon a prolonged reaction time, only decomposition was observed. In order to enhance the solubility and, hence, to increase the reaction progress and avoiding decomposition, the *N*-^{n}Pr derivative **17d,d'** was employed under otherwise same conditions (Scheme 6.3). This attempt was met with some success, and the conversion of **17d,d'** into the corresponding bis-thiazolium salt **22,22'** (only 70 % selectivity) was confirmed via ^{31}P NMR spectroscopy, *i.e.,* the resonances at 8.2 ppm and 9.6 ppm (Figure 6.9) were assigned to (*cis/trans* isomers ratio: 1:1.3).



Scheme 6.3. Attempted oxidative desulfurization of **17d,d'**.

The ^1H NMR spectrum of the reaction solution revealed resonances at 9.8 ppm and 10.0 ppm, being in the typical range for the acidic C^2–H protons of thiazolium salts (Figure 6.10). Unfortunately, despite several attempts of crystallization from different solvents (or mixture of solvents) or washing, further purification of the product could not be achieved which hindered the isolation and further investigations.

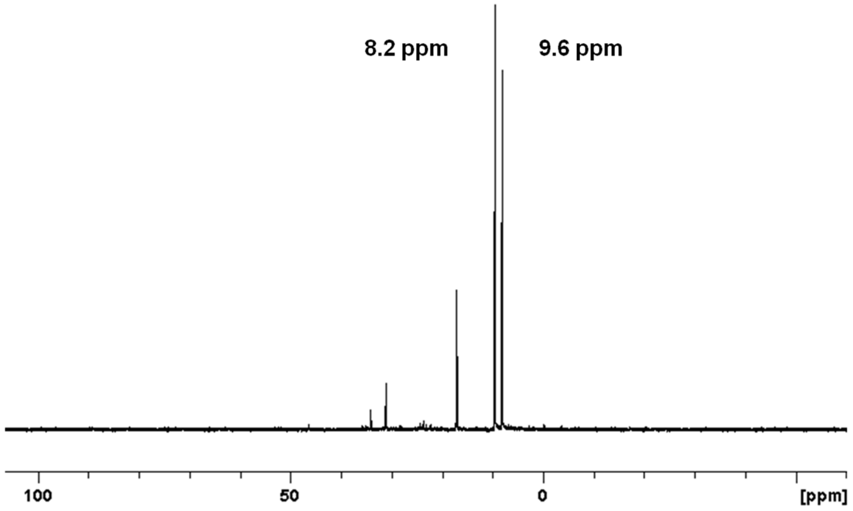


Figure 6.9.$^{31}P\{^{1}H\}$ NMR of reaction of **17d,d'** with H_2O_2 (D_2O, 25 °C)

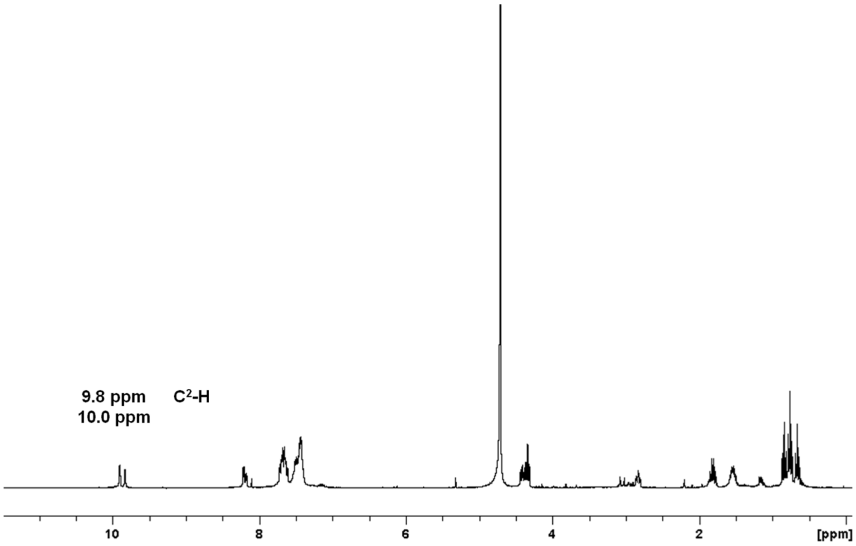


Figure 6.10. ^{1}H NMR of reaction of **17d,d'** with H_2O_2 (D_2O, 25 °C).

6.4 Reaction with electrophile and comparison with imidazole-based tricyclic 1,4-dihydro-1,4-diphosphinines (X, R' = Et_2N)

The extensive, theoretical and experimental investigations conducted upon the recently published imidazole-based 1,4-dihydro-1,4-diphosphinine **X** has explained the behavior towards different electrophiles.[14b] The theoretical calculations conducted by Fronterainspected the relative nucleophilicities of the S- and P-centers, and the reported calculated isosuface for **X** showed that molecular electrostatic potential (MEP) value at the *S*-centers is more negative than that of the P-centers (Figure 6.11). They also reported that the

HOMO orbital coefficients of the molecules are located more at theS- than at the P-centers thus made the pronounced nucleophilicity of the S-centers evident.

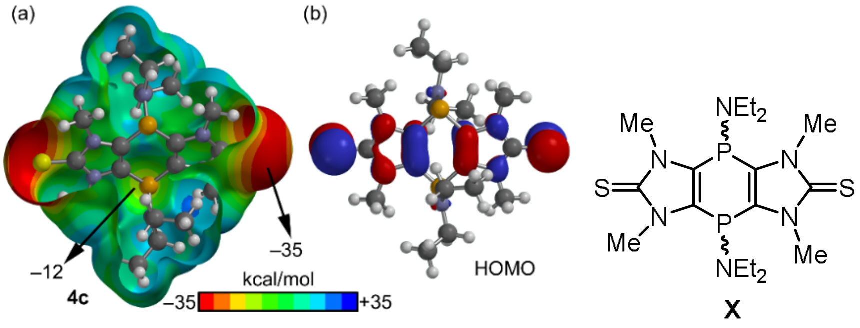
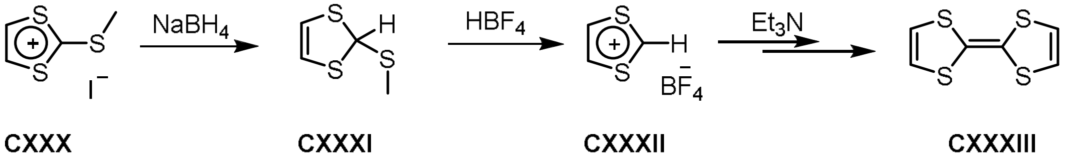


Figure 6.11. Reported MEP isosurface (0.002 a.u.) of compound **X** (a) and HOMO plot of compound **X**. (b).[14b]

To investigate and compare the nucleophilicity of the *S*- vs P-centers of tricyclic thiazole-based 1,4-dihydro-1,4-diphosphinines, similar reactivity studies were undertaken for **17a,a'**.

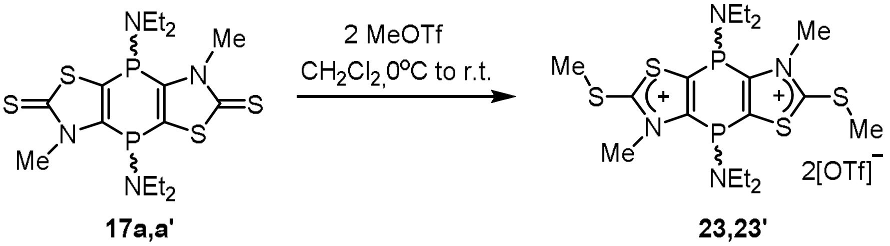
6.4.1 Reaction of tricyclic 1,4-dihydro-1,4-diphosphinine (17a,a') with MeOTf

Methyl trifluoromethanesulfonate (MeOTf) was chosen to react with 1,4-dihydro-1,4-diphosphinine (**17a**,**a'**) as a case study for two reasons: (i) to understand and compare the nature of C=S moiety of thiazole-2-thione-based tricyclic 1,4-dihydro-1,4-diphosphinines with the reported case of **X**(R' = Et$_2$N), for which the theoretically suggested nucleophilic nature of the C=S moiety was experimentally proven,[14b] and (ii) to investigate an alternative route which may finally lead to Biewlaski type bis-NHCs. But there is another potential problem: coupling of two *in situ* generated unstable carbenes leading to C=C bond formation. This is best illustrated using the well established synthesis of tetrathiafulvalene (TTF) **CXXXIII**, obtained after *S*-methylation of diathiole-2-thione followed by reduction and deprotonation,[124] schematically shown below in (Scheme 6.4).

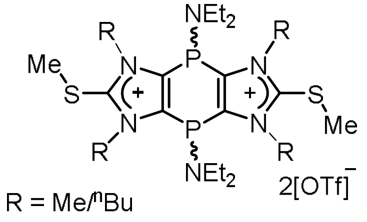


Scheme 6.4. Synthetic protocol for TTF.[124]

A dichloromethane solution of **17a,a'** was treated with two molar equivalents of MeOTf at 0 °C and the reaction mixture was stirred for three hours (0 °C to r.t.). The $^{31}P\{^{1}H\}$ spectrum of an aliquot separated from the reaction mixture showed two closely spaced signals at 22.8 ppm and 23.3 ppm (1.3:1) which were very similar to the starting material **17a,a'** ($\delta^{31}P$ = 18.8, 19.5 ppm, ratio = 1:1) (Scheme 6.5).



Scheme 6.5. Reaction of **17a,a'** with MeOTf.



CXXXIV

Figure 6.12. Literature known based *S*-methylated 1,4-dihydro-1,4-diphosphinine.[14b]

However, upon comparison to the Δδ value (2 to 4 ppm) of the ^{31}P resonance of the recently reported imidazole-based *S*-methylated 1,4-dihydro-1,4-diphosphinine **CXXXIV** and its parent compound**X** (R' = Et_2N),[14b] it became evident that the *S*-methylated *cis*/*trans* products **23,23'** have been formed (Figure 6.13). Products **23,23'** were isolated in excellent yield (94 %) after removal of solvent *in vacuo* and washing with *n*-pentane and unequivocally established via $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR and IR spectroscopy. In the ^{1}H NMR spectrum characteristic signals were observed at 3.07 ppm and 3.08 ppm assigned to the S-CH_3 protons of the two isomers of **23,23'**.Likewise in the $^{13}C\{^{1}H\}$ NMR spectrum also signals at 19.7 ppm and 9.8 ppm were assigned to the S-CH_3 carbon nuclei of the two isomers. $^{31}P\{^{1}H\}$ and selected $^{13}C\{^{1}H\}$ NMR data of **23,23'** are given in Table 6.3. The proposed composition of **23,23'** was further confirmed by elemental analysis and neg. ESI-MS spectrometry having *m/z* 149.2 $[OTf]^-$ and in the pos. ESI-MS spectrum an m/z value of 247.049 corresponding to$[C_{18}H_{32}N_4P_2S_4]^{2+}$.

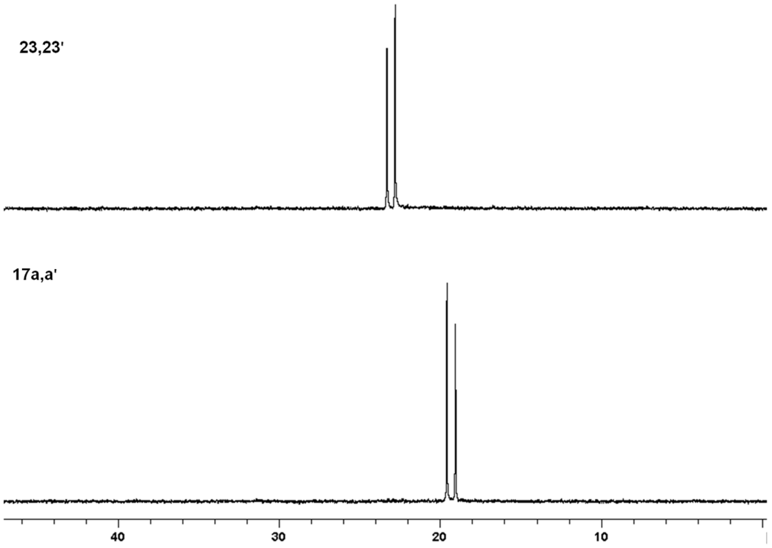


Figure 6.13..^{31}P{^{1}H} NMR comparison of **17a,a'** (THF, 25 °C) and **23,23'** (CH$_2$Cl$_2$, 25 °C).

Table 6.3. Selected NMR data and yield of **23,23'**.

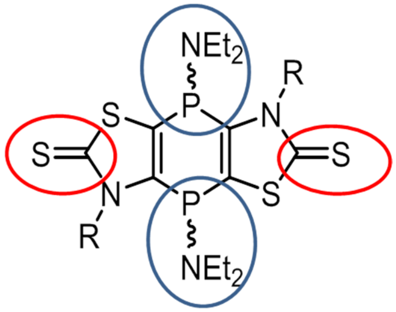
	δ^{31}P{^{1}H}(ppm)	Isomer ratio	δ ^{13}C{^{1}H} of thiazole ring carbon (ppm)	Yield (%)
23´,23'	22.8, 23.3	(1.3:1)	120.9 (q, $^1J_{P.F}$ = 320.7 Hz, *C*F$_3$), 136.0 (dd, $^1J_{P,C}$ = 26.3 Hz, $^2J_{P,C}$ = 4.2 Hz, C$^{5/4}$)138.7 (m, C$^{4/5}$), 143.3 (dd, $^1J_{P,C}$ = 28.1 Hz, $^2J_{P,C}$ = 4.5 Hz, C$^{5/4}$ *2nd isomer*) 150. (m, $^{4/5}$ *2nd isomer*),183.7 (t, $J_{P,C}$ = 4.0 Hz, *C*^{2}), 184.0 (t, $^3J_{P,C}$ = 2.4 Hz, *C*^{2}*2nd isomer*)	94

Chapter 7

Chapter 7: Chemistry of thiazole-2-thione-based 1,4-diphosphinines

The establishment of a multigram synthetic protocol to access the thiazole-based 1,4-dihydro-1,4-diphosphinine (**17**) has created the possibility to explore their chemistry mainly in two interesting fields: (i) The alkylamino group at the phosphorus centers of the tricyclic unit might offer access to the very promising 1,4-diphosphinine chemistry and (ii) the thione moieties might enable access to bis-NHCs having two P(III) and/or P(V) phosphorus units (Figure 7.1). Any of these synthetic approaches may lead to interesting outcomes as the 1,4-diphosphinine chemistry is rather less explored and, due to the intense research conducted on phosphinines [47] and their wide range of applications,[48] 1,4-diphosphinines deserve intense investigations as initial results showed for imidazole-2-thione based derivatives.[14a, 73]

On the other hand, despite the wide investigation conducted upon NHCs, thiazole-based NHCs are rather less explored, in general, and tricyclic thiazole-based bis-NHCs could open a new area of research on multi-topic[125] heterocyclic ligand arrays.



17

Figure 7.1. Potentially reactive centers of the 1,4-dihydro-1,4-diphosphinine **17** (R = Alkyl group).

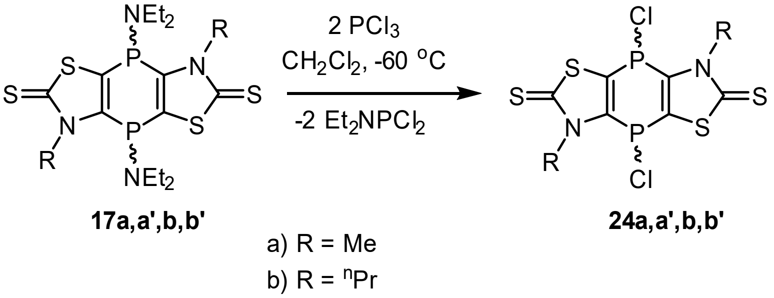
7.1 First indications of a newtricyclic 1,4-diphosphinine

The first indication to have the possibility to access 1,4-diphosphinines was obtained from EI-MS analysis of **17a,a',b,b'** (while **a** and **a'** represent the *cis/trans* isomers of **17a** and so on) as for both derivatives the fragment ions corresponding to the 1,4-diphosphinine were observed in the EI-MS spectrum in remarkably high percentages (**17a,a'**: R = Me (78%), **17b,b'**: R = ^{n}Pr (70%)). On the other hand, the thermal stability of **17a,a',b,b'** in solution was examined because earlier investigations on the *N*-^{n}Butyl substituted imidazole-2-thione-based 1,4-dihydro-1,4-diphosphinine, has shown thermal cleavage of the P-N bonds.[126] But in the present case, **17a,a',b,b'** did not show thermal conversion in toluene at 100°C into the 1,4-diphosphinines **25a,b**. Therefore, a more promising starting point was chosen: the 1,4-dichloro derivatives.

7.2 Synthesis of 1,4-dichloro-1,4-dihydro-1,4-diphosphinines 24

In order to synthesize the corresponding 1,4-dichloro-1,4-dihydro-1,4-diphosphinines (**24**), a PCl_3-initiated P-N bond cleavage in **17a,a',b,b'** was achieved using *cis/trans* mixtures of **17** (**a,a'**: 1:1.6 and **b,b'**: 1:1.3) and two equivalents of PCl_3 in dichloromethane at 0 °C (Scheme 7.1). In case of **17a,a'**, an orange colored precipitate was obtained having extremely low solubility in common organic solvents and only a signal of low intensity was observed at 132.7 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture. After removal of the solvent and drying (*in vacuo* ($8 \cdot 10^{-3}$ mbar), the EI-MS spectrum of the obtained orange precipitate showed a base peak m/z 319.8 (100%) together with the molecular ion peak for **24a,a'** (m/z 389.7 (10 %)). Altogether the ^{31}P NMR resonance (132.7 ppm) and also the EI-MS result (m/z 319.8 (100 %)) suggested that **24a,a'** was initially formed but could not be detected via $^{31}P\{^{1}H\}$ NMR spectroscopy due to low solubility. However, itdecomposed to the 1,4-diphosphinine which has relatively enhanced solubility and, hence, could be detected via $^{31}P\{^{1}H\}$ NMR spectroscopy. Furthermore, the proposed composition of **24a,a'** was also supported by HRMS (EI) and the experimentally found value (389.8265) was in good agreement with the calculated one (389.8266). The low solubility and decomposition hindered isolation and full characterization of the product.

However, in case of **17b,b'** a yellow precipitate was obtained possessing enhanced solubility thus **24b,b'** could be unambiguously identified to be formed. $^{31}P\{^{1}H\}$ NMR spectroscopy of this reaction solution revealed a mixture of *cis/trans* isomers in a 1:1.1 ratio, together with the expected by-product Et_2NPCl_2. The $^{31}P\{^{1}H\}$ NMR spectrum of the isolated product showed resonances at 12.7 and 21.3 ppm (ratio 1:1.1), assigned to the *cis* and *trans* isomers of **24b** respectively, based on comparison with the *cis and trans* assignment in case of **XCI**.[14a]. The constitution and composition of the product was further supported by HRMS (EI) *m/z*445.8896 which was found to be in agreement with the calculated *m/z* value of 445.8892. However, in the EI-MSspectrum of **24b,b'** also the loss of both Cl atoms was observed under the EI-MS conditions (m/z 375.9 (85 %) $[M-2Cl]^+$). Crystals of *trans***24b,b'** were obtained via slow diffusion of *n*-pentane into a dichloromethane solution at −35 °C. **24b** crystallized in triclinic crystal system with space group$P\bar{1}$and the X-ray diffraction analysis confirmed the constitution of the *trans* isomer (Figure 7.2).[127] Crystal structure with numbering scheme is given in Figure 7.2 and selected bond lengths and bond angles in figure caption. Although the X-ray crystal structure is not known for **CXXXV**[119] and **XCI**[14a], however the P-Cl bond length **24b** was found to be in the expected range, upon comparison the previously discussed compounds: **9** [dP-Cl = 2.0796(4)], **CV** [dP-Cl = 2.1029(6) Å],[84]**CVIII** [dP-Cl = 2.0982(2) Å][86] and **CIX**[dP-Cl = 2.061(1) Å].[87]



Scheme 7.1. Synthesis and of 1,4-dichloro-1,4-dihydro1,4-diphosphinines (**24a,a',b,b'**).

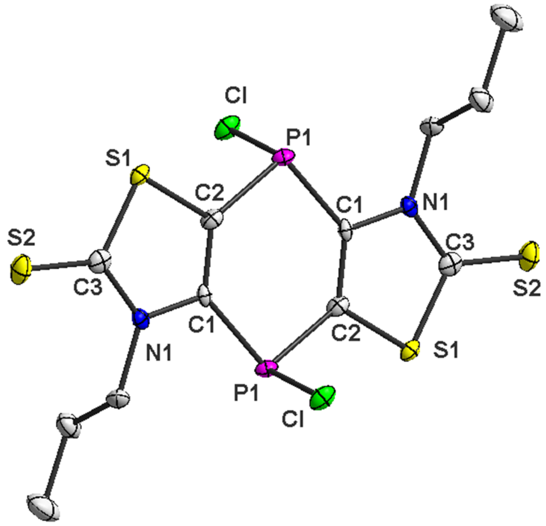
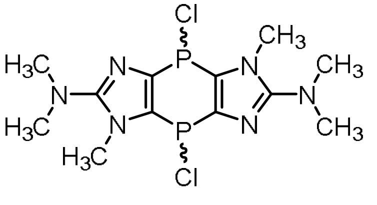
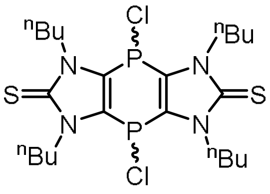


Figure 7.2. Displacement ellipsoids plot (50% probability) of molecular structure of **24b** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.828(4), P1-C2 1.817(4), C1-C2 1.350(5), P1-Cl 2.0973(13),C1-P-C2 98.32(17).

The ^{31}P NMR resonances of **24b,b'** (12.7 and 21.3 ppm) were found to be quite comparable to the values for the literature known 1,4-dichloro-1,4-dihydro-1,4-diphosphinines **CXXXV**[119] (25.8 ppm) and (2.6 and 10.9 ppm) **XCI**.[14a]



CXXXV

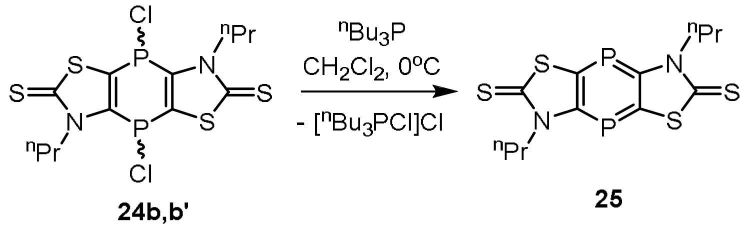


XCI

Figure 7.3. Literature known 1,4-dichloro-1,4-dihydro-1,4-diphosphinines **CXXXV**[119] and **XCI**.[14a]

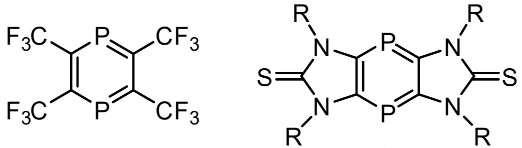
7.3 Reduction of 1,4-chloro-1,4-dihydro-1,4-diphosphinine 24b,b'

Upon treatment of a dichloromethane solution of **24b,b'** with ^{n}Bu$_3$P at 0 °C, a color change from yellow to red was observed which gave initial indication for the formation of 1,4-diphosphinine **25** (Scheme 7.2), as it was in close accordance with the color change in case of the recently reported imidazole-based derivative **XCII**;[14a] prolonged stirring of the reaction mixture at ambient temperature (16 h) led to the completion of the reaction as revealed by ^{31}P{^{1}H} NMR spectroscopic monitoring.



Scheme 7.2. Synthesis of the first thiazole-based 1,4-diphosphinine **25**.

The ^{31}P{^{1}H} NMR spectrum of an aliquot ofthe reactions solution of **25** showed two signals, a singlet at 134.7 ppm and another one at 105.2 ppm. The latter could be assigned to the chlorophosphonium chloride salt and the former was tentatively assigned to **25**. However, the downfield-shifted singlet resonance indicated a low-coordinate phosphorus compound when compared to **XCII.**[14a] But it should be also noted that the resonance was found in the upfield region when compared to **LXXXIV**.[71]



LXXXIV **XCII**

Figure 7.4. The literature known 1,4-diphosphinines **LXXXIV**[71] and **XCII**.**[14a]**

1,4-Diphosphinine **25** was isolated in good yields (77 %) via filtration of the reaction mixture at −40 °C, followed by washing of the residue with dichloromethane and then with *n*-pentane at low temperature. Further confirmation of the constitution of the productwas obtained from the HRMS (EI) experiment: the m/z value 375.9516 was in close agreement to the calculated one (375.9515). Elemental analysis also strongly supported the proposed composition of the product. Final confirmation came from the single crystal X-ray diffraction analysis of crystals grown from a dichloromethane solution at −35 °C. Single crystal X-ray diffraction analysis of 2, being in good agreement with the theoretical results, confirms the tricyclic structure with trans-oriented npropyl groups. Molecules of **25** crystallize centrosymmetrically in $P\bar{1}$ and display off-set planar stacking with equal inter-ring separations of 3.595 Å such that the N atoms of each thiazole-2-thione ring lie over centroids of 1,4-diphosphinine moieties above or below (Figure 7.5). The P–C bond lengths (P–C1 1.7390(15) Å, P–C3 1.7494(15) Å) of the central rings are in good agreement with literature values for phosphinines (Figure 7.6).[47e, 47f, 128] The symmetry-equivalent C–C bond lengths of 1.406(2) Å are comparable with those in benzene (1.397 Å);[129] all these parameters are consistent with a high degree of aromaticity in **25**.[127]

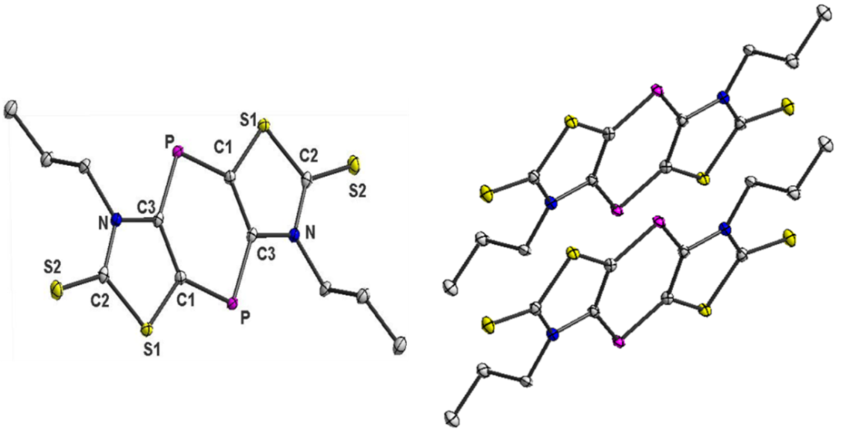
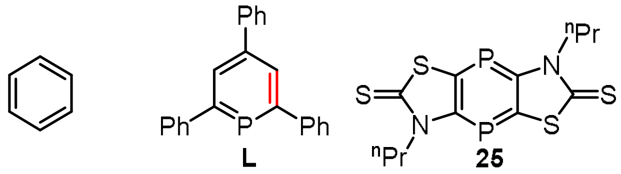


Figure 7.5. Displacement ellipsoids plot (50% probability) of molecular structure of **25** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P-C1 1.7390(15), P-C3 1.7494(15) C1-C3 1.406(2), C1-P-C3 100.02(7).



P=C (Å)	-	1.758	1.7494
C=C (Å)	1.397	1.385	1.406

Figure 7.6. Comparison of the endocyclic P=C and/or C=C bonds in the six-membered aromatic rings of benzene[129], phosphinine **L**,[47e, 47f, 128] and **25**.

7.4 Further investigations upon the properties of 1,4-diphosphinine 25

Owing to the rigid conjugated π–electronic system of compound **25**, its UV/Vis spectrum was recorded and cyclovoltammetric studies were conducted, and to get further insight into the electronic properties, theoretical calculations were also performed. All these aspects are discussed in the chapter below.

7.4.1 UV/Vis spectroscopy and TD DFT calculations

The UV/Vis spectrum of **25** was measured from its dilute (concentration~ 10^{-6} molar) dichloromethane solution in a sealed quartz cell at room temperature. A strong absorption in the UV/Vis spectrum of**25** (Figure 7.7) was observed at λmax = 497 nm. This value was found to be in a very good agreement with the TD DFT calculated value of 502 nm (at B3LYP/6-311+G**//M06-2X/6-311+G**), which is basically the HOMO(π)–LUMO(π*) transition with a high transition probability. So, the structurally indicated aromaticity of the 1,4-diphosphinine is also strongly supported by the UV/Vis spectroscopic data and by TD-DFT calculations too.

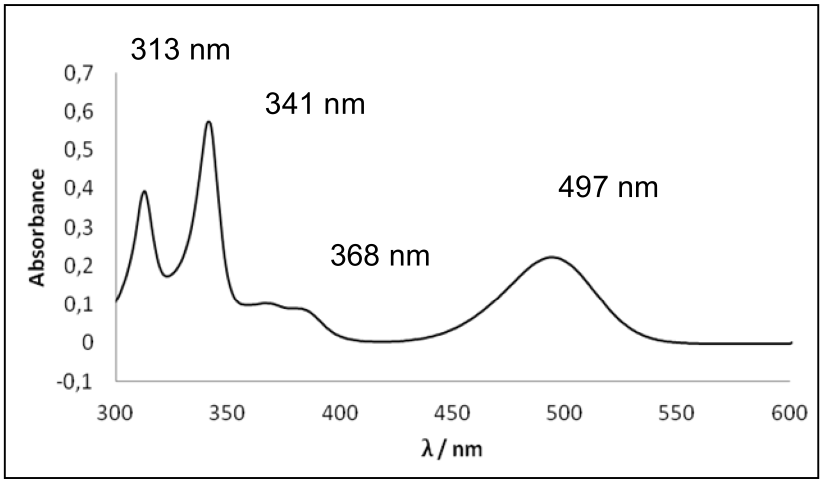


Figure 7.7. UV/Vis spectrum of **25** (CH_2Cl_2).

According to the calculated NICS(1)[130] values (M06-2X/6-311+G**) all of the three rings of **25'**(the notation ' stands for using Me substituents instead of ^{n}Pr) are aromatic, but the diphosphinine unit is more aromatic (NICS(1) = −8.8) than the outer rings (NICS(1) = −4.9) while that of benzene[131] was reported to be −12.8.

Theoretical investigations (B3LYP/6-311+G**) of Nyulaszi suggested that the HOMO of compound **25'** was relatively high in energy (−6.19 eV) and essentially represents the antibonding combination of the HOMOs of the two thiazole-2-thione fragments (Figure 7.8). The LUMO of compound **25** was found to be low lying (−3.20 eV) being largely stabilized. In conclusion, this high lying HOMO and low lying LUMO resulted in a rather small HOMO-LUMO (2.99 eV) gap which in turn lowers the excitation energy thus being in agreement with the observed dark red color of compound **25.**

If the theoretical investigations on **25'** arecompared to the previously reported imidazole-2-thioned based 1,4-diphosphinine **XCII'** (B3LYP/6-311+G**), asimilar energetic situationfor the LUMO (−2.93 eV) and HOMO (−5.79 eV) energies was found. The HOMO was found to be relatively high in energy and is responsible for the ylidic character of the C=S bond, while the LUMO is strongly stabilized and is basically the lowest π* orbital of the diphosphinine unit.[127] Parallel to the results of theoretical investigation on **25**, for **XCII**alsothe rather small HOMO–LUMO gap resulted into small excitation energy which explains the red color of compound **XCII.**

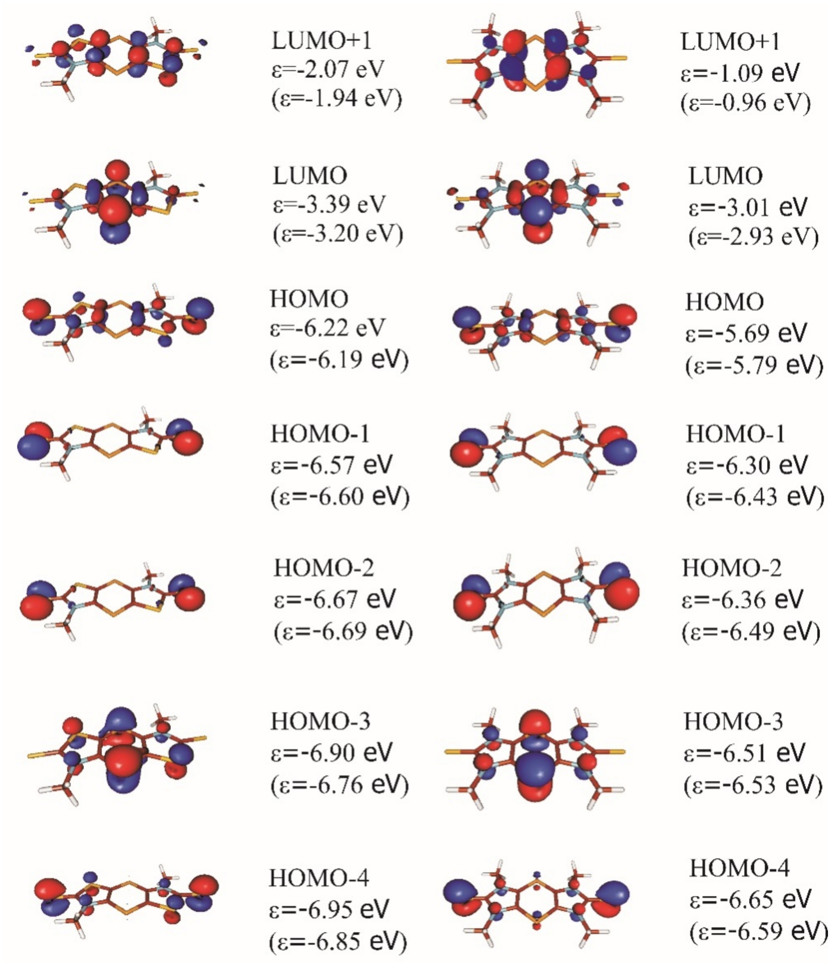


Figure 7.8: Comparative orbital energy manifolds for (left) **25’** and (right)**XCII’**[14a]from B3LYP/6-311+G** and (in brackets) B3LYP/6-311+G**(PCM:THF) calculations.

Table 7.1. M062x/6-311+G** (PCM: THF) relative energies (with respect to the neutral molecule in eV) of the calculated cationic (dicationic) and anionic (dianionic) states for **25** ‘ and **XCII** ‘.

M062x/6-311+G**					
	Dication	monocation	neutral	monoanion	Dianion
25’	19.53	7.80	0.0	-2.27	-0.60
XCII’	18.47	7.24	0.0	-1.93	+0.04
M062x/6-311+G** (PCM: THF)					
25’	14.10	6.49	0.0	-3.50	-5.67
XCII’	13.49	6.11	0.0	-3.20	-5.23

7.4.2 Cyclovoltammetric studies

Solution voltammetry on **25** in THF/$[^nBu_4N][PF_6]$ at Pt (Figure 7.9) and Au working electrodes identified two central reduction processes that are very closely spaced ($E_p^c(2)$ = -1.28 V and $E_p^c(3)$ = -1.45 V vs. the ferrocene/ferrocenium redox couple,[132] hereafter $Fc^{+/0}$) and are not electrochemically reversible. Nevertheless, return peaks $E_p^a(3)$ and $E_p^a(2)$ are observed and the general appearance of the solid trace (—) in Figure 7.9, including off-set re-oxidation $E_p^a(')$, is constant over multiple cycles and variation in scan rates from 0.1–1.0 $V{\cdot}s^{-1}$, except that the re-oxidation peak $E_p^a('')$ increases in intensity with slower scanning but loses intensity with multiple cycles that do not go negative of the starting potential.

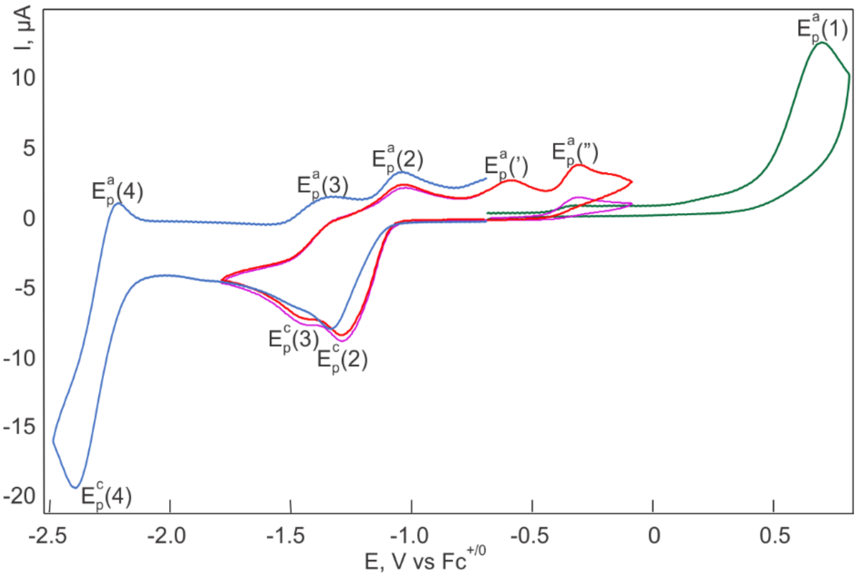


Figure 7.9. Composite CVs obtained on 2 2.0 mM in THF (0.2 M $[^nBu_4N][PF_6]$, v = 0.2 $V{\cdot}s{-}1$; scans start from o.c.p. = −0.69 V). (—–) Anodic scan through E(1). (—) Cycle in cathodic direction through E(2,3); (·····) same but starting anodic.

The oxidation process $E_p^a(1)$ at +0.70 V vs. $Fc^{+/0}$is irreversible and no further processes can be observed before the solvent limit is reached (compound reactivity limits solvent selection). There are also further reduction processes observable at much more negative potentials.

Justification for treating the radical anion and the dianion as *chemically* stable species (although quite reactive towards Pt and Au electrode materials) is provided by the recent NMR observation of a related imidazole-2-thione-based dianion[14c] (i), computational results showing that the dianion is more stable than the neutral species at M06-2X/6-311+G** (PCM: THF) as shown in Table 7.1 (ii), observation of further well-behaved reduction waves

(iii) and the great similarity to the CV behavior of analogue compound **XCII**[14a] (iv). The most important feature of the voltammetry is that $E_p^c(2)$ and $E_p^c(3)$ are at significantly *lower* potential than in **XCII** (by 0.52 and 0.50 V). This is in full agreement with the calculated LUMO energies of the two compounds, which are −3.20 eV and −2.93 eV at B3LYP/6-311+G**(PCM:THF) (see Figure 7.8). Also the M06-2X/6-311+G** (PCM:THF) anion and dianion is more stable for **25'** than for **XCII'** by 0.30 and 0.44 eV, respectively (see Table 7.1).

The origins of the very close spacings of $E_p^c(2)$ and $E_p^c(3)$, in both **25** and **XCII**, which approach but do not reach potential inversion,[133]might be sought in the structural changes that accompany the *second* reduction: the geometry of **25**$^{-\bullet}$ remains planar, whilst **25**$^{2-}$ bends appreciably.[133a] Indeed, at M06-2X/6-311+G** (PCM:THF) **25'**$^{2-}$ and **XCII'**$^{2-}$ exhibit pyramidalized phosphorus atoms (although, the barrier to planarization is only 4 and 2.3 kcal/mol, respectively). The calculated stability of the anion is larger than that of the dianion in the gas phase calculation, however, using the PCM:THF model the dianionic state is significantly stabilized (see Table 7.1) in reasonable agreement with the observed CV behavior. In this regard, diphosphinines **25** and **XCII** appear to be less structurally robust towards reduction than the comparably-sized PAH anthracene, which remains robustly planar also in the dianion at B3LYP/6-311+G**. Correspondingly, the separation of E(2) and E(3) in anthracene is 0.83 V in DMF and 0.60 V in (more strongly solvating) $HNMe_2$ solutions.[133b, 134] In further comparisons to the PAH analogue, the electrochemical stability window for **25**, defined as $\Delta E_{SW} = E_p^a(1) - E_p^a(2)$, is 1.74 V. In anthracene, $\Delta E_{SW} \approx 3.2$ V with an uncertainty caused by measurements of reduction and oxidation in separate experiments using DME and ACN, respectively.[133d, 135] Consistent with this, the HOMO-LUMO gap in anthracene is correspondingly larger at 3.55 eV than in **25'** (2.99 eV; gas phase computations).[127]

Chapter 8

Chapter 8: Reactivity studies of 1,4-diphosphinine25

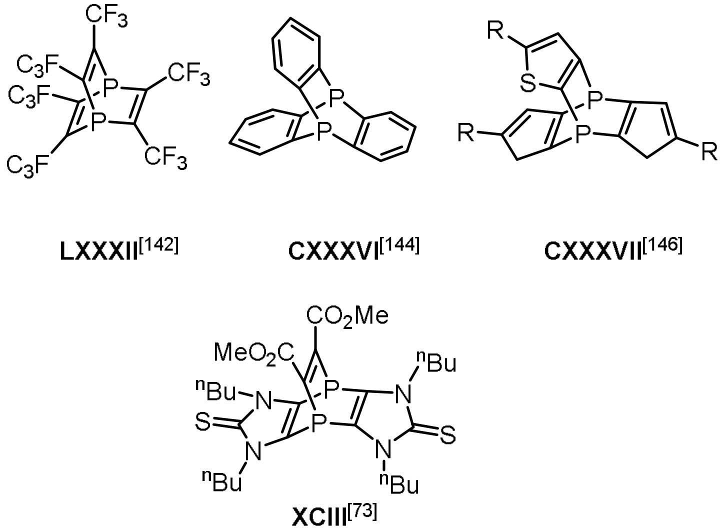
After their first discovery, intense research for more than five decades was devoted to phosphinines.[47] As mentioned beforehand in the introduction, a broad spectrum of studies have revealed complexation,[45, 136] P-alkylation,[57] P-oxidation,[58a-f, 137] P-reduction[59a-c] and cycloaddition reactions.[60a, 60b] In particular, phosphinines have interesting π-ligand accepting properties and a decidedly electrophilic phosphorus center and, therefore, they readily react with Grignard and organolithium compounds.[55]

In contrast, reactivity studies of 1,4-diphosphinines are not well explored and only few properties and reactions have been reported from the first known compound: formal [4+1] and [4+2] cycloaddition and one example of a photoisomerization.[72] Recently, new reactivity studies have been conducted by Streubel and co-workers on the imidazole-based 1,4-diphosphinine **XCIV**, which has re-opened this research area.[14a, 73]

8.1 [4+2]-Cycloaddition reactions

An interesting aspect of the phosphinine chemistry is their ability to generate phosphabarrelenes owing to some dienic nature of the π-system.[138] First synthesis of the phosphabarrelene was achieved by Märkl in 1968 via reaction of a phosphinine with different alkynes.[60a] Later on, they also reported other examples generated via cycloaddition reactions of phosphinines with arynes.[60c] Besides other applications,[139] phosphabarrelenes are used in hydrogenation[139a] of alkenes and rhodium-catalyzed hydroformylation,[140] An interesting addition to this field was the recently reported Rh-catalyzed one-pot tandem reaction sequence under hydroformylation conditions using phosphabarrelene by Müller and co-workers.[141]

Interestingly, the first diphosphabarrelene was reported even before the phosphabarrelene by Krespan in 1961.[142] Compound **LXXXII** was obtained via thermolysis of hexafluoro-2-butyne in the presence of red phosphorus, using iodine as catalyst. This methodology needs a long reaction time (8 h) at elevated temperatures (200 °C) under autogenous pressure, and the maximum yield reported was only 43 %. However, later on Kobayashi and co-workers synthesized the same compound via reaction of tetrakis(tri-fluoromethyl)-1,4-diphosphabenzene with hexafluoro-2-butyne.[71, 72b, 143] The same tetrakis-(trifluoromethyl)-1,4-diphosphabenzene was used to synthesize few other 1,4-diphospha-barrelenes, as explained in the introduction. Besides, several other 1,4-diphosphabarrelenes are known, being listed in Figure 8.1, and different synthetic methodologies were used to access these compounds.For example, Weinberg and co-workers reported the synthesis of **CXXXVI**in 1971 via thermolysis of *ortho*-dichlorobenzene and white phosphorus in the presence of catalytic amount of $FeCl_3$(20 % yield).[144] Attempts to optimize the synthetic protocol by Mazaki and co-workers did not achieve any noticeable improvements, and the yields were even lower (9 %).[145] Synthesis of 4,8-diphospha[3,4-a:7,8-a]thiophenotriptycene **CXXXVII**was reported by Nakayama and co-workers by reaction of tris(thiophen-2-yl)phosphane oxide with tris(phenoxy)phosphane using ^{n}BuLi as base.[146] However, the yield was less than 11 %. Very recently, the reactivity of the imidazole-based 1,4-diphosphinine **XCII** was investigated towards few dienophiles by Streubel and co-workers under relatively mild reaction conditions and the corresponding 1,4-diphosphabarrelenes, for example **XCIII**, were obtained in good yields (up to 95 %).[73]



LXXXII[142] **CXXXVI**[144] **CXXXVII**[146]

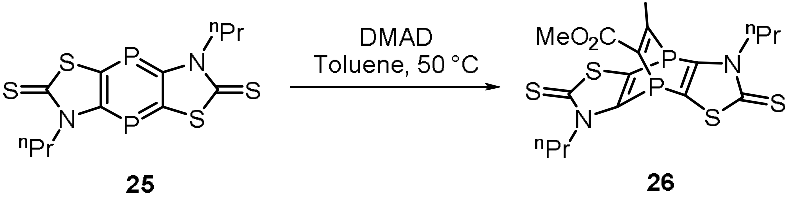
XCIII[73]

Figure 8.1. Selected examples of 1,4-diphosphabarrelenes.

Motivated by this easy access to the desired 1,4-diphosphabarrelenes, we wanted to investigate if the methodology can be extended to thiazole-based tricyclic systems.

8.1.1 Reaction of tricyclic 1,4-diphosphinine 25 with DMAD

In order to investigate the dienic nature of the 1,4-diphosphinine **25,** it was reacted with a typical electron-deficient alkyne, dimethyl acetylenedicarboxylate, at 50 °C in toluene (Scheme 8.1). After 45 min the red color of the 1,4-diphosphinine had disappeared and a yellow-orange turbid solution was formed. Compound **26** was isolated in very good yield (73 %) by removal of solvent under reduced pressure followed by washing with *n*-pentane (2•5 mL). The $^{31}P\{^1H\}$ NMR spectrum showed only one signal at −75.4 ppm which was comparable to literature known compounds (−87.1 and −93.4 ppm for **CXXXVII**[146]and −87.3 ppm for **XCIII**[73]), so it was tentatively assigned to the 1,4-diphosphabarrelene **26**. The ^1H NMR spectrum showed, besides signals of the substituent of the tricyclic system, a characteristic signal at 3.82 ppm for the OCH_3 group of compound **26**. The latter group could also be assigned to the signal in $^{13}C\{^1H\}$ NMR spectrum at 53.4 ppm and the carbon resonance at 157.6 ppm (dd, $^1J_{P,C}$ = 15.1 Hz, $^2J_{P,C}$ = 14.0 Hz,CCO_2Me) was assigned to the sp^2–hybridized carbon atom. The product **26** was further confirmed by EI-MS*, i.e.,* the molecular ion peak of **26** was observed at m/z 518.0 (68 %) which was further supported by the HRMS m/z value (517.9777) being in agreement with the calculated value (517.9781). Interestingly, one fragmentation pathway under EI-MS conditions of **26** was the cleavage of the alkyne moiety, to give the **25**-cation (376.0) (75 %). Compound **26** was also characterized by micro analysis and single crystal X-ray diffraction analysis. The molecular structure in the solid state is displayed in Figure 8.2, and selected bond lengths and angles are given in the figure caption. The C13-C14 bond distance: 1.336(4) Å, is in the normal range when compared to literature values of **XCIII** (1.329(9) Å for),[73] while the distance P1-C1 (1.846(3) Å) is within the range of phosphabarrelenes (1.864(2) Å)[147] or 1,4-diphosphabarrelenes **XCIII**(1.820(6) Å).[73]



Scheme 8.1. Reaction of 1,4-diphosphinine **25** with DMAD.

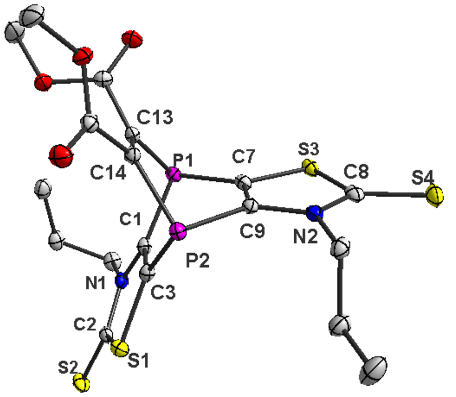
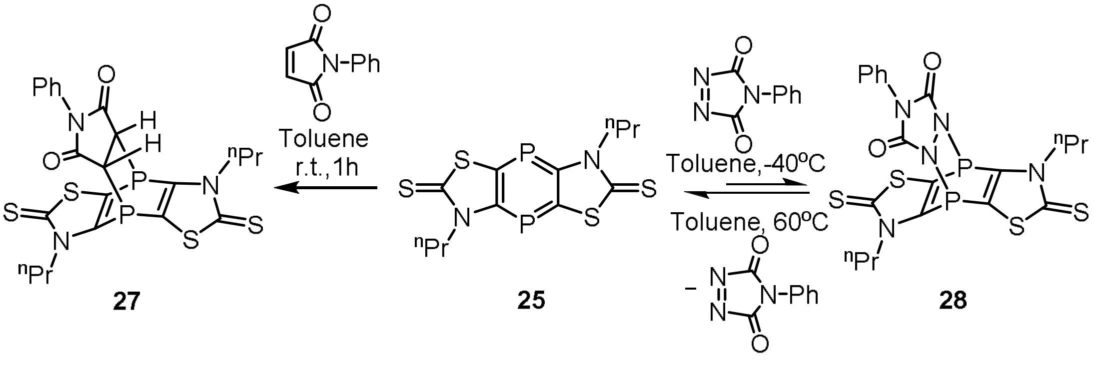


Figure 8.2. Displacement ellipsoids plot (50% probability) of molecular structure of **26** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.846(3), P1-C7 1.818(3), C1-C3 1.348(4), P1-C13 1.870(3), C13-C14 1.336(4), C1-P1-C7 95.63(13).

8.1.2 Reaction of 1,4-diphosphinine 25 with C=C and N=N containing systems

After the successful reaction with DMAD, it seemed to be interesting to investigate other potential 2π-systems as dienophiles in [4+2]-cycloaddition reactions. The reaction of **25** with 1-phenylpyrrole-1,5-dione also proceeded selectively to give a single product **27** as revealed by $^{31}P\{^{1}H\}$ NMR spectroscopy (Scheme 8.2).



Scheme 8.2.[4+2]-Cycloaddition reactions of 1,4-diphosphinine **25** to afford **27** and **28**.

In comparison to the singlet $^{31}P\{^{1}H\}$ NMR resonance of **26**,two doublets at −74.3 ppm and −74.7 ppm were observed with a coupling constant $^{3}J_{P,P}$ of 28.8 Hz (Figure 8.3). Upon comparison with the literature knownimidazole-derived compound **XCIV**($\delta^{31}P$ = −86.3),[73] both resonances were assigned to the two phosphorus atoms of **27**. However, in contrast to the singlet resonance of symmetric molecule **XCIV, 27** possesses two chiral phosphorus centers due to the presence of sulfur in the five-membered heterocyclic ring. Therefore, the two phosphorus atoms become inequivalentand appeear as doublets in the ^{31}P NMR spectrum.

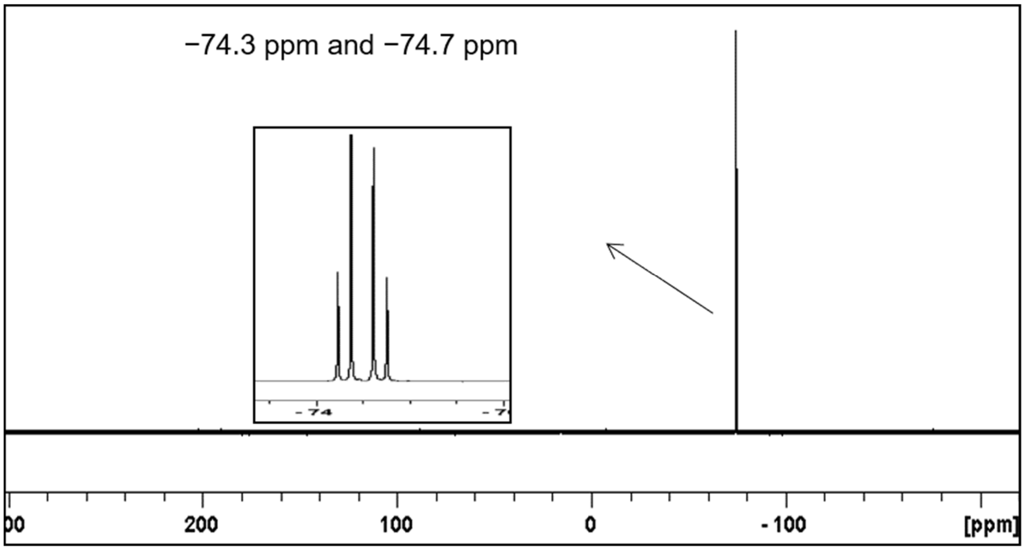


Figure 8.3.$^{31}P\{^1H\}$ NMR spectrum of **27** (CD_2Cl_2, 25 °C).

27 was isolated in excellent yields (94 %) as white powder after washing with *n*-pentane (2•2 mL) and drying *in vacuo* ($8\cdot10^{-3}$ mbar). and has been fully characterized including MS and elemental analysis. In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **27**, also two sets of signals were observed for each group of different moieties which confirms the lower symmetry in **27**.

The constitution of **27**was further confirmed by single crystal X-ray analaysis. A reduced molecular structure with numbering scheme is given in Figure 8.4 and selected bond lengths and bond angles are given in the figure caption. Two molecules (enantiomers) were present in the unit cell (Figure 8.4). Both C=O bond lengths [C15-O1 1.20(2), C16-O2 1.20(2)] were found to be very similar and the sum of bond angles at N3 atom was found to be around 360°($\Sigma\angle N3 = 360.1°$) which confirmed N3 to be planar and suggest the delocalization of the N electron pair along the CO-CN-CO centers.

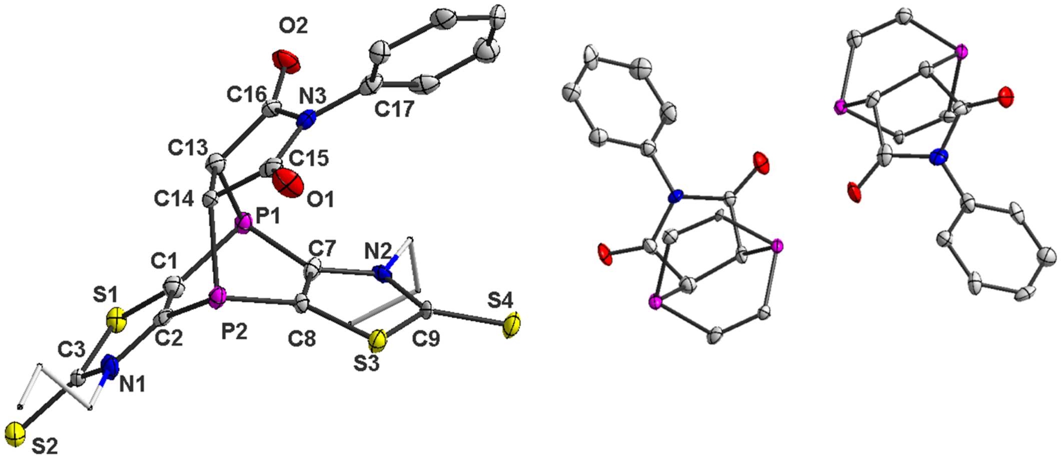


Figure 8.4.Displacement ellipsoids plot (50% probability) of molecular structure of **27** in the crystal; right: selected view along the six membered ring. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.82(2), P1-C7 1.839(18), P2-C2 1.833(19), P2-C8 1.819(16), C1-C2 1.36(3), C7-C8 1.34(2), P1-C13 1.892(18), P2-C14 1.880(18), C13-C14 1.53(2), C15-O1 1.20(2), C16-O2 1.20(2) , N3-C15 1.39(2), N3-C16 1.41(2), N3-C17 1.44(2) , C1-P1-C7 96.9(9).

Interestingly, 4-phenyl-1,2,4-triazoline-3,5-dione, a well known strong dienophile, reacted already at low temperature (−40 °C) in toluene with **25** (Scheme 8.2). Initially, a clean reaction was observed as monitored via $^{31}P\{^{1}H\}$ NMR spectroscopy showing two broad signal at −45.5 ppm and −46.0 ppm along with the signal of the starting material (**25**); this downfield-shift was expected due to the electron-withdrawing effect of the electronegative nitrogen atoms.In order to push the reaction towards completion, the solution was stirred overnight and warmed to ambient temperature. However, the ratio of the reactant and the product remained unchanged (1:2) as revealed via $^{31}P\{^{1}H\}$ NMR spectroscopic monitoring. To get further insights variable temperature (VT) $^{31}P\{^{1}H\}$ NMR experiments were conducted (Figure 8.5). This NMR study clearly demonstrated that the reaction proceeds in the forward direction until 0 °C. However, an equilibrium is established at this temperature and the reaction progression stops. Upon heating to room temperature and/or beyond, a backward reaction (retro-[4+2]) starts and the content of the diphosphinine **25** increased, reaching a maximum of about 95 % at +60 °C.

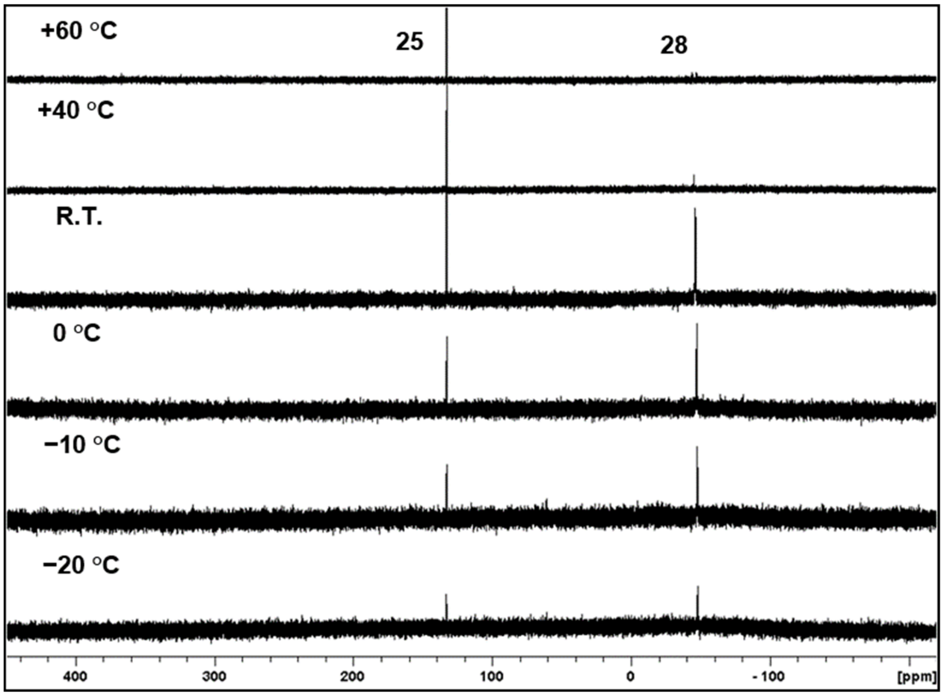


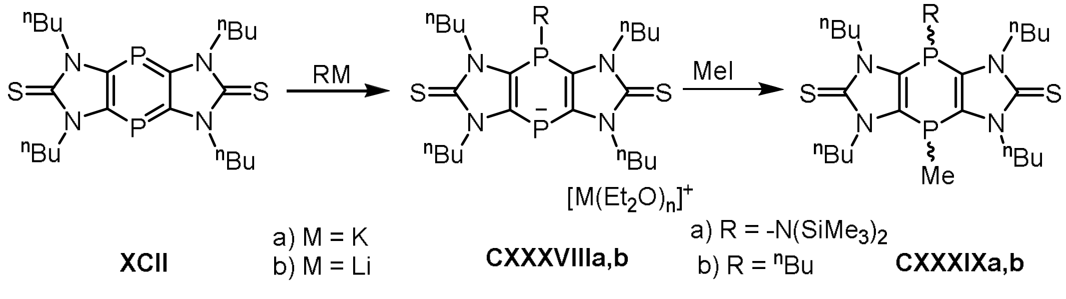
Figure 8.5.VT $^{31}P\{^1H\}$ NMR (toluene) study of the reaction of **25** with 4-phenyl-1,2,4-triazoline-3,5-dione to give **28**.

In order to achieve characterization of **28**, the reaction was performed again at −40 °C and the solvent removed from a 1:2 mixture of **25**:**28b** at ambient temperature. In the EI-MS spectrum of this mixture, a peak corresponding to the molecular ion of **28** was observed at *m/z* 551.0 (40 %) which supports the proposed composition of the product **28**. Apart from this other fragmentation ions were observed and could be assigned to the following fragments, *e.g. m/z* 376.0 (85 %) $[C_{12}H_{14}N_2P_2S_4]^+$, 334.0 (35 %) $[M-C_{12}H_{14}N_2P_2S_4-^nPr]^+$ and 177.1 (40%) $[C_8H_5N_3O_2]^+$. Further confirmation for the composition of **28** was obtained from a HRMS spectrum (*m/z* 550.9893) which was in agreement with the calculated m/z value (550.9897).

8.2 Synthesis and reactions of mono anions derived from 1,4-diphosphinine 25

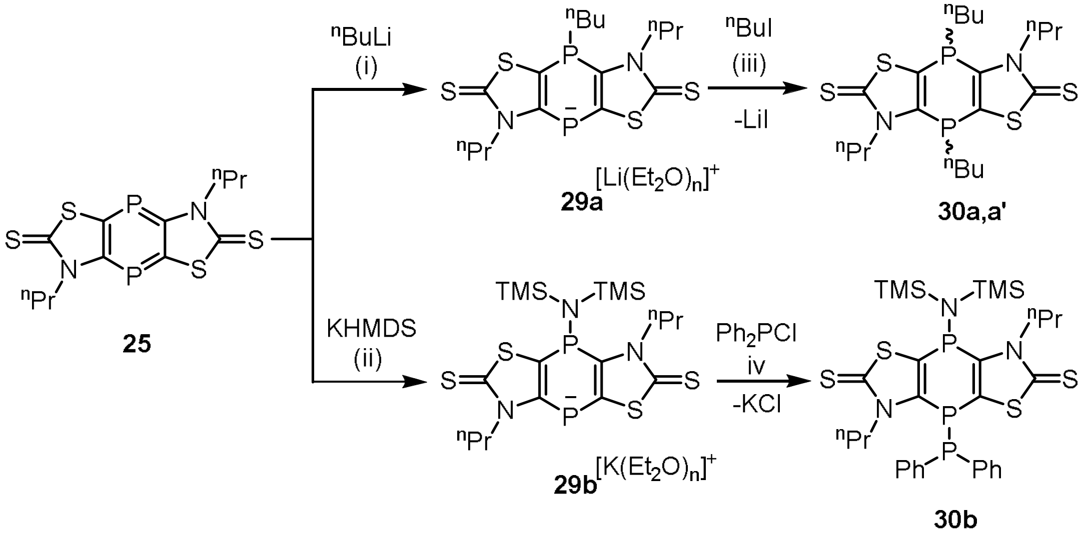
The addition of nucleophiles to phosphinines giving rise to anionic σ^3-P derivatives has been extensively studied, as explained and illustrated in the introduction.[55] In case of phosphinines, as it is a well known fact by now that the phosphorus lone pair resides in the less directional, low lying LUMO leading to its increased electron affinity,[46, 148] and a high electrophilic reactivity.[55] However for 1,4-diphosphinines no such study was reported until quite recently. In 2018, Streubel and co-workers reported the first study in this area, showing the addition of nucleophiles (KHMDS or ^{n}BuLi) to the imidazole-based 1,4-diphosphinine

(**XCII**) to generate the corresponding mono anions (**CXXXVIIIa,b**).[14c] However due to lower stability the aforementioned mono anions were not isolated and only generated *in situ* and detected via ^{31}P NMR spectroscopy (δ =12.1 (d), -76.1 (d) $^{3}J_{P,P}$ = 5.7 Hz for **a**, δ = -74.3 (d), -82.5 (d) $^{3}J_{P,P}$ = 4.1 Hz for **b**). The *in situ* generated mono anions (**CXXXVIIIa,b**) were then reacted with the electrophile MeI and 1,4-disubstituted compounds (**CXXXIXa,b**) were isolated and characterized (Scheme 8.3).



Scheme 8.3. Recently reported reactivity of a 1,4-diphosphinine towards a nucleophile electrophilesequence, according to Streubel.[14c]

For the first investigation of the electrophilic reactivityof 1,4-diphosphinine **25** a renowned good nucleophile such as ^{n}BuLi was used. Upon treatment of an ether suspension of **25** with ^{n}BuLi at –78 °C, a dark red solution was formed And the ^{31}P{^{1}H} NMR spectrum of the reaction mixture showed two signals at $\delta = -59.1$ and -21.1 assigned to the anionic and neutral phosphorus centers of product **29a,** respectively (Scheme 8.4). Upon treatment of freshly prepared **29a** with ^{n}BuI at −78 °C, an immediate color change from red to yellow was observed. The reaction progress was monitored via ^{31}P{^{1}H}-NMR spectroscopy which showed a fast and clean conversion to **30a,a'** (Scheme 8.4). The two signals in the ^{31}P{^{1}H} NMR spectrum of **30a,a'**;($\delta = -44.1$ ppm and -38.3 ppm) were assigned to the two *cis*/*trans* isomers of **30a** (2:1).[127]



Scheme 8.4. Addition of nucleophiles to 1,4-diphosphinine **25** and reactions with electrophiles to give **30a,b** (i = Et_2O, -78 °C, ii = Et_2O, r.t., iii = Et_2O, -78 °C, iv = Et_2O, -70 °C.

Compound **30a,a'**was isolated in rather good yield (55 %) via filtration of a dichloromethane solution to remove the formed LiI and subsequent washing of the residue with *n*-pentane. Besides NMR measurements, the proposed constitution of**30a,a'**was also supported by HRMS (EI) in which the experimental and calculated values are in good agreement (490.0921 vs. 490.0924) and also by elemental analysis. The chemical constitution of **30a,a'** was firmely established by single crystal X-ray diffraction studies. Crystals were grown by slow evaporation of concentrated dichloromethane solution. *Trans* isomer of **30a** crystalized in triclinic crystal system with space group $P\overline{1}$. The crystal structure of **30a** is given in Figure 8.6 while the selected bond lengths and bond angles are given the figure caption. The bond lengths and bond angles of **30a** are comparable with thore of **17**c so will not be discussed further

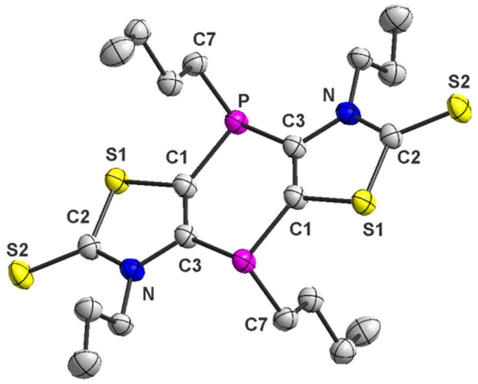
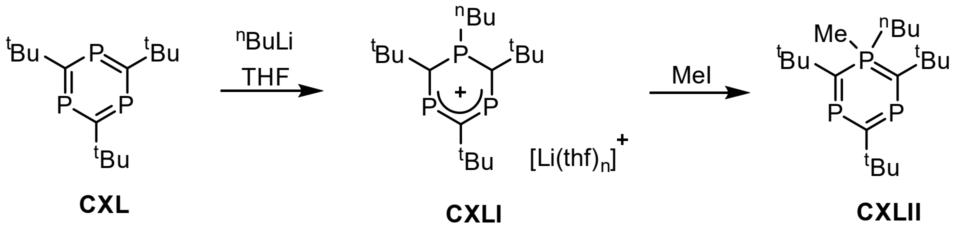


Figure 8.6. Displacement ellipsoids plot (50% probability) of molecular structure ofof **30a** in the crystal. Hydrogen atoms have been omitted for clarity.C2-S2 1.662(4), C1-P 1.821(4),C3-P 1.822(4), C7-P 1.864(5), CI-C3 1.351(6), C1-P-C3 98.27(19).

A noteworthy contrast stems from the chemistry of a 1,3,5-triphosphabenzene: a similar reaction sequence, as described beforehand (1. BuLi; 2. MeI and 2,4,6-tri-^{t}Bu-1,3,5 triphosphabenzene), resulted in the 1,1'-dialkylation of the same phosphorus atom, thus yielding $1\lambda^5,3\lambda^3,5\lambda^3$-triphosphabenzene **CXLII**(Scheme 8.5).[149]



Scheme 8.5. Addition of ^{n}butyl lithium and methyl iodide to triphosphabenzene according to Lawless.[149]

In order to examine the scope of the nucleophilic addition and reactivity of **25**, a very weak nucleophile (KHMDS) was chosen (Scheme 8.4). But to our surprise, treatment of **25** with KHMDS in diethyl ether at ambient temperature resulted in a sequence of color change from red to green and after few minutes, to bright red. In accord with the appearance and then fast disappearance of the green color, the formation of the radical anion of **25** ($\mathbf{25}^{\cdot-}$) is suggested. This finding was also supported by the calculated TD-DFT spectra of $\mathbf{25}^{\cdot-}$, performed by Nyulaszi, which suggests a green color (B3LYP/6-311+G**//M06-2X/6-311+G**)). Finally, the bright red color can be attributed to the anion of **29b** (B3LYP/6-311+G**//M06-2X/6-311+G**).[127]

The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed two rather broad singlets at −28.6 and 6.7 ppm, assigned to the anionic and neutral phosphorus centers of product

29b,respectively. Compound **29b** was isolated as reddish powder in good yields (70 %) by immediate solvent removal and washing with *n*-pentane. However, to get excellent NMR data, all NMR experiments were conducted at low temperature (−30 °C) in thf-d$_8$. The neg. ESI-MS experiment showed a peak at *m/z* 538.0453 (calc. 538.0451) which confirmed the composition of the product. The single crystal X-ray diffraction analysis confirmed the constitution; three solvent molecules were present in the unit cell. Within the 1D-coordination polymer each potassium cation is coordinated to the thione sulfur centers of two neighboring molecules and three Et$_2$O solvent molecules (Figure 8.7).

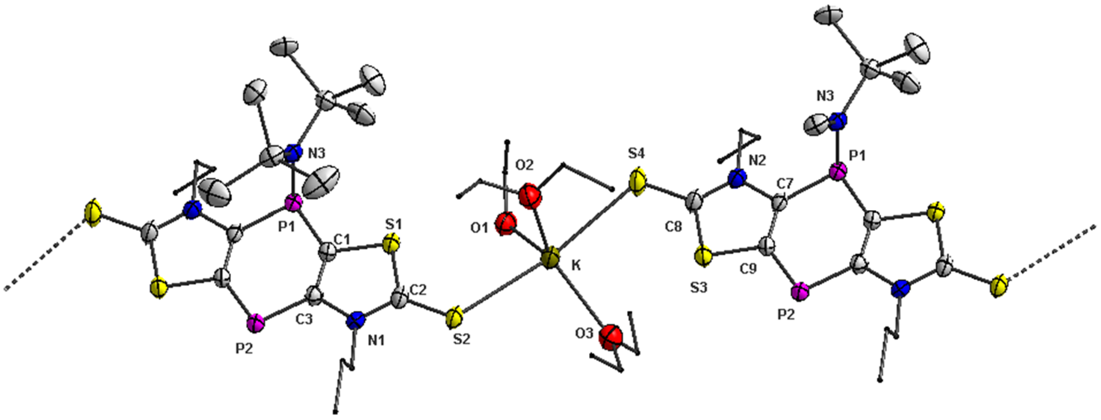


Figure 8.7. Displacement ellipsoids plot (50% probability) of a cut-out of the 1D-polymer structure of **29b** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.807(4), P1-C7 1.805(4), P2-C3 1.776(4), P2-C9 1.777(4), C1-C3, 1.376(6), C7-C9 1.373(6), P1-N3 1.744(4). C1-P1-C7 95.24(19), C3-P2-C9 96.6(9).

Having the isolated anionic compound **29b** in hand, its reactivity was investigated starting with the reaction of Ph$_2$PCl, representing a rather common main group element electrophile (Scheme 8.4). Upon addition of Ph$_2$PCl to a freshly prepared, pre-cooled Et$_2$O solution of **29b** immediate color change from red to yellow was observed. The ^{31}P{^{1}H} NMR spectrum showed an ABM spin habitus with three different $J_{P,P}$ couplings, *i.e.*, -50.8 ppm (dd, $^{1}J_{P,P}$ = 294.2 Hz, $^{4}J_{P,P}$ = 15.9 Hz), 9.5 ppm (dd, $^{1}J_{P,P}$ = 294.2 Hz, $^{3}J_{P,P}$ = 18.4 Hz), 15.0 ppm (t, $J_{P,P}$ = 17.1 Hz)}, revealing that the $^{3}J_{P,P}$ and $^{4}J_{P,P}$ coupling constant magnitudes are very similar. The product **30b** was isolated in good yields (65 %) after filtration and washing with *n*-pentane (2x3 mL).[127] The proposed composition of **30b** to have a newly formed P-P bond (cf. Scheme 5) was further supported by the experimentally found HRMS (APCI) value (723.1136) for [$C_{30}H_{42}N_3P_3S_4Si_2$]+H, which was in good agreement with the calculated one (723.1112). Single crystals were obtained via slow evaporation of its dichloromethane solution; the result of the X-ray analysis of **30b** (Figure 8.8) will be discussed together with that of **31.**

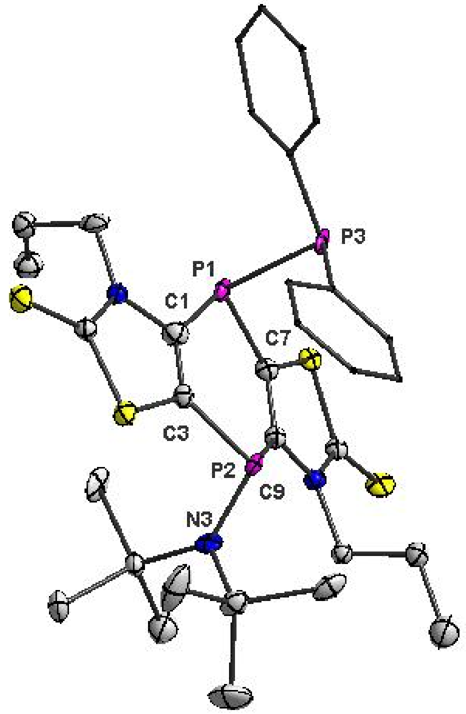
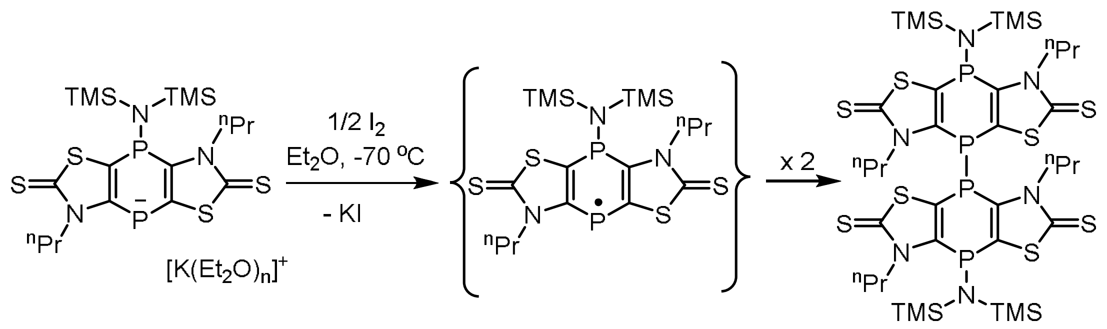


Figure 8.8. Displacement ellipsoids plot (50% probability) of molecular structure of **30b** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.81(2), P1-C7 1.813(19), P1-P3 2.246(6), P2-N3 1.691(16), P2-C3 1.856(19), P2-C9 1.845(19), C1-C3, 1.28(3). C1-P1-C7 96.6(8), C3-P2-C9 96.1(9), C1-P1-P3 106.6(7), P1-P3-C25 101.9(6).

8.3 Oxidation of the mono-anion 29b with elemental iodine

To examine the outcome of an oxidation of the anion **29b**, an etherial solution of **29b** was treated with half of an equivalent of iodine at low temperature (−70 °C). Again, an immediate color change from red to greenish yellow was observed (Scheme 8.6) suggesting the short-lived radical species. Calculation of the TD-DFT spectrum of the proposedradical species (Nyulaszi) resulted again in excitation energies (leading to absorptions in blue and red) which explains the observed (resulting) greenish color. The −63.5 kcal/mol dimerization Gibbs free energy of the radical speciesto give **31,31'** was also in good agreement with the observed short lifetime.[127]



Scheme 8.6. Oxidation reaction of the mono-anion **29b** with I_2 to afford **31,31'.**

The final product **31** was isolated by removing the solvent *in vacuo* (8 x10^{-3} mbar), dissolving the crude product in toluene and filtration to remove the formed KI (for more details see the experimental section). The $^{31}P\{^{1}H\}$ NMR spectrum of **31** showed two sets of signals for two isomers, one major (98 %) and one minor (2 %){−42.1 ppm (t, $^{3/4}J_{P,P}$= 20.1 Hz) −40.4 ppm (t, $^{3/4}J_{P,P}$ = 20.4 Hz), 17.9 ppm (t, $^{3/4}J_{P,P}$ = 20.2) 19.9 ppm (t, $^{3/4}J_{P,P}$ = 20.8)}.

Single crystal X-ray diffraction studies were performed for both **30b** (discussed in section 8.2) and **31**. The structures of **30b** and **31** are given in Figure 8.8 and 8.9, respectively, and selected bond lengths and bond angles are given in the respective figure captions.

Single crystal X-ray diffraction studies of **30b** and **31** show very similar P-C bond lengths in the central 1,4-dihydro-1,4-diphosphinine rings. However, a slightly longer P1-P3 bond distance of 2.2893(7) Å is found in **31**,compared to 2.246(6) Å in **30b**. As in case of **30b** only one isomer (*trans*) was observed which suggests a directional effect of the $N(SiMe_3)_2$ moiety onto the incoming group. Furthermore, one of the phenyl groups in **30b** is observed to have π–π interactions with the central 1,4-dihydro-1,4-diphosphinine ring on the same molecule. The molecular structure of **31** shows an orientation of the two tricyclic units with a torsion angle of 60.5° between the P1-P3-C1 and P1-P3-C19 planes. It seems that dispersive forces are responsible for the observed arrangement of substituents in **31'** (which is similar to that in **31**) since there was no sign of secondary orbital interactions in a second-order perturbation theory analysis made on the NBO basis. Indeed, optimization of a structure with the two tricycles in a *trans* arrangement results in a geometry which is ~12 kcal/mol higher in energy when using functionals that account for dispersion interactions (12.6 kcal/mol for M06-2X and 12.2 kcal/mol forωB97XD), whereas with the B3LYP functional (no dispersion correction), the energy of the two structures is nearly identical (ΔE = 0.2 kcal/mol; basis set used is 6-311+G**). For calculations of rotation about the P–P bond in the case of **30b'**, the energy difference using M06-2X is 2.5 kcal/mol, whereas with B3LYP it is 0.8 kcal/mol). Altogether, the dispersive forces operating between the planes of the two tricycles has a sizeable contribution to the energy of the adopted structure.[127]

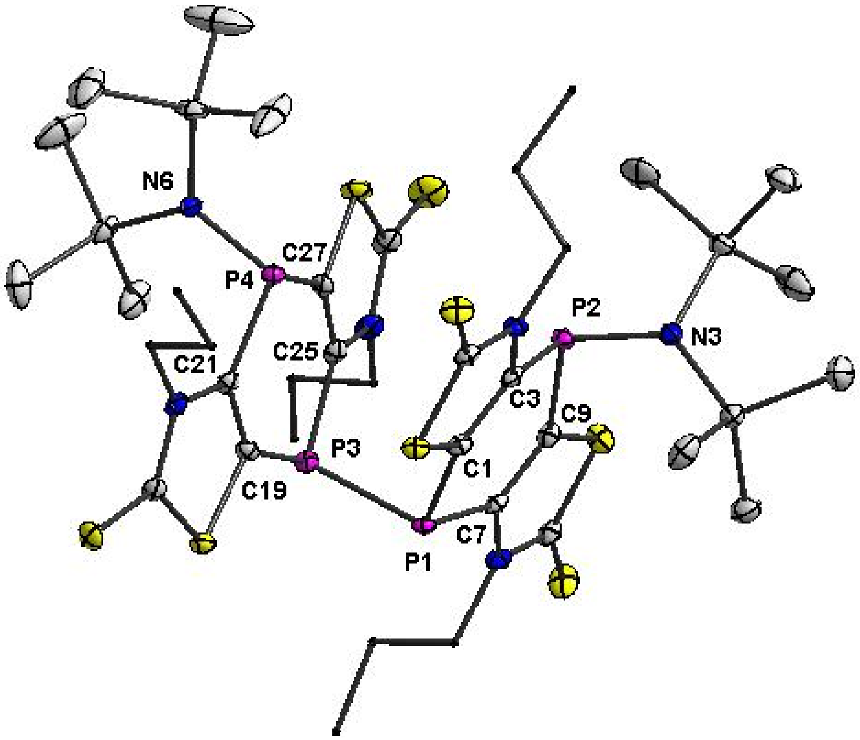
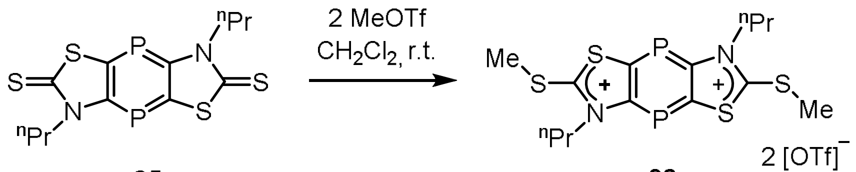


Figure 8.9. Displacement ellipsoids plot (50% probability) of molecular structure of **31** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.793(2), P1-C7 1.811(2), P1-P3 2.2893(7), P2-N3 1.7048(18), P2-C3 1.831(2), P2-C9 1824(2), C1-C3, 1.364(3). C1-P1-C7 99.43(9), C3-P2-C9 97.55(9), C1-P1-P3 101.64(7), P1-P3-C25 105.88(7).

8.4 Reaction of 1,4-diphosphinine 25 with MeOTf

Theoretical investigations suggested that the HOMO of compound **25** is relatively high in energy (-6.19 eV) and represents the antibonding combination of the HOMOs of the two thiazole-2-thione fragments. The LUMO of compound **25** was found to be low lying (-3.19 eV) and largely stabilized by the involvement of the π*P=C orbitals {Chapter 7, Figure 8 (comparative orbital energy manifolds for **25'** and **XCII'**)}. The theoretically suggested electrophilic nature of the P-center of the 1,4-diphosphinine was also experimentally confirmed (see section 8.2). However, equally interesting would be to experimentally proove the nucleophilic nature of the C=S unit of 1,4-diphosphinine through reaction with an electrophile such as MeOTf, as several examples of a similar reactivity were found for the hetazole-2-thione family *i.e.,* imidazole-2-thiones,[150] thiazole-2-thiones[151] and dithiole-2-thiones[124]. So, a dichloromethane solution of **25** wastreated with two equivalents of MeOTf at room temperature (Scheme 8.7). After stirring for 16 h the red color of the reaction mixture got changed to yellow. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a signal at 163.0 ppm which was assigned to the salt **32**.The proton-coupled^{31}P NMR spectrum did not show a coupling which provided the first indication that S-methylation has occurred. Compound **32** was isolated as white powder in excellent yield (92 %) after removal of the solvent and washing with *n*-pentane (2x5 mL). In the ^1H NMR spectrum of **32** a signal corresponding to the S-Me protons was observed at 5.20 ppm. Besides, in the $^{13}C\{^1H\}$ NMR spectrum a resonance corresponding to the SMe carbon was observed at 20.0 ppm. The proposed chemical composition of the product was further supported by HRMS (pos. ESI) m/z 203.0000 (calc.*m/z*202.9999). Single crystals of **32** were obtained via slow evaporation of its dichloromethane solution at low temperature. Single crystal X-ray analysis finally confirmed the S-methylation. **32** crystallized in the monoclinic crystal system with space group $P2_1/c$. Molecular structure of **32** is given in Figure 8.10 and selected bond lengths and angles are given in figure caption. It was found to be an all planar structure having the ^{n}Pr and -SMe groups trans to eachother. The bond lengths and bond angles of **32** are comparable with those of **25,** the S2-C7 bond length of **32** is also comparable with that of the literature known 4,8-dihydro-1,4-diphosphinine-2,5-bis(imidazolium)trifluoromethane sulfo-nate [dS2-C7 = 1.8114(1)].[126]



25 **32**

Scheme 8.7. Reaction of **25** with MeOTf.

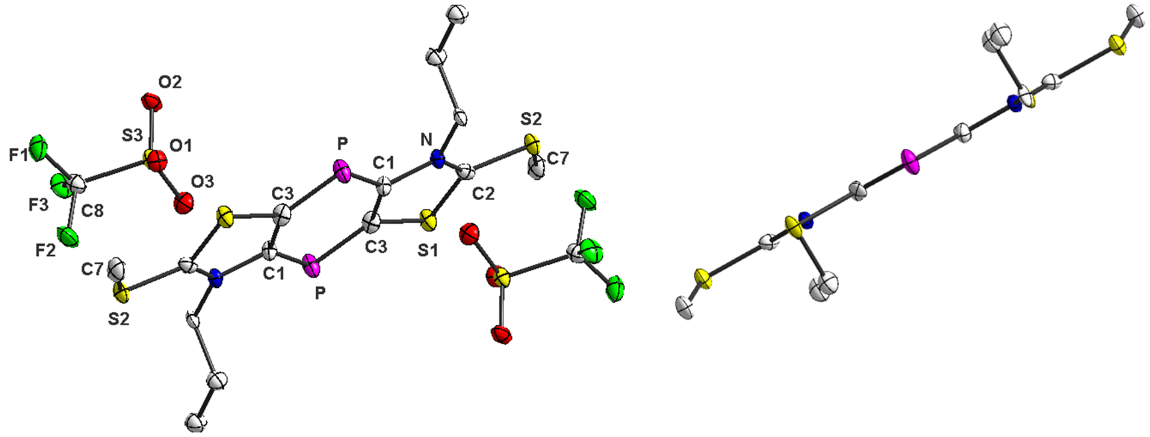
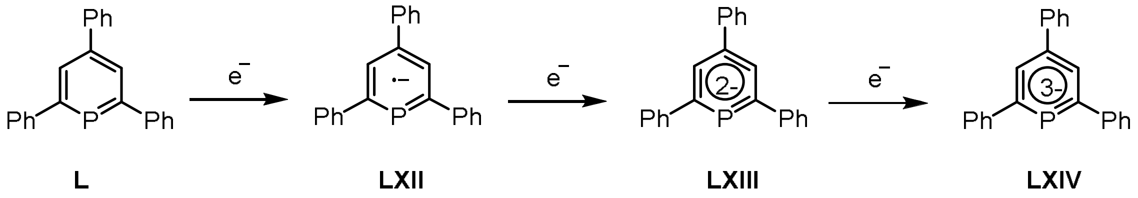


Figure 8.10. Displacement ellipsoids plot (50% probability) of molecular structure of **32** in the crystal (left: top-view, right_ in-plane-view without anions). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P-C1 1.757(5), P-C3 1.749(5), C1-C3 1.391(7), S2-C7 1.799(6), C1-P-C3 98.5(2).

8.5 Reduction of 1,4-diphosphinine 25

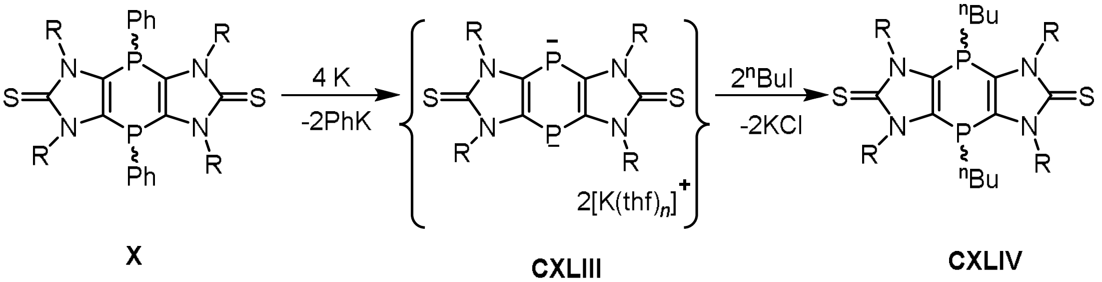
As discussed before in the introduction, the reduction of phosphinines has been well established and several examples of λ^3-phosphinines were found to be easily reducible by alkali metals to generate paramagnetic anion radicals and diamagnetic dianions.[59a-c]Dimroth and co-workers reported that reduction of 2,4,6-triphenylphosphinine with potassium metal in THF generates even paramagnetic trianion radicals, however the ESR spectrum of that was not resolved.[59a] Later on, Märkl extended the investigations via combined CV and ESR studies of stepwise reduction of **L** (Scheme 8.8).[61]It has been demonstrated that in **LXII** the singly occupied orbital is symmetric with respect to the vertical mirrorplane passing through the phosphorus atom. **LXII** possess the large positive ^{31}P coupling constant (+3.31 mT), giving rise to a noticeable hyperfne anisotropy and thereby it was regarded to be a P-centered radical with $g = 2.00456 \pm 0.00005$.[61]

Märkl characterized **LXIV** by virtue of ^{31}P and proton hyperfine coupling data.The ENDOR (Electron nuclear double resonance) experiment showed,in contrast to **LXII**, that the orbital of **LXIV**being occupied by a single electron has a vertical nodal plane through the P-atom, and this and the small and negative ^{31}P coupling value (−0.267 mT) suggested a hydrocarbon-centered radical with a $g$value of 2.0027.[61]



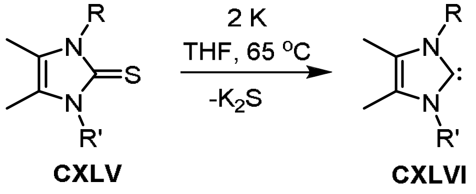
Scheme 8.8. Reduction of a phosphinine according to Märkl.[61]

However, none of such studies have been conducted for 1,4-diphosphinines successfully, so far; earlier attempts by Streubel and co-workers of twofold reductive cleavage of P-C bonds of 1,4-dihydro-1,4-diphosphinine (**X**) havehad some success to generate (*in situ*) the tricyclic *bis*-phosphanide (**CXLIII**). However, it was not stable enough to be isolated (under these conditions) and, hence, was reacted with an electrophile (^{n}BuI); the final product (**CXLIV**) was isolated and characterized (Scheme8.9).[14c]



Scheme 8.9. Reductive cleavage of P-C bonds to generate *in situ* tricyclic bis-phosphanide and its follow-up reaction with ^{n}BuI.[14c]

On the other hand reduction of thiones with potassium metal to generate carbenes (**CXLVI**) has been well established by Kuhn and co-workers for imidazole-2-thiones (Scheme 8.10).[152]

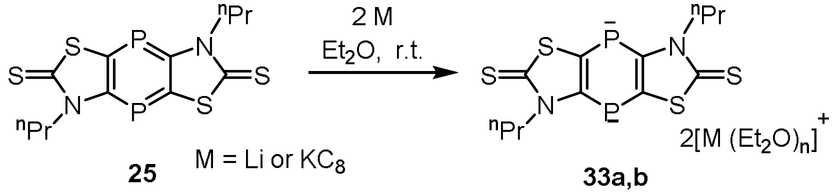


Scheme 8.10. Reduction of thiones to generate imidazole-2-ylidines accoring to Kuhn (R,R' = alkyl groups).[152]

Therefore, the thiazole-2-thione based 1,4-diphosphinine **25** represent a potential system that might undergo two-or even six-fold reduction processes, thus opening access to a dianionic and/or dianionic bis-carbenes, respectively. Both of which could open new areas of research.

8.5.1 Two-fold reduction of 1,4-diphosphinine 25

In order to study the reduction, an ether suspension of **25**was first treated with two equivalents of Li in diethyl ether. The mixture was stirred at ambient temperature for three days (Scheme 8.11). During this time the red colored suspension of the reaction mixture changed to form a dark blackish redprecipitate and a yellow solution. The precipitateshowed no solubility in Et_2O, so it was filtered and dissolved in THF. The $^{31}P\{^1H\}$ NMR spectrum of this solution showed two major broad signals at −40.0 and −36.0 ppm which were tentatively assigned to the dianion **33a**, constituting 96% of the reaction mixture according to NMR integration; the rest could not be identified. However, the proposed dianion **33a** was found to be not stable as decomposition always occurred during theNMR experiments, thus precluding further characterization of the product.



25 **33a,b**

Scheme 8.11. Two-fold reduction of 1,4-diphosphinine **25**.

In an attempt to optimize the reaction and/or getting to a more stable product, KC_8 was used as reducing agent in ether (Scheme 8.11). Initially two equivalents of KC_8 were used which resulted in a fast reaction and generated dark reddish-black precipitate. Upon dissolution of the precipitate in THF, the $^{31}P\{^1H\}$ NMR monitoring revealed a faster reaction which was more selective compared to Li. The formed dianionic salt **33b** was stable enough to be characterized via NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum in THF-d_8 solution showed two broad signals at −40.7 and−43.7 ppm which were tentatively assigned to the dianionic compound **33b** being quite comparable with the imidazole-derived *in situ* prepared bis-phoaphanide **CXLIV**($\delta^{31}P$ = −73.6) [14c](Figure 8.11). The appearance of two broad signals, rather than just one, can be explained with different (potential) coordination sides of the dianion and additional interactions of the counter cation with the solvent molecules acting here as ligands. **33b**was isolated in good yield (70 %) by filtration of its THF solution to remove the graphite and then subsequent drying *in-vacuo* ($8x10^{-3}$). It is noteworthy to mention that selective reaction was only obtained in the absence of other potentially strong coordinating ligands, for example crown ethers or cryptands. This has been shown by the use of such ligands under otherwise constant conditions which led only to unselective reactions.

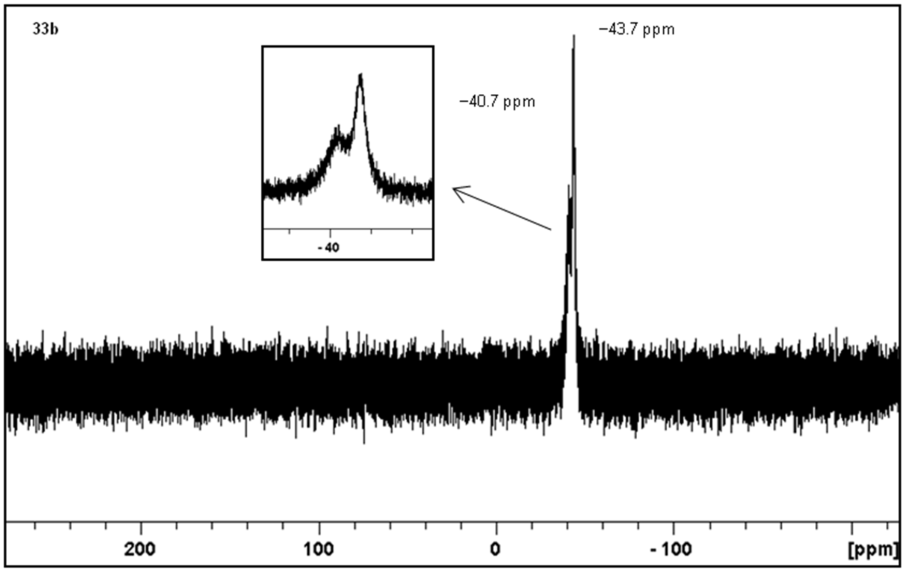


Figure 8.11. The $^{31}P\{^{1}H\}$ NMR spectrum of **33b** in thf-d_8.

The ^{1}H NMR spectrum of **33b** (thf-d_8) showed signals which were assigned to the protons of ^{n}Pr groups: $\delta = 0.92$ (br, 6H, $CH_2CH_2CH_3$), 1.76 (br, 4H, $CH_2CH_2CH_3$), 4.11 (br, 2H, CH_2-CH_2-CH_3). In the $^{13}C\{^{1}H\}$ NMR spectrum all signals could be assigned to all carbon atoms of the proposed product: $\delta = 11.7$ (s, $CH_2CH_2CH_3$), 21.5 (s, $CH_2CH_2CH_3$), 50.5 (s, br, $CH_2CH_2CH_3$), 122.2 (br, $^{4/5}$), 143.6 (br, $^{4/5}$), 185.2 (br, C=S), 186.2 (br, C=S). Furthermore, the MS spectrum (neg. ESI) showed a peak at 376.9670 which was not close to the expected m/z value of 187.9763. But it was more in agreement with the calculated m/z value of the mono anion $[C_{12}H_{14}N_2P_2S_4S)H]^{-}$ (376.9599). This points to a protonation under the conditions of the ESI-MS measurement.

Compound **33b** crystallized by cooling a concentrated THF solution at −35 °C. The single crystal X-ray diffraction analysis was conducted (Figure 8.12) which confirmed the proposed constitution of this interesting low-coordinate phosphorus containing molecule which is the first example of its kind. **33b** crystallized in monoclinic crystal system with space group $P2_1/c$. Four molecules were found to be present in the unit cell having one potassium cation

(K1) coordinated to the thione sulfur atoms of fourmolecules and one THF molecule. While the other potassium cation (K2) is coordinated with the thione sulfur atoms of two molecules, together with three THF molecules.Furthermore, the two potassium cations had alinkagewith K1-K2 distance of 4.4004(4) Å. Upon comparison of the bond lengths and bond angles of **33b** with the mono anionic compound **29b**, it was concluded that the bond lengths and bond angles are quite similar except the P-C bond, which are somewhat longer in **29b** [P1-C1 1.807(4), P1-C7 1.805(4), P2-C3 1.776(4), P2-C9 1.777(4)than those of **33b** P1-C1 1.786(8), P1-C9 1.768(8), P2-C3 1.778(8), P2-C7 1.771(9).Likewise, the K-S23.2492(16) and K-S43.2715(17) distances in **29b** are also slightly shorter than those in **33b** [K1-S4 3.191(3), K1-S6 3.194(4), K1-S10 3.164(4), K1-S14 3.113(3)].

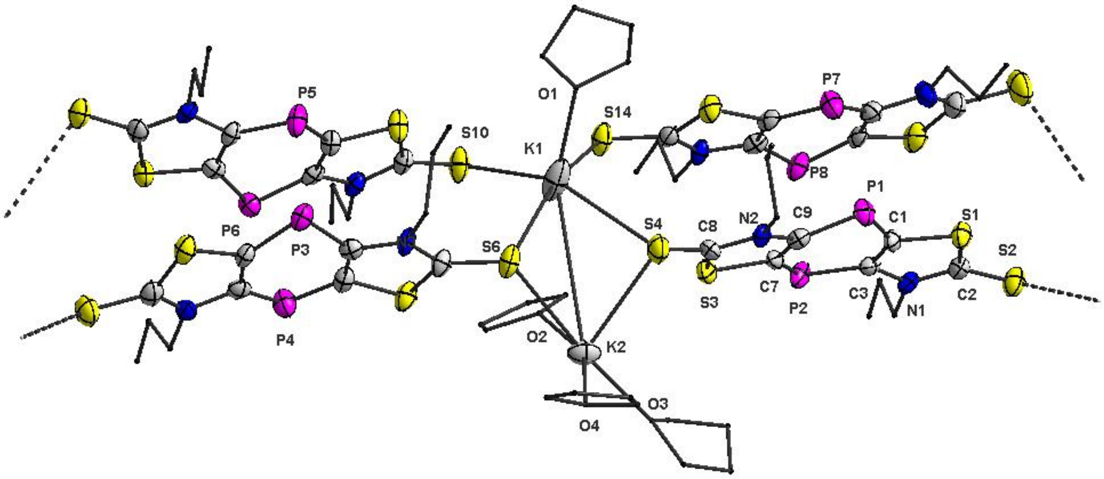
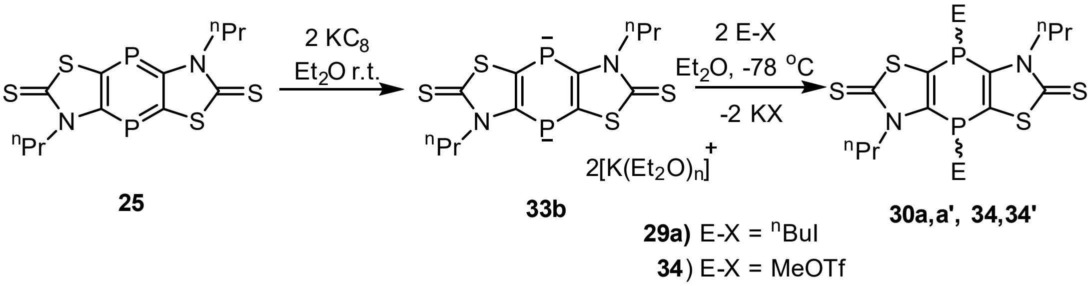


Figure 8.12. Displacement ellipsoids plot (50% probability) of molecular structure of **33b** in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.786(8), P1-C9 1.768(8), P2-C3 1.778(8), P2-C7 1.771(9), C1-C3 1.371(11), C7-C9 1.380(11). C1-P1-C9 96.8(4), C3-P2-C7 97.0(4).

In order to get chemical support for the two-fold reduction of **25**, 2 eq. of^{n}BuI (or MeOTf) were added to the ether suspension of freshly prepared **33b**at -78 °C,. This led to an immediate dissolution of the dark precipitate and a light yellow colored reaction solution was formed. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture with ^{n}BuI (Figure 8.13) showed resonances at −44.0 and −38.4 pm which were easy to assign to the *cis* and *trans* isomers of **30a,a'**of this compound. This was independently synthesized using another route: the sequential reaction of 1,4-diphosphinine **25** with ^{n}BuLi and ^{n}BuI (see section 8.2). **30a,a'**was completely characterized via various means (NMR, MS, IR and EA and single crystal X-ray diffraction). A similar reactivity was recently reported of an *in situ* prepared bis-phosphanide by Streubel and co-workers (Figure 8.9), and the ^{31}P NMR resonances of **30a,a'** (δ^{31}P =−44.0

& −38.4) are comparable to the follow-up product, *i.e.*, 1,4-dihydro-1,4-diphosphinine ($\delta^{31}P$ = –58.5 & –66.3).[14c]In case of MeOTf also a very selective reaction was observed, the ^{31}P NMR spectrum of the reaction mixture showed the formation of two isomers having resonances at δ = −50.2 ppm (s) 16 % and −54.2 ppm (s *2nd isomer*) 84 %, assigned to the *cis/trans* isomers of **34**. Compound **34,34'** was isolated by *in vacuo* solvent removal yielding crude product, which was redissolved in toluene and filtered to remove the formed KOTf. **34,34'** was isolated in excellent yield (88 %) and characterized via NMR, MS and elemental analysis.



Scheme 8.12. Synthesis of the dianion**33b** and subsequent reaction with ^{n}BuI and MeOTf.

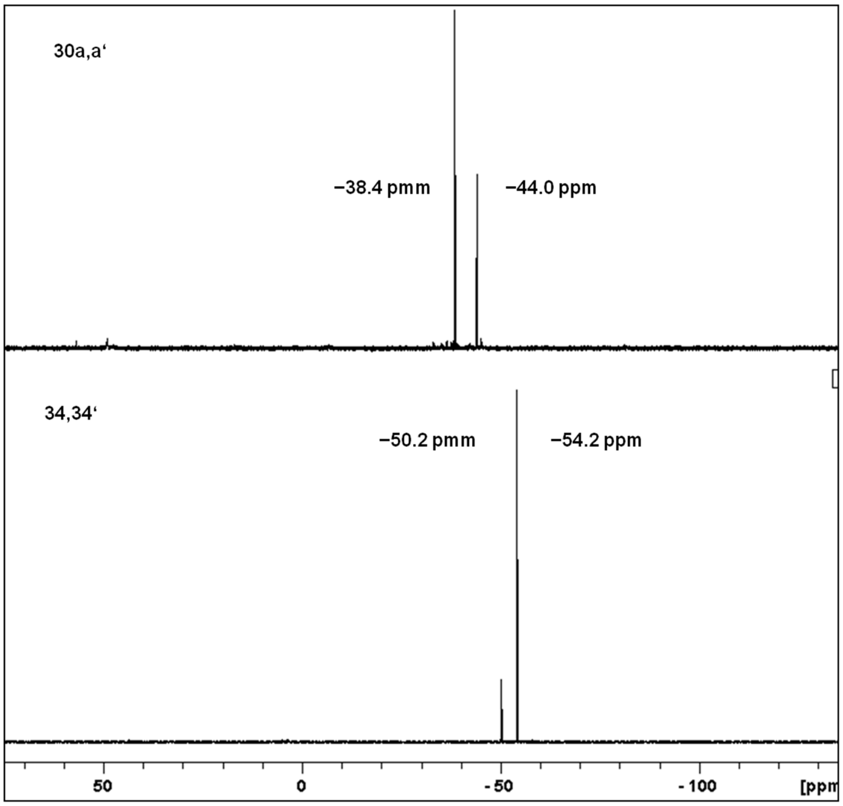


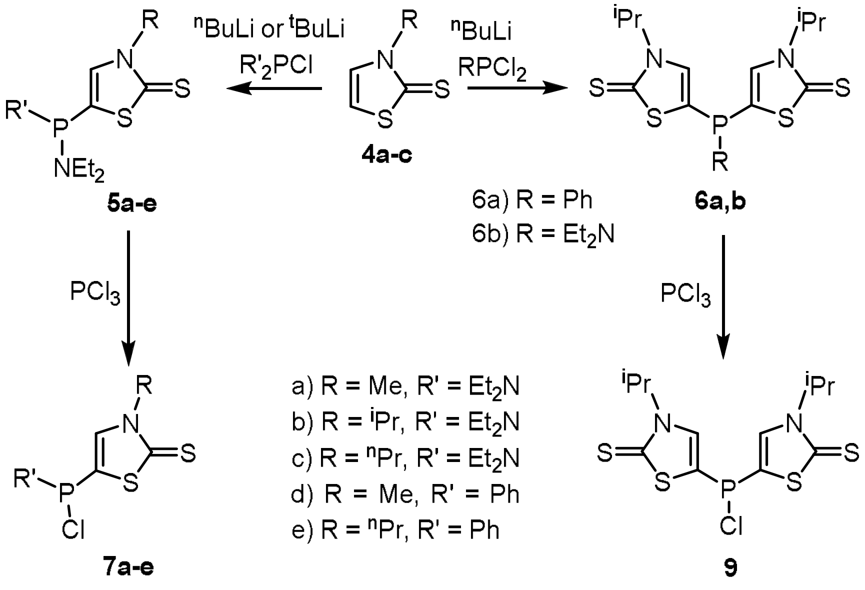
Figure 8.13. The $^{31}P\{^{1}H\}$NMR spectrum (THF) of the reaction e of dianion **33b** with ^{n}BuI (upper) and MeOTf (lower).

Chapter 9

Chapter 9: Summary

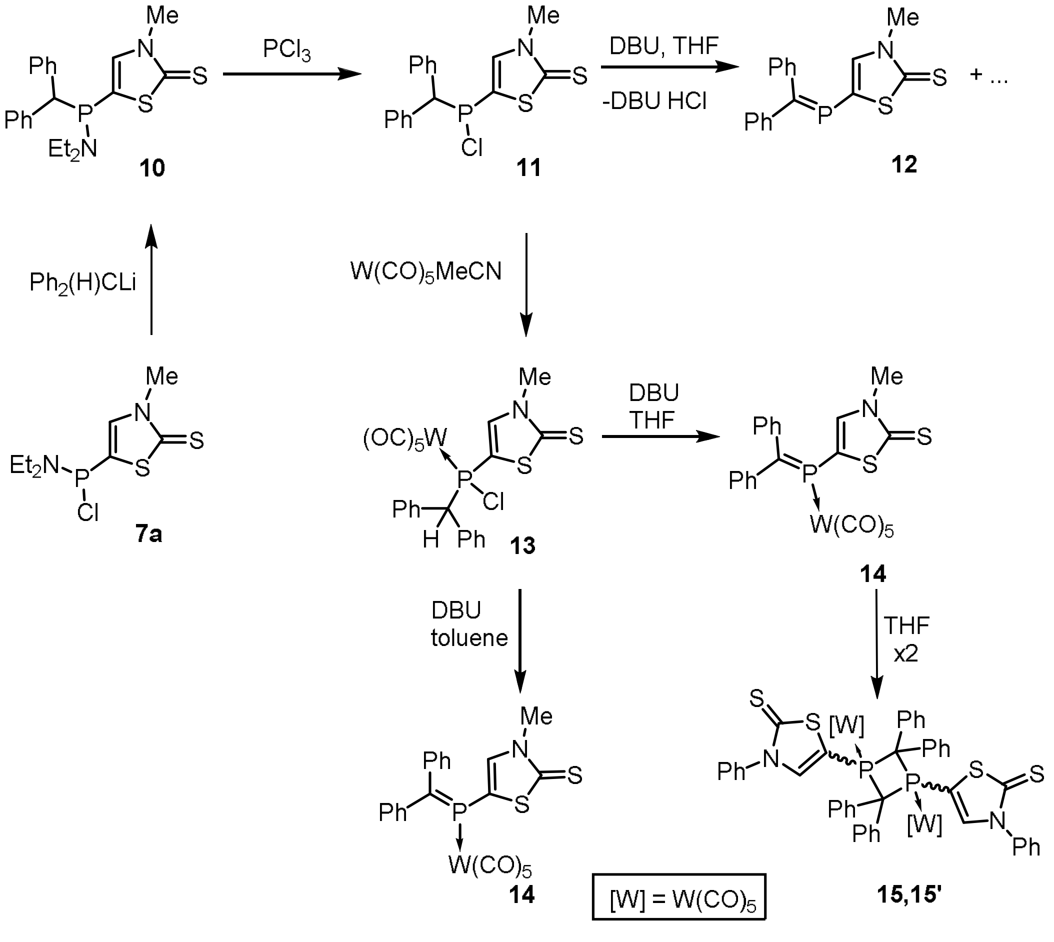
This PhD Thesis describes multigram syntheses of the first examples of C^5-phosphanylated thiazole-2-thiones including P-functional derivatives. It further details synthesis and reactions of thiazole-derived phosphaalkene and its tungsten(0) complex, 1,4-dihydro-1,4-diphosphinines and their conversion into 1,4-diphosphinines; initial reactivity studies on the latter were performed, too. First examples of two-fold reduction of a 1,4-diphosphinine leading to a novel, isolable 1,4-dianionic species.All of the new compounds were fully characterized by spectroscopic means including X-ray diffraction studies in most cases.

In chapter 3 a detailed protocol for the synthesis of C^5-phosphanylated thiazole-2-thiones possessing various N- and P-substituents is presented. The key steps are (i) backbone lithiation of the heterocycle, (ii) *in situ* reactions with chloro(diorgano)phosphanes to afford **5a-e,** (iii) and *in situ* reactions with dichloro(organo)phosphanes to give **6a,b** (Scheme 9.1). Subsequent scrambling reaction of **5a-e** and **6b** with PCl_3 furnished the corresponding chlorophosphanes **7a-e** and **9,** respectively.



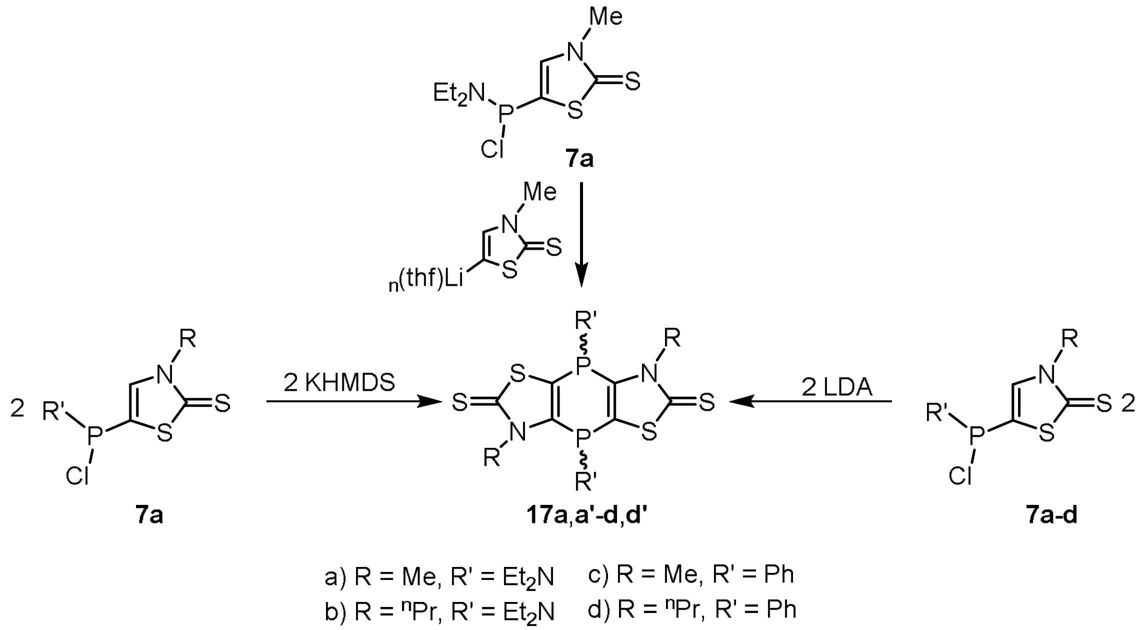
Scheme 9.1. Synthesis of the *C*-phosphanylated thiazole-2-thiones **5**, **6** and their conversion to *P*-chloro derivatives **7** and **9**.

Chapter 4 describes the use of the C^5-chlorophosphanyl-thiazole-2-thione **7a** into suitable precursors of a *P*-thiazolyl-phosphaalkene, including the *P*-diphenylmethyl-substituted compound **10**, followed by the introduction of the P-Cl functionality (**11**) and its dehydrohalogenation reaction with DBU to generate phosphaalkene **12** which suffered from decomposition (Scheme 9.2). To enhance the stability of the phosphaalkene, *end*-on pentacarbonyltungsten(0) complexation of **11** was performed andafforded **13** (Scheme 9.3). The subsequent dehydrohalogenation of using DBU in toluene furnished the phosphaalkene tungsten(0) complex **14,** while a solvent-dependent dimerization afforded the dinuclear complex of 1,3-diphosphetane **15,15'** which was further studied by DFT calculations.The comparison of the relative energies suggested that the Gibbs free energies are very similar for both regioisomeric species having a*trans* conformation. Same was true for thedimer formation energy for both solvents: −23.5 kcal/mol in CH_2Cl_2 and −23.9 kcal/mol in THF, thus, leading to the conclusion that the stability of reactants/products could not be differentiated via DFT analysis using the standard solvation methods.



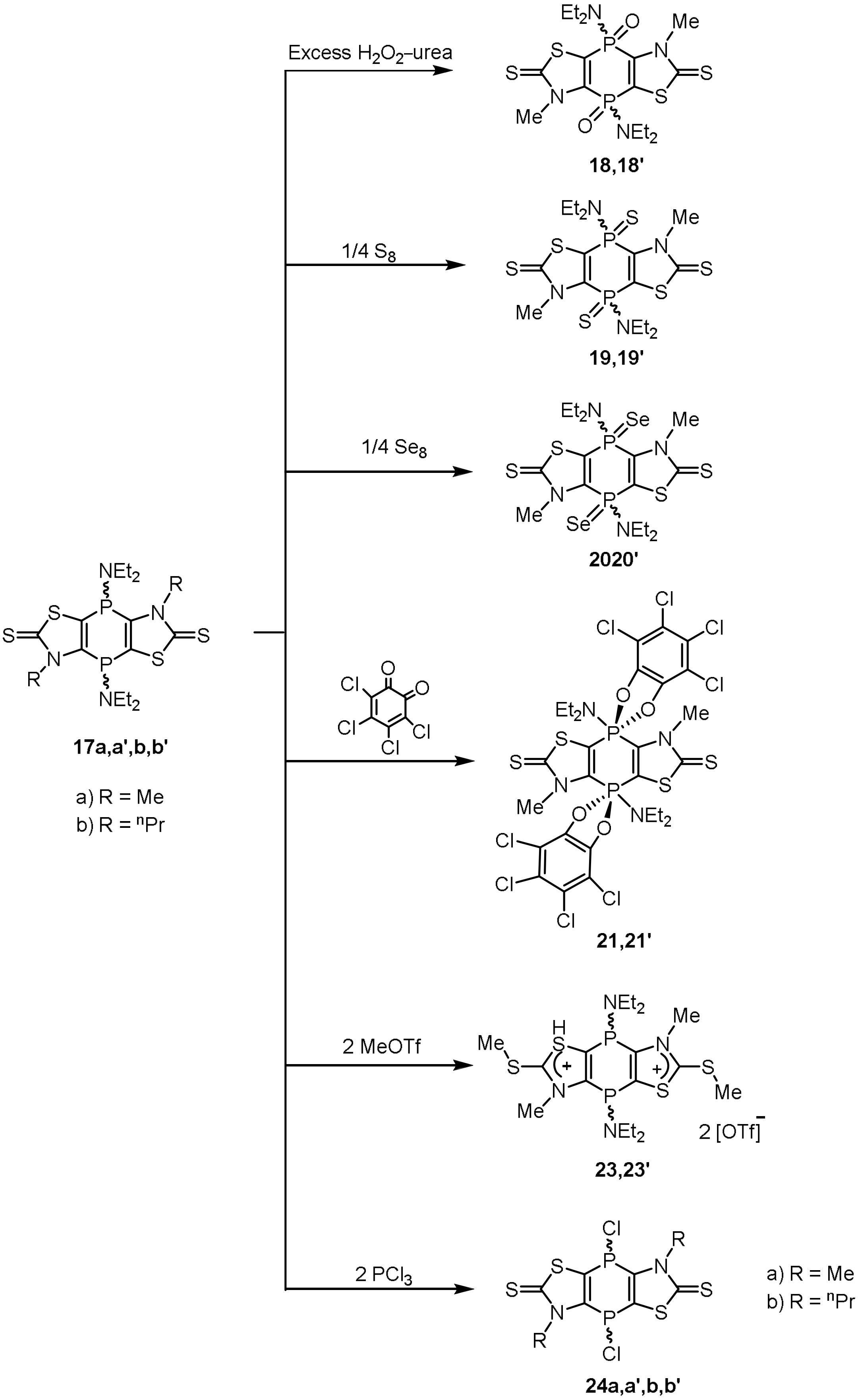
Scheme 9.2. Synthesisof phosphaalkene complex **14** and itsdimer **15**.

Chapter 5 describes the synthesis of the first thiazole-2-thione-based tricyclic 1,4-dihydro-1,4-diphosphinines employing **7a** as starting material. Different conditions and bases were tested resulting, finally, in a high-yield synthetic protocol of **17a** using LDA as base. This was then expanded to other derivatives with different N- and P-substituents to access derivatives**17b-d**(Scheme 9.3).



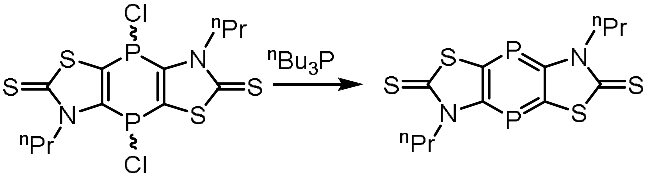
Scheme 9.3. Synthesis of tricyclic 1,4-dihydro-1,4-diphosphinines **17**.

Chapter 6 describes the reactivity studies on the tricyclic 1,4-dihydro-1,4-diphosphinines **17**. In particular, oxidation reaction with H_2O_2-urea, elemental sulfur and selenium resulted in the corresponding P(V),P'(V) dioxide (**18,18'**), disulfide (**19,19'**) and diselenide (**20,20'**) derivatives, respectively. Reaction of **17** with *O*-chloranil resulted in the formation of spirocyclic derivatives **21,21'** in high yields. Reactions of **17** with a hard electrophile resulted in the formation of bis-thiazolium salts **23,23'** via preferred *S*-methylation (Scheme 9.4). In order to achieve further P-functionalization the *P*-NEt$_2$ derivatives **17a,a',b,b'** were reacted with PCl_3 thus giving 1,4-dichloro-1,4-diphosphinines **24a,a',b,b'**.


17a,a',b,b'
a) R = Me
b) R = ⁿPr
Excess H2O2–urea
18,18'
1/4 S8
19,19'
1/4 Se8
2020'
21,21'
2 MeOTf
2 [OTf]⁻
23,23'
2 PCl3
24a,a',b,b'
a) R = Me
b) R = ⁿPr

Scheme 9.4. Reactions of 1,4-dihydo-1,4-diphosphinine **17.**

Chapter 7 describes the reduction of 1,4-dichloro-1,4-diphosphinine **24b** using $^{n}Bu_3P$ as mild reducing agent leading to the novel thiazole-derived tricyclic aromatic 1,4-diphosphinine **25** in high yield (Scheme 9.5). The compound possesses anall-planar tricyclic structure with negative NICS(1) values [NICS(1) = −8.8 (diphosphinine ring) (NICS(1) = −4.9 (outer rings)] indicating aromaticity in all rings.

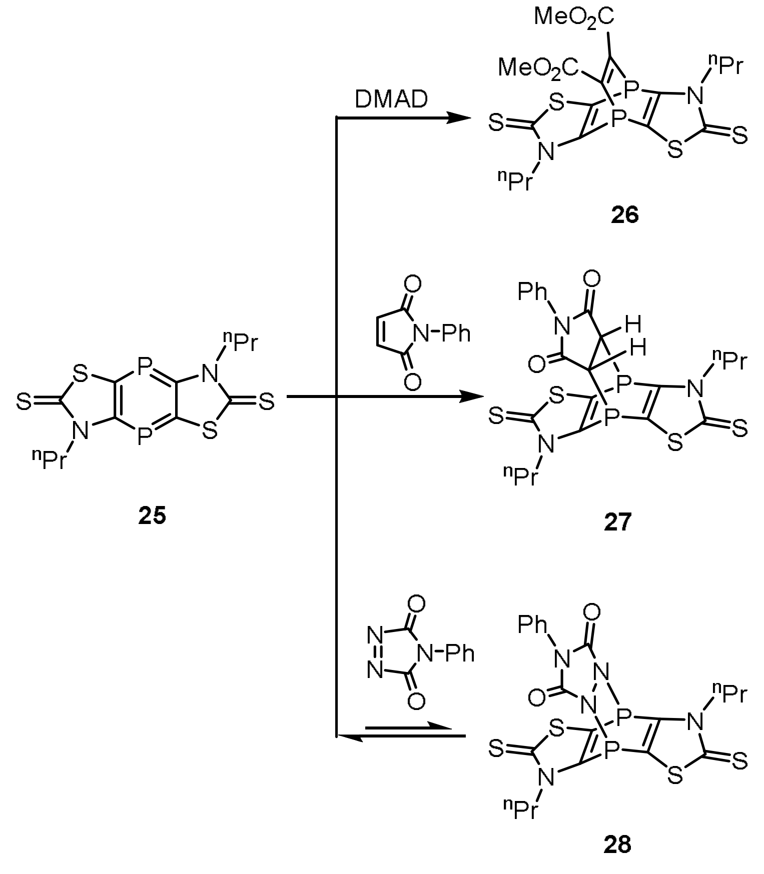


24b,b' **25**

Scheme 9.5. Synthesis of 1,4-diphosphinine **25**.

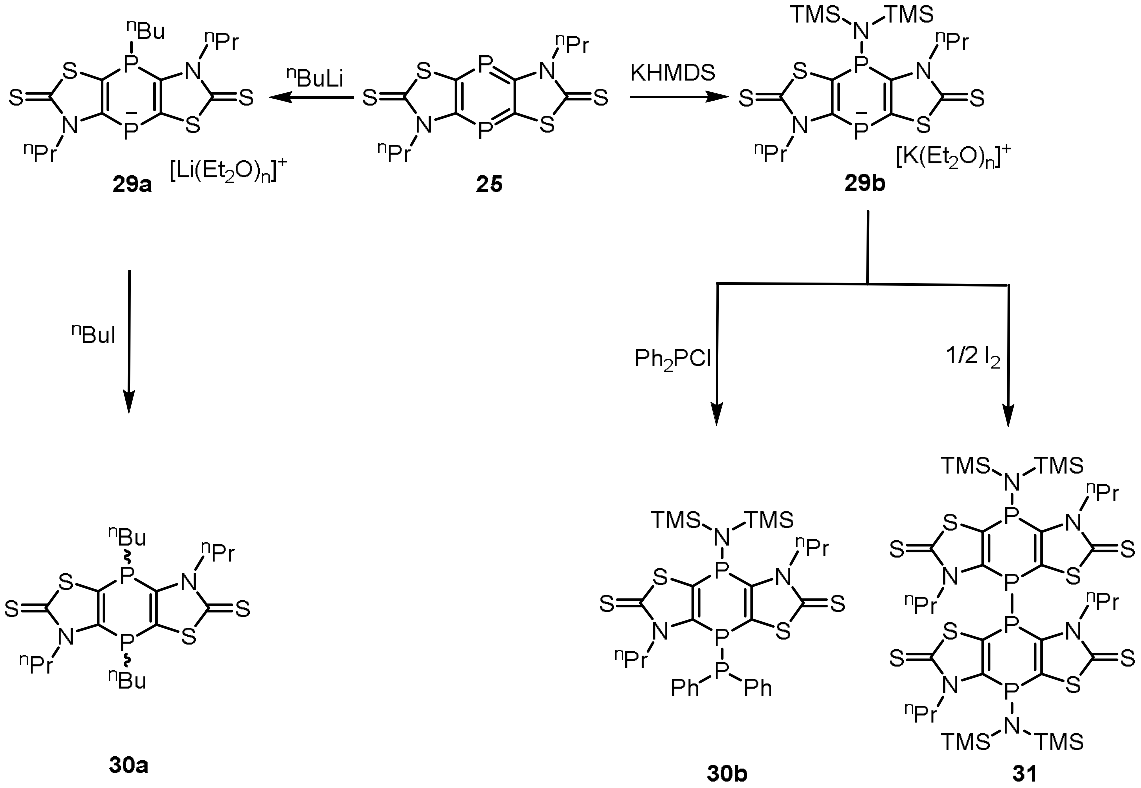
The intense red color of **25**, determined via UV/vis spectra showing an absorption at λ_{max} 497 nm, was analyzed by TD-DFT calculations, thus enabling attribution to a π-π* excitation; the latter is in accordance with the calculated HOMO-LUMO gap (2.99 eV). Cyclo voltammetric studieson **25** showed two reversible reduction process at E = −1.28 and −1.45 V vs the ferrocene/ferrocenium redox couple.

Chapter 8 describes reactions of 1,4-diphosphinine **25** including [4+2] cycloadditions with electron deficient dienophiles such as DMAD and *N*-phenyl maleimide to yield selectively **26** and **27**, respectively (Scheme 9.6). However, the reaction of **25** with 4-phenyl-1,2,4-triazoline-3,5-dione to give **28**was reversible under given conditions; at a temperature of 60 °C the ratio of 25:28 was determined (95:5) via $^{31}P\{1H\}$ NMR signal integration.



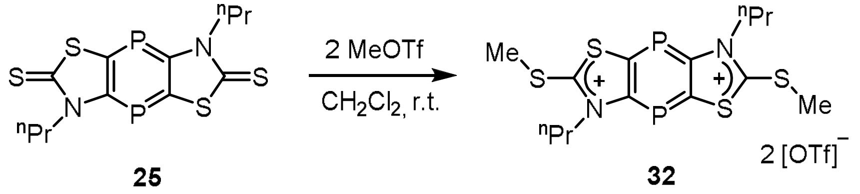
Scheme 9.6. Synthesis of 1,4-diphosphinine **25** and some [4+2]-cycloaddition reactions.

Furthermore, fundamental reactions of the 1,4-diphosphinine **25** with nucleophiles followed by addition of electrophiles are detailed. In particular, reactivity towards nucleophiles (^{n}BuLi and KHMDS) was investigated, and even a week nucleophile such as KHMDS was found to react selectively via addition to the P-center (Scheme 9.7). In both cases, selective formation of the corresponding novel mono-anions **29a,b** were achieved.Whereas **29a** could be generated only and *in situ* reacted with ^{n}BuI to afford **30a.** In contrast, **29b** was isolated and fully characterized including X-ray diffraction wrevealing a 1D-coordination polymer structure with K-S linkages in the solid state. **29b** reacted selectively with Ph_2PCl to give the substitution product **30b**. Even more interesting was the oxidation of **29b**with a half equivalent of I_2 selectively affording the P-P coupled product **31**.



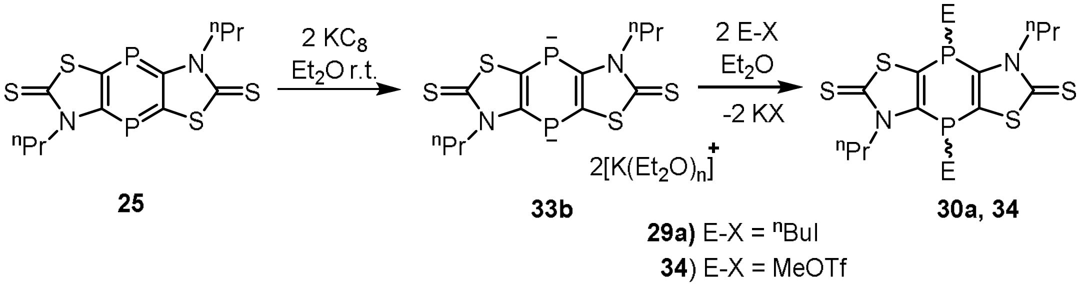
Scheme 9.7. Sequential addition of nucleophiles/electrophiles to 1,4-diphosphinine **25** to give **30a,b** and its oxidation with I_2 to give **31**.

Furthermore, initial efforts towards the synthesis of bis-carbenes were undertaken. Firstly and based on the theoretically proposed frontier orbital situation, the nucleophilicity of the S-centers of 1,4-diphosphinine **25** was experimentally examined using areaction with the hard electrophile MeOTf. This resulted in a selective formation of the corresponding doubly *S*-methylated bis-thiazolium salt **32** possessing an unaffected tricyclic 1,4-diphosphinine unit which was fully characterized and structurally confirmed by X-ray diffraction analysis (Scheme 9.8).



Scheme 9.8. Reaction of **25** with 2 eq. of MeOTf to give **32**.

Of particular importance was the outcome of reduction studies of 1,4-diphosphinine **25.** With two equivalents of potassium graphite in diethyl ether the corresponding dianionic compound **33b**was obtained selectively which was characterized via NMR spectroscopy and firmly established via single crystal X-ray diffraction analysis. Further derivatization using 2 eq. of ^{n}BuI or MeOTf as electrophiles yielded**30a**and **34**,respectively (Scheme 9.9).



Scheme 9.9. Reduction of 1,4-diphosphinine **25** with KC$_8$ to give **33b** and its follow-up reactions with ^{n}BuI and MeOTf.

Chapter 10

Chapter 10: Experimental section

10.1 General

All reactions were performed using standard Schlenk techniques under dried (using molecular sieve and phosphorus pentoxide) and deoxygenated (using preheated BTS catalyst at 100-130 °C) Argon gas environment. All air and/or moister-sensitive chemicals were stored in either Schlenk flasks or handled in the glovebox. All the solvents used in reactions were dried; Tetrahydrofuran, diethyl ether and *n*-pentane were dried over sodium wire/benzophenon. Dichloromethane was dried over calcium hydride and further purification was done by distillation and stored in brown glass bottles having Schlenk connections. All glass wares used were dried by heating in the oven prior to use. Schlenk flasks or tubes were prepared before use, by heating under high vacuo and subsequently refilling with Argon gas. OKS grease type 1112 was used for lubrication of all glass joints. The high temperature reactions were done with an oil bath whereas the low temperature ones were performed using a liquid nitrogen/ethanol bath. For the purpose of removing salts formed in the reaction mixture common G3 frits having two Schlenk joints were used, along with either silica gel (Merck 60-200) or Celite. For transferring solvents or filtering, stainless steel double needle or filter cannula were used, which were preheated and dried in the oven at 75 °C. Whatman filter papers or glass microfiber filter papers were used for filtration purposes. All the used glass wares were soaked overnight in a KOH-isopropanol bath having some NaOCl (for oxidizing the metal impurities) and then dipped into a HCl-water bath for the sake of neutralization prior to washing with soap water. Then the cleaned glass wares were rinsed with deionized water and acetone simultaneously before drying at 120 °C in the oven overnight.

10.2 Melting point determination

A Büchi 535 Type S melting point apparatus was used for melting points (or decomposition temperatures) determination, where the sample were placed inside a both sided closed glass capillary tubes; the values are not corrected.

10.3 Elemental analysis

All the elemental analyses were performed with an Elementar Vario Micro elemental analyser by the micro analysis section of the Chemical Institute of the University of Bonn. The given values are the mean of at least three values.

10.4 NMR spectroscopy

Bruker Avance DMX-300, DPX-300, DPX-400 or DMX-500 spectrometers were used to record all the NMR spectra. Dried ($CDCl_3$, CD_2Cl_2, THF-d_8 or C_6D_6) using literature procedures were used for the multinuclear NMR characterizations and the chemical resonances are given relative to Tetramethylsilane (^1H, ^{13}C, ^{29}Si NMR), 1M LiCl in D_2O (^7Li NMR), 15 % $BF_3{\cdot}OEt_2$ in $CDCl_3$ (^{11}B NMR), $CFCl_3$ (^{19}F NMR) or 85% H_3PO^4 (^{31}P NMR), respectively. The following abbreviations were used for expression of the multiplicities of the resonance signals: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet and br = broad signal. The chemical shifts are expressed in parts per million, ppm. Coupling constants are abbreviated as $^nJ_{X,Y}$ whereas X and Y express the coupling nuclei (In decending order of atomic number, n denote the number of bonds that separate X and Y). Generally the measurements were performed at 298K unless some specific temperature is given. For the assignment of ^1H NMR and ^{13}C NMR signals, HMQC, HMBC and DEPT experiments were used.

10.5 Mass spectrometry

Electron ionization mass spectra were recorded on a 95 XL Finnigan using EI (70 eV). ESI mass spectra were recorded on a Bruker Daltonik micrOTOF-Q. LIFDI mass spectra were recorded on a Thermo Finnigan MAT 90 sector instrument equipped with a LIFDI ion source (Linden CMS).

10.6 UV/vis spectroscopy

A Shimadzu UV-1650PC spectrometer (λ = 190-900 nm) was used to obtain UV/vis spectra using dichloromethane/THF as the solvent and quartz glass cells (Hellma) of optical path 1cm at ambient temperature.

10.7 Infrared spectroscopy

IR-spectra were recorded on a Thermo IR spectrometer with an attenuated total reflection (ATR) attachment or on a Bruker Alpha Diamond ATR FTIR spectrometer at room temperature. Following are the abbreviations used for expression of the intensities of the absorption bands:

vs = very strong, s = strong, m = medium, w = weak.

10.8 Cyclic voltammetry

Cyclic voltammograms (CVs) were measured under rigorous exclusion of the atmosphere by working in an argon-filled glove box. CVs measured at Au and Pt electrodes "screen printed" onto patterned ceramic plates were very similar and the analysis is here reported in detail only for results at the Pt-surfaced electrodes. The starting potential of -0.690 V (versus $Fc^{+/0}$; all potentials are quoted on this scale) was determined from an open circuit potential (o.c.p.) experiment. Electrochemical samples were recorded with scan rates of 10–500 mVs_{-1} at r.t. under Ar atmosphere. Ferrocene was used as internal/external reference to determine the potentials. Sample solutions (THF) were 2 mM in analyte and 0.2 M in *n*-Bu_4NPF_6 as the supporting electrolyte

10.9 Single crystal X-ray diffraction studies

Single crystal were grown mostly by slow evaporation of saturated solutions of the compounds at -35°C or bydiffusion of non polar solvent into the sample solution. Once grown the single crystalas were separated from thesupernatantsolution and were covered with Fomblin to avoid decomposition.A suitable single crystal was selected under the microscope and loaded onto the diffractometer. Thecrystallographic data was collected on Brucker D8-Venture diffractometer, Bruker X8-KappaApexII,Bruker APEX-II CCD, Nonius KappaCCD or STOE IPDS 2T diffractometer equipped with a lowtemperaturedevice at 100.0 K using graphite monochromated Cu-K_α radiation (λ = 1.54178 Å) orCu-$K_\alpha$radiation (λ = 1.54178). The absorption correction, structure solution and structurerefinementwasperformed by Patterson methods or by fullmatrix least squares on F_2 using theSHELXL-97 programs. The non-hydrogen atoms were refined anisotropically, the hydrogen atomswere included isotropically using the riding model on the bound carbon atoms. For data analyses and further picture preparation of the molecular structure for compounds were done using Diamond3.0 program.

10.10 Chemicals used

All the commercially available chemicals used for experiments are listed below along with the supplier name in the brackets. The chlorophosphanes were further purified by fractional distillation.

10.11 List of chemicals used (commercially available)

Chemicals Supplier Chemicals Supplier

- Acetonitrile (Fisher Scientific)
- *n*-Butylamine (Acros)
- *n*-Butyllithium (Acros)
- Carbondisulfide (Sigmaaldrich)
- Chloroform (Fisher Scientific)
- Chloroform-d (Eurisotop)
- Chloroacetaldehyde (Acros)
- Diethylether (VWR)
- Dichloromethane (Biesterfeld)
- Diisopropylamine (Acros)
- Dimethylaminodichlorophosphane (Sigmaaldrich)
- Dimethylsulfoxide (Acros)
- Dimethylacetylenedicarboxylate (Acros)
- Diphenylmethane (Acros)
- Diphenylchlorophosphane (Alfa Aesar)
- Ethanol (Hofmann)
- Lithium metal (Sigmaaldrich)

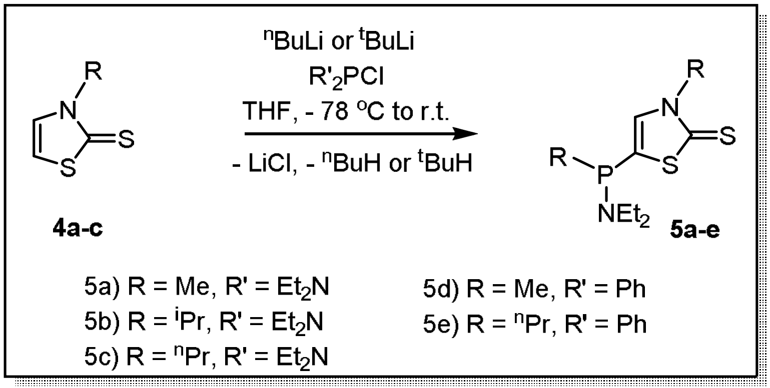
- Methanol (Aldrich)
- Methyamine (Sigmaaldrich)
- Potassium metal (Riedel de Haen)
- *n*-Pentane (Grüssing)
- *o*-Chronil (Across)
- Petrol ether 40/60 (Biesterfeld)
- Phenyldichlorophosphane (Acros)
- 1-Phenylpyrrole-1,5-dione (abcr)
- 4-phenyl-1,2,4-triazoline-3,5-dione (abcr)
- Phosphorustrichloride (Acros)
- Sodium Metal (Riedel de Haen)
- Sodium hydroxide(Sigmaaldrich)
- Selenium (Acros)
- Sulfur (Acros)
- Sulfuricacid (Fluka)
- Tetrahydrofuran (Fisher Scientific)
- THF-d8 (Eurisotop)
- Triflicacid methyl ester (Sigmaaldrich)
- Tributylphosphane (Acros)
- Triethylamine (Sigmaaldrich)
- Toluene (Fisher Scientific)
- Tungstenhexacarbonyl (Across)

- Hydrogen peroxide (Acros)
- Hydrogen peroxide-urea adduct (Acros)
- Iodine (Grüssing)
- Isopropylamine(Sigmaaldrich)
- Isopropanol (Biesterfeld)
- Water-*d*2 (Eurisotop)

The following compounds were synthesized according to literature known protocols:

- Bis(diethylamino)chlorophosphane,[153]
- N-methyl thiazole-2-thione,[74a]
- N-isopropyl thiazole-2-thione,[74b]
- N-^{n}propyl thiazole-2-thione.[74b]
- Potassium graphite[154]

10.12 Synthesis of 5-phosphanyl-thiazole-2-thiones (5a-e)

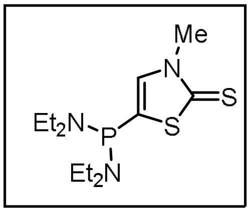


To a solution of the thiazole-2-thiones **4a-c** in THF, ^{t}butyllithium (for **4a**) or ^{n}butyllithium (for **4b,c**) was added at −78 °C and the reaction mixture was slowly warmed to −70 °C where it was stirred for 3 h. Subsequently, the reaction mixture was cooled again to −90 °C whereupon $Et_2N(R')PCl$ was added. The reaction mixture was stirred overnight as it slowly warmed up to ambient temperature. The orange colored solution was concentrated *in vacuo*

(8•10−3 mbar) and the residue was taken up in dry dichloromethane and filtered through a 3G frit having a celite pad to remove the formed lithium chloride. The solvent was removed from the filtrate and the product was dried *in vacuo* ($8•10^{-3}$ mbar). The residue was washed twice with *n*-pentane (2-3 mL/g of the product) and dried *in vacuo* ($8•10^{-3}$ mbar). Yellow to white solids (**5a**-**5e**) were thus obtained.

10.12.1 3-Methyl-5-bis(diethylamino)phosphanyl-thiazole-2-thione (5a)

	amount used (g/mL)	mmol
4a	4.09 g	31.17
^{t}BuLi (1.9 M in hexane)	17.21 mL	32.70
$(Et_2N)_2PCl$	7.20 mL	34.24
THF	130 mL	



Yield: 8.42 g (27.56 mmol) 88.4 %; light yellow solid.

Melting point: 83 °C

Elemental composition: $C_{12}H_{24}N_3PS_2$

Molecular weight: 305.43 g/mol

^{1}H-NMR (300.1 MHz, $CDCl_3$): δ = 1.0 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, CH_2CH_3), 3.02 (m, 8H, CH_2CH_3), 3.6 (s, 3H, CH_3), 6.73 (s br, 1H, ^{4}C-*H*).

$^{13}C\{^1H\}$-NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (d, $^3J_{P,C}$ = 3.2 Hz, CH_2CH_3), 36.6 (s, CH_3), 41.5 (d, $^2J_{P,C}$ = 17.9 Hz, CH_2CH_3), 128.9 (d, $^1J_{P,C}$ = 14.0 Hz, C^5), 132.1 (d, $^2J_{P,C}$ = 17.6 Hz, C^4), 189.5 (s, *C*=S).

$^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ = 79.6 (s).

IR (ATR, ṽ {cm^{-1}}): ṽ = 2970 (s), 2929 (s), 2859 (m), 2705 (s), 2518 (s), 1556 (vs), 1558 (vs), 1375 (vs), 1335 (vs), 1193 (vs), 1133 (vs), 1023 (s), 987 (vs), 917 (vs), 902 (s), 847 (s), 791 (s), 703(s), 665(s).

MS (EI, 70 eV): *m/z* (%) 305.1152 (48) $[M]^+$, 233 (100) $[M-C_4H_{10}N]^+$, 175.1 (8) $[C_8H_{20}N_2P]^+$, 130.9 (10) $[M-C_8H_{20}N_2P]^+$, 72.0 (5) $[C_4H_{10}N]^+$.

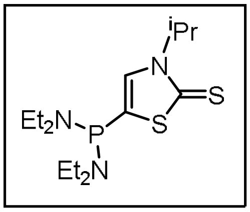
HR-MS: found: 305.1152 calc. 305.1149.

Elemental analysis for: $C_{12}H_{24}N_3PS_2$:

Calculated	C	47.19	H	7.92	N	13.76	S	20.99
Found	C	46.81	H	7.68	N	13.67	S	20.89

10.12.2 3-Isopropyl-5-bis(diethylamino)phosphanyl-thiazole-2-thione (5b)

	amount used (g/mL)	mmol
4b	2.77 g	17.38
^{n}BuLi (1.6 M in hexane)	11.95 mL	19.12
$(Et_2N)_2PCl$	4.38 mL	20.86
THF	110 mL	



Yield: 5.64 g (16.91 mmol) 98 %, white solid

Melting point: 84.5 °C

Elemental composition: $C_{14}H_{28}N_3PS_2$

Molecular weight: 333.49 g/mol

^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.07 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, CH_2CH_3), 1.37 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, $CH(CH_3)_2$),3.09 (m, 8H, CH_2CH_3), 5.32 (heptet, $^3J_{H,H}$ = 6.8 Hz, IH, $CH(CH_3)_2$, 6.9 (s br, 1H, ^{4}C-*H*).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 14.7 (d, $^3J_{P,C}$ = 3.2 Hz, CH_2CH_3), 21.9 (s, $CH(CH_3)_2$), 42.5 (d, $^2J_{P,C}$ = 17.9 Hz, CH_2CH_3), 50.6 (s, $CH(CH_3)_2$) 128.3 (d, $^2J_{P,C}$ = 18.2 Hz, C^4), 130.6 (d, $^1J_{P,C}$ = 13.6 Hz, C^5), 189.5 (s, *C*=S*)*.

$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 79.7$ (s).

IR (ATR, $\tilde{\upsilon}$ {cm^{-1}}): $\tilde{\upsilon}$ = 665 (m), 703 (vs), 778 (vs), 795 (s), 810 (vs), 901 (vs), 920 (m), 996 (m), 1010 (m), 1022 (vs), 1051 (vs), 1082 (s), 1094 (vs), 1176 (m), 1192 (m), 1284 (m), 1316 (m), 1326 (w), 1368 (s), 1374 (s), 1396 (s), 1454 (vs), 1543 (vs), 2856 (vs), 2927 (vs), 2967 (vs).

MS (EI, 70 eV): *m/z* (%) 333.1 (38) $[M]^+$, 261.0 (100) $[M\text{-}Et_2N]^+$.

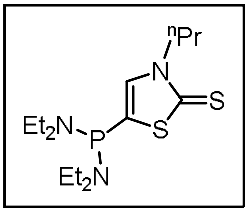
HR-MS: found: 333.1461 calc. 333.1464.

Elemental analysis: for $C_{14}H_{28}N_3PS_2$:

Calculated	C	50.42	H	8.46	N	12.60	S	19.23
Found	C	50.19	H	8.44	N	12.57	S	19.34

10.12.3 **3-^{n}Propyl-5-bis(diethylamino)phosphanyl-thiazole-2-thione (5c)**

	amount used (g/mL)	mmol
4c	2.53 g	15.92
^{n}BuLi (1.6 M in hexane)	10.9 mL	17.52
$(Et_2N)_2PCl$	3.85 mL	18.31
THF	82 mL	



Yield: 4.92 g (14.75 mmol) 93 %; Light yellow sticky solid.

Melting point: 49 °C

Elemental composition: $C_{14}H_{28}N_3PS_2$

Molecular weight: 333.49 g/mol

^{1}H-NMR (300.1 MHz, $CDCl_3$): δ = 0.98 (t, $^3J_{H,H}$ = 7.30 Hz, 3H, $CH_2CH_2CH_3$), 1.07 (t, $^3J_{H,H}$ = 7.10 Hz, 12H, CH_2CH_3), 1.84 (m, 2H, $CH_2CH_2CH_3$), 3.09 (m, 8H, CH_2CH_3), 4.09 (t, $^3J_{H,H}$ = 7.50 Hz, 2H, $CH_2CH_2CH_3$) 6.79 (s br, 1H, $^4C\text{-}H$).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 11.1 (s, $CH_2CH_2CH_3$), 14.6 (d, $^3J_{P,C}$ = 3.2 Hz, CH_2CH_3), 21.9 (s, $CH_2CH_2CH_3$), 42.5 (d, $^2J_{P,C}$ = 17.9 Hz, CH_2CH_3), 51.5 (s, $CH_2CH_2CH_3$), 129.9 (d, $^1J_{P,C}$ = 14.0 Hz, C^5), 132.4 (d, $^2J_{P,C}$ = 18.0 Hz, C^4), 190.2 (d, $^3J_{P,C}$ = 1.0 Hz, *C*=S).

$^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ = 79.2 (s).

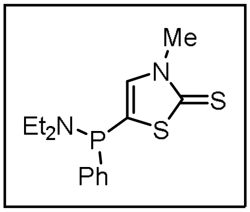
IR (ATR, $\tilde{\nu}$ {cm^{-1}}): $\tilde{\nu}$ = 2960 (s), 2930 (vs), 2865 (vs), 1449 (vs), 1436 (vs), 1370 (w), 1320 (s), 1294 (s), 1225 (m), 1191 (m), 1176 (m), 1138 (w), 1105 (s), 1072 (vs), 1048 (vs), 1009 (m), 989 (w), 919 (w), 884 (s), 876 (s), 805 (m), 794 (m), 752 (vs), 710 (s), 665 (w).

MS (EI, 70 eV): *m/z* (%) 333.1 (38) $[M]^+$, 261.0 (100) $[M\text{-}Et_2N]^+$, 189.9 (50) $[M\text{-}2Et_2N]^+$, 175.1 (7) $[(Et_2N)_2P]^+$.

HR-MS: found: 333.1465 calc. 333.1462.

10.12.4 3-Methyl-5-phenyl(diethylamino)phosphanyl-thiazole-2-thione (5d)

	amount used (g/mL)	mmol
4a	2.50 g	19.05
^{t}BuLi (1.7 M in hexane)	12.32 mL	20.95
Ph(Et_2N)PCl	4.12 mL	20.95
THF	80 mL	



Yield: 5.00 g (16.10 mmol) 84 %; white sticky solid.

Elemental composition: $C_{14}H_{19}N_2PS_2$

Molecular weight: 310.41 g/mol

^1H-NMR (300.1 MHz, $CDCl_3$): δ = 1.05 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, CH_2CH_3), 3.0 (m, 4H, CH_2CH_3), 3.70 (s, 3H, CH_3), 7.23 (d, $^3J_{P,H}$ = 4.5 Hz, 1H, $^4C\text{-}H$), 7.30-7.40 (m, 5H, C_6H_5).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 14.3 (d, $^3J_{P,C}$ = 3.6 Hz, CH_2CH_3), 37.4 (s, CH_3), 44.2 (d, $^2J_{P,C}$ = 14.9 Hz, CH_2CH_3), 126.6 (d, $^1J_{P,C}$ = 55.6 Hz, C^5), 128.4 (d, $J_{P,C}$ = 5.0 Hz, C_6H_5), 128.5 (d, $J_{P,C}$ = 1.0 Hz, C_6H_5), 130.2 (d, $J_{P,C}$ = 17.8 Hz, C_6H_5), 138.3 (d, $^2J_{P,C}$ = 46.9 Hz, C^4), 138.4 (d, $^1J_{P,C}$ = 1.3 Hz, *ipso*-C_6H_5) 191.2 (d, $^4J_{P,C}$ = 1.6 Hz *C*=S).

$^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ = 44.4 (s).

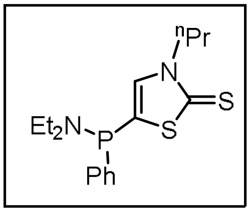
IR (ATR, ṽ {cm^{-1}}): ṽ = 3010 (vs), 2964 (vs), 1540 (vs), 1455 (vs), 1430 (s), 1414 (vs), 1378 (s), 1333 (w), 1292 (vs), 1219 (vs), 1193 (vs), 1169 (vs), 1134 (m), 1108 (s), 1052 (vs), 1019 (s), 989 (w), 920 (m), 908 (s), 861 (vs), 791 (vs), 779 (vs), 748 (w), 700 (m), 694 (s), 655 (m).

MS (EI, 70 eV): *m/z* (%)237.1 (10) $[M\text{-}Et_2N]^+$, 180.0 (100) $[P(Et_2N)Ph]^+$, 130.9 (30) $[M\text{-}P(Et_2N)Ph]^+$,

HR-MS: found: 310.0727 calc. 310.0727.

10.12.5 3-^{n}Propyl-5-phenyl(diethylamino)phosphanyl-thiazole-2-thione (5e)

	amount used (g/mL)	mmol
4c	6.58 g	41.33
^{n}BuLi (1.6 M in hexane)	27.13 mL	43.40
Ph(Et_2N)PCl	8.54 mL	43.40
THF	215 mL	



Yield: 11.36 g (33.56 mmol) 80 %; white solid

Melting point: 99 °C

Elemental composition: $C_{16}H_{23}N_2PS_2$

Molecular weight: 338.47 g/mol

^1H-NMR (500.1 MHz, $CDCl_3$): δ = 0.98 (t, $^3J_{H,H}$ = 7.15 Hz, 3H, $CH_2CH_2CH_3$), 1.04 (t, $^3J_{H,H}$ = 7.34 Hz, 6H, CH_2CH_3),1.86 (m, 2H, $CH_2CH_2CH_3$), 3.04 (m, 4H, CH_2CH_3), 4.12 (m, 2H, $CH_2CH_2CH_3$), 7.24 (d, $^3J_{P,H}$ = 4.78 Hz, 1H, C^4-*H*), 7.26-7.36 (m, 5H, C_6H_5).

^{13}C{^{1}H} -NMR (125.7 MHz, CDCl$_3$:δ = 11.1 (s, CH$_2$CH$_2$*C*H$_3$), 14.38 (d, $^{3}J_{P,C}$ = 3.5 Hz, CH$_2$*C*H$_3$), 21.9 (s, CH$_2$*C*H$_2$CH$_3$), 44.3 (d, $^{2}J_{P,C}$ = 14.7 Hz, *C*H$_2$CH$_3$), 51.4 (s, *C*H$_2$CH$_2$CH$_3$), 126.6 (d, $^{1}J_{P,C}$ = 54.7 Hz, C^5), 128.5 (d, $J_{P,C}$ = 4.9 Hz, *C*$_6$H$_5$), 128.6 (s, *C*$_6$H$_5$), 130.2 (d $J_{P,C}$ = 17.3 Hz *C*$_6$H$_5$), 137.8 (d, $^{2}J_{P,C}$ = 47.3 Hz, C^4), 138.5 (d, $^{1}J_{P,C}$ = 0.7 Hz, *ipso*-C$_6$H$_5$), 190.9 (d, $^{3}J_{P,C}$ = 1.3 Hz *C*=S),

^{31}P{^{1}H} -NMR (202.4 MHz, CDCl$_3$):δ = 44.3 (s).

IR (ATR, ῦ {cm^{-1}}):ῦ = 2962 (vs), 2927 (vs), 2872 (vs), 2483 (vs), 1541 (vs), 1477 (vs), 1452 (vs), 1433 (s), 1373 (m), 1318 (vs), 1288 (s), 1211 (s), 1194 (s), 1165 (s), 1132 (w), 1110 (m), 1072 (m), 1050 (m), 1014 (m), 982 (w), 924 (m), 880 (s), 824 (s), 795 (s), 747 (m), 702 (m), 658 (s), 584 (vs), 546 (s), 528 (m), 514 (m), 481 (m), 436 (m), 406 (w).

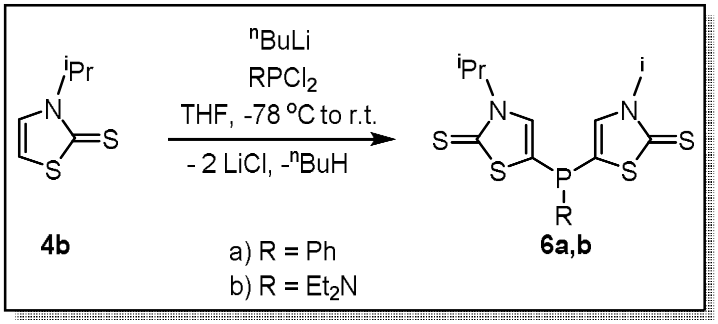
MS (EI, 70 eV):*m/z* (%) 338.1 (25) [M]$^+$, 295.0 (5) [M-^{n}Pr]$^+$, 266.0 (27) [M-Et$_2$N]$^+$, 261.0 (3) [M-Ph]$^+$.

HR-MS: found: 338.1035 calc. 338.1040.

Elemental analysis: for C$_{16}$H$_{23}$N$_2$PS$_2$: found:

Calculated	C	56.78	H	6.85	N	8.28	S	18.94
Found	C	56.42	H	6.72	N	8.29	S	18.83

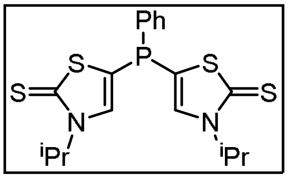
10.13 Synthesis of bis(thiazolyl)phosphanes 6a,b.



To a solution of the thiazole-2-thione **4b** in THF, ^{n}butyllithium was added at −78 °C and the reaction mixture was slowly warmed to −70 °C where it was stirred for 3 h. Subsequently, the reaction mixture was cooled again to −90 °C whereupon RPCl$_2$ was added. The reaction mixture was stirred overnight as it slowly warmed up to ambient temperature. The orange colored solution was concentrated *in vacuo* (8•10^{-3} mbar) and the residue was taken up in dry dichloromethane and filtered through a 3G frit having a celite pad to remove the formed lithium chloride. The solvent was removed from the filtrate and the product was dried *in vacuo* ($8 \cdot 10^{-3}$ mbar). The residue was washed twice with pentane (3-4 mL/g of the product) and dried *in vacuo* ($8 \cdot 10^{-3}$ mbar). Both **6a** and **6b** were obtained as white solid.

10.13.1 Bis(3-isopropyl-thiazole-2-thione-5-yl)-phenylphosphane (6a)

	amount used (g/mL)	**mmol**
4b	8.00 g	50.22
nBuLi (1.6 M in hexane)	34.53 mL	55.25
$PhPCl_2$	3.91 mL	28.81
THF	270 mL	



Yield: 18.00 g (42.39 mmol) 84.4 %; white solid.

Melting point: 233 °C

Elemental composition: $C_{18}H_{21}N_2PS_4$

Molecular weight: 424.59 g/mol

^{1}H-NMR (500.1 MHz, CD_2Cl_2): δ = 1.40 (t, $^3J_{H,H}$ = 6.83 Hz, 12H, CH(C*H*$_3$)$_2$), 5.30 (heptet, $^3J_{H,H}$ = 6.89 Hz, 2H, C*H*(CH$_3$)$_2$), 7.38-7.40 (m, 5H, C$_6$*H*$_5$), 7.44 (d, $^3J_{P,H}$ = 5.77 Hz, 2H, ^{4}C-*H*).

^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): δ = 21.9 (s, CH(*C*H$_3$)$_2$), 51.3 (s, *C*H(CH$_3$)$_2$, 120.6 (d, $^1J_{P,C}$ = 30.4 Hz, *C*^{5}), 129.3 (d, $J_{P,C}$ = 6.7. Hz, *C*$_6$H$_5$), 130.1 (s, *C*$_6$H$_5$), 132.0 (d, $J_{P,C}$ = 18.6. Hz, *C*$_6$*H*$_5$), 134.4 (s, *ipso*-*C*$_6$H$_5$), 136.2 (d, $^2J_{P,C}$ = 49.4 Hz, *C*^{4}), 191.1 (s, *C*=S).

^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ = -42.0 (s).

IR (ATR, ῦ {cm^{-1}}): ῦ = 3120 (vs), 2975 (vs), 2931 (vs), 1545 (s), 1536 (s), 1459 (vs), 1433 (s), 1391 (m), 1376 (s), 1367 (s), 1321 (s), 1309 (m), 1274 (m), 1190 (m), 1167 (s), 1135 (vs), 1084 (m), 993 (m), 967 (s), 916 (s), 846 (vs), 822 (m), 742 (m), 695 (m).

MS (EI, 70 eV):*m/z* (%) 424.1 (50) $[M]^+$, 363.0 (18) $[M-2S]^+$, 267.1 (60) M-$[C_6H_8NS_2]^+$, 77.1 (20) $[Ph]^+$.

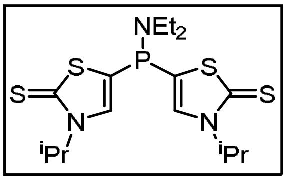
HR-MS: found: 424.0322 calc. 424.0325.

Elemental analysis: for $C_{18}H_{21}N_2PS_4$:

Calculated	C	50.92	H	4.99	N	6.60	S	30.20
Found	C	50.72	H	4.94	N	6.65	S	30.62

10.13.2 Bis(3-isopropyl-thiazole-2-thione-5-yl)-diethylaminophosphane (6b)

	amount used (g/mL)	mmol
4b	1.72 g	10.79
^{n}BuLi (1.6 M in hexane)	7.4 mL	11.85
Et_2NPCl_2	0.86 mL	5.91
THF	60 mL	



Yield: 4.32 g (10.29 mmol) 95.5 %, white solid:

Melting point: 166 °C

Elemental composition:$C_{16}H_{26}N_3PS_4$

Molecular weight: 419.62 g/mol

^{1}H-NMR (300.1 MHz, CDCl$_3$):δ = 1.03 (t, $^{3}J_{H,H}$ = 7.03 Hz, 6H, CH$_2$CH_3), 1.39 (t, $^{3}J_{H,H}$ = 7.55 Hz, 12H, CH(CH_3)$_2$), 3.03 (m, 4H, CH_2CH$_3$), 5.30 (heptet, $^{3}J_{H,H}$ = 6.79 Hz, 2H, C*H*(CH$_3$)$_2$), 7.12 (d, $^{3}J_{P,H}$ = 3.5, 2H, ^{4}C-*H*).

^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$):δ = 14.3 (d, , $^{3}J_{P,C}$ = 3.7 Hz CH$_2$*C*H$_3$), 21.9 (s, CH(*C*H$_3$)$_2$), 44.2 (d, $^{2}J_{P,C}$ = 15.6 Hz, *C*H$_2$CH$_3$), 51.0 (s, (s, *C*H(CH$_3$)$_2$), 125.3 (d, $^{1}J_{P,C}$ = 34.9 Hz, C^{5}), 132.2 (d, $^{2}J_{P,C}$ = 37.9 Hz, C^{4}), 189.9 (s, *C*=S).

^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$):δ = 28.3 (s).

IR (ATR, ṽ {cm^{-1}}):ṽ = 3094 (vs), 3032 (vs), 2967 (vs), 1538 (s), 1462 (vs), 1398 (m), 1385 (s), 1369 (s), 1322 (m), 1314 (m), 1280 (w), 1202 (m), 1169 (s), 1133 (vs), 1094 (m), 1082 (w), 1019 (s), 1002 (w), 990 (w), 923 (s), 855 (vs), 830 (vs), 812 (s), 799 (s), 780 (vs), 737 (vs), 703 (s), 687 (vs), 658 (s).

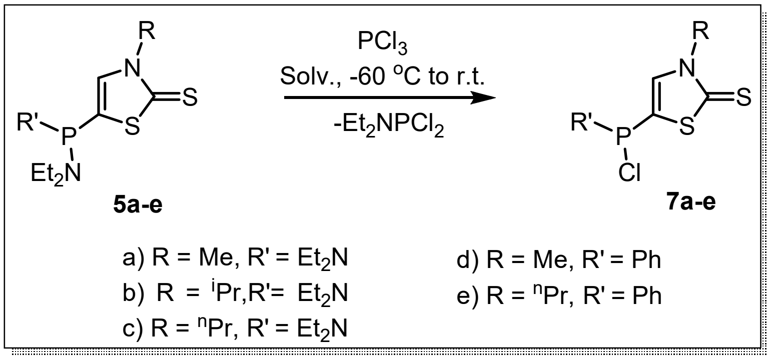
MS (EI, 70 eV):*m/z* (%) 419.1 (80) [M]$^+$, 347 (100) [M-Et$_2$N]$^+$, 262.9 (40) [M-C$_6$H$_8$NS$_2$]$^+$, 72.1 (18) [Et$_2$N]$^+$

HR-MS: found: 419.0750 calc. 419.0747.

Elemental analysis: for C$_{16}$H$_{26}$N$_3$PS$_4$: found:

Calculated	C	45.80	H	6.25	N	10.01	S	30.56
Found	C	42.72	H	5.84	N	9.29	S	28.73

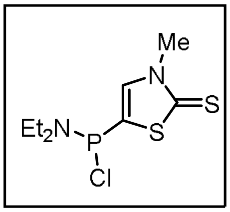
10.14 Synthesis of 5-(chloro)phosphanyl substituted thaizole-2-thiones 7a-e



C^{5-}Phosphanyl-thiazole-2-thione (**5a-e**) was dissolved in dry diethyl ether (or dichloromethane for **7d**, **7e**) in a Schlenk flask and cooled to −60 °C. Phosphorus trichloride (ρ = 1.570 g/cm^3) was added dropwise and the reaction mixture was slowly warmed up to room temperature and stirred for two hours. The solvent was removed *in vacuo* ($8 \cdot 10^{-3}$ mbar), and the residue was washed twice with *n*-pentane (2-3 mL/g of the product) and dried *in vacuo* ($8 \cdot 10^{-3}$ mbar). A white to yellow solid was thus obtained.

10.14.1 3-Methyl-5-diethylamino(chloro)phosphanyl-thiazole-2-thione (7a)

	amount used (g/mL)	mmol
5a	5.06 g	16.56
PCl_3	1.58 mL	17.39
Et_2O	130 mL	



Yield: 4.28 g (15.92 mmol) 96 %; white solid.

Melting point: 80 °C.

Elemental composition: $C_8H_{14}ClN_2PS_2$

Molecular weight: 268.75 g/mol

^{1}H-NMR (400.1 MHz, $CDCl_3$): δ = 1.0 (t, $^3J_{H,H}$ = 7.0 Hz, 6H, CH_2CH_3), 3.1 (m, 4H, CH_2CH_3), 3.6 (s, 3H, CH_3), 7.2 (s, 1H, C^4-*H*).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 14.0 (d, $^3J_{P,C}$ = 6.0 Hz, CH_2CH_3), 37.7 (s, CH_3), 43.5 (d, $^2J_{P,C}$ = 14.8 Hz, CH_2CH_3), 126.0 (d, $^1J_{P,C}$ = 48.5.0 Hz, C^5), 136.5 (d, $^2J_{P,C}$= 20.5 Hz, C^4), 191.0 (s, *C*=S).

^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ = 114.5 (s).

IR (ATR, $\tilde{\upsilon}$ {cm^{-1}}): $\tilde{\upsilon}$ = 2971 (s), 2821 (m), 2774 (m), 2751 (w), 2482 (s), 2387 (w), 1555 (vs), 1538 (m), 1453 (m), 1376 (s), 1322 (vs), 1238 (m), 1206 (vs), 1139 (s), 1023 (vs), 1000 (s), 1007 (s), 981 (s), 942 (vs), 826 (s), 666 (s).

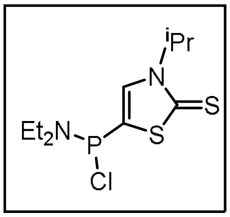
MS (EI, 70 eV): m/z (%): 234.9 (10) $[M-Cl]^+$, 194.9 (18) $[M-C_4H_{10}N]^+$, 130.9 (82) $[M-C_4H_{10}ClNP]^+$, 58.0 (90) $[C_4H_{20}]^+$.

Elemental analysisfor: $C_8H_{14}ClN_2PS_2$:

Calculated	C	35.75	H	5.25	N	10.42	S	23.86
Found	C	35.37	H	5.40	N	10.19	S	23.19

10.14.2 3-Isopropyl-5-diethylamino(chloro)phosphanyl-thiazole-2-thione (7b)

	amount used (g/mL)	mmol
5b	5.00 g	14.99
PCl_3	1.37 mL	15.74
Et_2O	100 mL	



Yield: 4.41 g (14.85 mmol) 99 %; white solid.

Melting point: 55 °C.

Elemental composition:$C_{10}H_{18}ClN_2PS_2$

Molecular weight: 296.81 g/mol.

^{1}H-NMR (400.1 MHz, $CDCl_3$): δ = 1.10 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_2CH_3), 1.40 (d, $^3J_{H,H}$ = 11.0 Hz, 6H, $CH(CH_3)_2$) 3.10-3.20 (m, 4H, CH_2CH_3), 5.27 (heptet, 1H, $CH(CH_3)_2$), 7.27 (s, 1H, C^4-*H*).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$):δ = 14.1 (d, $^3J_{P,C}$ = 5.1 Hz, CH_2CH_3), 21.8 (s, $CH(CH_3)_2$), 43.6 (d, $^2J_{P,C}$ = 14.9 Hz, CH_2CH_3), 51.1 (s, $CH(CH_3)_2$) 127.1 (d, $^1J_{P,C}$ = 48.8 Hz, C^5), 132.1 (d, $^2J_{P,C}$ = 14.8 Hz, C^4), 190.2 (s, *C*=*S*).

$^{31}P\{^1H\}$ -NMR (161.9 MHz, $CDCl_3$): δ = 115.1 (s).

IR (ATR, ṽ {cm^{-1}}): ṽ = 2970 (s), 2933 (vs), 2866 (vs), 2821 (vs), 2775 (vs), 2481 (vs), 1549 (vs), 1533 (s), 1452 (vs), 1393 (m), 1381 (m), 1314 (w), 1279 (w), 1197 (w), 1162 (w), 1135 (s), 1093 (w), 1078 (m), 1042 (m), 1019 (w), 1003 (w), 942 (w), 911 (m), 851 (w), 828 (s), 806 (vs), 787 (w), 697 (s), 666 (w).

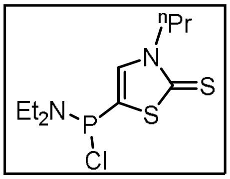
MS (EI, 70 eV): m/z (%): 158.9 (30) $[M\text{-}P(Et_2N)PCl]^+$, 116.8 (40) $[M\text{-}{}^{i}pr\text{-} P(Et_2N)PCl]^+$, 72.9 (10) $[Ph]^+$.

Elemental analysis: for $C_{10}H_{18}ClN_2PS_2$: found:

Calculated	C	40.47	H	6.11	N	9.44	S	21.60
Found	C	39.00	H	6.61	N	9.06	S	20.46

10.14.3 3-^{n}Propyl-5-diethylamino(chloro)phosphanyl-thiazole-2-thione (7c)

	amount used (g/mL)	mmol
5c	4.02 g	12.35
PCl_3	1.13 mL	12.95
Et_2O	130 mL	



Yield: 3.52 g (11.85 mmol) 96 %; white solid:

Melting point: 66 °C.

Elemental composition: $C_{10}H_{18}ClN_2PS_2$

Molecular weight: 296.81 g/mol

^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 1.0 (t, $^{3}J_{H,H}$ = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.16 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6H, CH_2CH_3) 1.88 (m, 2H, $CH_2CH_2CH_3$), 3.2 (m, 4H, CH_2CH_3), 4.13 (m, 2H, $CH_2CH_2CH_3$), 7.25 (s, 1H, C^4-*H*).

^{13}C{1H} NMR (75.5 MHz, CDCl$_3$): δ = 11.1 (s, $CH_2CH_2\mathit{C}H_3$), 14.0 (d, $^3J_{P,C}$ = 6.0 Hz, $CH_2\mathit{C}H_3$), 21.8 (s, $CH_2\mathit{C}H_2CH_3$), 43.6 (d, $^2J_{P,C}$ = 14.9 Hz, $\mathit{C}H_2CH_3$), 51.7 (s, $\mathit{C}H_2CH_2CH_3$), 126.2 (d, $^1J_{P,C}$ = 48.2.0 Hz, C^5), 135.7 (d, $^2J_{P,C}$= 21.0 Hz, C^4), 191.0 (s, C=S).

^{31}P{1H} NMR (121.5 MHz, CDCl$_3$): δ = 114.3 (s).

IR (ATR, ṽ {cm^{-1}}): ṽ = 2973 (vs), 2931 (vs), 2873 (vs), 2821 (vs), 2774 (vs), 2481 (vs), 1544 (s), 1461 (vs), 1435 (vs), 1367 (w), 1324 (s), 1292 (s), 1225 (w), 1194 (w), 1166 (w), 1138 (w), 1112 (s), 1082 (vs), 1022 (w), 992 (w), 939 (w), 886 (m), 876 (s), 838 (w), 803 (w), 788 (m), 744 (s), 708 (s), 668 (w).

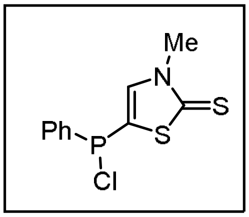
MS: EI, 70 eV): m/z (%): 295.3 (8) $[M-H]^+$, 267.2 (10) $[M-Et]^+$, 159.0 (35) $[M-Et_2NPCl]^+$.

Elemental analysis for: $C_{10}H_{18}ClN_2PS_2$:

Calculated	C	40.47	H	6.11	N	9.44	S	21.60
Found	C	39.91	H	6.26	N	9.23	S	21.09

10.14.4 3-Methyl-5-phenyl(chloro)phosphanyl-thiazole-2-thione (7d)

	amount used (g/mL)	mmol
5d	4.54 g	14.64
PCl$_3$	1.40 mL	16.38
CH$_2$Cl$_2$	140mL	



Yield: 3.68 g (13.44 mmol) 92 %; white solid.

Melting point: 111 °C.

Elemental composition: $C_{10}H_9ClNPS_2$

Molecular weight: 273.73 g/mol

^{1}H NMR (500.1 MHz, CDCl$_3$): δ = 3.65 (s, 3H, CH_3), 7.42 (d, $^3J_{P,H}$ = 4.28 Hz, 1H, C^4-H), 7.44-7.48 (m, 3H,C$_6H_5$) 7.64-7.70 (s, 2H, C$_6H_5$).

^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ = 37.5 (s, CH$_3$), 125.0 (d, $^1J_{P,C}$ = 59.4 Hz, C^5), 129.0 (d, $J_{P,C}$ = 7.7 Hz, C_6H$_5$); 130.6 (d, $J_{P,C}$ = 25.0 Hz, C_6H$_5$), 131.2 (s, C_6H$_5$), 135.9 (d, $J_{P,C}$ = 25.0 Hz, *ipso*-C$_6$H$_5$), 139.5 (d, $^2J_{P,C}$= 51.6 Hz, C^4), 192.1 (s, C=S).

^{31}P{^{1}H} NMR (202.5 MHz, CDCl$_3$): δ = 55.3 (s).

IR (ATR, ṽ {cm^{-1}}): ṽ = 3045 (vs), 2971 (vs), 2818 (vs), 2773 (vs), 2480 (vs), 1692 (vs), 1541 (m), 1478 (s), 1463 (s), 1434 (m), 1418 (s), 1390 (vs), 1338 (w), 1317 (w), 1207 (m), 1142 (w), 1113 (m), 1033 (m), 1010 (w), 971 (m), 913 (w), 844 (w), 805 (s), 750 (w), 698 (w), 689 (w).

MS (EI, 70 eV): m/z (%): 272.9 (100) [M]$^+$, 237.9 (25) [M-Cl]$^+$, 195.8 (10) [M-PPh]$^+$, 164.9 (12) [M-PPhCl]$^+$.

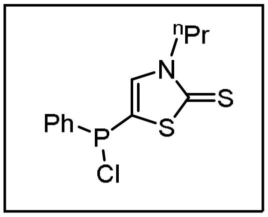
HR-MS: found: 272.9602 calc. 272.9603.

Elemental analysis: for $C_{10}H_9ClNPS_2$:

Calculated	C	43.88	H	3.31	N	5.12	S	23.42
Found	C	44.59	H	3.73	N	5.09	S	24.50

10.14.5 3-^{n}Propyl-5-phenyl(chloro)phosphanyl-thiazole-2-thione (7e)

	amount used (g/mL)	mmol
5e	11.36 g	33.56
PCl$_3$	3.08 mL	35.24
CH$_2$Cl$_2$	370 mL	



Yield: 9.71 g (32.17 mmol) 96 %; white sticky solid.

Elemental composition:$C_{12}H_{13}ClNPS_2$

Molecular weight: 301.78 g/mol

^{1}H-NMR (500.1 MHz, $CDCl_3$):δ = 1.0 (t, $^3J_{H,H}$= 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.83 (m, 2H, $CH_2CH_2CH_3$), 4.07 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, $CH_2CH_2CH_3$), 7.42 (d, $^3J_{P,H}$ = 4.5 Hz, 1H, C^4-*H*), 7.42-7.49 (m, 3H,C_6H_5) 7.64-7.70 (s, 2H, C_6H_5).

^{13}C-NMR (125.7 MHz, $CDCl_3$):δ = 11.2 (s, $CH_2CH_2CH_3$), 21.9 (s, $CH_2CH_2CH_3$), 51.7 (s, $CH_2CH_2CH_3$), 125.0 (d, $^1J_{P,C}$ = 59.2 Hz, C^5), 129.1 (d, $J_{P,C}$ = 7.9 Hz, C_6H_5); 130.8 (d, $J_{P,C}$ = 25.1 Hz, C_6H_5), 131.3 (s, C_6H_5), 136.1 (d, $J_{P,C}$ = 25.1 Hz, *ipso*-C_6H_5), 138.8 (d, $^2J_{P,C}$= 51.8 Hz, C^4), 192.0 (s, *C*=S).

^{31}P{1H} NMR (202.4 MHz, $CDCl_3$):δ = 55.3 (s).

IR (ATR, ῦ {cm^{-1}}):ῦ = 3041 (vs), 2959 (vs), 2928 (vs), 2871 (vs), 1541 (vs), 1461 (vs), 1431 (m), 1366 (m), 1348 (m), 1320 (s), 1290 (m), 1213 (m), 1133 (w), 1097 (m), 1006 (w), 928 (m), 884 (s), 842 (m), 741 (m), 690 (m), 640 (vs), 595 (vs), 548 (vs), 517 (w), 495 (w), 457 (w).

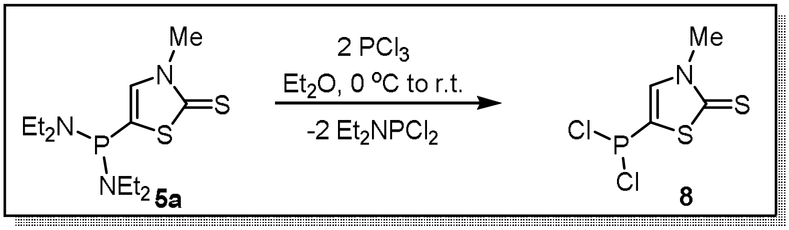
MS (EI, 70 eV): m/z (%): 267.0 (80) $[M-Cl]^+$, 116.9 (38) $[M-{}^nPr-PPhCl]^+$, 109.0 (25) $[PPh]^+$, 77.0 (30) $[Ph]^+$.

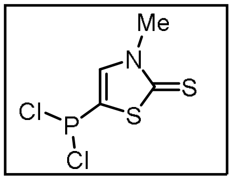
Elemental analysis: for $C_{12}H_{13}ClNPS_2$:

Calculated	C	47.76	H	4.34	N	4.64	S	21.25
Found	C	48.14	H	4.76	N	4.99	S	21.13

10.15 Synthesis of 3-methyl-5-dichlorophosphanyl-thiazole-2-thione (8)

3-Methyl-5-bis(diethylamiono)phosphanyl-thiazole-2-thione **5a** (1.50 g, 4.91 mmol) was dissolved in dry 50 mL of diethylether in a Schlenk flask and cooled to 0 °C. Phosphorus trichloride (0.94 mL, 10.8 mmol, ρ = 1.570 g/cm^3) was added dropwise and the reaction mixture was warmed up to room temperature and stirred for three days. The solvent was removed *in vacuo* ($8•10^{-3}$ mbar), and the residue was washed twice with *n*-pentane (2•3 mL) and dried *in vacuo* ($8•10^{-3}$ mbar). A yellow solid was thus obtained.





Yield: = 1.00 g (4.30 mmol) 88 %; yellow solid

Melting point: 80 °C

Elemental composition: $C_4H_4Cl_2NPS_2$

Molecular weight: 232.07 g/mol

^{1}H NMR (300.1 MHz, CDCl$_3$):δ = 3.6 (s, 3H, C*H*$_3$), 7.4 (d, $^{3}J_{\mathrm{P,H}}$ = 4.3 Hz, 1H, ^{4}C-*H*).

^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$):δ = 37.7 (s, *C*H$_3$), 125.8 (d, $^{1}J_{\mathrm{P,C}}$= 76.3. Hz, C^5), 138.3 (d, $^{2}J_{\mathrm{P,C}}$= 60.7 Hz, C^4), 192.1 (s,*C*=S).

^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$):δ = 131.4 (s).

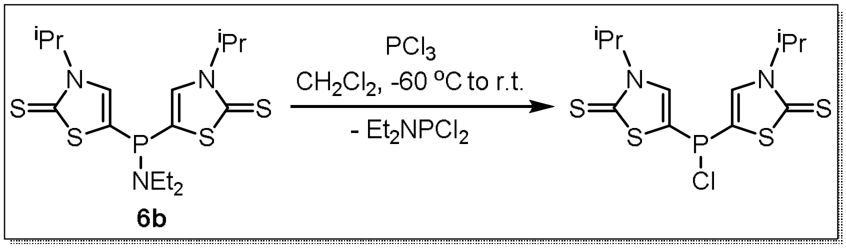
IR (ATR, $\tilde{\upsilon}$ {cm^{-1}}):$\tilde{\upsilon}$ = 3094(s), 3038(s), 1539 (m), 2751(vs), 1459 (m), 1418 (m), 1338 (s), 1313 (vs), 1210 (s), 1134(vs), 1116(s), 1012(vs), 916(vs), 855(s), 701(s), 1000(s).

MS (EI, 70 eV): m/z (%):230.9 (100) [M].+, 195.9 (75) [M-Cl]+, 131.0 (78) [M- PCl2]+.

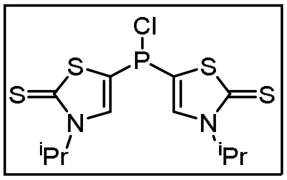
HR-MS: Found 230.8897 calc. 230.8900.

Elemental analysis: for $C_4H_4Cl_2NPS_2$:

10.16 Synthesis of bis(3-isopropyl-thiazole-2-thione-5-yl)chlorophosphane (9)



Bis(3-isopropyl-thiazole-2-thione-5-yl)-diethyamionophosphane **6b** (3.36 g, 8.00 mmol) was dissolved in dry 100 mL of dichloromethane in a Schlenk flask and cooled to −60 °C. Phosphorus trichloride (0.77 mL, 8.80 mmol, ρ = 1.570 g/cm^3) was added dropwise and the reaction mixture was warmed up to room temperature, and stirred for one hour. The solvent was removed *in vacuo* (8•10^{-3} mbar), and the residue was washed twice with *n*-pentane (2•5 mL) and dried *in vacuo* (8•10^{-3} mbar). A white solid was thus obtained.



Yield:2.80 g (7.31 mmol) 91 %; white solid.

Melting point: 201 °C.

Elemental composition:$C_{12}H_{16}ClN_2PS_4$

Molecular weight: 382.94 g/mol.

^{1}H-NMR (300.1 MHz, CD_2Cl_2):δ = 1.39 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 5.24 (heptd, $^3J_{H,H}$ = 6.9 Hz, $^5J_{P,H}$ = 1.2 Hz, 2H, C*H*(CH$_3$)$_2$), 7.51 (d, $^3J_{P,H}$ = 5.73 Hz, 2H, ^{4}C-*H*).

^{13}C{^{1}H} NMR (75 5 MHz, CD_2Cl_2):δ = 21.9 (s, CH(CH$_3$)$_2$), 51.6 (s, *C*H(CH$_3$)$_2$), 122.4 (d, $^1J_{P,C}$ = 48.6 Hz, C^5), 136.0 (d, $^2J_{P,C}$ = 57.8 Hz, C^4), 191.3 (s, br, *C*=S).

^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2):δ = 34.9 (s)

IR (ATR, $\tilde{\upsilon}$ {cm^{-1}}): $\tilde{\upsilon}$ = 3097 (vs), 3027 (vs), 2970 (vs), 1534 (s), 1394 (s), 1381 (s), 1311 (s), 1272 (w), 1197 (m), 1169 (vs), 1138 (vs), 1078 (m), 1011 (w), 916 (vs), 847 (s), 824 (vs), 524 (m), 498 (s), 472 (s), 459 (m), 405 (s).

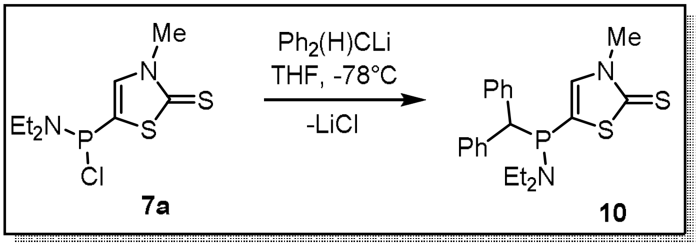
MS (EI, 70 eV): *m/z* (%) 382.1 (100) $[M]^+$, 348.1 (90) $[M-Cl]^+$, 298.0 (65) $[M-2^iPr]^+$

HR-MS: found: 381.9624 calc. 381.9622.

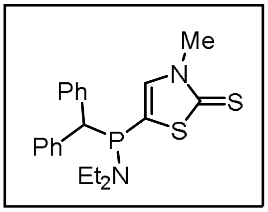
Elemental analysis for: $C_{12}H_{16}ClN_2PS_4$:

Calculated	C	37.64	H	4.21	N	7.32	S	33.49
Found	C	37.62	H	4.19	N	7.31	S	34.09

10.17 Synthesis of 3-methyl-5-diphenylmethyl(diethylamino)phosphanyl-thiazole-2-thione (10)



To a solution of **7a**(7.60 g, 28.27 mmol) in 200 mL of dry THF, the *in situ* prepared Ph_2CHLi (1 28.27 mmol, in 115 mL THF) was added dropwise using cannula at −78 °C and the reaction mixture was stirred for 15 min. The orange colored solution was concentrated *in vacuo* ($8•10^{-3}$ mbar) and the residue was taken up in dry toluene and filtered via cannula to remove the formed lithium chloride. The solvent was removed from the filtrate *in vacuo* ($8•10^{-3}$ mbar) and the residue was dried *in vacuo*. The residue was recrystallized from THF/*n*-hexane mixture at low tem-perature (−40 °C), washed twice with pentane (10 mL, 7 mL) and dried *in vacuo* ($8•10^{-3}$ mbar). A white solid was thus obtained.



Yield: Yield: 7.00 g (17.47 mmol), 61.8 %, white solid.

Melting point: 151 °C.

Elemental composition: $C_{21}H_{25}N_2PS_2$

Molecular weight: 400.53 g/mol.

^{1}H-NMR (300.1 MHz, CDCl$_3$): δ = 0.76 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH$_2$C*H$_3$*), 3.02 (m, 4H, C*H$_2$*CH$_3$), 3.4 (s, 3H, C*H$_3$*), 4.5 (d, $^2J_{P,H}$ = 5.4 Hz, 1H, P-C*H*Ph$_2$), 6.4 (d, $^3J_{P,H}$ = 2.8 Hz, 1H, C^4-*H*),7.13-7.50 (m, 10H, C$_6$*H$_5$*).

^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ = 14.0 (d, $^3J_{P,C}$ = 3.0 Hz, CH$_2$*C*H$_3$), 37.2 (s, *C*H$_3$), 43.8 (d, $^2J_{P,C}$ = 15.2 Hz, *C*H$_2$CH$_3$), 53.5 (d, $^1J_{P,C}$ = 11.2 Hz, P-*C*HPh$_2$), 126.6 (d, $J_{P,C}$= 2.0 Hz, *C*$_6$H$_5$), 126.9 (d, $J_{P,C}$= 2.1 Hz, *C*$_6$H$_5$), 127.4 (d, $^1J_{P,C}$= 51.8 Hz, *C*^{5}), 128.7 (d, $J_{P,C}$= 12.5 Hz, *C*$_6$H$_5$), 128.8 (d, $J_{P,C}$= 13.3 Hz, *C*$_6$H$_5$), 129.0 (s, *C*$_6$H$_5$), 135.7 (d, $^2J_{P,C}$= 36.2 Hz, *C*^{4}), 140.1 (d, $J_{P,C}$= 16.3 Hz, *C*$_6$H$_5$), 141.3 (d, $J_{P,C}$= 12.5 Hz, *C*$_6$H$_5$), 189.6 (d, $^3J_{P,C}$= 1.1 Hz *C*=S).

^{31}P{^{1}H}-NMR (121.5 MHz, CDCl$_3$): δ = 47.9 (s).

IR (ATR, $\tilde{\upsilon}$ {cm^{-1}}): $\tilde{\upsilon}$= 3034 (w), 2969 (w), 1556 (s), 1493 (m), 1448 (s), 1339 (vs), 1199 (s), 1175 (m), 1140 (vs), 1123 (vs), 985 (vs), 936 (s), 772 (s), 704 (vs), 666 (vs).

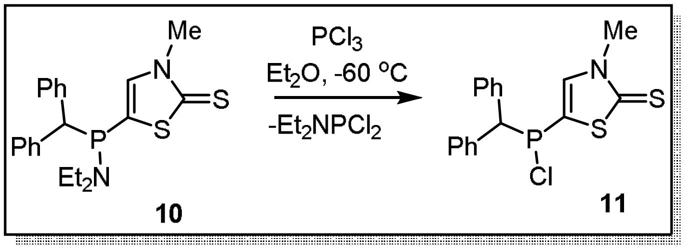
MS (EI, 70 eV): *m/z* (%) 400 (28) [M]$^+$, 233 (100) [M-C$_8$H$_{14}$N$_2$PS$_2$]$^+$, 162 (63) [C$_4$H$_4$NPS$_2$]$^+$.

HRMS: found: 400.1194, calc.: 400.1196.

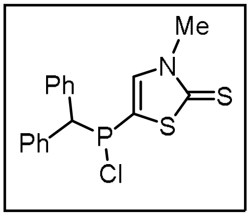
Elemental analysis for: C$_{21}$H$_{25}$N$_2$PS$_2$: found:

Calculated	C	62.97	H	6.29	N	6.99	S	16.01
Found	C	62.18	H	6.37	N	7.02	S	15.99

10.18 Synthesis of 3-methyl-5-diphenylmethyl(chloro)phosphanyl-thiazole-2-thione (11)



Compound **10**(6.71 g, 16.75 mmol) was dissolved in 200 mL of dry dichloromethane in a Schlenk flask and cooled to −60 °C. Phosphorus trichloride (1.60 mL, 18.42 mmol) was added dropwise, the reaction mixture was slowly warmed up to room temperature, and stirred for two hours. The solvent was removed i*n vacuo* (8•10^{-3} mbar). The residue was washed twice with *n*-pentane (15 mL, 10 mL) and dried *in vacuo* (8•10^{-3} mbar). A white solid was thus obtained.



Yield:6.0 g (16.48 mmol) 98.5 %; white solid.

Melting point: 148 °C.

Elemental composition: $C_{17}H_{15}ClNPS_2$

Molecular weight: 363.85 g/mol.

^{1}H NMR (300.1 MHz, CDCl$_3$):δ = 3.49 (s, 3H, CH_3), 4.65 (d, $^2J_{P,H}$ = 2.4 Hz, 1H, C*H*Ph$_2$), 7.0 (d, $^3J_{P,H}$ = 4.5 Hz, 1H, C^4-*H*), 7.16-7.57 (m, 10H, $C_6\mathit{H}_5$).

13C{1H} NMR (75.5 MHz, CDCl$_3$):δ = 37.4 (s, *C*H$_3$), 59.5 (d, $^1J_{P,C}$ = 24.6 Hz, *C*HPh$_2$), 122.6 (d, $^1J_{P,C}$ = 61.1 Hz, C^5), 127.5 (d, $J_{P,C}$ = 1.9 Hz, C_6H_5), 127.7 (d, $J_{P,C}$ = 2.2 Hz, C_6H_5), 128.5 (d, $J_{P,C}$ = 3.5 Hz C_6H_5), 128.7 (d, $J_{P,C}$ = 3.9 Hz C_6H_5), 129.0 (d, $J_{P,C}$ = 13.1 Hz C_6H_5), 137.6 (d, $J_{P,C}$ = 15.0 Hz C_6H_5), 138.5 (d, $J_{P,C}$ = 14.5 Hz C_6H_5), 139.8 (d, $^2J_{P,C}$ = 50.32 Hz, C^4), 191.4 (d, $^3J_{P,C}$ = 1.4 Hz *C*=S).

31P{1H} NMR (121.5 MHz, CDCl$_3$):δ = 57.9 (s).

IR (ATR, ῦ {cm−1}):ῦ= 3021 (w), 1556 (s), 1597 (w), 1548 (s), 1494 (m), 1335 (s), 13215 (s), 1205 (s), 1070 (m), 1006 (vs), 915 (s), 819 (s), 781 (vs), 743 (s), 704 (vs), 700 (s).

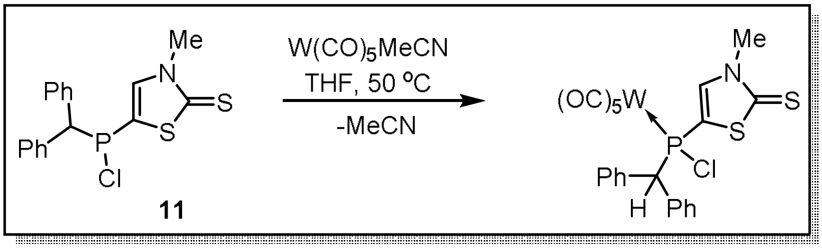
MS (EI, 70 eV): m/z (%) 363 (60) [M]$^+$, 167 (100) [Ph$_2$C]$^+$.

HR-MS: found: 363.0070, calc. 363.0072.

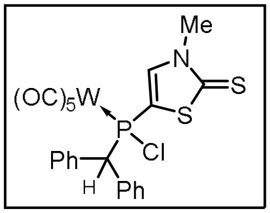
Elemental analysis for: $C_{17}H_{15}ClNPS_2$:

Calculated	C	56.12	H	4.16	N	3.85
Found	C	55.70	H	4.26	N	3.90

10.19 Synthesis of {pentacarbonyl[chloro(3-methyl-thiazole-2-thione-5-yl)-diphenylmethyl-]-phosphane}tungsten(0)} (13)



To a solution of **11** (1.00 g, 2.74 mmol) in 30 mL of dry THF was added dropwise at ambient temperature a solution of W(CO)$_5$MeCN in 20 mL of THF (1.00 g, 2.74 mmol). The reaction mixture was warmed to 50 °C and stirred at this temperature for 48 h. The greenish yellow solution was then concentrated *in vacuo* ($8 \cdot 10^{-3}$ mbar) and then purified via column chromatography (−20 °C using cryostat) using silica gel as stationary phase and Et$_2$O/petrol ether (40/60) as eluent. The obtained bright yellow powder was washed with *n*-pentane (3 mL) and dried *in vacuo* ($8 \cdot 10^{-3}$ mbar).



Yield:1.33 g (1.93 mmol) 70.3 %; Yellow solid.

Melting point: 80 °C.

Elemental composition: $C_{22}H_{15}ClNO_5PS_2W$

Molecular weight: 687.74 g/mol.

^{1}H NMR (300.1 MHz, CDCl$_3$):δ = 3.56 (s, = 3H, CH_3, 3.64 (s, = 3H, CH_3*2nd isomer*), 4.82 (d, $^2J_{P,H}$ = 3.26 Hz, 1H, C*H*Ph$_2$), 4.89 (d, $^2J_{P,H}$ = 3.63 Hz, 1H, C*H*Ph$_2$ *2nd isomer*), 6.72 (d, $^3J_{P,H}$ = 5.23 Hz, 1H, C^4-*H*), 6.90 (d, $^3J_{P,H}$ = 4.37 Hz, 1H, C^4-*H 2nd isomer*), 7.31-7.52 (m, 10H, C$_6H_5$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): = 37.7 (s, *C*H$_3$), 38.4 (s, *C*H$_3$ *2nd isomer*), 65.9 (d, $^1J_{P,C}$ = 7.5 Hz, *C*HPh$_2$), 66.5 (d, $^1J_{P,C}$ = 6.2 Hz, C*H*Ph$_2$ *2nd isomer*),122.7 (d, $^1J_{P,C}$ = 20.9 Hz, *C*^{5}), 127.4 (d, $^1J_{P,C}$ = 17.3 Hz, *C*^{5} *2nd isomer*), 128.3 (d, $J_{P,C}$ = 2.6 Hz, *C*$_6$H$_5$), 128.6 (d, $J_{P,C}$ = 2.3

Hz, C_6H_5), 128.7 (d, $J_{P,C}$ = 1.5 Hz, C_6H_5), 129.0 (d, $J_{P,C}$ = 7.0 Hz, C_6H_5), 129.7 (d, $J_{P,C}$ = 7.1 Hz, C_6H_5), 129.8 (d, $J_{P,C}$ = 6.0 Hz, C_6H_5), 130.0 (d, $J_{P,C}$ = 7.6 Hz, C_6H_5), 130.1 (d, $J_{P,C}$ = 7.6 Hz, C_6H_5), 135.8 (d, $J_{P,C}$ = 1.0 Hz, C_6H_5), 135.8 (d, $J_{P,C}$ = 0.8 Hz, C_6H_5), 139.0 (d, $^2J_{P,C}$ = 13.3 Hz, C^4), 140.5 (d, $^2J_{P,C}$= 10.9 Hz, *C 2nd isomer* ^{4}), 190.2 (d, $^3J_{P,C}$ = 2.1 Hz C=S), 192.9 (d, $^3J_{P,C}$= 1.7 Hz C=S *2nd isomer*), 194.5 (d_{sat}, $^2J_{P,C}$ = 6.9 Hz, $^1J_{W,C}$ = 126.7 Hz, *C*O), 194.8 (d_{sat}, $^2J_{P,C}$ = 7.0 Hz, $^1J_{W,C}$ = 126.7 Hz, *C*O *2nd isomer*), 196.3 (d, $^2J_{P,C}$ = 35.9 Hz, *C*O), 196.8 (d, $^2J_{P,C}$ = 35.3 Hz, *C*O *2nd isomer*).

^{31}P NMR (121.5 MHz, CDCl3): δ = 84.7 ($s_{sat,}$ $^1J_{W,P}$ = 299.5 Hz), 85.7 ($s_{sat,}$ $^1J_{W,P}$ = 294.8 Hz *2nd isomer*).

IR (ATR, ṽ {cm^{-1}}): ṽ= 2079 (s), 2068 (w), 1906 (vs), 1541 (w), 1493 (w), 1449 (w), 1342(s), 1141 (m), 1002 (s), 746 (s), 699 (vs).

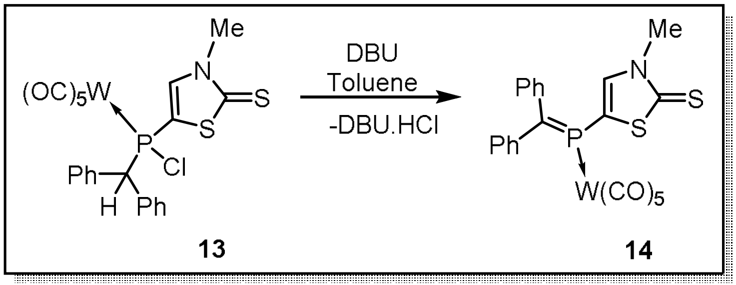
MS: EI, 70 eV): m/z (%): 687.0 (30) $[M]^+$, 323 (4) $[W(CO)5]^+$, 166.9 (100) $[PPh_2C]^+$.

HR-MS: found: 684.9304, calc. 684.9300.

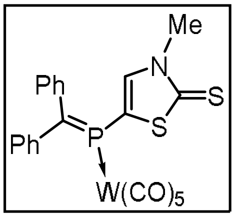
Elemental analysis for: $C_{22}H_{15}ClNO_5PS_2W$:

Calculated	C	38.42	H	2.20	N	2.04	S	9.32
Found	C	38.14	H	2.22	N	1.97	S	9.04

10.20 Synthesis of [pentacarbonyl[{(diphenylmethylene)3-methyl-thiazole-2-thione-5-yl-]-phosphane}]tungsten(0)] (14)



In a Schlenk tube, DBU (0.05 mL, 0.33 mmol) was added dropwise to a toluene (5 mL) solution of **13** (0.19 g, 0.27 mmol) at ambient temperature. Upon mixing, orange colored precipitate was formed.The precipitate was filtered and the obtained solid was dissolved in dichloromethane and filtered over a frit having silica pad. The filtrate was collected, solvent was removed *in vacuo* ($8{\bullet}10^{-3}$ mbar) andwashed twice with *n*-pentane (2•3 mL). Yellow solid was obtained after drying *in vacuo* ($8{\bullet}10^{-3}$ mbar).



Yield:0.12 g (0.18 mmol) 67 %; yellow solid.

Elemental composition: $C_{22}H_{14}NO_5PS_2W$

Molecular weight: 651.29 g/mol.

^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$):δ = 3.58 (s, 3H, C*H$_3$*), 7.15-7.18 (m, 2H, C_6*H*$_5$). 7.20 (d, $^3J_{P,H}$ = 7.63 Hz, 1H, C^4-*H*), 7.32-7.44 (m, 8H, C_6*H*$_5$).

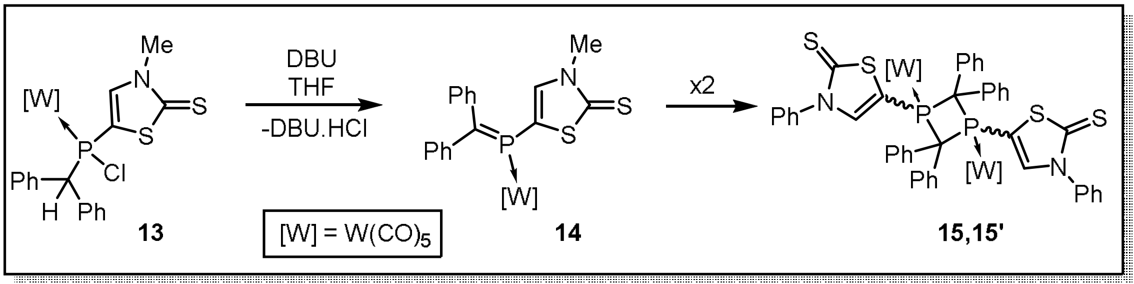
13C{^{1}H} NMR (125.7 MHz, CD$_2$Cl$_2$):δ = 38.0 (s, *C*H$_3$), 124.6 (d, $^1J_{P,C}$ = 8.1 Hz, *C*^{5}), 129.1 (d, $J_{P,C}$ = 1.4 Hz, *C*$_6$H$_5$), 129.4 (d, $J_{P,C}$ = 1.4 Hz, *C*$_6$H$_5$), 130.0 (d, $J_{P,C}$ = 2.6 Hz *C*$_6$H$_5$), 130.1 (d, $J_{P,C}$ = 3.5 Hz *C*$_6$H$_5$), 130.3 (d, $J_{P,C}$ = 16.1 Hz *C*$_6$H$_5$), 130.8 (d, $J_{P,C}$ = 11.7 Hz *C*$_6$H$_5$), 142.1 (d, $^2J_{P,C}$ = 16.8 Hz, *C*^{4}), 142.6 (d, $^2J_{P,C}$ = 16.1 Hz, *ipso*-*C*$_6$H$_5$), 143.0 (d, $^2J_{P,C}$ = 12.1 Hz, *ipso*-*C*$_6$H$_5$), 185.1 (d, $^1J_{P,C}$ = 60.0 Hz, P=*C*), 190.6 (s, *C*=S), 195.1 (d$_{sat}$, $^2J_{P,C}$ = 9.7 Hz, $^1J_{W,C}$ = 125.6 Hz, *cis*-*C*O), 197.8 (d, $^2J_{P,C}$ = 34.2 *trans*-*C*O).

^{31}P{^{1}H} NMR (202.4 MHz, CD$_2$Cl$_2$):δ = 140.7 ppm ($^1J_{W,P}$ =283.4 Hz).

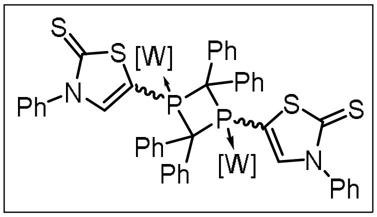
IR (ATR, ῦ {cm−1}):ῦ = 2070 (s), 1990 (vs), 1907 (m), 1642 (vs), 1541 (vs), 1440 (vs), 1339 (s), 1324 (s), 1208 (vs), 1133 (s), 1001 (m), 926 (vs), 891 (vs), 806 (s), 757 (m), 697 (m), 605 (vs), 590 (m), 566 (m), 518 (m), 502 (m), 420 (m).

MS (EI, 70 eV): m/z (%) 651 (30) $[M]^+$, 327 (100) $[M\text{-}W(CO)_5]^+$, 167.1 (100) $[PPh_2C]^+$).

10.21 Synthesis of [decacarbonyl[{μ(3,3,4,4-diphenyl)(1,2-di(3-methyl-thiazole-2-thione-5-yl-)1,3-diphosphetane}]ditungsten(0)] (15)



DBU (0.02 mL, 0.16 mmol) was added dropwise to a THF (3 mL) solution of **13** (0.10 g, 0.14 mmol) at −78 °C. The bright red colored reaction mixture was kept at −30 °C for 12 h. Then the formed salt was filtered via cannula at −30 °C; the color of the filtrate was yellow at this point. The solvent was removed *in vacuo* ($8{\bullet}10^{-3}$ mbar) to afford a yellow powder. The powder was washed with *n*-pentane (2 mL) at −30 °C and dried *in vacuo* ($8{\bullet}10^{-3}$ mbar).



Yield:0.05 g (0.04 mmol), 53 %; yellow solid.

Elemental composition: $C_{44}H_{28}N_2O_{10}P_2S_4W_2$

Molecular weight: 1302.58 g/mol.

^{1}H NMR (300.1 MHz, THF d$_8$, −30 °C):δ = 3.5 (s, = 6H, C*H$_3$*), 6.9-7.8 (m, 22H, C^4-*H*, C$_6$*H$_5$*).

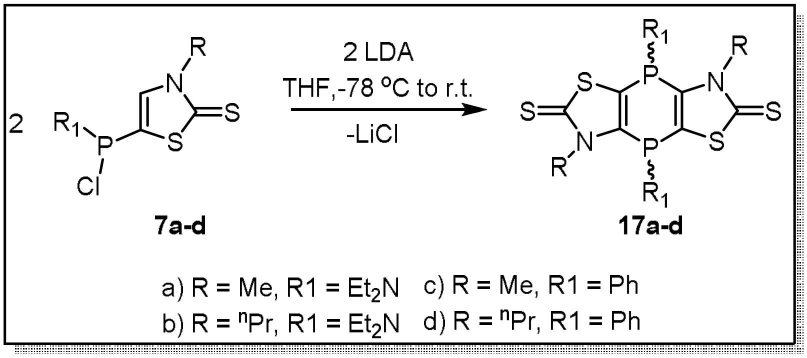
^{13}C{^{1}H} NMR (75.5 MHz, THFd8,-30 °C):δ = 37.0 (s, *C*H$_3$), 68.0 (t, $^1J_{P,C}$ = 7.0 Hz, *C*Ph$_2$), 125.9 (s, *C*$_6$H$_5$), 126.9 (s, *C*$_6$H$_5$), 127.8 (s, *C*$_6$H$_5$), 128.8 (s, *C*$_6$H$_5$), 129.7 (d, $J_{P,C}$ = 3.9 Hz, *C*$_6$H$_5$), 131.0 (d, $J_{P,C}$ = 7.2 Hz, *C*$_6$H$_5$), 132.7 (d, $^2J_{P,C}$= 11.9 Hz, *C*^{4}), 138.1 (d, $J_{P,C}$= 8.5 Hz, *ipso*-*C*$_6$H$_5$), 141.7 (d, $J_{P,C}$= 6.7 Hz, *ipso*-*C*$_6$H$_5$), 143.4 (d, $^1J_{P,C}$= 11.9 Hz, *C*^{5})189.2 (s, C=S), 199.8 (d$_{sat}$, $^2J_{P,C}$ = 9.3 Hz, $^1J_{W,C}$ = 126.2 Hz, *C*O), 203.0 (d$_{sat}$, $^2J_{P,C}$ = 18.2 Hz, $^1J_{W,C}$= 141.4 Hz,*C*O).

^{31}P{^{1}H} NMR (121.5 MHz, THFd$_8$, −30 °C): δ = 71.3 {(s_{sat} = $J_{W,P}$ = 270.5Hz) 97 %}73.1, {(s_{sat} = $J_{W,P}$ = 272.7 Hz *2nd isomer*) 3%}.

IR (ATR, ῦ {cm−1}): ῦ = 2928 (s), 2058 (s), 1895 (vs), 1793 (s), 1640 (s), 1578 (s), 1489 (w), 1445 (m), 1315 (s), 1261 (w), 1205 (w), 1040 (s), 989 (s), 800 (s), 732 (m), 705 (s), 695 (s).

MS (neg. ESI-MS): [$C_{44}H_{28}N_2O_{10}P_2S_4W_2$]Cl found = 1337.8830, calc. = 1337.8836.

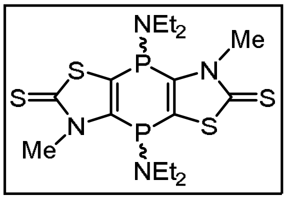
10.22 Synthesis of tricyclic 1,4-dihydro-1,4-diphosphinines 17a-d



In a Schlenk flask **7a-d** (individually) was dissolved in dry THF and cooled to −78 °C. A THF solution of LDA was added to it at −78 °C, and the reaction mixture was warmed up to ambient temperature. It was stirred for two hours at this temperature. The solvent was removed *in vacuo* ($8 \cdot 10^{-3}$ mbar) and the residue was taken in dicholoromethane and filtered over frit having silica gel. The filtrate was collected; solvent was removed *in vacuo* ($8 \cdot 10^{-3}$ mbar). The obtained solid was washed twice with *n*-pentane (2-3 mL/g of the product) and dried *in vacuo* ($8 \cdot 10^{-3}$ mbar). White solids were obtained (**17a-d**).

10.22.1 4,8-Bis(dimethylamino)-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-dithione (17a)

	amount used (g/mL)	**mmol**
7a	3.18 g	11.84
LDA	1.52 g	14.21
THF	100 mL	



Yield:2.20 g (4.73 mmol), 80 %; white solid.

Melting point:232 °C

Elemental composition:$C_{16}H_{26}N_4P_2S_4$

Molecular weight: 464.60 g/mol

^{1}H NMR (300.1 MHz, $CDCl_3$): δ =0.85-1.03 (m, 24H, ($CH_2C\mathit{H}_3$)), 2.86 (br, 8H, $C\mathit{H}_2CH_3$), 3.01 (br 8H, $C\mathit{H}_2CH_3$ *2nd isomer*), 3.70 (s, 6H, $C\mathit{H}_3$), 3.80 (s, 6H, $C\mathit{H}_3$ *2nd isomer*),

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$):δ = 14.1 (br, $CH_2\mathit{C}H_3$), 14.2 (br, $CH_2\mathit{C}H_3$ *2nd isomer*), 34.9 (m, $\mathit{C}H_3$),36.8 (t, $^{3/4}J_{P,C}$ = 6.7 Hz, $\mathit{C}H_3$ *2nd isomer*), 43.7 (br, $\mathit{C}H_2CH_3$), 44.1 (br, $\mathit{C}H_2CH_3$ *2nd isomer*),124.9 (dd, $^1J_{P,C}$ = 19.3 Hz, $^2J_{P,C}$ = 9.6 Hz, $C^{5/4}$)127.6 (m, $^1J_{P,C}$ =11.3 Hz, $^2J_{P,C}$ = 10.4 $C^{4/5}$ *2nd isomer*), 137.6 (dd, $^1J_{P,C}$ = 21.4 Hz, $^2J_{P,C}$ = 8.6 Hz, $C^{5/4}$) 144.1 (dd, $J_{P,C}$ = 9.0 Hz, $^2J_{P,C}$ = 7.4 $C^{4/5}$ *2nd isomer*),190.3 (t, $J_{P,C}$ = 2.3 Hz, *C*=S), 190.5 (t, $J_{P,C}$ = 3.5 Hz, *C*=S *2nd isomer*).

^{31}P NMR (121.5 MHz, $CDCl_3$):δ = 18.8 (s), 19.5 (s, *2nd isomer*).

IR (ATR, ṽ {cm^{-1}}):ṽ = 2963(s), 2924(m), 285 (m), 1493(m), 1435(m), 1412 (m), 1375(s), 1363(m), 1313(vs), 1293 (s), 1261(s), 1197(s), 1137 (s), 1092 (m), 1061(s), 1019(vs), 1000(vs), 929(vs), 819(vs), 786 (vs), 671(vs), 655(vs).

MS (EI, 70 eV): *m/z* (%) 464.0 (100) $[M]^+$,392.9 (23) $[M- NEt_2]^+$,319.8 (78)) $[M- 2Et_2]^+$, 72 (100)) $[NEt_2]^+$.

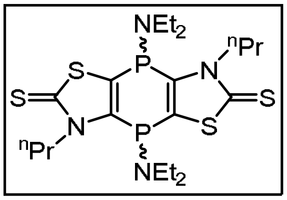
HR-MS: found: 464.0514,calc. 464.0515.

Elemental analysis for: $C_{16}H_{26}N_4P_2S_4$: found:

Calculated	C	41.36	H	5.64	N	12.06	S	27.60
Found	C	40.17	H	5.58	N	11.28	S	26.15

10.22.2 4,8-Bis(dimethylamino)-3,7-di^{n}propyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-dithione (17b)

	amount used (g/mL)	mmol
7b	2.60 g	8.75
LDA	1.03 g	9.63
THF	85 mL	



Yield: 2.22 g (4.26 mmol), 97 %, white solid.

Melting point:181°C.

Elemental composition:$C_{20}H_{34}N_4P_2S_4$

Molecular weight: 520.71 g/mol

^{1}H NMR (500.1 MHz, CDCl$_3$):δ = 0.95-1.02 (m, 24H, $CH_2C\mathit{H}_3$), 1.03-1.12 (br, 12H, $CH_2CH_2C\mathit{H}_3$), 1.80-2.04 (m, 8H, $CH_2C\mathit{H}_2CH_3$), 2.74-2.99 (br, 8H, $C\mathit{H}_2CH_3$), 2.99-3.16 (br, 8H, $CH_2C\mathit{H}_3$ *2nd isomer*) 3.87-4.03 (m, 4H $C\mathit{H}_2CH_2CH_3$), 4.48-4.59 (m, 4H, $C\mathit{H}_2CH_2CH_3$ *2nd isomer*).

^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$): δ = 11.2 (s, $CH_2CH_2\mathit{C}H_3$), 11.3 (s, $CH_2CH_2\mathit{C}H_3$ *2nd isomer*), 14.4 (br, $CH_2\mathit{C}H_3$), 14.6 (br, $CH_2\mathit{C}H_3$ *2nd isomer*), 20.7 (t $^{4/5}J_{P,C}$ = 2.2 Hz, $CH_2\mathit{C}H_2CH_3$), 20.8 (t, $^{4/5}J_{P,C}$ = 2.6 Hz, $CH_2\mathit{C}H_2CH_3$ *2nd isomer*) 44.7 (br, $\mathit{C}H_2CH_3$), 44.8 (br, $\mathit{C}H_2CH_3$ *2nd isomer*), 49.4 (t, $^{3/4}J_{P,C}$ = 3.4 Hz $\mathit{C}H_2CH_2CH_3$), 51.3 (t, $^{3/4}J_{P,C}$ = 4.8 Hz $\mathit{C}H_2CH_2CH_3$ *2nd isomer*), 126.4 (dd, $^1J_{P,C}$ = 21.0 Hz, $^2J_{P,C}$ = 10.5 Hz,$C^{4/5}$), 129.1 (dd, $^1J_{P,C}$ = 12.4 Hz, $^2J_{P,C}$ = 10.4 Hz,$C^{4/5}$ *2nd isomer*), 137.4 (dd, $^1J_{P,C}$ = 24.3 Hz, $^2J_{P,C}$ = 9.3 Hz,$C^{4/5}$), 143.7 (dd, $^1J_{P,C}$ = 9.0 Hz, $^2J_{P,C}$ = 7.8 Hz,$C^{4/5}$ *2nd isomer*) 190.3 (t, $^3J_{P,C}$ = 2.8 Hz, *C*=S), 190.5 (t, $^3J_{P,C}$ = 3.6 Hz, *C*=S *2nd isomer*).

^{31}P{^{1}H} NMR (202.5 MHz, CDCl$_3$):δ= 16.5 (s), δ= 19.3 (s, *2nd isomer*).

IR (ATR, ῦ {cm^{-1}}):ῦ = 2961 (m), 2926 (w), 2867 (w), 1458 (m), 1377 (m), 1348 (s), 1294 (m), 1212 (s), 1177 (s), 1139 (vs) 1039 (vs), 1019 (vs), 1001 (vs), 928 (vs) 817 (s), 817 (vs), 661 (vs).

MS (EI,70 eV): m/z (%) = 520.1 (100) $[M]^+$, 449.0 (10) $[M-Et_2N]^+$, 376.0 (70) $[M-2Et_2N]^+$, 434.0 (10) $[M-2^nPr]^+$, 72.1 (85) $[Et_2N]^+$.

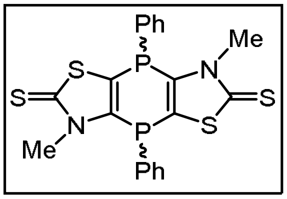
HR-MS: found = 520.1141, calc. = 520.1142.

Elemental analysis for: $C_{20}H_{34}N_4P_2S_4$: found: C 45.21, H 6.35, N 10.7, S 24.01. calc.: C 46.13, H 6.58, N 10.76, S 24.63.

Calculated	C	46.13	H	6.58	N	10.76	S	24.63
Found	C	45.07	H	6.34	N	10.70	S	24.01

10.22.3 4,8-Diphenyl-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-dithione (17c)

	amount used (g/mL)	mmol
7c	2.58 g	9.42
LDA	1.16 g	10.83
THF	85 mL	



Yield:2.0 g (4.21 mmol) 89 %; white solid.

Melting point:280 °C.

Elemental composition: $C_{20}H_{16}N_2P_2S_4$

Molecular weight: 474.55 g/mol

^{1}H-NMR (300.1 MHz, CDCl$_3$):δ = 3.50 (s, 6H, CH_3), 7.36-7.58 (m, 10H, C_6H_5).

^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$):δ = 37.4 (t, $^{3/4}J_{P,C}$ = 7.14 Hz, CH_3), 123.4 (dd, $^1J_{P,C}$ = 8.4 Hz, $^2J_{P,C}$ = 7.0 Hz, $C^{4/5}$), 130.0 (t, $J_{P,C}$ = 4.3 Hz, C_6H_5), 131.8 (s, C_6H_5), 132.1 (m, *ipso*- C_6H_5), 133.3 (t, $J_{P,C}$ = 11.3 Hz, C_6H_5), 135.4 (m, $C^{4/5}$), 190.6 (t, $J_{P,C}$ = 3.2 Hz C=S).

^{31}P{^{1}H}-NMR (121.5 MHz, CDCl$_3$):δ = −40.1 (s) 10 %, −37.9 (s, *2nd isomer*) 90%

IR (ATR, ῦ {cm^{-1}}):ῦ = 3052 (vs), 2925 (vs), 2200 (vs), 1966 (vs), 1495 (vs), 1475 (vs), 1454 (vs), 1434 (s), 1415 (vs), 1313 (w), 1201 (vs), 1178 (vs), 1141 (w), 1070 (m), 1023 (vs), 1000 (m), 996 (m), 914 (vs), 827 (s), 741 (m), 690 (w), 672 (m).

MS (EI, 70 eV): *m/z* (%) 474.0 (50) $[M]^+$, 239.0 (90) $[M\text{-}C_{10}H_8NPS_2]^+$, 129.1(30) $[C_3H_3NS_2]^+$.

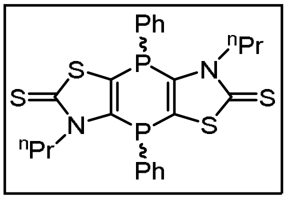
HR-MS: found: 473.9675, calc. 473.9672.

Elemental analysis for: for $C_{20}H_{16}N_2P_2S_4$:

Calculated	C	50.62	H	3.40	N	5.90	S	27.02
Found	C	50.36	H	3.47	N	5.82	S	26.71

10.22.4 4,8-Diphenyl-3,7-di^{n}propyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bis-thiazole-2,6-dithione (17d)

	amount used (g/mL)	mmol
7d	9.56 g	31.67
LDA	3.73 g	34.84
THF	300 mL	



Yield:7.6 g (14.32 mmol) 90 %; white solid.

Melting point:257 °C.

Elemental composition: $C_{24}H_{24}N_2P_2S_4$

Molecular weight: 530.66 g/mol.

^{1}H-NMR (300.1 MHz, CDCl$_3$):δ = 0.76 (t, 6H, $^3J_{H,H}$ = 7.25 Hz, $CH_2CH_2CH_3$), 0.81 (t, 6H, $^3J_{H,H}$ = 7.38 Hz, $CH_2CH_2CH_3$ *2ndisomer*), 1.02-1.51 (m, 4H, $CH_2CH_2CH_3$), 1.68-1.95 (m, 4H, $CH_2CH_2CH_3$ *2ndisomer*), 3.58-3.89 (m, 4H, $CH_2CH_2CH_3$), 4.05-4.32 (m, 4H, $CH_2CH_2CH_3$ *2ndisomer*), 7.30-7.39 (m, 10H, C_6H_5).7.40-7.55 (m, 10H, C_6H_5 *2ndisomer*).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 10.9 (s, $CH_2CH_2CH_3$), 11.1 (s, $CH_2CH_2CH_3$ *2ndisomer*), 20.2 (s, br, $CH_2CH_2CH_3$), 20.8 (s, br, $CH_2CH_2CH_3$ *2ndisomer*), 50.8 (t, $^{3/4}J_{P,C}$ = 5.9 Hz, $CH_2CH_2CH_3$), 51.9 (t, $^{3/4}J_{P,C}$ = 6.5 Hz, $CH_2CH_2CH_3$ *2ndisomer*), 124.6 (dd, $^1J_{P,C}$ = 17.5 Hz, $^2J_{P,C}$ = 9.2 Hz,$C^{4/5}$), 129.8 (t, $J_{P,C}$ = 4.0 Hz, C_6H_5), 130.0 (t, $J_{P,C}$ = 4.6 Hz, C_6H_5 *2ndisomer*), 131.5 (s, C_6H_5), 132.2 (s, C_6H_5 *2ndisomer*), 132.5 (dd, $^1J_{P,C}$ = 6.9 Hz, $^3J_{P,C}$ = 5.9 Hz, *ipso*-C_6H_5), 132.8 (dd, $^1J_{P,C}$ = 6.1 Hz, $^3J_{P,C}$ = 3.0 Hz, *ipso*-C_6H_5 *2ndisomer*), 133.0 (t, $J_{P,C}$ = 11.03 Hz, C_6H_5), 133.9 (m,C_6H_5 *2ndisomer*), 135.6 (t, $J_{P,C}$ = 4.0 Hz, 3.9 Hz, $C^{5/4}$), 138.1(dd, $^1J_{P,C}$ = 8.1 Hz, $^2J_{P,C}$ = 4.8 Hz,$C^{5/4}$ *2ndisomer*). *Other signal for $C^{4/5}$ was not observed.*

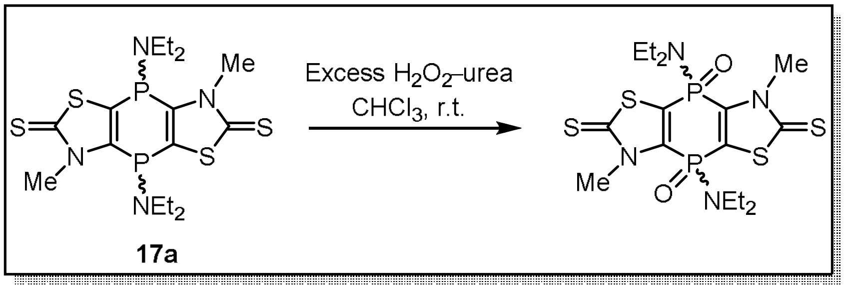
$^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ = −39.8 (s) 36 %, −38.9 (s, *2ndisomer*)64 %

IR (ATR, ṽ {cm^{-1}}): ṽ = 2961 (vs), 2921 (vs), 2867 (vs), 2159 (vs), 2035 (vs), 1457 (vs), 1433 (s), 1395 (vs), 1375 (vs), 1349 (m), 1287 (s), 1211 (m), 1137 (m), 1106 (s), 1073 (m), 999 (m), 923 (s), 872 (s), 827 (s), 744 (m), 691 (m), 666 (s), 642 (s), 600 (s), 545 (s), 495 (m), 478 (m), 458 (m), 437 (m), 425 (m).

MS (EI, 70 eV): *m/z* (%) 530.0 (10) $[M]^+$, 487.9 (10) $[M-^nPr]^+$, 445.9 (1w0) $[M-2^nPr]^+$.

HR-MS: found: 530.0296, calc. 530.0298.

10.23 Oxidation reaction of 1,4-dihydro-1,4-diphosphinine (17a) with H_2O_2-urea



In a round bottom flask **17a** (0.32 g, 0.69 mmol) was dissolved in 15 mL of chloroform and H_2O_2-urea (0.14 g, 1.53 mmol) was added at ambient temperature. The reaction mixture was stirred for 16 hours. The reaction solution was filtered to remove the excess urea and dried *in vacuo* (8•10^{-3} mbar).The obtained solid was washed twice with *n*-pentane (2•2 mL) and dried *in vacuo* (8•10^{-3} mbar).

10.23.1 4,8-Bis(dimethylamino)-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-dithione-4,8-dioxide (18)

Yield:0.30 g (0.60 mmol) 86.7 %; white solid:

Elemental composition: $C_{16}H_{26}N_2O_2P_2S_4$

Molecular weight: 496.60 g/mol

^{1}H NMR (300.1 MHz, CDCl$_3$: δ = 1.02-1.18 (m, 24H, $CH_2C\mathit{H}_3$), 2.96-3.17 (m, 8H, $C\mathit{H}_2CH_3$), 3.17-3.37 (m, $C\mathit{H}_2CH_3$ *2nd isomer*), 3.83 (s, 6H, $C\mathit{H}_3$), 3.84 (s, 6H, $C\mathit{H}_3$ *2nd isomer*).

^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$):δ = 13.7 (s, $CH_2\mathit{C}H_3$), 13.9 (s, $CH_2\mathit{C}H_3$ *2nd isomer*), 36.1 (s, *C*H$_3$), 36.2 (s, *C*H$_3$ *2nd isomer*), 38.2 (t, $J_{P,C}$ = 2.7 Hz,*C*H$_2$CH$_3$), 38.5 (t, $J_{P,C}$ = 2.6 Hz,*C*H$_2$CH$_3$ *2nd isomer*),125.7(dd, $^1J_{P,C}$ = 13.2 Hz, $^2J_{P,C}$ = 7.8 Hz, C$^{5/4}$), 127.7 (dd, $^1J_{P,C}$ = 13.3 Hz, $^2J_{P,C}$ = 9.1 Hz, *C*$^{5/4}$ *2nd isomer*),140.8 (dd, $^1J_{P,C}$ = 46.4 Hz, $^2J_{P,C}$ = 11.2 Hz,C$^{4/5}$), 142.6 (dd, $^1J_{P,C}$ = 45.3 Hz, $^2J_{P,C}$ = 11.2 Hz,C$^{4/5}$ *2nd isomer*), 190.9 (t, $^3J_{P,C}$ = 8.4 Hz, *C*=S)**,** 192.0 (t, $^3J_{P,C}$ = 8.4 Hz, *C*=S *2nd isomer*).

^{31}P{^{1}H}NMR (121.5 MHz, CDCl$_3$):δ = −4.2 ppm (s) 50 %, −3.3 ppm (s, *2nd isomer*) 50 %

IR (ATR, ṽ {cm^{-1}}):ṽ = 2971 (vs), 2930 (vs), 2869 (vs), 1509 (vs), 1457 (vs), 1421 (vs), 1380 (vs), 1323 (s), 1294 (s), 1228 (m), 1199 (s), 1151 (m), 1080 (s), 1067 (s), 1019 (m), 948 (m), 926 (s), 842 (m), 785 (s), 701 (m), 673 (m).

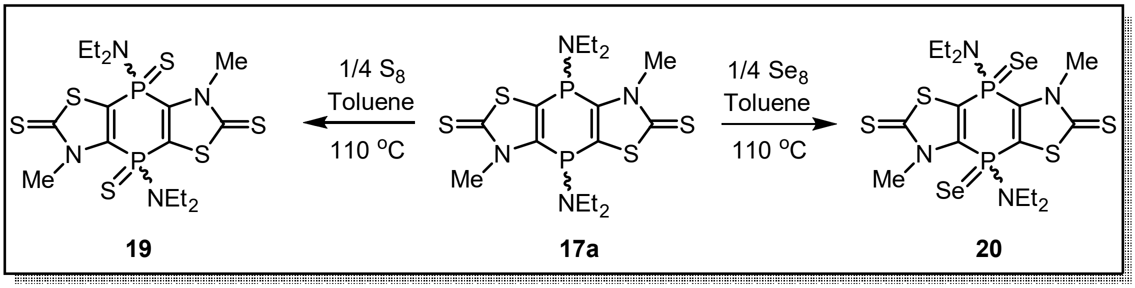
MS (EI, 70 eV): *m/z* (%) 721.0 (100) [C_4H_{10}]$^+$,351.9 (8) [M- 2NEt$_2$]$^+$, 424.0 (5)) [M-Et$_2$]$^+$.

HR-MS: found: 496.0416,calc.: 496.0413.

Elemental analysis for: $C_{16}H_{26}N_4P_2S_4$:

Calculated	C	38.70	H	5.82	N	11.28	S	25.82
Found	C	38.52	H	5.12	N	11.06	S	25.28

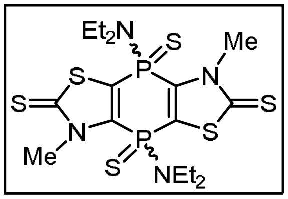
10.24 Oxidation of 17a with elemental sulfur and selenium



In a Schlenk flask **17a** was dissolved in toluene and sulfur (for **19**) or selenium (for **20**) was added at ambient temperature. The reaction mixtures were heated to 110 °C and stirred for 5 days. The reaction solutions were concentrated and kept at −35 °C, whereupon cooling crystalline solids were obtained. After filtration the obtained solids were washed twice with *n*-pentane (2•5 mL) and dried *in vacuo* (8•10^{-3} mbar).

10.24.1 4,8-Bis(dimethylamino)-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-dithione-4,8-disulfide (19)

	amount used (g/mL)	mmol
17a	0.39 g	0.84
1/4S_8	0.06 g	1.87
toluene	20 mL	



Yield:0.40 g (0.75 mmol), 88.8 %, White crystalline solid

Melting point:180°C

Elemental composition: $C_{16}H_{26}N_4P_2S_6$

Molecular weight: 528.72 g/mol

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.09-1.18 (m, 24H, CH_2CH_3), 3.04-3.21 (m, 8H, CH_2CH_3), 3.38-3.53 (m, CH_2CH_3 *2nd isomer*), 3.86 (s, 6H, CH_3), 4.00 (s, 6H, CH_3 *2nd isomer*).

^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ = 13.9 (s, CH$_2$*C*H$_3$), 14.0 (s, CH$_2$*C*H$_3$ *2nd isomer*), 35.9 (s, *C*H$_3$), 36.2 (s, *C*H$_3$ *2nd isomer*), 39.5 (t, $J_{P,C}$ = 2.6 Hz,*C*H$_2$CH$_3$), 39.7 (t, $J_{P,C}$ = 2.4 Hz,*C*H$_2$CH$_3$ *2nd isomer*),128.5 (dd, $^{1}J_{P,C}$ = 93.6 Hz, $^{2}J_{P,C}$ = 10.7 Hz, C$^{5/4}$), 129.5 (dd, $^{1}J_{P,C}$ = 94.0 Hz, $^{2}J_{P,C}$ = 10.6 Hz, *C*$^{5/4}$ *2nd isomer*),138.2 (dd, $^{1}J_{P,C}$ = 99.2 Hz, $^{2}J_{P,C}$ = 8.0 Hz,C$^{4/5}$), 139.1 (dd, $^{1}J_{P,C}$ = 95.8 Hz, $^{2}J_{P,C}$ = 8.6 Hz,C$^{4/5}$ *2nd isomer*), 190.4 (t, $^{3}J_{P,C}$ = 8.2 Hz, *C*=S), 190.4 (t, $^{3}J_{P,C}$ = 8.1 Hz, *C*=S *2nd isomer*).

^{31}P{^{1}H}NMR (202.5 MHz, CDCl$_3$): δ = 22.4 (s) 50 %, 23.3 (s, *2nd isomer*) 50 %

IR (ATR, ṽ {cm^{-1}}): ṽ = 2967 (vs), 2929 (vs), 1504 (vs), 1458 (vs), 1380 (vs), 1315 (s), 1288 (s), 1198 (vs), 1151 (s), 1073 (s), 1012 (m), 945 (s), 921 (vs), 842 (m), 783 (s), 738 (vs), 710 (m), 687 (m), 628 (s), 541 (vs), 494 (s), 462 (s), 431 (m).

MS (EI, 70 eV): *m/z* (%) 528.0 (85) [M]$^{+}$,496.0 (10) [M-S]$^{+}$, 383.8 (60) [M-2NEt$_2$]$^{+}$, 320.9 (80) [M-2S-2NEt$_2$]$^{+}$, 72.1 [C$_4$H$_{10}$N]$^{+}$.

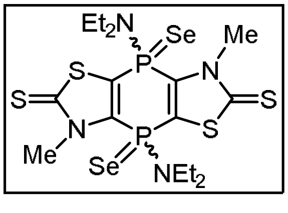
HR-MS: found: 527.9961, calc. 527.9957.

Elemental analysis for: C$_{16}$H$_{26}$N$_4$P$_2$S$_6$:

Calculated	C	36.35	H	4.96	N	10.60	S	36.38
Found	C	37.73	H	5.04	N	10.34	S	35.46

10.24.2 4,8-Bis(dimethylamino)-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-dithione-4,8-diselenide (20)

	amount used (g/mL)	mmol
17a	0.29 g	0.63
Se	0.11 g	1.40
toluene	20 mL	



Yield: 0.30 g (0.48), 76.5 %; White crystalline solid

Melting point: 244°C

Elemental composition: $C_{16}H_{26}N_4P_2S_4Se_6$

Molecular weight: 622.52 g/mol

^{1}H NMR (500.1 MHz, CDCl$_3$: δ = 1.09-1.17 (m, 24H, CH$_2$C*H*$_3$), 3.12-3.26 (m, 8H, C*H*$_2$CH$_3$), 3.45-3.60 (m, C*H*$_2$CH$_3$ *2nd isomer*), 3.86 (s, 6H, C*H*$_3$), 4.00 (s, 6H, C*H*$_3$ *2nd isomer*).

^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$):δ = 13.9 (s, CH$_2$*C*H$_3$), 14.0 (s, CH$_2$*C*H$_3$ *2nd isomer*), 36.0 (s, *C*H$_3$), 36.2 (s, *C*H$_3$ *2nd isomer*), 40.3 (t, $J_{\mathrm{P,C}}$ = 2.4 Hz,*C*H$_2$CH$_3$), 40.4 (t, $J_{\mathrm{P,C}}$ = 2.4 Hz,*C*H$_2$CH$_3$ *2nd isomer*),127.5 (dd, $^{1}J_{\mathrm{P,C}}$ = 110.6 Hz, $^{2}J_{\mathrm{P,C}}$ = 9.5 Hz, *C*$^{5/4}$), 129.0 (dd, $^{1}J_{\mathrm{P,C}}$ = 109.3 Hz, $^{2}J_{\mathrm{P,C}}$ = 9.0 Hz, *C*$^{5/4}$ *2nd isomer*),136.1 (dd, $^{1}J_{\mathrm{P,C}}$ = 108.2 Hz, $^{2}J_{\mathrm{P,C}}$ = 6.4 Hz,*C*$^{4/5}$), 136.5 (dd, $^{1}J_{\mathrm{P,C}}$ = 104.1 Hz, $^{2}J_{\mathrm{P,C}}$ = 7.7 Hz,*C*$^{4/5}$ *2nd isomer*), 190.1 (t, $^{3}J_{\mathrm{P,C}}$ = 7.6 Hz, *C*=S).

^{31}P{^{1}H} NMR (202.5 MHz, CDCl$_3$):δ = 13.4 (S$_{\mathrm{sat}}$$^{1}J_{\mathrm{Se,P}}$ = 812.0 Hz), 54 % 14.3 (S$_{\mathrm{sat}}$$^{1}J_{\mathrm{Se,P}}$ = 830.0 Hz *2nd isomer*) 46 %

IR (ATR, ῦ {cm^{-1}}):ῦ = 2964 (vs), 1495 (vs), 1452 (vs), 1440 (vs), 1412 (vs), 1379 (vs), 1312 (s), 1284 (m), 1197 (vs), 1149 (m), 1063 (s), 1014 (m), 939 (s), 917 (s), 837 (m), 780 (s), 714 (vs), 688 (m), 675 (m).

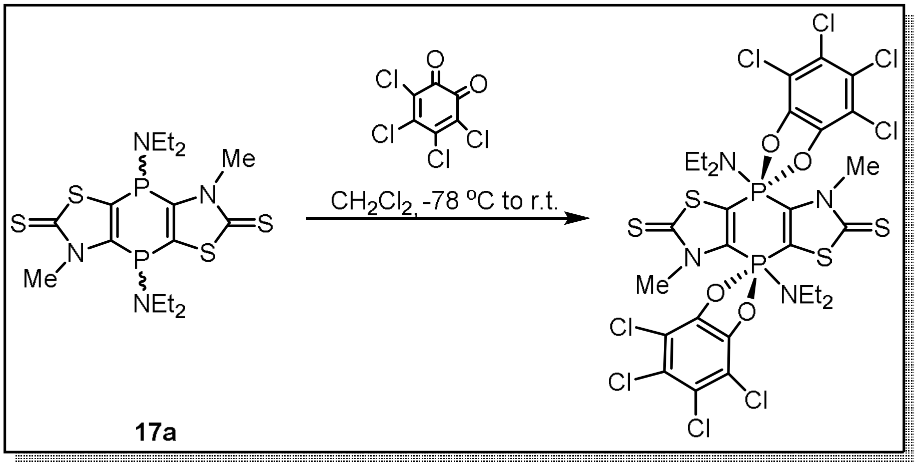
MS (EI, 70 eV): *m/z* (%) 623.8 (60) [M]$^{+}$,543.9 (20) [M- Se]$^{+}$, 464.0 (20) [M-2Se]$^{+}$, 399.8 (10) [M-Se-NEt$_2$]$^{+}$, 319.9 (60) [M-2Se-2NEt$_2$]$^{+}$, 288.9 (30) [M-2Se-2NEt$_2$-S]$^{+}$, 72.1 [$C_4H_{10}N$]$^{+}$.

HR-MS: found: 615.8901, calc. 615.8900.

Elemental analysis for: $C_{16}H_{26}N_4P_2S_4Se_2$:

Calculated	C	30.87	H	4.21	N	9.00	S	20.60
Found	C	30.81	H	4.37	N	8.66	S	19.17

10.25 Oxidation of tricyclic 1,4-dihydro-1,4-diphosphinine (17a) with *ortho*-chloranil



In a Schlenk flask **17a** (0.70 g, 1.50 mmol) was dissolved in 30 mL of dichloromethane and cooled −78 °C. *O*-chloranil (0.74 g, 3.01 mmol) was added and the reaction mixture was stirred for 24 hours and warmed up to ambient temperature. Solvent was removed *in vacuo* ($8 \cdot 10^{-3}$ mbar) and the obtained solid was washed twice with *n*-pentane (2•7 mL) and dried *in vacuo*($8 \cdot 10^{-3}$ mbar). White solid was thus obtained.

10.25.1 4,8-bis(dimethylamino)-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-dithione-4,8-bis(tetracholorobenzodioxaphosphole) (21)

Yield:1.40 g (1.46 mmol) 97 %; white solid.

Melting point: 339 °C.

Elemental composition:$C_{28}H_{26}Cl_8N_4O_4P_2S_4$

Molecular weight: 956.33 g/mol.

^{1}H NMR (500.1 MHz,CD_2Cl_2): δ =1.41 (t, 12H, $^3J_{H,H}$ = 7.23 Hz, CH_2CH_3), 3.00 (br 8H, CH_2CH_3), 3.80 (s, 6H, N-CH_3).

^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2):δ = 11.4 (s, CH_2CH_3), 39.4 (s, CH_2CH_3), 42.4 (s, CH_3), 115.6 (t, $J_{P,C}$ = 7.4 Hz, *o-chloranil ringC*)122.0 (dd, $^1J_{P,C}$ = 194.1 Hz, $^2J_{P,C}$ = 9.3 Hz, $C^{5/4}$), 125.8 (s, *o-chloranil ringC*), 140.2 (s, *o-chloranil ringC*),158.3 (dd, $^1J_{P,C}$ = 120.0 Hz, $^2J_{P,C}$ = 24.2 Hz, $C^{4/5}$), 193.2 (t, $J_{P,C}$ = 7.6 Hz, *C*=S).

^{31}P NMR (202.5 MHz, CD$_2$Cl$_2$):δ =−60.1 ppm (s) 6 %, −59.2 ppm (s, *2nd isomer*) 94 %

IR (ATR, ṽ {cm^{-1}}):ṽ = 2929 (w), 1453 (vs), 1390 (m), 1277(s), 1194 (m), 1141 (s), 1065 (s), 1006 (vs), 994(s), 944 (m), 928 (m), 814 (vs), 790 (m), 708 (s), 682 (m), 659 (m).

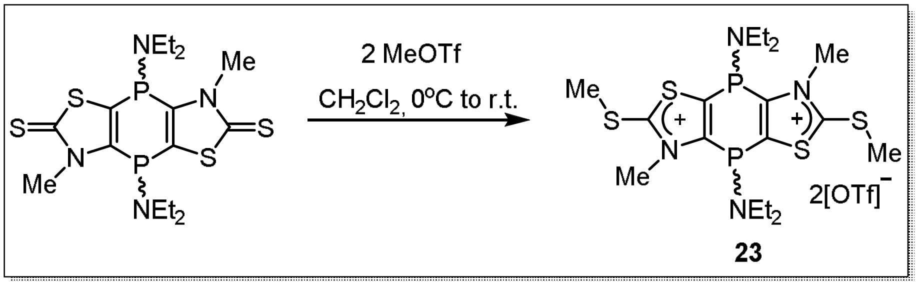
MS (EI, 70 eV): *m/z* (%) 955.7 (3) [M]$^+$, 883.7 (35) [M-Et$_2$N]$^+$, 710.0 (5) [M-C$_6$Cl$_4$O$_2$]$^+$, 464.0 (3) [M-2C$_6$Cl$_4$O$_2$]$^+$, 72 (58) [NEt$_2$]$^+$.

FTMS- pos ESI for [C$_{28}$H$_{26}$Cl$_8$N$_4$O$_4$P$_2$S$_4$]H: found = 956.7840, calc. = 956.7840.

Elemental analysis: for C$_{28}$H$_{26}$Cl$_8$N$_4$O$_4$P$_2$S$_4$:

Calculated	C	35.17	H	2.74	N	5.86	S	13.41
Found	C	34.60	H	3.03	N	5.62	S	12.98

10.26 Reaction of tricyclic 1,4-dihydro-1,4-diphosphinine (17a) with MeOTf



In a Schlenk flask **17a** (0.50 g, 1.07 mmol) was dissolved in 25 mL of dichloromethane and cooled 0 °C. MeOTf (0.25 mL, 2.28 mmol) was added and the reaction mixture was stirred for 3 hours and warmed up to ambient temperature. Solvent was removed *in vacuo* (8•10^{-3} mbar) and the obtained solid was washed twice with *n*-pentane (2•3 mL) and dried *in vacuo* (8•10^{-3} mbar). Yellow solid was thus obtained.

10.26.1 [4,8-bis(dimethylamino)-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bisthiazole-2,6-bis(thiazolium)]trifluoromethanesulfonate (23)

Yield:0.80 g (1.00 mmol), 94.3 %; Yellow solid.

Melting point:78 °C

Elemental composition: C$_{20}$H$_{32}$F$_6$N$_4$O$_6$P$_2$S$_6$

Molecular weight: 792.80 g/mol

^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$):δ = 1.05 (br, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 1.13 (br, 12H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ *2nd isomer*), 3.01 (br, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 3.07 (s, $\mathrm{SC}\mathit{H}_3$), 3.08 (s, $\mathrm{SC}\mathit{H}_3$ *2nd isomer*), 3.20 (br, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ *2nd isomer*), 4.03 (s, $\mathrm{NC}\mathit{H}_3$), 4.12 (s, $\mathrm{NC}\mathit{H}_3$ *2nd isomer*).

^{13}C{^{1}H} NMR (125.75 MHz, CD$_2$Cl$_2$):δ = 14.7 (br, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 15.0 (br, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$ *2nd isomer*), 19.7 (s, $\mathrm{S}\mathit{C}\mathrm{H_3}$), 19.8 (s, $\mathrm{S}\mathit{C}\mathrm{H_3}$ *2nd isomer*), 40.0 (m, $\mathit{C}\mathrm{H_3}$),40.7 (t, $^{3/4}J_{\mathrm{P,C}}$ = 7.3 Hz, $\mathit{C}\mathrm{H_3}$ *2nd isomer*), 45.5 (br, $\mathit{C}\mathrm{H_2CH_3}$), 46.1 (br, $\mathit{C}\mathrm{H_2CH_3}$ *2nd isomer*),120.9 (q, $^1J_{\mathrm{P.F}}$ = 320.7 Hz, $\mathit{C}\mathrm{F_3}$), 136.0 (dd, $^1J_{\mathrm{P,C}}$ = 26.3 Hz, $^2J_{\mathrm{P,C}}$ = 4.2 Hz, $\mathit{C}^{5/4}$)138.7 (m, $\mathrm{C}^{4/5}$), 143.3 (dd, $^1J_{\mathrm{P,C}}$ = 28.1 Hz, $^2J_{\mathrm{P,C}}$ = 4.5 Hz, $\mathit{C}^{5/4}$ *2nd isomer*) 150. (m, $^{4/5}$ *2nd isomer*),183.7 (t, $J_{\mathrm{P,C}}$ = 4.0 Hz, *C*=S), 184.0 (t, $^3J_{\mathrm{P,C}}$ = 2.4 Hz, *C*=S *2nd isomer*).

^{31}P{^{1}H} NMR (102.5 MHz, CD$_2$Cl$_2$):δ = 22.8 (s) 59 %, 23.3 (s, *2nd isomer*) 41 %

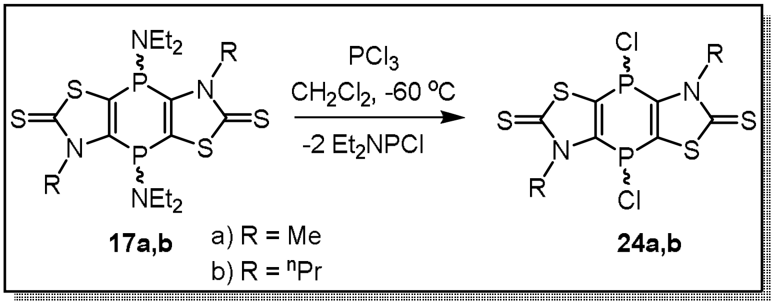
IR (ATR, ṽ {cm^{-1}}):ṽ = 2973 (vs), 2933 (vs), 2872 (vs), 1430 (vs), 1381 (s), 1253 (w), 1221 (m), 1196 (s), 1145 (m), 1051 (s), 1026 (w), 936 (s), 814 (s), 788 (s), 753 (s), 707 (vs), 663 (vs).

MS (neg. ESI-MS): m/z =149.2 [OTf]$^-$, (pos. ESI-MS): m/z = 247.049 [$\mathrm{C_{18}H_{32}N_4P_2S_4}$]$^{2+}$.

Elemental analysis for: $\mathrm{C_{20}H_{32}F_6N_4O_6P_2S_6}$:

Calculated	C	30.30	H	4.07	N	7.07	S	24.26
Found	C	30.42	H	4.26	N	7.99	S	23.26

10.27 Synthesisof *cis/trans* 1,4-dihydro-1,4-dichloro-1,4-diphosphinines (24a,b)



To a solution of **17a**(0.14 g, 0.30 mmol)or **17b**(1.7 g, 3.3 mmol) in dichloromethane (10 mL for 1a, 65 mL for 1b), PCl$_3$ (0.06 mL, 0.68 mmol for 1a, 0.62 mL, 7.18 mmol for 1b) was added (dropwise with a syringe) at 0 °C in a Schlenk flask. The reaction mixture was warmed to ambient temperature and stirred for two days. In case of **17a** orange colored precipitate was obtained having no solubility in common organic solvents, so it was filtered, washed with *n*-pentane (3•7 mL) and dried *in vacuo* (8•10^{-3} mbar). In case of **17b** the solvent was removed *in vacuo* (8•10^{-3} mbar) and the remaining yellow colored precipitate was dried *in vacuo* (8•10^{-3} mbar). The obtained solid was washed twice with *n*-pentane (2•5 mL) and dried in vacuo (8•10^{-3} mbar). Compound **24b** was obtained as 1:1.1 mixture of *cis* and *trans* isomers. This mixture was used for the following characterization and measurements; further assignments to the isomers was not achieved (due to extremely low solubility, characterization of **24a** could not be achieved).

10.27.1 4,8-Dichloro-3,7-dimethyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bis-thiazole-2,6-dithione (24a)

Elemental composition:$C_8H_6Cl_2N_2P_2S_4$

Molecular weight: 391.23 g/mol.

MS (EI, 70 eV):m/z (%) = 389.7 (10) [M]$^+$, 319.8 (100) [M−2Cl]$^+$.

HR-MS ($C_8H_6Cl_2N_2P_2S_4$): found = 389.8266, calc. = 389.8265.

10.27.2 4,8-Dichloro-3,7-di^{n}propyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bis-thiazole-2,6-dithione (24b)

Yield:1.24 g (2.77 mmol), 85.0 %, yellow solid.

Melting point:235 °C.

Elemental composition:$C_{12}H_{14}Cl_2N_2P_2S_4$

Molecular weight: 447.35 g/mol.

^{1}H NMR (500.1 MHz, CDCl$_3$):δ = 1.05 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, $CH_2CH_2CH_3$), 1.85-2.10 (m, 4H, $CH_2CH_2CH_3$), 4.20 (m, 2H, CH_2-CH_2-CH_3), 4.55 (m, 2H, CH_2-CH_2-CH_3).

^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$): δ = 11.2 (s, $CH_2CH_2CH_3$), 21.s (s, $CH_2CH_2CH_3$), 21.5 (s, $CH_2CH_2CH_3$ *2nd isomer*), 50.8 (s, $CH_2CH_2CH_3$), 52.2 (s, $CH_2CH_2CH_3$*2nd isomer*), 124.6 (d, $J_{P,C}$ = 42.0 Hz,$C^{4/5}$), 141.5 (d, $J_{P,C}$ = 37.4 Hz,$C^{4/5}$), 189.8 (s, br C=S).

^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$):δ = 12.7 (s), δ= 21.3 (s).

IR (ATR, ῦ {cm^{-1}}): ῦ = 2927 (w), 2867 (w), 1480 (m), 1352 (s), 1280 (s), 1214 (s), 1136 (s), 1011 (s) 924 (m), 833 (vs), 669 (vs), 583 (s), 546 (s), 437 (vs).

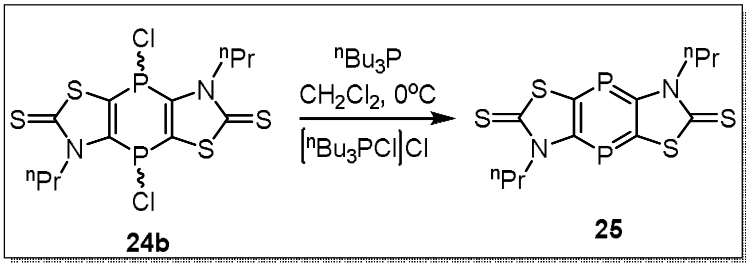
MS (EI, 70 eV):m/z (%) = 445.9 (28) [M]$^+$, 412.9 (15) [M−Cl]$^+$, 375.9 (85) [M-2Cl]$^+$, 345.0 (6) [M-S]$^+$, 291.8 (100) [M-2^{n}Pr,-2Cl]$^+$.

HR-MS ($C_{12}H_{14}Cl_2N_2P_2S_4$): found = 445.8896, calc. = 445.8892.

Elemental analysisfor $C_{12}H_{14}Cl_2N_2P_2S_4$:

Calculated	C	32.22	H	3.15	N	6.26	S	28.67
Found	C	30.92	H	3.21	N	6.02	S	27.35

10.28 Synthesis of thiazole-based 1,4-diphosphinine 25



In a Schlenk flask, ^{n}Bu$_3$P (0.4 mL, 1.65 mmol) was added to a suspension of the 1:1.1 mixture of **24b** (0.62 g, 1.38 mmol) in 15 mL of dichloromethane at 0 °C. The reaction mixture was warmed to ambient temperature and stirred overnight. The reaction mixture was filtered via a cannula and the obtained red residue was washed with dichloromethane (1.5 mL) and then with *n*-pentane (2•5 mL). The obtained bright red color solid was dried *in vacuo* (8•10^{-3} mbar).

10.28.1 3,7-Di^{n}propyl-[2,3-d:5,6-d']bis-thiazole-2,6-dithione-4,8-[1,4]diphosphinine (25)

Yield:0.40 g (1.06 mmol), 77.0 %, red solid.

Melting point:249 °C.

Elemental composition:$C_{12}H_{14}N_2P_2S_4$

Molecular weight: 376.45 g/mol.

^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 1.07 (t, 6H, $^{3}J_{H,H}$ = 7.4 Hz, $CH_2CH_2CH_3$), 4.57 (m, 4H, $CH_2CH_2CH_3$), 4.57 (m, 4H, $CH_2CH_2CH_3$).

^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2): δ = 11.3 (s, $CH_2CH_2CH_3$), 19.6 (t, $^{4/5}J_{P,C}$ = 2.3 Hz, $CH_2CH_2CH_3$), 50.7 (t, $^{3/4}J_{P,C}$ = 7.8 Hz, $CH_2CH_2CH_3$), 154.2 (dd, $^{1}J_{P,C}$ = 36.0 Hz, $^{2}J_{P,C}$ = 32.1 Hz, $C^{4/5}$), 164.0 (dd, $^{1}J_{P,C}$ = 33.4 Hz, $^{2}J_{P,C}$ = 30.1 Hz, $C^{4/5}$), 190.0 (t, $^{3}J_{P,C}$ = 3.5 Hz, *C*=S).

^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ = 134.3 (s).

IR (ATR, ṽ {cm^{-1}}): ṽ = 1455 (w), 1348 (m), 1307 (s), 1287 (s), 1158 (s), 1105 (vs), 1017 (vs), 932 (s), 888 (s), 848 (s) 746 (s), 678 (s).

MS (EI, 70 eV): m/z (%) = 376.0 (75) $[M]^+$, 333.9 (37) $[M-{}^{n}Pr]^+$, 301.0 (8) $[M-{}^{n}Pr-S]^+$, 291.9 (100) $[M-2{}^{n}Pr]^+$,

HR-MS ($C_{12}H_{14}N_2P_2S_4$): found = 375.9516, calc. = 375.9515.

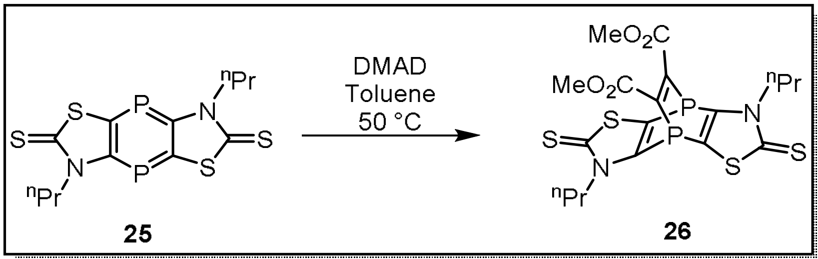
Elemental analysis for $C_{12}H_{14}N_2P_2S_4$:

Calculated	C	38.29	H	3.75	N	7.44	S	34.07
Found	C	38.20	H	3.77	N	7.34	S	33.94

10.29 [4+2]-Cycloaddition reactions of 1,4-diphosphinine 25

In a Schlenk tube, reagent (see the table below) was added to a suspension of 1,4-diphosphinine **25** in dry toluene (temperature is given in the table below). It was stirred (time is given in the table below). Solvent was removed under reduced pressure (8•10^{-3} mbar) and the obtained solid was washed with *n*-pentane (2•2 mL **26** and **27a**) and dried *in vacuo* (8•10^{-3} mbar).

10.29.1 7,8-Bis(methyloxocarbonyl)-[2,3-d:5,6-d']bis(3-^{n}butyl-thiazole-2-thione)-1,4-diphospha-bicyclo[2.2.2]octa-2,5,7-triene (26)



	amount used (g/mL)	mmol	min/°C
25	0.50 g	1.32	
DMAD	0.17 mL	1.39	
Toluene	20 mL		
Reaction time/temp			45/50

Yield:0.50 g (0.96 mmol), 73 %, yellow orange solid.

Melting point:205°C.

Elemental composition:$C_{18}H_{20}N_2O_4P_2S_4$

Molecular weight: 518.56 g/mol.

^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 1.01 (t, 6H, $^3J_{H,H}$ = 7.41 Hz, $CH_2CH_2CH_3$), 1.80 (m, 4H, $CH_2CH_2CH_3$), 3.82 (s, OCH_3), 4.27-4.51 (m, 4H, CH_2-CH_2-CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2):δ = 10.9 (s, $CH_2CH_2CH_3$), 22.3 (t, $^{4/5}J_{P,C}$ = 1.62 Hz,N $CH_2CH_2CH_3$), 51.5 (t, $^{3/4}J_{P,C}$ = 4.8 Hz, $CH_2CH_2CH_3$), 53.4 (s, OCH_3), 131.7 (dd, $^1J_{P,C}$ = 17.2 Hz, $^2J_{P,C}$ = 15.0 Hz, C^5), 157.6 (dd, $^1J_{P,C}$ = 15.1 Hz, $^2J_{P,C}$ = 14.0 Hz,CCO_2Me), 160.1 (dd, $^1J_{P,C}$ = 11.1 Hz, $^2J_{P,C}$ = 9.3 Hz,C^4), 165.5 (t, $J_{P,C}$ = 17.1 Hz, CCO_2Me), 189.4 (br, C=S).

^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2):δ= -75.4 (s).

IR (ATR, $\tilde{\upsilon}$ {cm^{-1}}): $\tilde{\upsilon}$ = 2953 (w), 1711 (vs), 1572 (m), 1430 (m), 1359 (s), 1332 (m),1253 (vs), 1212 (vs),1141 (vs), 1060 (s),1020 (s), 915 (m), 879 (s), 815 (vs), 744 (m), 653 (s), 618 (s), 468 (s).

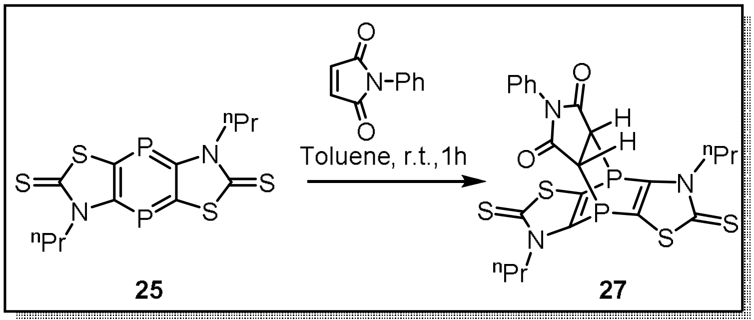
MS (EI, 70 eV):m/z (%) = 292.0 (100) $[C_6N_2P_2S_4]^+$, 301 (10) $[C_9H_7N_2P_2S_3]^+$, 376.0 (75) $[C_{12}H_{14}N_2P_2S_4]^+$, 518.0 (68) $[M]^+$.

HR-MS: found = 517.9777, calc. = 517.9781.

Elemental analysis:for $C_{18}H_{20}N_2O_4P_2S_4$:

Calculated	C	41.69	H	3.89	N	5.40	S	24.73
Found	C	41.53	H	3.72	N	5.37	S	24.82

10.29.2 7,8-(*N*-Phenylmaleimide)-[2,3-d:5,6-d']bis(3-ⁿpropyl-thiazole-2-thione)-1,4-diphospha-7,8-dihydro-bicyclo[2.2.2]octa-2,5-diene (27)



	amount used (g/mL)	mmol	min/°C
25	0.35 g	0.92	
1-phenyl pyrrole-1,5-dione	0.16 g	0.97	
Toluene	15 mL		
Reaction time/temp			120/25

Yield:0.48 g (0.87 mmol), 94 %, white solid.

Melting point:289 °C.

Elemental composition:$C_{22}H_{21}N_3O_2P_2S_4$

Molecular weight: 549.62 g/mol.

^{1}H NMR (300.1 MHz, CD_2Cl_2):δ = 1.01 (t, 3H, $^3J_{H,H}$ = 7.37 Hz, $CH_2CH_2CH_3$), 1.10 (t, 3H, $^3J_{H,H}$ = 7.40 Hz, $CH_2CH_2CH_3$), 1.68-1.83 (m, 2H, $CH_2CH_2CH_3$), 1.84-1.94 (m, 2H, $CH_2CH_2CH_3$), 3.86 (m, 1H, $(CHCO)_2$N-Ph), 3.95 (m, 1H, $(CHCO)_2$ N-C_6H_5), 4.23-4.54 (m, 4H, CH_2-CH_2-CH_3), 6.90-7.00 (m, 2H, N-C_6H_5), 7.44-7.51 (m, 3H, C_6H_5).

^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2):δ = 11.2 (s, $CH_2CH_2CH_3$), 11.3 (s, $CH_2CH_2CH_3$) 22.3 (d, $^4J_{P,C}$ = 3.0 Hz,$CH_2CH_2CH_3$), 22.8 (d, $^4J_{P,C}$ = 3.4 Hz,$CH_2CH_2CH_3$), 44.1 (dd, $^1J_{P,C}$ = 16.4 Hz, $^2J_{P,C}$ = 2.3 Hz, P-CH), 44.6 (dd, $^1J_{P,C}$ = 16.3 Hz, $^2J_{P,C}$ = 2.2 Hz, P-CH) 51.6 (d, $^3J_{P,C}$ = 10.2 Hz, $CH_2CH_2CH_3$), 125.4 (dd, $^1J_{P,C}$ = 29.5 Hz, $^2J_{P,C}$ = 5.8 Hz,C^5), 126.8 (s, N-C_6H_5),127.2 (dd, $^1J_{P,C}$ = 25.1 Hz, $^2J_{P,C}$ = 5.5 Hz,C^5), 128.8 (s, C_6H_5), 129.9 (s, C_6H_5), 131.3 (s, C_6H_5), 151.7 (dd, $^2J_{P,C}$ = 21.5 Hz, $^2J_{P,C}$ = 3.5 Hz, C^4), 152.5 (dd, $^2J_{P,C}$ = 17.1 Hz, $^2J_{P,C}$ = 2.3 Hz, C^4), 172.2 (d, $^2J_{P,C}$ = 6.5 Hz, (CH*CO*)$_2$ N-C_6H_5), 172.7 (d, $^2J_{P,C}$ = 6.5 Hz, (CH*CO*)$_2$ N-C_6H_5), 191.0 (d, $^3J_{P,C}$ = 2.0 Hz, *C*=S), 191.2 (d, $^3J_{P,C}$ = 1.9 Hz, *C*=S).

$^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = -75.7 (d, $^3J_{P,P}$ = 28.8 Hz, P), -74.3 (d, $^3J_{P,P}$ = 28.8 Hz, P).

IR (ATR, ῦ {cm^{-1}}): ῦ = 2966 (w), 2869 (w), 1769 (m), 1705 (vs), 1491 (w), 1458 (m), 1360 (vs), 1286 (s), 1214 (s), 1140 (s), 1024 (s), 925 (s), 821 (s), 735 (s), 696 (s), 621 (m),735 (s), 696 (s), 621 (m), 541 (m), 452 (s).

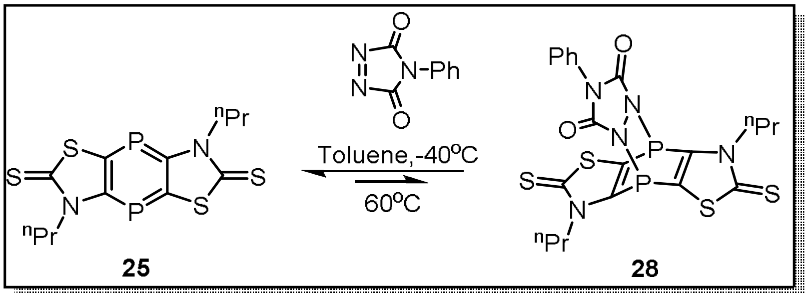
MS (EI, 70 eV): m/z (%) = 549.1 (10) $[M]^+$, 549.1 (10) $[M]^+$, 376.0 (85) $[C_{12}H_{14}N_2P_2S_4]^+$, 291.9 (100) $[M\text{-}2^nPr\text{-} C_{10}H_7NO_2]^+$ 173.2 (50) $[C_{10}H_7NO_2]^+$.

Elemental analysis: for $C_{22}H_{21}N_3O_2P_2S_4$:

Calculated	C	48.08	H	3.85	N	7.65	S	23.33
Found	C	48.20	H	3.89	N	7.50	S	23.14

10.29.3 7,8-(4-Phenyl-1,2,4-triazoline-3,5-dione)-[2,3-d:5,6-d']bis(3-^{n}propylthiazole-2-thione)-1,4-diphospha-7,8-dihydro-bicyclo[2.2.2]octa-2,5-diene (28)

The reaction did not proceed to completion and at aconversion of almost 50 % an equilibrium was established (as revealed by ^{31}P-NMR monitoring). The solvent was removed from this mixture, and the obtained solid was used for the analysis.



	amount used (g/mL)	mmol	min/°C
25	0.50 g	1.32	
4-Phenyl-1,2,4-triazolinedione	0.24 g	2.39	
Toluene	25 mL		
Reaction time/temp			60/–40-r.t.

$^{31}P\{^1H\}$ NMR (121.5 MHz, Toluene): δ = −47.4 (s)

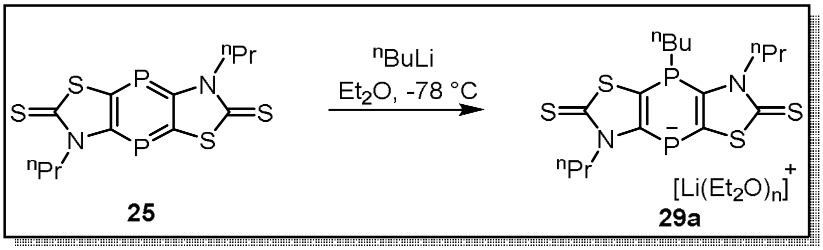
MS (EI, 70 eV): m/z (%) *m/z* = 551.0 (40) $[M]^+$, *m/z* = 376 (85 %) $[C_{12}H_{14}N_2P_2S_4]^+$, 334.0 (35 %) $[M\text{-}C_{12}H_{14}N_2P_2S_4\text{-}^nPr]^+$, 177.1 (40%) $[C_8H_5N_3O_2]^+$.

HR-MS: found = 550.9893, calc. = 550.9897.

10.30 Reaction of 1,4-diphosphinine 25 with nucleophiles

To a suspension of **25** in a Schlenk tube in dry diethylether, the reagent (^{n}BuLi for **29a** and KHMDS solution in 7 mL Et_2O for **29b**) was added at −78 °C (for **29a)** or at r.t. (for **29b**). Red solutions were formed (in both cases) which were stirred for 10 min. Only **29b** was isolated by immediate solvent removal under reduced pressure ($8•10^{-3}$ mbar) and washing with *n*-pentane (2•3 mL). **29b** wasobtainedas red powder after drying *in vacuo* ($8•10^{-3}$ mbar). However, the NMR data are given below of the *in situ* prepared thf-analogue of **29b** measured at -30 °C.

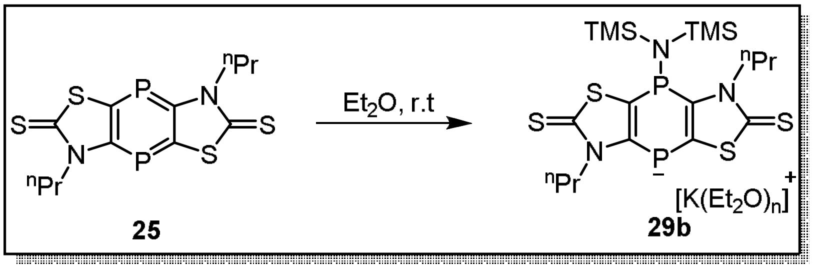
10.30.1 Lithium(Et_2O)$_n$ [3,7-di^{n}propyl-[2,3-d:5,6-d']bis-thiazole-2,6-dithione-4-^{n}butyl-8-phosphan-1-ide](29a)



	amount used (g/mL)	mmol
25	0.13 g	0.33
^{n}BuLi	0.21 mL	0.35
Ether	10 mL	

$^{31}P\{^1H\}$ NMR (202.4 MHz, Et_2O): δ = −59.1 (s), −21.1 (s).

10.30.2 Potassium (Et$_2$O)$_n$ [3,7-di^{n}propyl-[2,3-d:5,6-d']bis-thiazole-2,6-dithione-4-bis(trimethylsilyl)amino-8-phosphan-1-ide] (29b)



Note: The exact number of solvent ligands (in solution) could not be determined due to *in situ* preparation and characterization in THF-d$_8$ because of stability issues in THF.

	amount used (g/mL)	mmol
25	0.15 g	0.39
KHMDS	0.09 9	0.44
Ether	10 mL	

Yield:0.23 g (0.28 mmol), 70 %, red solid.

Elemental composition:$C_{18}H_{31}N_3P_2S_4Si_2^-$(Except for $[K(solv)_n]^+$)

^{1}H NMR (500.1 MHz, THF-d$_8$, -30 °C): δ = −0.11 (s, br, 9H, –Si(C*H$_3$*)$_3$), 0.30 (s, br, 9H, = –Si(C*H$_3$*)$_3$), 0.90 (t, 3H, $^3J_{\mathrm{H,H}}$ = 7.43 Hz, CH$_2$CH$_2$C*H$_3$*), 0.97 (t, 3H, $^3J_{\mathrm{H,H}}$ = 7.43 Hz, CH$_2$CH$_2$C*H$_3$*), 1.74-193 (m, 4H, CH$_2$C*H$_2$*CH$_3$), 3.78-3.96 (br, 2H, C*H$_2$*CH$_2$CH$_3$), 4.23 (br, 1H C*H$_2$*CH$_2$CH$_3$), 4.58 (td, 1H $^2J_{\mathrm{H,H}}$ = 5.3 Hz, $^3J_{\mathrm{H,H}}$ = 12.2 Hz, C*H$_2$*CH$_2$CH$_3$).

^{13}C{^{1}H} NMR (125.75 MHz, THF-d$_8$, -30 °C): δ = 2.7 (s, br, -Si(*CH$_3$*)$_3$), 4.9 (d, $^3J_{\mathrm{P,C}}$ = 17.4 Hz, Si(*CH$_3$*)$_3$), 11.5 (s, CH$_2$CH$_2$*C*H$_3$), 20.6 (d, $^4J_{\mathrm{P,C}}$ = 4.4 Hz, CH$_2$*C*H$_2$CH$_3$), 21.8 (d, $^4J_{\mathrm{P,C}}$ = 8.4 Hz,CH$_2$*C*H$_2$CH$_3$) 49.3 (d, $^3J_{\mathrm{P,C}}$ = 21.3 Hz, *C*H$_2$CH$_2$CH$_3$), 49.6 (d, $^3J_{\mathrm{P,C}}$ = 13.9 Hz, *C*H$_2$CH$_2$CH$_3$), 106.7 (dd, $^1J_{\mathrm{P,C}}$ = 17.3 Hz, $^2J_{\mathrm{P,C}}$ = 8.2 Hz, *C*$^{4/5}$), 126.5 (dd, $^1J_{\mathrm{P,C}}$ = 12.0 Hz, $^2J_{\mathrm{P,C}}$ = 8.9 Hz, C$^{4/5}$), 148.5 (dd, $^1J_{\mathrm{P,C}}$ = 54.0 Hz, $^2J_{\mathrm{P,C}}$ = 8.2 Hz, *C*$^{4/5}$), 161.2 (dd, $^1J_{\mathrm{P,C}}$ = 51.1, $^2J_{\mathrm{P,C}}$ = 5.9 Hz,C$^{4/5}$), 184.3 (d, $^3J_{\mathrm{P,C}}$ = 5.83 Hz *C*=S), 188.7 (d, $^3J_{\mathrm{P,C}}$ = 11.1 Hz *C*=S).

^{31}P{^{1}H} NMR (202.4 MHz, THF-d$_8$,-30 °C): δ = −28.8 (s, P), 6.7 (s, N-P).

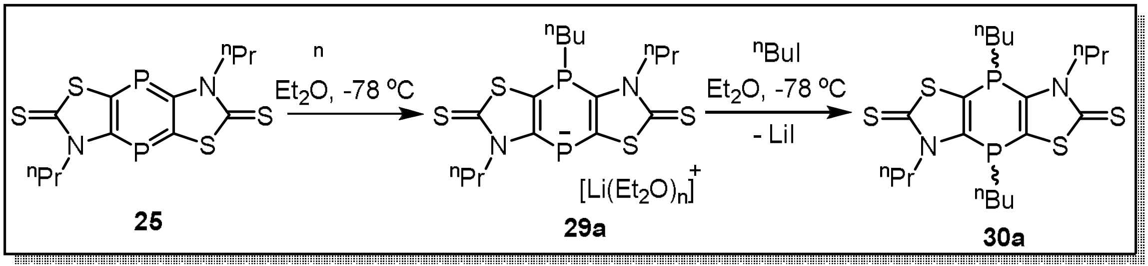
IR (ATR, ṽ {cm^{-1}}): ṽ = 2959 (m), 1436 (w), 1397 (m), 1254 (s), 1251 (s), 1207(s), 1133 (vs), 1102 (s), 998 (vs), 856 (vs) 819 (s), 761 (s), 676 (vs), 430 (vs).

MS (neg. ESI-MS): $C_{18}H_{31}N_3P_2S_4Si_2^-$ =: found = 538.0499, calc. = 538.0499.

10.31 General procedure for the reaction of mono anions 29a, 29b with electrophiles: ^{n}BuI and Ph_2PCl

In a Schlenk tube to an ether solution of freshly prepared **29a**/**29b**,reagent (^{n}BuI for **29a** and Ph_2PCl for **29b**) was added dropwise at −78 °C for **29a** or −70 °C for **29b**. The reaction mixture was stirred (for two h **30a** and 30 min **30b**) and warmed up to ambient temperature. The solvent was removed *in vacuo* ($8{\bullet}10^{-3}$ mbar) and the residue was taken in dicholoromethane for **30a** and toluene for **30b** and filtered to remove the formed salt (over frit having silica gel for **30a** and via canula for **30b)** The filtrate was collected, solvent was removed *in vacuo* ($8{\bullet}10^{-3}$ mbar). The obtained solid was washed twice with *n*-pentane (3 mL each) and dried *in-vacuo*($8{\bullet}10^{-3}$ mbar).

10.31.1 4,8-Di^{n}butyl-3,7-di^{n}propyl-4,8-dihydro-1,4-diphosphinine[2,3 -d:5,6-d']bis-thiazole-2,6-dithione (30a)



	amount used (g/mL)	mmol
25	0.13 g	0.33
^{n}BuLi	0.21 mL	0.35
^{n}BuI	0.1 mL	0.33
Ether	10 mL	

Yield:0.09 g (0.18 mmol), 55 %, white solid.

Melting point:165 °C.

Elemental composition:$C_{20}H_{32}N_2P_2S_4$

Molecular weight: 490.68 g/mol.

^{1}H NMR (300.1 MHz, $CDCl_3$):δ = 0.82 (t, 6H, ${}^{3}J_{H,H}$ = 7.12 Hz, N–$CH_2CH_2CH_3$), 0.91 (t, 6H, ${}^{3}J_{H,H}$ = 7.23 Hz, N–$CH_2CH_2CH_3$*2*nd *isomer*), 1.00 (t, 12H, ${}^{3}J_{H,H}$ = 7.40 Hz, P–CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.05-1.19 (m, 4H, N–CH$_2$C*H*$_2$CH$_3$) 1.21-1.31 (m, 4H, N-CH$_2$C*H*$_2$CH$_3$ *2nd isomer*), 1.31-1.50 (m, 4H, P-CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.51-1.66 (m, 4H, P-CH$_2$CH$_2$C*H*$_2$CH$_3$ *2nd isomer*), 1.67-1.74 (m, 4H, P-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.74-1.82 (m, 4H, P-CH$_2$C*H*$_2$CH$_2$CH$_3$ *2nd isomer*), 1.83-1.89 (m 4H, P-C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.91-214 (m, 4H, P-C*H*$_2$CH$_2$CH$_2$CH$_3$ *2nd isomer*), 3.79-3.93 (m, 4H, N-C*H*$_2$CH$_2$CH$_3$), 4.42-4.60 (m. 4H, N-C*H*$_2$CH$_2$CH$_3$ *2nd isomer*).

^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$):δ = 11.1 (s, br, P-CH$_2$CH$_2$CH$_2$*C*H$_3$), 11.2 (s, br, P-CH$_2$CH$_2$CH$_2$*C*H$_3$*2nd isomer*), 13.6 (s, br, N-CH$_2$CH$_2$*C*H$_3$), 13.7 (s, br, N-CH$_2$CH$_2$*C*H$_3$ *2nd isomer*), 20.8 (s, br, P-CH$_2$CH$_2$*C*H$_2$CH$_3$), 21.3 (s, br, P-CH$_2$CH$_2$*C*H$_2$CH$_3$ *2nd isomer*), 23.7 (t, $^{4/5}J_{P,H}$ = 5.0 Hz, N-CH$_2$*C*H$_2$CH$_3$), 24.03 (t, $^{4/5}J_{P,H}$ = 6.1 Hz, N-CH$_2$*C*H$_2$CH$_3$ *2nd isomer*), 26.7 (s, br, P-CH$_2$*C*H$_2$CH$_2$CH$_3$), 28.5 (t, $^{2/5}J_{P,H}$ = 6.3 Hz, P-CH$_2$*C*H$_2$CH$_2$CH$_3$ *2nd isomer*), 31.0 (dd, $^{1}J_{P,C}$ = 19.9 Hz, $^{4}J_{P,C}$ = 5.6 Hz, P-*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.4 (dd, $^{1}J_{P,C}$ = 25.0, Hz, $^{4}J_{P,C}$ = 11.0 Hz, P-*C*H$_2$CH$_2$CH$_2$CH$_3$ *2nd isomer*), 50.7 (t, $^{3/5}J_{P,C}$ = 7,0, Hz, N-*C*H$_2$CH$_2$CH$_3$), 51.8 (dd, $^{3}J_{P,C}$ = 13.7 Hz, $^{5}J_{P,C}$ = 6,9 Hz, N-*C*H$_2$CH$_2$CH$_3$ *2nd isomer*), 122.5 (dd, $^{1}J_{P,C}$ = 13.6 Hz, $^{2}J_{P,C}$ = 8.0 Hz, C$^{4/5}$), 123.4 (dd, $^{1}J_{P,C}$ = 12.1 Hz, $^{2}J_{P,C}$ = 10.2 Hz, C$^{4/5}$ *2nd isomer*),139.2 (dd, $^{1}J_{P,C}$ = 13.5 Hz, $^{2}J_{P,C}$ = 6.8 Hz, C$^{4/5}$), 141.5 (dd, $^{1}J_{P,C}$ = 7.9 Hz, $^{2}J_{P,C}$ = 6.8 Hz, C$^{4/5}$ *2nd isomer*), 189.9 (br, *C*=S), 190.1 (br, *C*=S *2nd isomer*).

^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$):δ = −44.1 (s), −38.3 (s).

IR (ATR, ṽ {cm^{-1}}):ṽ = 2961 (m), 2926 (w), 2867 (w), 1458 (w), 1348 (s), 11294 (m), 1212 (m), 1177 (m), 1139 (vs), 1097 (s), 1001 (s), 928 (s) 817 (s), 795 (m), 780 (m), 661 (s).

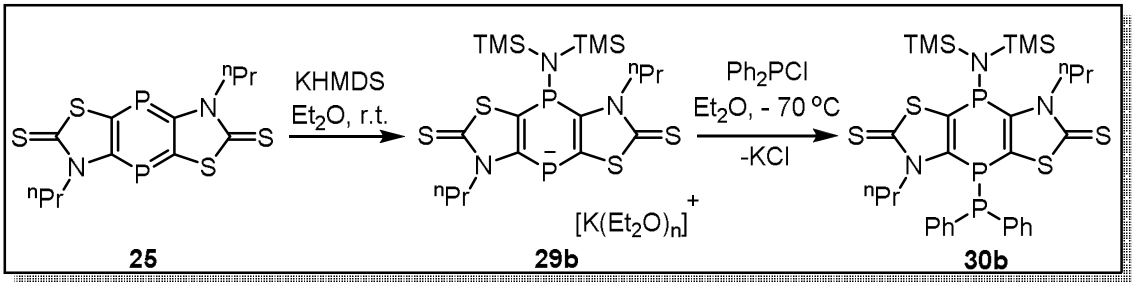
MS (EI,70 eV):m/z (%) = 549.0 (90) [M]$^{+}$, 433.0 (10) [M−^{n}Bu]$^{+}$, 390.9 (65) [M-^{n}Bu-^{n}Pr]$^{+}$, 376.9 (50) [M-2^{n}Bu]$^{+}$, 348.9 (25) [M-^{n}Bu-2^{n}Pr]$^{+}$, 291.8 (80) [M-2^{n}Bu-2^{n}Pr]$^{+}$, 57.1 (60) [^{n}Bu]$^{+}$.

HR-MS: found = 490.0921, calc. = 490.0924.

Elemental analysis:for C$_{20}$H$_{32}$N$_2$P$_2$S$_4$:

Calculated	C	48.96	H	6.57	N	5.71	S	26.14
Found	C	48.37	H	6.68	N	5.62	S	23.79

10.31.2 4-Bis(trimethylsilyl)amino-8-diphenylphosphanyl-3,7-di^{n}propyl-4,8-dihydro[1,4]diphosphinine[2,3-d:5,6-d']bis-thiazole-2,6-dithione (30b)



	amount used (g/mL)	mmol
25	0.15 g	0.39
KHMDS	0.09 9	0.44
Ph$_2$PCl	0.08 mL	0.49
Ether	10 mL	

Yield:0.19 g (0.26 mmol), 66 %, yellow solid.

Melting point:147 °C.

Elemental composition:$C_{30}H_{42}N_3P_3S_4Si_2$

Molecular weight: 722.02 g/mol.

^{1}H NMR (300.1 MHz, CDCl$_3$):δ = −0.10 (s, br, 9H, −Si(CH_3)$_3$), 0.33 (d, 9H, $^4J_{P,H}$ = 2.7 Hz, −Si(CH_3)$_3$), 1.01 (m, 6H, CH$_2$CH$_2$CH_3), 1.41-2.10 (m, 4H, CH$_2$CH_2CH$_3$), 3.75-3.9 (m, 2H, CH_2CH$_2$CH$_3$), 4.36-4.68 (m, 2H, CH_2CH$_2$CH$_3$), 7.05 (t, 2H, $^{3/4}J_{P,H}$= 7.56 Hz, *o*-C$_6$$\mathit{H}_5$), 7.26 (t, 2H, $^{3/4}J_{P,H}$= 7.64 Hz, *o*-C$_6$$\mathit{H}_5$), 7.38-7.51 (m, 6H, *m,p*-C$_6$H$_5$).

^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$):δ= 3.5 (s, −Si(*C*H$_3$)$_3$), 4.1 (d, $^3J_{P,C}$ = 15.2 Hz, −Si(*C*H$_3$)$_3$), 11.2 (s, CH$_2$CH$_2$*C*H$_3$), 11.3 (s, CH$_2$CH$_2$*C*H$_3$), 21.2 (dd, $^4J_{P,C}$ = 4.5, Hz, $^5J_{P,C}$ = 1.6 Hz, CH$_2$*C*H$_2$CH$_3$), 21.5 (d, $^4J_{P,C}$ = 4.6 Hz, CH$_2$*C*H$_2$CH$_3$), 50.9 (d, $^3J_{P,C}$ = 6.2 Hz *C*H$_2$CH$_2$CH$_3$), 51.6 (dd, $^3J_{P,C}$ = 10.5, Hz, $^4J_{P,C}$ = 7.0 Hz, *C*H$_2$CH$_2$CH$_3$), 116.5 (dd, $^1J_{P,C}$ = 9.3 Hz, $^2J_{P,C}$ = 1.4 C$^{4/5}$), 117.0 (dd, $^1J_{P,C}$ = 9.0 Hz, $^2J_{P,C}$ = 1.3 C$^{4/5}$),129.0 (d, $^3J_{P,C}$ =7.5 Hz, *m*-C$_6$H$_5$), 129.3 (d, $^3J_{P,C}$ = 5.0 Hz, *m*-C$_6$H$_5$), 129.6 (d, $^4J_{P,C}$ = 2.0 Hz, *p*-C$_6$H$_5$), 130.4 (s, br, *p*-C$_6$H$_5$), 130.4 (dd, $^1J_{P,C}$ = 28.2 Hz, $^2J_{P,C}$ = 12.6 Hz, *ipso*-*C*$_6$H$_5$), 131.4 (dd, $^1J_{P,C}$ = 20.1 Hz, $^2J_{P,C}$ = 4.6 Hz *ipso*-*C*$_6$H$_5$), 132.7 (dd, $^2J_{P,C}$ = 15.3 Hz, $^3J_{P,C}$ = 11.5 Hz, *o*-C$_6$H$_5$), 133.4 (dd, $^2J_{P,C}$ =

20.6 Hz, $^3J_{P,C}$ = 3.7 Hz, *o*-C_6H_5), 147.5 (dd, $^1J_{P,C}$ = 5.1 Hz, $^2J_{P,C}$ = 4.4 Hz, $C^{4/5}$), 148.1 (dd, $^1J_{P,C}$ = 5.2 Hz, $^2J_{P,C}$ = 4.3 Hz,$C^{4/5}$), 189.3 (dd, $^3J_{P,C}$ = 6.6 Hz, $^4J_{P,C}$ = 1.2 Hz, *C*=S), 189.6 (d, $^3J_{P,C}$ = 5.2 Hz).

^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$):$\delta = -50.8$ ppm (dd, $^1J_{P,P}$ = 294.2 Hz, $^4J_{P,P}$ = 15.9 Hz, *P*Ph$_2$), 9.5 ppm (dd, $^1J_{P,P}$ = 294.2 Hz, $^3J_{P,P}$ = 18.4 Hz, P*P*Ph$_2$), 15.0 ppm (t, $J_{P,P}$ = 17.1 Hz, -*P*NSi(CH$_3$)$_3$).

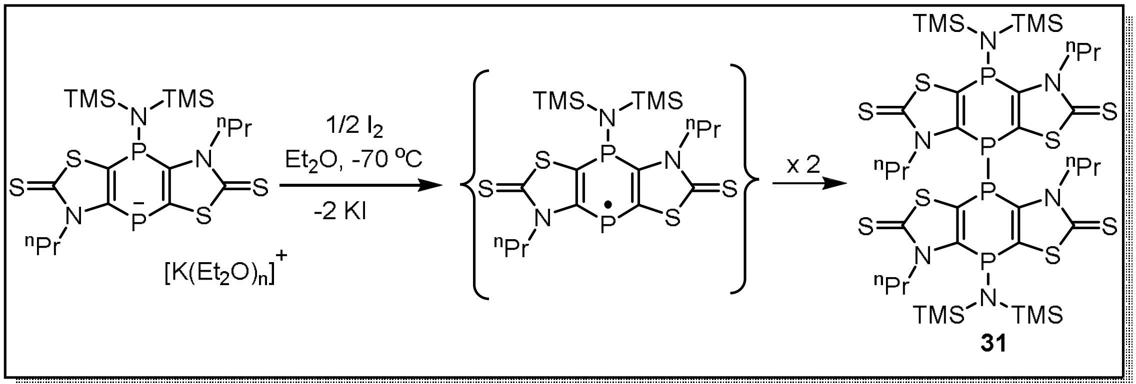
IR (ATR, ṽ {cm^{-1}}): ṽ = 2959 (m), 1436 (w), 1397 (m), 1354 (s), 1251 (s), 1207 (s), 1133 (vs), 1102 (s), 998 (s), 856 (vs) 761 (m), 734 (m), 676 (s), 620 (w).

MS (APCI):HR-MS: found for [$C_{30}H_{42}N_3P_3S_4Si_2$]H = 723.1136, calc. = 723.1112.

Elemental analysis: for $C_{30}H_{42}N_3P_3S_4Si_2$: found: C 50.00, H 5.96, N 5.70, S 17.34 Calc.: C 49.91, H 5.86, N 5.82, S 17.76.

Calculated	C	49.91	H	5.86	N	5.82	S	17.76
Found	C	50.17	H	5.95	N	5.75	S	17.43

10.32 Oxidation reaction of the mono anion 29b and formation of the P-P dimer of [3,7-di^{n}propyl-[2,3-d:5,6-d']bis-thiazole-2,6-dithione-4-bis(trimethylsilyl)amino-8-phosphan-1-yl] radical



In a Schlenk flask a suspension **25** (0.31 g, 0.85 mmol) was prepared using 20 mL of dry diethylether. To this suspension, ether (15 mL) solution of KHMDS (0.18 g, 0.90 mmol) was added at ambient temperature. Red solution was formed which was stirred for 10 min at ambient temperature and then cooled down to −70°C. Ether (10 mL) solution of iodine (0.06

g 0.44 mmol) was added dropwise and the reaction mixture turned greenish. The reaction solution was stirred for half an hour and then solvent was removed under reduced pressure ($8{\bullet}10^{-3}$ mbar). The residue was taken in dry toluene and filtered via cannula to remove the formed potassium chloride. Solvent was removed again in-vacuo ($8{\bullet}10^{-3}$ mbar) and the obtained greenish yellow solid was washed with *n*-pentane (2•5 mL) and dried *in vacuo* ($8{\bullet}10^{-3}$ mbar).

Yield:0.6 g (0.55 mmol), 65 %, Greenish yellow solid.

Melting point:260 °C.

Elemental composition:$C_{36}H_{64}N_6P_4S_8Si_4$

Molecular weight: 1073.67 g/mol.

^{1}H NMR (500.1 MHz, CDCl$_3$):$\delta = -0.10$ (s, br, 18H, $-\mathrm{Si}(\mathrm{C}H_3)_3$), 0.41 (d, 18H, $^4J_{\mathrm{P,H}} = 2.0$ Hz, $-\mathrm{Si}(\mathrm{C}H_3)_3$), 0.97 (t, 6H, $^3J_{\mathrm{H,H}} = 7.4$ Hz, $\mathrm{CH_2CH_2C}H_3$), 1.10 (t, 6H, $^3J_{\mathrm{H,H}} = 7.4$ Hz, $\mathrm{CH_2CH_2C}H_3$),1.62-1.75 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.78-1.88 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.88-1.98 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.10-2.23 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 3.23-3.35 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 3.96-4.05 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.45-4.60 (m, 4H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$).

^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$):$\delta = 3.6$ (s, $-\mathrm{Si}(C\mathrm{H_3})_3$), 4.1 (d, $^3J_{\mathrm{P,C}} = 13.6$ Hz, $-\mathrm{Si}(C\mathrm{H_3})_3$), 11.2 (s, $\mathrm{CH_2CH_2}C\mathrm{H_3}$), 11.4 (s, $\mathrm{CH_2CH_2}C\mathrm{H_3}$), 21.2 (s, br, $\mathrm{CH_2}C\mathrm{H_2CH_3}$), 22.0 (s, br, $\mathrm{CH_2}C\mathrm{H_2CH_3}$), 50.9 (t, $^{3/4}J_{\mathrm{P,C}} = 7.3$ Hz, $C\mathrm{H_2CH_2CH_3}$), 51.4 (d, $^3J_{\mathrm{P,C}} = 4.6$, Hz, -N $C\mathrm{H_2CH_2CH_3}$), 110.2 (m, C^4), 128.6 (m, C^4), 139.0 (d, $^1J_{\mathrm{P,C}} = 39.5$ Hz, C^5), 151.3 (d, $^1J_{\mathrm{P,C}} = 44.7$ Hz, C^5), 189.2 (d, $^3J_{\mathrm{P,C}} = 3.5$ Hz, C=S), 190.2 (d, $^3J_{\mathrm{P,C}} = 3.5$ Hz, C=S).

^{31}P{^{1}H} NMR (202.4 MHz, CDCl$_3$): $\delta = -42.1$ (t, $^{3/4}J_{\mathrm{P,P}} = 20.1$ Hz, P-P), -40.4 (t, $^{3/4}J_{\mathrm{P,P}} = 20.4$ Hz, P-P *2nd isomer*), 17.9 (t, $^{3/4}J_{\mathrm{P,P}} = 20.2$ Hz, -$P\mathrm{NSi_2(CH_3)_3}$) 19.9 (t, $^{3/4}J_{\mathrm{P,P}} = 20.8$ Hz, -$P\mathrm{NSi_2(CH_3)_3}$ *2nd isomer*).

IR (ATR, ṽ {cm^{-1}}): ṽ = 2963 (m), 1460 (w), 1432 (w), 1352 (vs), 1345 (s), 1213 (vs), 1141 (vs), 1001 (s), 898 (s), 844 (s) 824 (s), 764 (m), 681 (w), 664 (w), 548 (s), 433 (s).

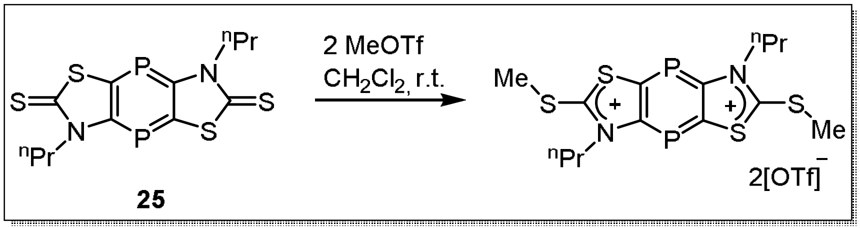
MS (APCI):HR-MS: found for $[C_{36}H_{64}N_6P_4S_8Si_4]H = 1073.1057$, calc. = 1073.1058.

Elemental analysis: for $C_{36}H_{64}N_6P_4S_8Si_4$:

Calculated	C	40.27	H	6.01	N	7.83	S	23.89

Found	C	40.17	H	5.88	N	7.48	S	23.22

10.33 Reaction of 1,4-diphosphinine 25 with MeOTf



A dichloromethane (15 mL) solution of **25** (0.35 g, 0.92 mmol) was prepared in a Schlenk tube. To this solution, MeOTf (0.23mL, 1.97 mmol) was added dropwise at ambient temperature. The reaction mixture was stirred overnight. The solvent was removed *in vacuo* ($8 \cdot 10^{-3}$ mbar) from the obtained yellow solution. The residue was washed with *n*-pentane (3•5 mL). White solid was obtained.

10.33.1 [3,7-Di^{n}propyl-[1,4]diphosphinine[2,3-d:5,6-d']bis-thiazole-2,6-bis(thiazolium)]bis-trifluoromethanesulfonate (32)

Yield:0.6 g (0.84 mmol), 92 %, White solid.

Melting point:150 °C.

Elemental composition: $C_{16}H_{20}F_6N_2O_6P_2S_6$

Molecular weight: 704.64 g/mol.

^{1}H NMR (300.1 MHz, $CDCl_3$):δ = 3.11 (t, 6H, $^3J_{H,H}$ = 7.43 Hz, $CH_2CH_2C\mathit{H}_3$), 4.10 (m, 4H, $CH_2C\mathit{H}_2CH_3$), 5.20 (s, 6H, S*Me*), 6.76 (m, 4H, $C\mathit{H}_2CH_2CH_3$).

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$):δ = 11.4 (s, $CH_2CH_2\mathit{C}H_3$), 20.0 (s, S*Me*), 20.7 (br, $CH_2\mathit{C}H_2CH_3$), 55.4 (t, $^{3/4}J_{P,C}$ = 8.6 Hz, $\mathit{C}H_2CH_2CH_3$), 120.8 (q, $^1J_{P,F}$ = 321.0 Hz, $\mathit{C}F_3$) 156.0 (t, $^{1/2}J_{P,C}$ = 37.0 Hz,$C^{4/5}$), 165.4 (t, $^{1/2}J_{P,C}$ = 34.0 Hz, $C^{4/5}$), 186.7 (t, $^3J_{P,C}$ = 4.6 Hz *C*=S).

^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$):δ = 164.8 (s).

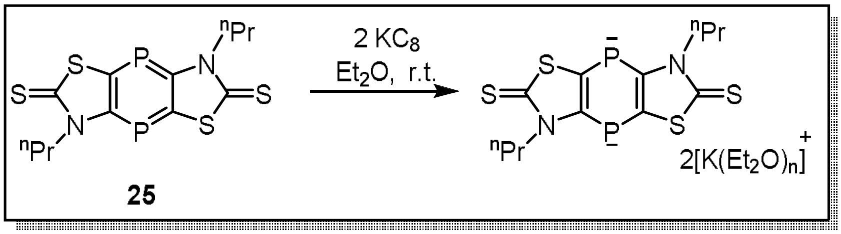
IR (ATR, $\tilde{\upsilon}$ {cm^{-1}}):$\tilde{\upsilon}$ = 3009 (vs), 2976 (vs), 2941 (vs), 2920 (vs), 2884 (vs), 1480 (vs), 1452 (vs), 1436 (s), 1423 (s), 1327 (vs), 1296 (vs), 1254 (w), 1219 (m), 1139 (w), 1122 (m), 1054 (vs), 1026 (w), 975 (s), 960 (s), 937 (vs), 891 (vs), 843 (s), 632 (w), 571 (m), 516 (m).

HR-MS : pos. ESI found = 203.0000, calc. = 202.9999.

EA: for $C_{16}H_{20}F_6N_2O_6P_2S_6$: found: C 27.36, H 2.86, N 3.85, S 27.32. calc.: C 27.27, H 2.86 N 3.98, S 27.30.

Calculated	C	27.27	H	2.86	N	3.98	S	27.30
Found	C	27.36	H	2.86	N	3.85	S	27.32

10.34 Two-fold reduction of 1,4-diphosphinine 25



25 (50.00 mg, 0.13 mmol), KC_8 (35.90 mg, 0.26 mmol) and Et_2O (2 mL) were stirred together in a Schlenk tube at ambient temperature for 20 minutes. Dark blackish red precipitate was formed. Precipitate was filtered and dissolved in THF and filtered again to remove the unreacted graphite. The filtrate was collected, solvent was removed and the obtained dark solid was dried *in vacuo* ($8 \bullet 10^{-3}$ mbar).

The exact number of solvent ligands (in solution) could not be determined because the reaction was performed in Et_2O and THF was used for work up, so it is not clear which solvent is coordinated to K^+in solution (as both Et_2O and THF are donating solvents). The ^{1}H NMR (measured in thf-d_8) showed only traces of ether.

10.34.1 Dipotassium(thf)$_n$[3,7-di^{n}propyl-[2,3-d:5,6-d']bisthiazole-2,6-dithione-4,8-[1,4]bis-phosphane-1,4-diide](33)

Yield: 42.0 mg (0.10 mmol 70 %), Blackish red solid (calculated without solvent molecules).

Elemental composition:$[C_{12}H_{14}N_2P_2S_4]^{2-}$(Except for the counter cation $2[K(solv.)_n]^{2+}$.

^{1}H NMR (300.1 MHz, THF-d_8):δ = 0.92 (br, 6H, $CH_2CH_2CH_3$), 1.76 (br, 4H, $CH_2CH_2CH_3$), 4.11 (br, 4H, $CH_2CH_2CH_3$).

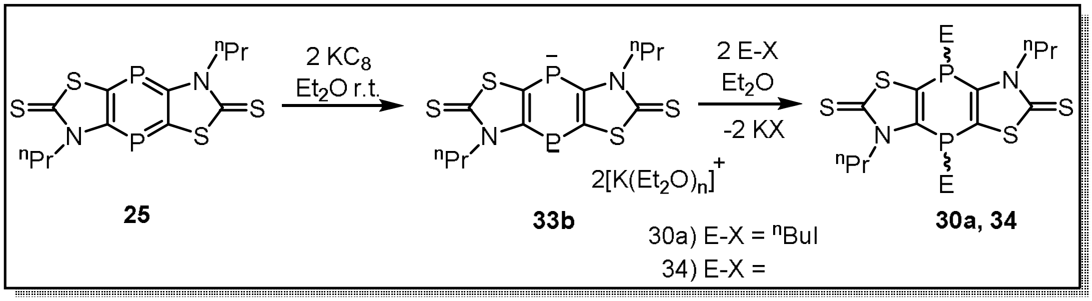
$^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8):δ = 11.7 (s, $CH_2CH_2CH_3$), 21.5 (s, $CH_2CH_2CH_3$), 50.5 (s, br, $CH_2CH_2CH_3$), 122.2 (s, br, $^{4/5}$), 143.6 (s, br, $^{4/5}$), 185.2 (s, br, C=S), 186.2 (s, br, C=S).

^{31}P NMR (121.5 MHz, THF-d_8): $\delta = -43.7$ (s, br), -40.7(s, br).

MS (neg. ESI-MS): $C_{12}H_{15}N_2P_2S_4S^-$ = found = 376.967, calc. = 376.9599.

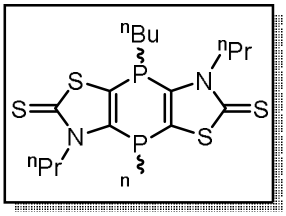
IR (ATR, $\tilde{\nu}$ {cm^{-1}}): $\tilde{\nu}$ = 2956 (w), 2922 (w), 2863 (w), 2134 (w), 1432 (m), 1389 (vs), 1268 (m), 1205 (vs), 1131 (vs), 1101 (s) 1045 (m), 992 (vs), 873 (s), 821 (s), 745 (m), 663 (w), 584 (w), 533 (w), 454 (w).

10.35 Reaction of 33 with electrophiles (^{n}BuI and MeOTf)



25 (50.00 mg, 0.13 mmol), KC_8 (35.90 mg, 0.26 mmol) and Et_2O (2 mL) were stirred together in a Schlenk tube at ambient temperature for 20 minutes. Dark blackish red precipitate was formed. Precipitate was filtered and dissolved in THF and filtered again to remove the unreacted carbon black. The obtained THF solution of **33b** was cooled to −78 °C and then precooled (−78 °C) THF solution of E-X [0.03 mL, 0.26 mmol (^{n}BuI) for **30a**; 0.03 mL, 0.26 mmol (^{n}BuI) for **34**]was added to it. The reaction mixture was stirred for two hours, then solvent was removed *in vacuo* ($8 \cdot 10^{-3}$ mbar), and the obtained solid was dissolved in toluene and filtered to separate the fomed salt. The filtrate was collected, solvent was removed, and the obtained white solid was dried *in vacuo* ($8 \cdot 10^{-3}$ mbar).

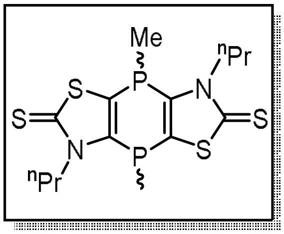
10.35.1 4,8-Di^{n}butyl-3,7-di^{n}propyl-4,8-dihydro-1,4-diphosphinine[2,3 -d:5,6-d']bis-thiazole-2,6-dithione (30a)



Yield: 0.052 g (0.10 mmol), 80 %, White solid.

See section 10.31

10.35.2 4,8-Di^{n}methyl-3,7-di^{n}propyl-4,8-dihydro-1,4-diphosphinine[2,3 -d:5,6-d']bis-thiazole-2,6-dithione (34)



Yield:0.047 g (0.11 mmol), 88 %, White solid.

Elemental composition: $C_{14}H_{20}N_2P_2S_2$

Molecular weight:406.52 g/mol

^{1}H NMR (300.1 MHz, THF-d$_8$):δ = 1.01 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, $CH_2CH_2C\mathit{H}_3$), 1.02 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, $CH_2CH_2C\mathit{H}_3$ *2nd isomer*), 1.80 (m, P-C*H*$_3$), 3.63 (m, 4H, $CH_2C\mathit{H}_2CH_3$), 4.0 (m, 2H, $C\mathit{H}_2CH_2CH_3$), 4.55 (m, 2H, $C\mathit{H}_2CH_2CH_3$).

^{13}C{^{1}H} NMR (75.5 MHz, THF-*d$_8$*):δ = 11.0 (s, $CH_2CH_2\mathit{C}H_3$), 18.2 ((dd, $^1J_{P,C}$ = 8.0 Hz, $^4J_{P,C}$= 6.0 Hz, P-*C*H$_3$), 21.6 (t, $^{4/5}J_{P,C}$ = 1.9 Hz, $CH_2\mathit{C}H_2CH_3$), 50.6 (t, br, $^{3/4}J_{P,C}$ = 7.2 Hz, $\mathit{C}H_2CH_2CH_3$), 124.4 (dd, $^1J_{P,C}$= 10.4 Hz, $^2J_{P,C}$ = 9.3 Hz, $C^{4/5}$), 143.3 (dd, $^1J_{P,C}$ = 7.5 Hz, $^2J_{P,C}$ = 6.9 Hz, $C^{5/4}$), 190.5 (t, $^3J_{P,C}$ = 4.0 Hz C^2).

^{31}P NMR (121.5 MHz, THF-*d$_8$*):δ = −50.2 ppm (s) 16 %, −54.2 ppm (s *2nd isomer*) 84 %

MS (EI,70 eV):m/z (%) = 406.0 (60) [M]$^+$, 363.9 (30) [M−^{n}Pr]$^+$, 348.9 (20) [M-Me-^{n}Pr]$^+$, 321.9 (70) [M-2^{n}Pr]$^+$, 306.9 (35) [M-2^{n}Bu-Me]$^+$, 291.9 (10) [M-2Me-2^{n}Pr]$^+$.

HR-MS: found = 405.9986, calc. = 405.9985.

Elemental analysis: for $C_{14}H_{20}N_2P_2S_4$:

Calculated	C	41.36	H	4.96	N	6.89	S	31.55
Found	C	41.65	H	5.01	N	6.31	S	28.76

Chapter 11

Chapter 11: References

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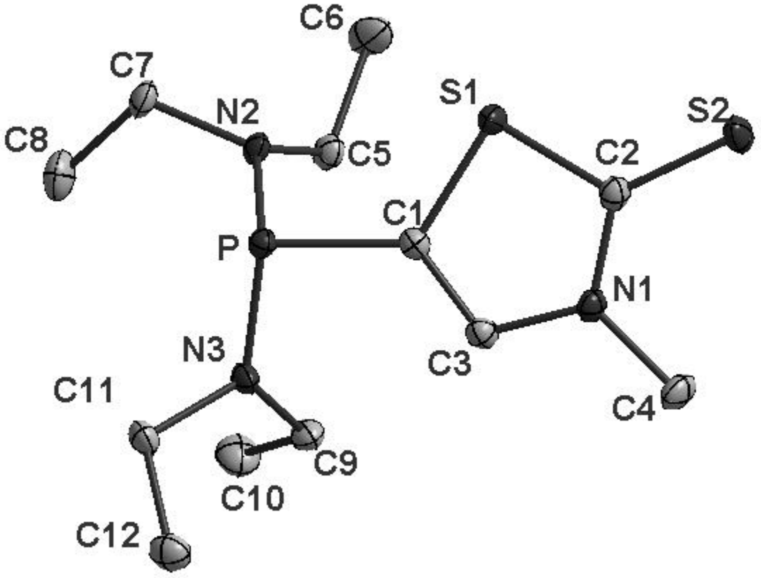
Chapter 12

Chapter 12: Appendix

12.1 Crystal data and structure refinement for 5a (IB-71).



Identification code	GSTR416, IB-71 // GXray4048f	μ/mm^{-1}	0.422
Device Type	Bruker X8-KappaApexII	F(000)	656
Empirical formula	$C_{12}H_{24}N_3PS_2$	Crystal size/mm^3	0.3 × 0.1 × 0.08
Moiety formula	C12 H24 N3 P S2	Absorption correction	empirical
Formula weight	305.43	Tmin; Tmax	0.6828; 0.7460
Temperature/K	100	Radiation	MoKα ($\lambda = 0.71073$)
Crystal system	monoclinic	2Θ range for data collection/°	6.33 to 55.988°
Space group	$P2_1/c$	Completeness to theta	0.995
a/Å	6.1742(5)	Index ranges	$-8 \le h \le 8$, $-31 \le k \le 31$, $-13 \le l \le 14$
b/Å	24.1038(19)	Reflections collected	15854
c/Å	10.8461(8)	Independent reflections	3848 [$R_{int} = 0.0322$, $R_{sigma} = 0.0299$]
α/°	90	Data/restraints/parameters	3848/0/168

β/°	97.663(2)	Goodness-of-fit on F^2	1.062
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0316, wR_2 = 0.0714
Volume/Å^3	1599.7(2)	Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0754
Z	4	Largest diff. peak/hole / e Å^{-3}	0.37/-0.27
ρ_{calc}g/cm^3	1.268		

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.7439(14)	N2	C5	1.4689(18)
S1	C2	1.7416(15)	N2	C7	1.4701(18)
S2	C2	1.6676(15)	N3	C9	1.4657(19)
P	N2	1.6979(12)	N3	C11	1.4721(18)
P	N3	1.6834(13)	C1	C3	1.349(2)
P	C1	1.8202(15)	C5	C6	1.522(2)
N1	C2	1.3544(19)	C7	C8	1.525(2)
N1	C3	1.3821(18)	C9	C10	1.521(2)
N1	C4	1.4629(19)	C11	C12	1.516(2)

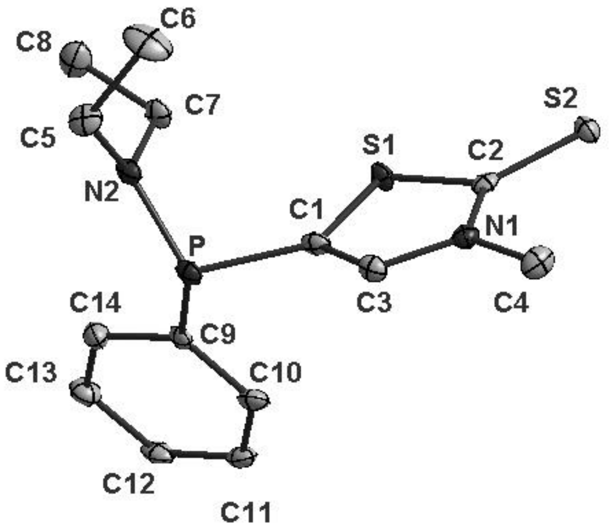
Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	92.93(7)	C11	N3	P	116.68(10)
N2	P	C1	98.51(6)	S1	C1	P	122.63(8)
N3	P	N2	113.51(6)	C3	C1	S1	108.79(11)
N3	P	C1	99.22(6)	C3	C1	P	127.66(11)
C2	N1	C3	115.49(12)	S2	C2	S1	125.34(9)
C2	N1	C4	122.39(13)	N1	C2	S1	108.16(11)
C3	N1	C4	122.09(12)	N1	C2	S2	126.50(12)
C5	N2	P	124.53(10)	C1	C3	N1	114.61(13)
C5	N2	C7	114.85(12)	N2	C5	C6	113.22(13)
C7	N2	P	113.96(9)	N2	C7	C8	115.11(13)
C9	N3	P	126.12(10)	N3	C9	C10	114.41(13)
C9	N3	C11	115.99(12)	N3	C11	C12	113.34(13)

Torsion Angles

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
S1	C1	C3	N1	-1.15(16)	C1	P	N2	C5	48.33(13)
P	N2	C5	C6	-39.18(13)	C1	P	N2	C7	-61.90(11)
P	N2	C7	C8	-77.63(15)	C1	P	N3	C9	-52.58(13)
P	N3	C9	C10	-07.13(14)	C1	P	N3	C11	140.58(11)
P	N3	C11	C12	-29.54(12)	C2	S1	C1	P	170.37(9)
P	C1	C3	N1	-70.28(10)	C2	S1	C1	C3	0.58(12)
N2	P	N3	C9	50.95(14)	C2	N1	C3	C1	1.34(19)
N2	P	N3	C11	-15.89(11)	C3	N1	C2	S1	-0.81(16)
N2	P	C1	S1	52.51(10)	C3	N1	C2	S2	179.64(11)
N2	P	C1	C3	-39.73(14)	C4	N1	C2	S1	177.23(11)
N3	P	N2	C5	-55.66(13)	C4	N1	C2	S2	-2.3(2)
N3	P	N2	C7	94.11(11)	C4	N1	C3	C1	-76.71(13)
N3	P	C1	S1	168.16(9)	C5	N2	C7	C8	75.17(16)
N3	P	C1	C3	-24.08(15)	C7	N2	C5	C6	71.29(17)
C1	S1	C2	S2	179.67(11)	C9	N3	C11	C12	62.26(18)
C1	S1	C2	N1	0.12(11)	C11	N3	C9	C10	59.79(18)

12.2 Crystal data and structure refinement for 5d (IB-190).



Identification code	GSTR559, IB-190 // GXraymo_5083f	ρ_{calc}g/cm^3	1.319
Crystal Habitus	clear colourless plate	μ/mm^{-1}	0.432
Device Type	Bruker D8-Venture	F(000)	656
Empirical formula	$C_{14}H_{19}N_2PS_2$	Crystal size/mm^3	0.26 × 0.15 × 0.02
Moiety formula	C14 H19 N2 P S2	Absorption correction	empirical
Formula weight	310.4	Tmin; Tmax	0.6113; 0.7459
Temperature/K	100.01	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	4.988 to 55.998°
Space group	P-1	Completeness to theta	0.999
a/Å	8.1963(10)	Index ranges	$-10 \leq h \leq 10$, $-16 \leq k \leq 16$, $-20 \leq l \leq 20$
b/Å	12.3995(14)	Reflections collected	71878
c/Å	15.4355(19)	Independent reflections	7516 [R_{int} = 0.1340, R_{sigma} = 0.0665]
α/°	91.257(6)	Data/restraints/parameters	7516/0/350
β/°	94.697(6)	Goodness-of-fit on F^2	1.083
γ/°	90.623(6)	Final R indexes [I>=2σ (I)]	R_1 = 0.0732, wR_2 = 0.1962
Volume/Å^3	1562.9(3)	Final R indexes [all data]	R_1 = 0.0965, wR_2 = 0.2133
Z	4	Largest diff. peak/hole / e Å^{-3}	0.81/-0.53

Bond Lengths

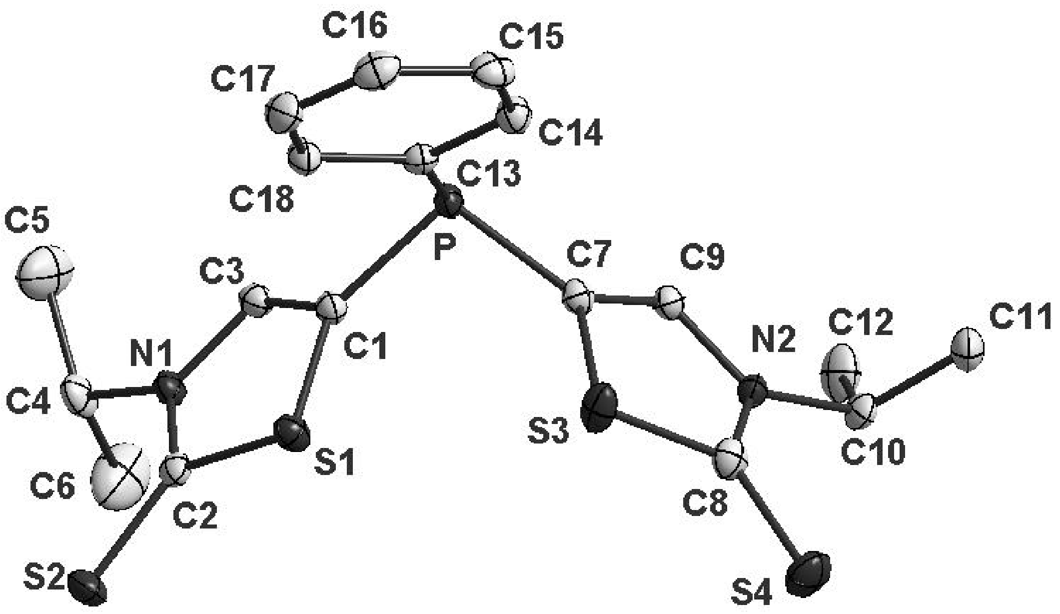
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.745(5)	S1'	C1'	1.754(5)
S1	C2	1.741(5)	S1'	C2'	1.731(5)
S2	C2	1.656(5)	S2'	C2'	1.672(5)
P	N2	1.697(5)	P'	N2'	1.684(5)
P	C1	1.826(6)	P'	C1'	1.819(6)
P	C9	1.831(6)	P'	C9'	1.827(5)
N1	C2	1.367(7)	N1'	C2'	1.364(7)
N1	C3	1.383(7)	N1'	C3'	1.388(7)
N1	C4	1.456(7)	N1'	C4'	1.460(7)
N2	C5	1.465(7)	N2'	C5'	1.475(6)
N2	C7	1.474(6)	N2'	C7'	1.467(6)
C1	C3	1.347(8)	C1'	C3'	1.350(7)
C5	C6	1.525(8)	C5'	C6'	1.521(8)
C7	C8	1.524(8)	C7'	C8'	1.524(8)
C9	C10	1.407(7)	C9'	C10'	1.396(7)
C9	C14	1.401(8)	C9'	C14'	1.408(7)
C10	C11	1.390(8)	C10'	C11'	1.400(7)
C11	C12	1.383(8)	C11'	C12'	1.398(8)
C12	C13	1.391(8)	C12'	C13'	1.380(8)
C13	C14	1.390(8)	C13'	C14'	1.378(8)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C1	93.5(3)	C2'	S1'	C1'	93.4(3)
N2	P	C1	107.8(2)	N2'	P'	C1'	107.2(2)
N2	P	C9	100.8(2)	N2'	P'	C9'	100.3(2)
C1	P	C9	101.0(2)	C1'	P'	C9'	102.0(2)
C2	N1	C3	115.2(4)	C2'	N1'	C3'	114.8(4)
C2	N1	C4	122.8(5)	C2'	N1'	C4'	123.4(4)
C3	N1	C4	122.0(5)	C3'	N1'	C4'	121.8(5)
C5	N2	P	116.4(4)	C5'	N2'	P'	115.9(4)
C5	N2	C7	116.2(4)	C7'	N2'	P'	122.2(3)
C7	N2	P	120.3(3)	C7'	N2'	C5'	114.7(4)

S1	C1	P	128.9(3)	S1'	C1'	P'	129.5(3)
C3	C1	S1	108.3(4)	C3'	C1'	S1'	108.1(4)
C3	C1	P	122.7(4)	C3'	C1'	P'	122.1(4)
S2	C2	S1	125.2(3)	S2'	C2'	S1'	125.3(3)
N1	C2	S1	107.7(4)	N1'	C2'	S1'	108.5(4)
N1	C2	S2	127.1(4)	N1'	C2'	S2'	126.2(4)
C1	C3	N1	115.3(5)	C1'	C3'	N1'	115.2(5)
N2	C5	C6	115.1(5)	N2'	C5'	C6'	114.9(5)
N2	C7	C8	112.5(4)	N2'	C7'	C8'	113.4(5)
C10	C9	P	121.5(4)	C10'	C9'	P'	122.3(4)
C14	C9	P	119.6(4)	C10'	C9'	C14'	118.8(5)
C14	C9	C10	118.4(5)	C14'	C9'	P'	118.6(4)
C11	C10	C9	120.6(5)	C9'	C10'	C11'	120.2(5)
C12	C11	C10	120.1(5)	C12'	C11'	C10'	120.0(5)
C11	C12	C13	120.1(5)	C13'	C12'	C11'	119.7(5)
C14	C13	C12	120.1(5)	C14'	C13'	C12'	120.8(5)
C13	C14	C9	120.6(5)	C13'	C14'	C9'	120.5(5)

12.3 Crystal data and structure refinement for 6a (IB-276).



Identification code	GSTR573, IB-276 //	μ/mm^{-1}	0.55

	GXray5183		
Crystal Habitus	clear colourless block	F(000)	888
Device Type	STOE IPDS-2T	Crystal size/mm^3	0.18 × 0.15 × 0.14
Empirical formula	$C_{18}H_{21}N_2PS_4$	Absorption correction	integration
Moiety formula	C18 H21 N2 P S4	Tmin; Tmax	0.8190; 0.9058
Formula weight	424.58	Radiation	MoKα (λ = 0.71073)
Temperature/K	123(2)	2Θ range for data collection/°	5.262 to 55.974°
Crystal system	orthorhombic	Completeness to theta	0.99
Space group	$P2_12_12_1$	Index ranges	$-13 \le h \le 15$, $-10 \le k \le 15$, $-20 \le l \le 20$
a/Å	11.3855(8)	Reflections collected	8682
b/Å	11.5308(6)	Independent reflections	4789 [R_{int} = 0.0260, R_{sigma} = 0.0422]
c/Å	15.4838(8)	Data/restraints/parameters	4789/0/230
α/°	90	Goodness-of-fit on F^2	0.933
β/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0252, wR_2 = 0.0533
γ/°	90	Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0540
Volume/Å^3	2032.8(2)	Largest diff. peak/hole / e Å^{-3}	0.50/-0.26
Z	4	Flack parameter	0.02(4)
ρ_{calc}g/cm^3	1.387		

Bond Lengths

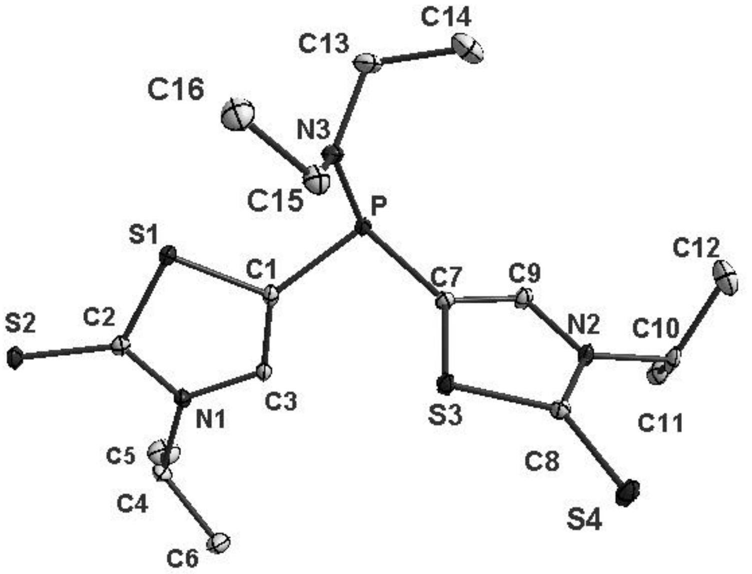
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.750(2)	N2	C10	1.489(3)
S1	C2	1.735(2)	C1	C3	1.345(3)
S2	C2	1.667(2)	C4	C5	1.522(4)
S3	C7	1.753(2)	C4	C6	1.493(4)
S3	C8	1.741(2)	C7	C9	1.344(3)
S4	C8	1.663(2)	C10	C11	1.522(4)
P	C1	1.808(2)	C10	C12	1.516(4)
P	C7	1.814(2)	C13	C14	1.396(4)
P	C13	1.838(2)	C13	C18	1.400(3)
N1	C2	1.367(3)	C14	C15	1.389(3)
N1	C3	1.383(3)	C15	C16	1.395(4)

N1	C4	1.483(3)	C16	C17	1.381(4)
N2	C8	1.357(3)	C17	C18	1.390(3)
N2	C9	1.386(3)			

Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	92.65(12)	C6	C4	C5	112.7(3)
C8	S3	C7	92.87(11)	S3	C7	P	126.84(13)
C1	P	C7	101.84(11)	C9	C7	S3	108.43(17)
C1	P	C13	101.65(10)	C9	C7	P	124.45(18)
C7	P	C13	101.08(11)	S4	C8	S3	123.58(14)
C2	N1	C3	113.7(2)	N2	C8	S3	108.51(17)
C2	N1	C4	121.98(19)	N2	C8	S4	127.90(19)
C3	N1	C4	124.32(19)	C7	C9	N2	115.3(2)
C8	N2	C9	114.85(19)	N2	C10	C11	109.7(2)
C8	N2	C10	121.1(2)	N2	C10	C12	111.2(2)
C9	N2	C10	124.04(19)	C12	C10	C11	112.8(2)
S1	C1	P	128.51(15)	C14	C13	P	119.45(18)
C3	C1	S1	108.44(17)	C14	C13	C18	119.1(2)
C3	C1	P	123.05(18)	C18	C13	P	120.98(19)
S2	C2	S1	123.34(15)	C15	C14	C13	120.7(2)
N1	C2	S1	109.24(17)	C14	C15	C16	119.8(3)
N1	C2	S2	127.42(18)	C17	C16	C15	119.7(2)
C1	C3	N1	116.0(2)	C16	C17	C18	120.9(2)
N1	C4	C5	111.1(2)	C17	C18	C13	119.7(2)
N1	C4	C6	110.9(2)				

12.4 Crystal data and structure refinement for 6b (IB-270).



Identification code	GSTR575, IB-270 // GXraymo_5182f	ρ_{calc}g/cm^3	1.346
Crystal Habitus	clear colourless block	μ/mm^{-1}	0.54
Device Type	Bruker D8-Venture	F(000)	888
Empirical formula	$C_{16}H_{26}N_3PS_4$	Crystal size/mm^3	0.25 × 0.21 × 0.18
Moiety formula	C16 H26 N3 P S4	Absorption correction	empirical
Formula weight	419.61	Tmin; Tmax	0.7017; 0.7460
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	monoclinic	2Θ range for data collection/°	5.778 to 55.994°
Space group	P2$_1$/n	Completeness to theta	0.996
a/Å	13.4783(9)	Index ranges	$-17 \leq h \leq 17$, $-9 \leq k \leq 9$, $-28 \leq l \leq 28$
b/Å	7.3226(5)	Reflections collected	60380
c/Å	21.8904(13)	Independent reflections	4985 [R_{int} = 0.0300, R_{sigma} = 0.0127]
α/°	90	Data/restraints/parameters	4985/1/223
β/°	106.580(2)	Goodness-of-fit on F^2	1.106
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0243, wR_2 = 0.0617
Volume/Å^3	2070.7(2)	Final R indexes [all data]	R_1 = 0.0264, wR_2 = 0.0629
Z	4	Largest diff. peak/hole / e	0.37/-0.34

Å^{-3}

Bond Lengths

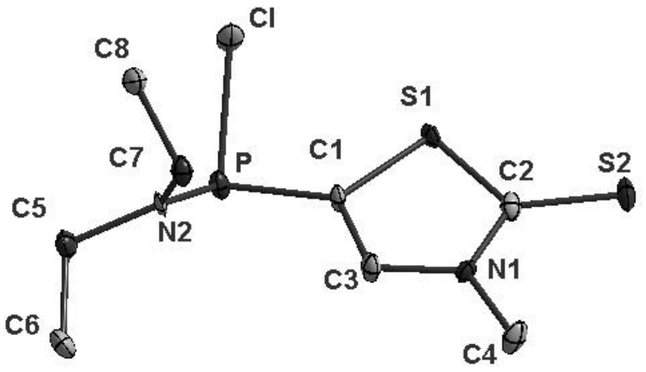
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.7404(11)	N2	C9	1.3797(14)
S1	C2	1.7317(12)	N2	C10	1.4829(14)
S2	C2	1.6688(12)	N3	C13	1.4734(15)
S3	C7	1.7485(12)	N3	C15	1.4724(16)
S3	C8	1.7382(12)	C1	C3	1.3498(16)
S4	C8	1.6762(12)	C4	C5	1.5219(18)
P	N3	1.6896(10)	C4	C6	1.5195(17)
P	C1	1.8149(12)	C7	C9	1.3559(16)
P	C7	1.8213(12)	C10	C11	1.5172(17)
N1	C2	1.3633(14)	C10	C12	1.5207(18)
N1	C3	1.3922(14)	C13	C14	1.5191(19)
N1	C4	1.4773(14)	C15	C16	1.5262(17)
N2	C8	1.3610(15)			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C1	93.00(5)	N1	C2	S1	108.73(8)
C8	S3	C7	92.84(6)	N1	C2	S2	127.89(9)
N3	P	C1	99.60(5)	C1	C3	N1	114.36(10)
N3	P	C7	108.19(5)	N1	C4	C5	109.67(10)
C1	P	C7	100.31(5)	N1	C4	C6	111.01(10)
C2	N1	C3	114.70(10)	C6	C4	C5	113.04(11)
C2	N1	C4	121.08(9)	S3	C7	P	132.03(7)
C3	N1	C4	124.16(10)	C9	C7	S3	108.53(8)
C8	N2	C9	114.90(10)	C9	C7	P	119.39(9)
C8	N2	C10	123.27(10)	S4	C8	S3	124.11(7)
C9	N2	C10	121.83(10)	N2	C8	S3	108.70(8)
C13	N3	P	113.36(8)	N2	C8	S4	127.18(9)
C15	N3	P	122.33(8)	C7	C9	N2	115.01(10)
C15	N3	C13	116.71(10)	N2	C10	C11	110.49(10)
S1	C1	P	120.06(7)	N2	C10	C12	109.68(10)

C3	C1	S1	109.21(8)	C11	C10	C12	111.89(10)
C3	C1	P	129.74(9)	N3	C13	C14	115.06(11)
S2	C2	S1	123.37(7)	N3	C15	C16	112.41(11)

12.5 Crystal data and structure refinement for 7a (IB-73).



Identification code	GSTR468, IB-73 // GXraycu_4500f_pl	ρ_{calc}g/cm^3	1.464
Crystal Habitus	clear colourless plank	μ/mm^{-1}	6.934
Device Type	Bruker D8-Venture	F(000)	560
Empirical formula	$C_8H_{14}ClN_2PS_2$	Crystal size/mm^3	0.16 × 0.08 × 0.08
Moiety formula	C8 H14 Cl N2 P S2	Absorption correction	empirical
Formula weight	268.75	Tmin; Tmax	0.2956; 0.7536
Temperature/K	123	Radiation	CuKα (λ = 1.54178)
Crystal system	monoclinic	2Θ range for data collection/°	6.588 to 135.47°
Space group	$P2_1/c$	Completeness to theta	0.999
a/Å	12.7695(5)	Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-8 \leq l \leq 8$
b/Å	13.4160(5)	Reflections collected	19438
c/Å	7.1453(3)	Independent reflections	2207 [R_{int} = 0.0613, R_{sigma} = 0.0334]
α/°	90	Data/restraints/parameters	2207/6/131
β/°	95.1700(10)	Goodness-of-fit on F^2	1.198
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0715, wR_2 = 0.1922
Volume/Å^3	1219.12(8)	Final R indexes [all data]	R_1 = 0.0733, wR_2 = 0.1932
Z	4	Largest diff. peak/hole / e Å^{-3}	1.46/-0.55

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl	P	2.152(2)	N1	C3	1.379(9)
S1	C1	1.736(6)	N1	C4	1.457(8)
S1	C2	1.729(7)	N2	C5	1.485(8)
S2	C2	1.673(7)	N2	C7	1.474(8)
P	N2	1.651(6)	C1	C3	1.364(9)
P	C1	1.807(7)	C5	C6	1.515(10)
N1	C2	1.356(9)	C7	C8	1.514(10)

Bond Angles

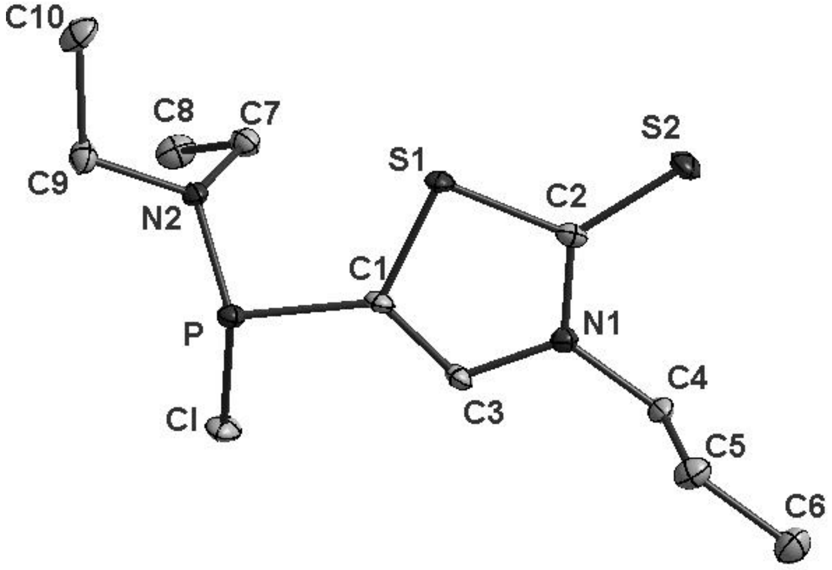
Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	92.9(3)	S1	C1	P	123.9(4)
N2	P	Cl	108.1(2)	C3	C1	S1	108.8(5)
N2	P	C1	101.8(3)	C3	C1	P	126.4(5)
C1	P	Cl	94.7(2)	S2	C2	S1	124.1(4)
C2	N1	C3	114.8(6)	N1	C2	S1	109.1(5)
C2	N1	C4	122.6(6)	N1	C2	S2	126.8(5)
C3	N1	C4	122.6(6)	C1	C3	N1	114.3(6)
C5	N2	P	116.3(4)	N2	C5	C6	111.8(6)
C7	N2	P	127.5(4)	N2	C7	C8	113.6(6)
C7	N2	C5	115.2(5)				

Torsion Angles

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Cl	P	N2	C5	110.5(4)	C1	P	N2	C5	-150.5(5)
Cl	P	N2	C7	-57.3(6)	C1	P	N2	C7	41.7(6)
Cl	P	C1	S1	-37.1(4)	C2	S1	C1	P	-167.9(5)
Cl	P	C1	C3	155.2(6)	C2	S1	C1	C3	1.7(5)
S1	C1	C3	N1	-0.8(8)	C2	N1	C3	C1	-0.9(9)
P	N2	C5	C6	108.4(6)	C3	N1	C2	S1	2.2(7)

P	N2	C7	C8	93.3(7)	C3	N1	C2	S2	-177.3(5)
P	C1	C3	N1	168.5(5)	C4	N1	C2	S1	-176.0(5)
N2	P	C1	S1	-146.7(4)	C4	N1	C2	S2	4.5(10)
N2	P	C1	C3	45.6(7)	C4	N1	C3	C1	177.3(6)
C1	S1	C2	S2	177.3(5)	C5	N2	C7	C8	-74.6(7)
C1	S1	C2	N1	-2.2(5)	C7	N2	C5	C6	-82.2(7)

12.6 Crystal data and structure refinement for 7c (IB-256).



Identification code	GSTR543, IB-256 // GXraymo_5045f	ρ_{calc}g/cm^3	1.378
Crystal Habitus	clear colourless plate	μ/mm^{-1}	0.648
Device Type	Bruker D8-Venture	F(000)	312
Empirical formula	$C_{10}H_{18}N_2PS_2Cl$	Crystal size/mm^3	0.2 × 0.11 × 0.06
Moiety formula	C10 H18 Cl N2 P S2	Absorption correction	empirical
Formula weight	296.8	Tmin; Tmax	0.5813; 0.7459
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	5.478 to 55.996°
Space group	P-1	Completeness to theta	0.999
a/Å	6.9041(6)	Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14

b/Å	9.7436(7)	Reflections collected	22072
c/Å	10.8226(8)	Independent reflections	3452 [R_{int} = 0.1530, R_{sigma} = 0.0932]
α/°	93.169(4)	Data/restraints/parameters	3452/0/148
β/°	98.014(5)	Goodness-of-fit on F^2	1.012
γ/°	95.990(5)	Final R indexes [I>=2σ (I)]	R_1 = 0.0465, wR_2 = 0.0768
Volume/Å^3	715.19(10)	Final R indexes [all data]	R_1 = 0.0928, wR_2 = 0.0890
Z	2	Largest diff. peak/hole / e Å^{-3}	0.48/-0.44

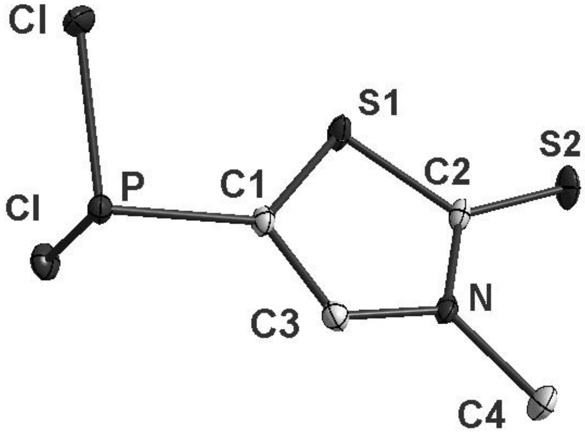
Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl	P	2.1350(10)	N1	C4	1.469(3)
S1	C1	1.745(3)	N2	C7	1.471(3)
S1	C2	1.735(3)	N2	C9	1.481(3)
S2	C2	1.670(3)	C1	C3	1.347(3)
P	N2	1.655(2)	C4	C5	1.520(3)
P	C1	1.817(3)	C5	C6	1.521(4)
N1	C2	1.356(3)	C7	C8	1.521(3)
N1	C3	1.384(3)	C9	C10	1.519(4)

Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	92.60(12)	C3	C1	S1	109.39(19)
N2	P	Cl	106.37(8)	C3	C1	P	130.3(2)
N2	P	C1	100.05(11)	S2	C2	S1	123.77(16)
C1	P	Cl	95.51(9)	N1	C2	S1	108.50(18)
C2	N1	C3	115.5(2)	N1	C2	S2	127.7(2)
C2	N1	C4	122.8(2)	C1	C3	N1	114.0(2)
C3	N1	C4	121.7(2)	N1	C4	C5	111.6(2)
C7	N2	P	124.47(17)	C4	C5	C6	111.5(2)
C7	N2	C9	116.29(19)	N2	C7	C8	113.9(2)
C9	N2	P	115.46(16)	N2	C9	C10	112.4(2)
S1	C1	P	119.67(14)				

12.7 Crystal data and structure refinement for 8 (IB-74).



Identification code	GSTR538, IB-74 // GXraymo_5002f	ρ_{calc}g/cm^3	1.805
Crystal Habitus	clear colourless plate	μ/mm^{-1}	1.357
Device Type	Bruker D8-Venture	F(000)	464
Empirical formula	$C_4H_4NPS_2Cl_2$	Crystal size/mm^3	0.1 × 0.06 × 0.04
Moiety formula	C4 H4 Cl2 N P S2	Absorption correction	empirical
Formula weight	232.07	Tmin; Tmax	0.6871; 0.7459
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	monoclinic	2Θ range for data collection/°	5.208 to 55.976°
Space group	$P2_1/c$	Completeness to theta	1
a/Å	6.5200(11)	Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 12$, $-18 \leq l \leq 18$
b/Å	9.4916(17)	Reflections collected	24109
c/Å	13.822(3)	Independent reflections	2062 [R_{int} = 0.1060, R_{sigma} = 0.0435]
α/°	90	Data/restraints/parameters	2062/6/92
β/°	93.257(7)	Goodness-of-fit on F^2	1.029
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0306, wR_2 = 0.0461
Volume/Å^3	854.0(3)	Final R indexes [all data]	R_1 = 0.0528, wR_2 = 0.0505
Z	4	Largest diff. peak/hole / e Å^{-3}	0.42/-0.38

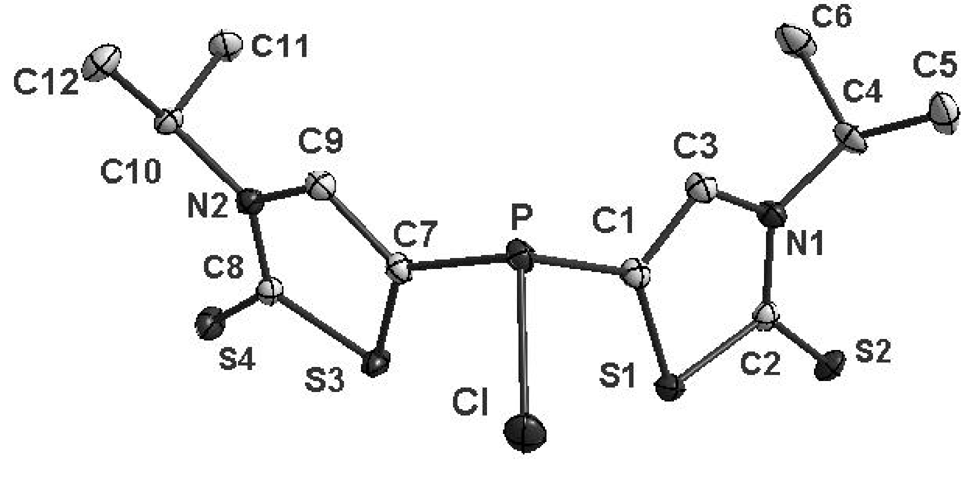
Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	P	2.0924(8)	P	C1	1.800(2)
Cl2	P	2.0717(8)	N	C2	1.360(3)
S1	C1	1.7403(19)	N	C3	1.373(2)
S1	C2	1.739(2)	N	C4	1.465(3)
S2	C2	1.663(2)	C1	C3	1.347(3)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C1	92.05(10)	S1	C1	P	128.19(12)
Cl2	P	Cl1	96.59(3)	C3	C1	S1	109.73(14)
C1	P	Cl1	99.12(7)	C3	C1	P	122.04(15)
C1	P	Cl2	98.94(7)	S2	C2	S1	124.90(13)
C2	N	C3	115.01(17)	N	C2	S1	108.83(14)
C2	N	C4	121.30(17)	N	C2	S2	126.25(16)
C3	N	C4	123.67(17)	C1	C3	N	114.35(18)

12.8 Crystal data and structure refinement for 9 (IB-285).



Identification code	GSTR579, IB-285 // GXray5251f	ρ_{calc}g/cm^3	1.483
Crystal Habitus	clear colourless block	μ/mm^{-1}	0.793
Device Type	Bruker X8-KappaApexII	F(000)	792

Empirical formula	$C_{12}H_{16}N_2PS_4Cl$	Crystal size/mm^3	0.32 × 0.2 × 0.19
Moiety formula	C12 H16 Cl N2 P S4	Absorption correction	empirical
Formula weight	382.93	Tmin; Tmax	0.6531; 0.7461
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	monoclinic	2Θ range for data collection/°	5.074 to 55.996°
Space group	$P2_1/c$	Completeness to theta	0.997
a/Å	12.5874(6)	Index ranges	$-14 \leq h \leq 16$, $-18 \leq k \leq 18$, $-13 \leq l \leq 9$
b/Å	13.8120(7)	Reflections collected	32997
c/Å	9.9208(5)	Independent reflections	4131 [R_{int} = 0.0298, R_{sigma} = 0.0174]
α/°	90	Data/restraints/parameters	4131/1/185
β/°	95.9307(15)	Goodness-of-fit on F^2	1.104
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0227, wR_2 = 0.0540
Volume/Å^3	1715.57(15)	Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0557
Z	4	Largest diff. peak/hole / e Å^{-3}	0.32/-0.23

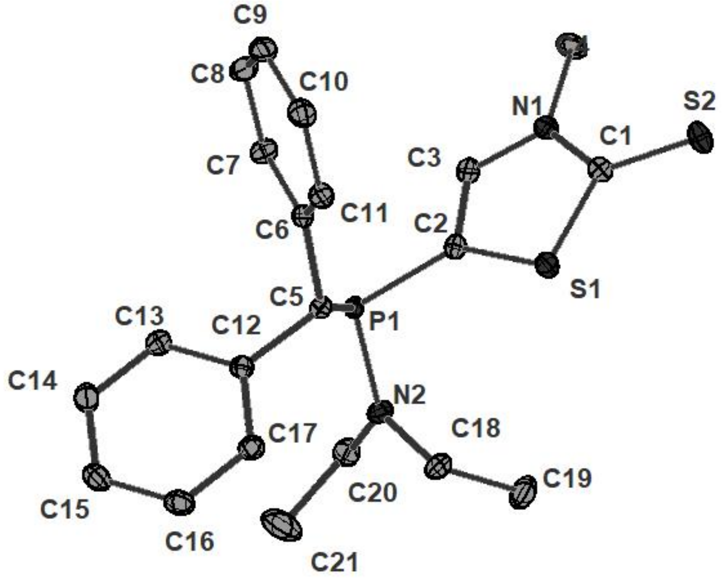
Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl	P	2.0796(4)	N1	C4	1.4889(16)
S1	C1	1.7414(12)	N2	C8	1.3655(15)
S1	C2	1.7379(13)	N2	C9	1.3747(16)
S2	C2	1.6658(13)	N2	C10	1.4876(15)
S3	C7	1.7448(12)	C1	C3	1.3504(17)
S3	C8	1.7445(13)	C4	C5	1.5187(19)
S4	C8	1.6590(13)	C4	C6	1.5179(19)
P	C1	1.8030(13)	C7	C9	1.3497(17)
P	C7	1.7909(13)	C10	C11	1.5199(17)
N1	C2	1.3661(16)	C10	C12	1.5232(17)
N1	C3	1.3827(16)			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C1	92.47(6)	N1	C2	S2	127.68(10)
C8	S3	C7	92.40(6)	C1	C3	N1	114.37(11)
C1	P	Cl	98.43(4)	N1	C4	C5	109.31(10)
C7	P	Cl	101.47(4)	N1	C4	C6	110.67(11)
C7	P	C1	101.95(6)	C6	C4	C5	112.01(11)
C2	N1	C3	114.79(10)	S3	C7	P	130.27(7)
C2	N1	C4	123.46(10)	C9	C7	S3	109.18(9)
C3	N1	C4	121.42(10)	C9	C7	P	120.25(9)
C8	N2	C9	114.86(10)	S4	C8	S3	124.02(7)
C8	N2	C10	121.58(10)	N2	C8	S3	108.59(9)
C9	N2	C10	123.32(10)	N2	C8	S4	127.38(9)
S1	C1	P	129.52(7)	C7	C9	N2	114.96(11)
C3	C1	S1	109.57(9)	N2	C10	C11	108.88(10)
C3	C1	P	120.90(9)	N2	C10	C12	111.49(10)
S2	C2	S1	123.52(8)	C11	C10	C12	112.67(11)
N1	C2	S1	108.80(9)				

12.9 Crystal data and structure refinement for 10 (dg407_a)



Bond precision:	C-C = 0.0016 A

Cell:	a=9.8047(9; b=21.6697(17); c=10.5847(9); alpha=90; beta=113.054(2; gamma=90	
Wavelength	0.71073	
Temperature:	100 K	
	Calculated	**Reported**
Volume	2069.3(3)	2069.3(3)
Space group	P 1 21/n 1	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H25 N2 P S2	C21 H25 N2 P S2
Sum formula	C21 H25 N2 P S2	C21 H25 N2 P S2
Mr	400.52	400.52
Dx,g cm-3	1.286	1.286
Z	4	4
Mu (mm-1)	0.342	0.342
F000	848.0	848.0
F000’		
h,k,lmax	14,30,15	14,30,15
Nref	6323	6323
Tmin,Tmax	0.682,0.746	0.682,0.746
Tmin’		
AbsCorr	MULTI-SCAN	
Theta(max)	30.612	30.612
wR2(reflections)	0.0829(6323)	0.0829(6323)
S	1.034	

Bond length

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.7460(11)	C13	H13	0.93
S1	C2	1.7529(10)	C13	C14	1.3940(15)
P1	N2	1.6692(9)	C18	H18A	0.97
P1	C5	1.8751(11)	C18	H18B	0.97
P1	C2	1.8226(10)	C18	C19	1.5244(15)
S2	C1	1.6649(10)	C17	H17	0.93
N2	C18	1.4669(13	C17	C16	1.3936(15)

N2	C20	1.4679(13)	C16	H16	0.93
N1	C3	1.3826(13)	C10	H10	0.93
N1	C1	1.3606(13)	C10	C9	1.3889(16)
N1	C4	1.4615(14)	C14	H14	0.93
C12	C5	1.5187(14)	C8	H8	0.93
C12	C13	1.4011(14)	C8	C9	1.3902(16)
C12	C17	1.3951(14)	C20	H20A	0.97
C5	H5	0.98	C20	H20B	0.97
C5	C6	1.5191(13)	C20	C21	1.5151(17)
C3	H3	0.93	C9	H9	0.93
C3	C2	1.3489(15)	C4	H4A	0.96
C6	C7	1.3993(14)	C4	H4B	0.96
C6	C11	1.3954(14)	C4	H4C	0.96
C7	H7	0.93	C19	H19A	0.96
C7	C8	1.3954(14)	C19	H19B	0.96
C11	H11	0.93	C19	H19C	0.96
C11	C10	1.3936(14)	C21	H21A	0.96
C15	H15	0.93	C21	H21B	0.96
C15	C16	1.3914(16)	C21	H21C	0.96
C15	C14	1.3891(16)			

Bond angle

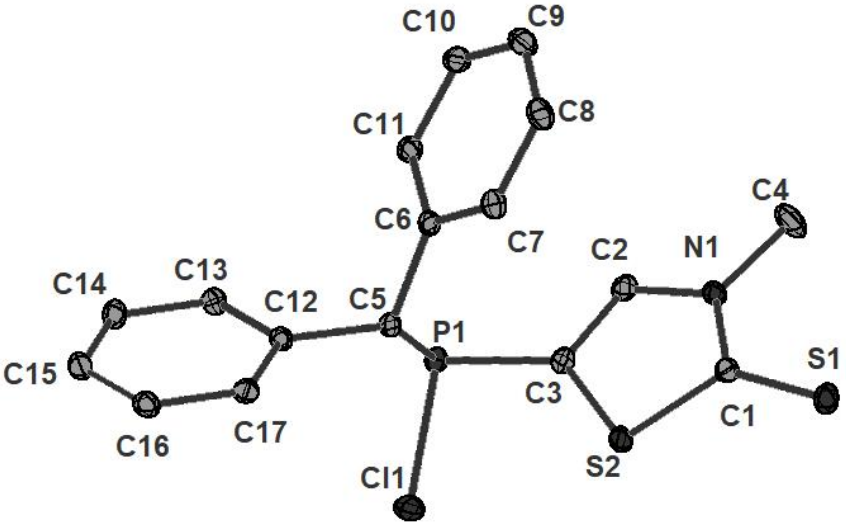
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	S1	C2	93.29(5)	H18A	C18	H18B	107.7
N2	P1	C5	104.41(5)	C19	C18	H18A	108.9
N2	P1	C2	107.76(4)	C19	C18	H18B	108.9
C2	P1	C5	98.30(5)	C12	C17	H17	119.6
C18	N2	P1	125.50(7)	C16	C17	C12	120.77(10)
C18	N2	C20	116.39(8)	C16	C17	H17	119.6
C20	N2	P1	118.07(7)	C15	C16	C17	119.97(10)
C3	N1	C4	122.56(9)	C15	C16	H16	120
C1	N1	C3	115.36(9)	C17	C16	H16	120
C1	N1	C4	121.95(9)	C11	C10	H10	120
C13	C12	C5	121.29(9)	C9	C10	C11	119.96(10)

C17	C12	C5	119.89(9)	C9	C10	H10	120
C17	C12	C13	118.81(9)	C15	C14	C13	120.26(10)
P1	C5	H5	108	C15	C14	H14	119.9
C12	C5	P1	109.12(7)	C13	C14	H14	119.9
C12	C5	H5	108	C7	C8	H8	119.9
C12	C5	C6	111.87(8)	C9	C8	C7	120.29(10)
C6	C5	P1	111.63(7)	C9	C8	H8	119.9
C6	C5	H5	108	N2	C20	H20A	108.9
N1	C3	H3	122.3	N2	C20	H20B	108.9
C2	C3	N1	115.39(9)	N2	C20	C21	113.20(11)
C2	C3	H3	122.3	H20A	C20	H20B	107.8
C7	C6	C5	122.72(9)	C21	C20	H20A	108.9
C11	C6	C5	118.88(9)	C21	C20	H20B	108.9
C11	C6	C7	118.32(9)	C10	C9	C8	119.64(10)
C6	C7	H7	119.7	C10	C9	H9	120.2
C8	C7	C6	120.62(10)	C8	C9	H9	120.2
C8	C7	H7	119.7	N1	C4	H4A	109.5
C6	C11	H11	119.4	N1	C4	H4B	109.5
C10	C11	C6	121.17(10)	N1	C4	H4C	109.5
C10	C11	H11	119.4	H4A	C4	H4B	109.5
C16	C15	H15	120.1	H4A	C4	H4C	109.5
C14	C15	H15	120.1	H4B	C4	H4C	109.5
C14	C15	C16	119.82(10)	C18	C19	H19A	109.5
S2	C1	S1	125.62(6)	C18	C19	H19B	109.5
N1	C1	S1	107.82(7)	C18	C19	H19C	109.5
N1	C1	S2	126.56(8)	H19A	C19	H19B	109.5
C12	C13	H13	119.8	H19A	C19	H19C	109.5
C14	C13	C12	120.37(10)	H19B	C19	H19C	109.5
C14	C13	H13	119.8	C20	C21	H21A	109.5
S1	C2	P1	130.36(6)	C20	C21	H21B	109.5
C3	C2	S1	108.08(7)	C20	C21	H21C	109.5
C3	C2	P1	121.46(8)	H21A	C21	H21B	109.5
N2	C18	H18A	108.9	H21A	C21	H21C	109.5
N2	C18	H18B	108.9	H21B	C21	H21C	109.5
N2	C18	C19	113.45(10)				

Torsion angle

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P1	N2	C18	C19	-114.47(10)	C7	C6	C11	C10	0.07(15)
P1	N2	C20	C21	-113.10(10)	C7	C8	C9	C10	-0.37(16)
P1	C5	C6	C7	36.08(12)	C11	C6	C7	C8	-0.52(15)
P1	C5	C6	C11	-147.09(8)	C11	C10	C9	C8	-0.08(16)
N2	P1	C5	C12	-61.36(7)	C1	S1	C2	P1	-177.23(8)
N2	P1	C5	C6	174.47(6)	C1	S1	C2	C3	-0.85(8)
N2	P1	C2	S1	-53.41(9)	C1	N1	C3	C2	2.01(13)
N2	P1	C2	C3	130.62(9)	C13	C12	C5	P1	-72.41(10)
N1	C3	C2	S1	-0.43(11)	C13	C12	C5	C6	51.62(13)
N1	C3	C2	P1	176.34(7)	C13	C12	C17	C16	-0.86(15)
C12	C5	C6	C7	-86.54(12)	C2	S1	C1	S2	-177.08(7)
C12	C5	C6	C11	90.30(11)	C2	S1	C1	N1	1.88(8)
C12	C13	C14	C15	-0.11(16)	C2	P1	N2	C18	54.71(10)
C12	C17	C16	C15	-0.03(16)	C2	P1	N2	C20	-122.73(8)
C5	P1	N2	C18	-49.10(10)	C2	P1	C5	C12	-172.20(7)
C5	P1	N2	C20	133.46(8)	C2	P1	C5	C6	63.63(7)
C5	P1	C2	S1	54.70(8)	C18	N2	C20	C21	69.22(13)
C5	P1	C2	C3	-121.27(9)	C17	C12	C5	P1	107.93(9)
C5	C12	C13	C14	-178.74(10)	C17	C12	C5	C6	-128.04(10)
C5	C12	C17	C16	178.81(10)	C17	C12	C13	C14	0.92(15)
C5	C6	C7	C8	176.33(9)	C16	C15	C14	C13	-0.79(17)
C5	C6	C11	C10	-176.90(9)	C14	C15	C16	C17	0.86(17)
C3	N1	C1	S1	-2.50(11)	C20	N2	C18	C19	63.02(12)
C3	N1	C1	S2	176.45(8)	C4	N1	C3	C2	178.01(9)
C6	C7	C8	C9	0.68(16)	C4	N1	C1	S1	-178.53(8)
C6	C11	C10	C9	0.23(16)	C4	N1	C1	S2	0.42(15)

12.10 Crystal data and structure refinement for 11 (dg408_a)



Bond precision	C-C = 0.0016 A	
Cell:	a=15.1719(19); b=7.8102(10);c=15.0707(19);alp ha=90;beta=110.848(2);gamma= 90	
Wavelength	0.71073	
Temperature:	90 K	
	Calculated	**Reported**
Volume	1668.9(4)	1668.9(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C17 H15 Cl N P S2	C17 H15 Cl N P S2
Sum formula	C17 H15 Cl N P S2	C17 H15 Cl N P S2
Mr	363.84	363.87
Dx,g cm-3	1.448	1.448
Z	4	4
Mu (mm-1)	0.570	0.570
F000	752.0	754.2
F000’	754.17	
h,k,lmax	21,11,21	21,11,21
Nref	5110	5095
Tmin,Tmax	0.843,0.945	0.654,0.746

Tmin’	0.843	
AbsCorr	MULTI-SCAN	
Data completeness=	0.997	
R(reflections)	0.0255(4620)	0.0707(5095)
S = 1.043	Npar= 199	
Theta(max)	30.54	

Bond length

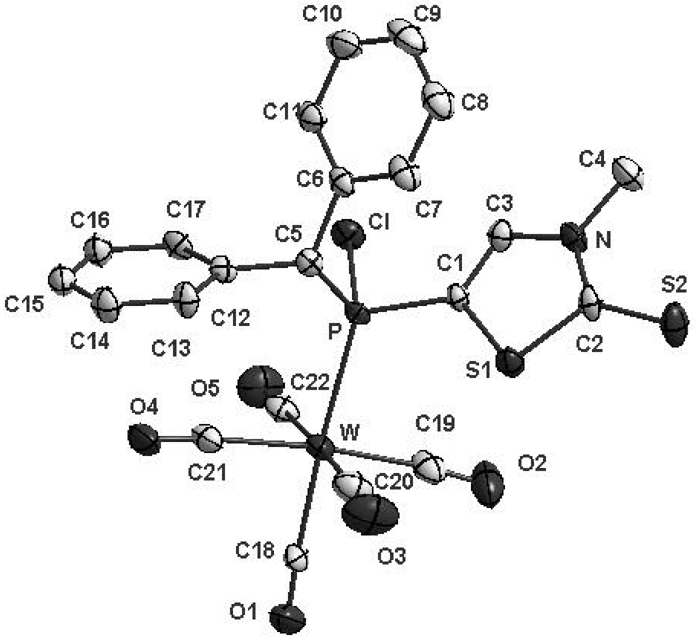
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	P1	2.0726(4)	C15	H15	0.93
S1	C1	1.6661(11)	C11	C6	1.4013(14)
S2	C1	1.7380(10)	C11	C10	1.3995(14)
S2	C3	1.7464(11)	C11	H11	0.93
P1	C5	1.8776(11)	C6	C7	1.4017(14)
P1	C3	1.8097(10)	C17	C16	1.3975(14)
N1	C2	1.3839(13)	C17	H17	0.93
N1	C1	1.3648(13)	C16	H16	0.93
N1	C4	1.4662(14)	C7	C8	1.3948(15)
C12	C5	1.5175(13)	C7	H7	0.93
C12	C13	1.3983(14)	C10	C9	1.3899(16)
C12	C17	1.4009(14)	C10	H10	0.93
C5	C6	1.5229(14)	C8	C9	1.3961(16)
C5	H5	0.98	C8	H8	0.93
C2	C3	1.3542(14)	C9	H9	0.93
C2	H2	0.93	C14	H14	0.93
C13	C14	1.3952(14)	C4	H4a	0.96
C13	H13	0.93	C4	H4b	0.96
C15	C16	1.3938(15)	C4	H4c	0.96
C15	C14	1.3954(15)			

Bond Angle

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	S2	C1	92.76(5)	N1	C1	S1	127.10(8)
C5	P1	Cl1	100.46(3)	N1	C1	S2	108.60(7)

C3	P1	Cl1	99.58(4)	C16	C17	C12	121.08(9)
C3	P1	C5	97.13(5)	H17	C17	C12	119.46(6)
C1	N1	C2	115.09(9)	H17	C17	C16	119.46(6)
C4	N1	C2	122.36(9)	C17	C16	C15	119.90(10)
C4	N1	C1	122.55(9)	H16	C16	C15	120.05(6)
C13	C12	C5	123.06(9)	H16	C16	C17	120.05(6)
C17	C12	C5	118.46(9)	C8	C7	C6	120.31(10)
C17	C12	C13	118.48(9)	H7	C7	C6	119.84(6)
C12	C5	P1	112.58(7)	H7	C7	C8	119.84(6)
C6	C5	P1	102.95(6)	P1	C3	S2	126.48(6)
C6	C5	C12	117.13(8)	C2	C3	S2	109.14(8)
H5	C5	P1	107.92(3)	C2	C3	P1	123.27(8)
H5	C5	C12	107.92(5)	C9	C10	C11	119.86(10)
H5	C5	C6	107.92(5)	H10	C10	C11	120.07(6)
C3	C2	N1	114.42(9)	H10	C10	C9	120.07(6)
H2	C2	N1	122.79(6)	C9	C8	C7	120.45(10)
H2	C2	C3	122.79(6)	H8	C8	C7	119.77(6)
C14	C13	C12	120.56(9)	H8	C8	C9	119.77(6)
H13	C13	C12	119.72(6)	C8	C9	C10	119.75(10)
H13	C13	C14	119.72(6)	H9	C9	C10	120.12(6)
C14	C15	C16	119.42(9)	H9	C9	C8	120.12(6)
H15	C15	C16	120.29(6)	C15	C14	C13	120.56(10)
H15	C15	C14	120.29(6)	H14	C14	C13	119.72(6)
C10	C11	C6	120.84(10)	H14	C14	C15	119.72(6)
H11	C11	C6	119.58(6)	H4a	C4	N1	109.5
H11	C11	C10	119.58(6)	H4b	C4	N1	109.5
C11	C6	C5	121.65(9)	H4b	C4	H4a	109.5
C7	C6	C5	119.23(9)	H4c	C4	N1	109.5
C7	C6	C11	118.73(9)	H4c	C4	H4a	109.5
S2	C1	S1	124.29(6)	H4c	C4	H4b	109.5

12.11 Crystal data and structure refinement for 13 (IB-241)



Identification code	GSTR539, IB-241 // GXray5003f_pl	ρ_{calc}g/cm^3	1.836
Crystal Habitus	clear dark yellow block	μ/mm^{-1}	5.015
Device Type	Bruker X8-KappaApexII	F(000)	664
Empirical formula	$C_{22}H_{15}ClNO_5PS_2W$	Crystal size/mm^3	0.12 × 0.09 × 0.06
Moiety formula	C22 H15 Cl N O5 P S2 W	Absorption correction	empirical
Formula weight	687.74	Tmin; Tmax	0.5481; 0.7459
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	2.832 to 56°
Space group	P-1	Completeness to theta	0.994
a/Å	8.8458(5)	Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-19 \leq l \leq 19$
b/Å	10.6789(7)	Reflections collected	28743
c/Å	14.9336(10)	Independent reflections	5974 [R_{int} = 0.0531, R_{sigma} = 0.0444]
α/°	85.736(4)	Data/restraints/parameters	5974/24/299
β/°	74.522(4)	Goodness-of-fit on F^2	1.08
γ/°	66.311(3)	Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1102
Volume/Å^3	1244.10(14)	Final R indexes [all data]	R_1 = 0.0524, wR_2 = 0.1151
Z	2	Largest diff. peak/hole / e Å^{-3}	2.20/-1.75

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W	P	2.4671(15)	N	C3	1.373(8)
W	C18	2.027(6)	N	C4	1.460(8)
W	C19	2.046(8)	C1	C3	1.331(9)
W	C20	2.042(8)	C5	C6	1.522(8)
W	C21	2.056(7)	C5	C12	1.502(8)
W	C22	2.064(8)	C6	C7	1.398(9)
Cl	P	2.069(2)	C6	C11	1.381(9)
S1	C1	1.747(6)	C7	C8	1.392(11)
S1	C2	1.735(7)	C8	C9	1.376(13)
S2	C2	1.655(6)	C9	C10	1.372(12)
P	C1	1.807(6)	C10	C11	1.394(10)
P	C5	1.875(6)	C12	C13	1.390(9)
O1	C18	1.106(8)	C12	C17	1.403(9)
O2	C19	1.124(10)	C13	C14	1.384(9)
O3	C20	1.133(10)	C14	C15	1.383(10)
O4	C21	1.139(9)	C15	C16	1.387(10)
O5	C22	1.131(9)	C16	C17	1.393(9)
N	C2	1.359(8)			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	W	P	176.57(19)	S2	C2	S1	125.2(4)
C18	W	C19	86.4(3)	N	C2	S1	108.5(4)
C18	W	C20	86.7(3)	N	C2	S2	126.3(5)
C18	W	C21	87.0(3)	C1	C3	N	114.7(6)
C18	W	C22	91.6(3)	C6	C5	P	112.8(4)
C19	W	P	90.2(2)	C12	C5	P	112.9(4)
C19	W	C21	173.2(3)	C12	C5	C6	116.5(5)
C19	W	C22	92.2(3)	C7	C6	C5	119.0(6)
C20	W	P	92.7(2)	C11	C6	C5	122.4(6)
C20	W	C19	89.9(3)	C11	C6	C7	118.6(6)
C20	W	C21	91.2(3)	C8	C7	C6	120.5(7)
C20	W	C22	177.2(3)	C9	C8	C7	120.1(8)

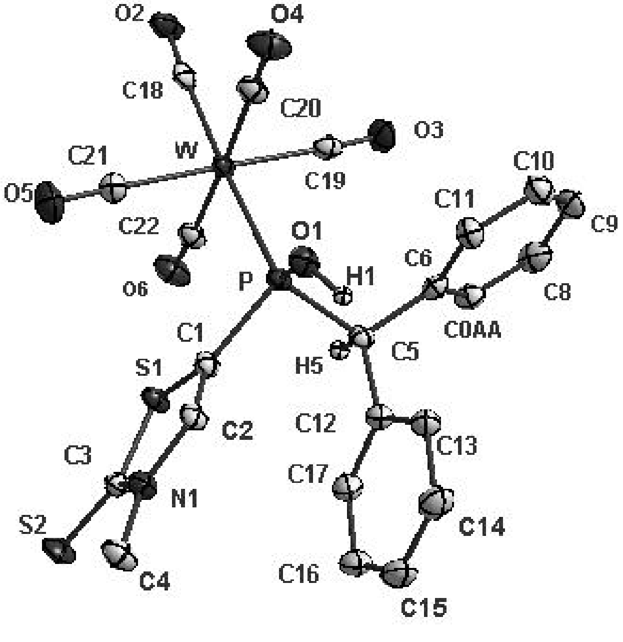
C21	W	P	96.44(19)	C10	C9	C8	119.8(7)
C21	W	C22	86.5(3)	C9	C10	C11	120.6(8)
C22	W	P	89.09(19)	C6	C11	C10	120.3(7)
C2	S1	C1	92.1(3)	C13	C12	C5	118.8(5)
Cl	P	W	115.25(8)	C13	C12	C17	118.6(6)
C1	P	W	116.2(2)	C17	C12	C5	122.6(5)
C1	P	Cl	97.6(2)	C14	C13	C12	121.0(6)
C1	P	C5	101.0(3)	C15	C14	C13	120.4(6)
C5	P	W	120.11(19)	C14	C15	C16	119.4(6)
C5	P	Cl	103.33(19)	C15	C16	C17	120.6(6)
C2	N	C3	115.2(5)	C16	C17	C12	120.0(6)
C2	N	C4	122.2(6)	O1	C18	W	176.6(6)
C3	N	C4	122.5(6)	O2	C19	W	174.9(7)
S1	C1	P	121.5(3)	O3	C20	W	175.8(8)
C3	C1	S1	109.5(5)	O4	C21	W	174.8(6)
C3	C1	P	128.6(5)	O5	C22	W	178.7(7)

Torsion Angles

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
W	P	C1	S1	-41.4(4)	C4	N	C2	S2	-5.8(10)
W	P	C1	C3	146.0(6)	C4	N	C3	C1	-177.1(7)
W	P	C5	C6	177.4(3)	C5	P	C1	S1	90.3(4)
W	P	C5	C12	-47.9(5)	C5	P	C1	C3	-82.3(6)
Cl	P	C1	S1	-164.5(3)	C5	C6	C7	C8	177.6(6)
Cl	P	C1	C3	22.9(6)	C5	C6	C11	C10	-178.7(6)
Cl	P	C5	C6	-52.5(4)	C5	C12	C13	C14	177.8(6)
Cl	P	C5	C12	82.2(4)	C5	C12	C17	C16	-177.0(6)
S1	C1	C3	N	0.0(7)	C6	C5	C12	C13	-103.0(7)
P	C1	C3	N	173.4(5)	C6	C5	C12	C17	75.9(8)
P	C5	C6	C7	-89.4(6)	C6	C7	C8	C9	1.6(12)
P	C5	C6	C11	90.5(6)	C7	C6	C11	C10	1.2(10)
P	C5	C12	C13	124.1(6)	C7	C8	C9	C10	0.3(12)

P	C5	C12	C17	-57.0(7)	C8	C9	C10	C11	-1.4(12)
C1	S1	C2	S2	-176.3(5)	C9	C10	C11	C6	0.7(11)
C1	S1	C2	N	1.4(5)	C11	C6	C7	C8	-2.3(10)
C1	P	C5	C6	48.2(5)	C12	C5	C6	C7	137.7(6)
C1	P	C5	C12	-177.2(4)	C12	C5	C6	C11	-42.5(8)
C2	S1	C1	P	-174.8(4)	C12	C13	C14	C15	0.0(11)
C2	S1	C1	C3	-0.9(5)	C13	C12	C17	C16	1.9(10)
C2	N	C3	C1	1.2(9)	C13	C14	C15	C16	0.3(11)
C3	N	C2	S1	-1.7(7)	C14	C15	C16	C17	0.4(11)
C3	N	C2	S2	175.9(5)	C15	C16	C17	C12	-1.6(11)
C4	N	C2	S1	176.5(6)	C17	C12	C13	C14	-1.2(10)

12.12 Crystal data and structure refinement for hydrolysis product of 14 (IB-407-B).



Identification code	GSTR620, IB-407-B // GXray5625f	ρ_{calc}g/cm^3	1.624
Crystal Habitus	clear yellow block	μ/mm^{-1}	3.332
Device Type	Bruker X8-KappaApexII	F(000)	940
Empirical formula	$C_{68}H_{76}Cl_4N_6O_{13}P_2S_4W_2$	Crystal size/mm^3	0.24 × 0.19 × 0.17

Moiety formula	2(C22 H16 N O6 P S2 W), 2(C H2 Cl2), C4 H10 O, 2(C9 H15 N2)	Absorption correction	empirical
Formula weight	1885.02	Tmin; Tmax	0.4884; 0.7459
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	5.554 to 55.996°
Space group	P-1	Completeness to theta	0.996
a/Å	12.4512(9)	Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
b/Å	12.9084(10)	Reflections collected	87672
c/Å	14.8449(13)	Independent reflections	9281 [R_{int} = 0.0463, R_{sigma} = 0.0244]
α/°	98.754(4)	Data/restraints/parameters	9281/43/491
β/°	110.579(4)	Goodness-of-fit on F^2	1.148
γ/°	113.432(4)	Final R indexes [I>=2σ (I)]	R_1 = 0.0328, wR_2 = 0.0830
Volume/$Å^3$	1927.5(3)	Final R indexes [all data]	R_1 = 0.0378, wR_2 = 0.0863
Z	1	Largest diff. peak/hole / e $Å^{-3}$	2.29/-1.50

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W	P	2.5095(10)	C10	C11	1.395(6)
W	C18	2.009(4)	C12	C13	1.398(6)
W	C19	2.039(4)	C12	C17	1.396(6)
W	C20	2.048(4)	C13	C14	1.383(6)
W	C21	2.034(4)	C14	C15	1.386(7)
W	C22	2.036(4)	C15	C16	1.372(8)
S1	C1	1.731(4)	C16	C17	1.382(7)
S1	C3	1.736(4)	Cl1	C36	1.739(5)
S2	C3	1.666(4)	Cl2	C36	1.750(5)
P	O1	1.521(3)	O7	C33	1.410(9)
P	C1	1.831(4)	O7	C34	1.400(10)
P	C5	1.892(4)	C32	C33	1.544(9)
O2	C18	1.151(5)	C34	C35	1.510(9)
O3	C19	1.139(5)	N2	C23	1.473(6)
O4	C20	1.137(5)	N2	C28	1.325(5)
O5	C21	1.148(6)	N2	C29	1.464(6)

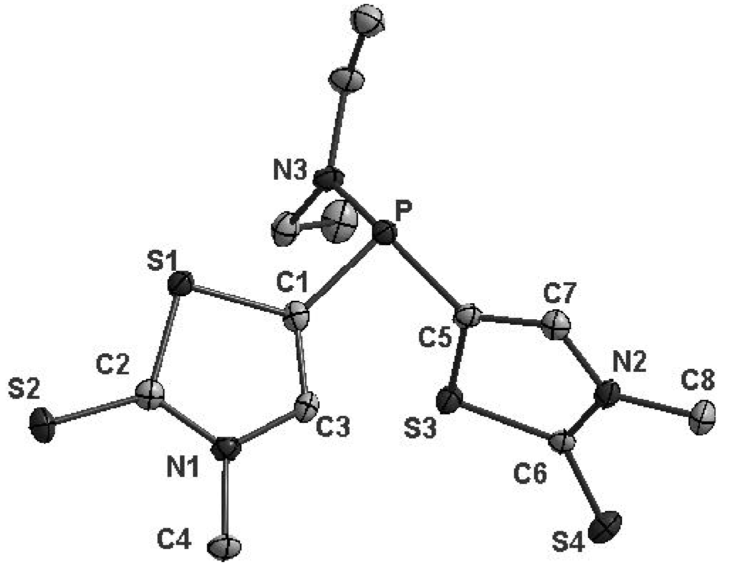
O6	C22	1.140(5)	N3	C28	1.316(6)
N1	C2	1.385(5)	N3	C31	1.466(18)
N1	C3	1.355(5)	N3	C31S	1.509(15)
N1	C4	1.470(5)	C23	C24	1.519(6)
C0AA	C6	1.400(6)	C24	C25	1.526(6)
C0AA	C8	1.381(6)	C25	C26	1.525(6)
C1	C2	1.343(5)	C26	C27	1.536(6)
C5	C6	1.522(5)	C27	C28	1.498(6)
C5	C12	1.513(5)	C29	C30	1.345(11)
C6	C11	1.388(6)	C29	C30S	1.598(11)
C8	C9	1.391(7)	C30	C31	1.598(19)
C9	C10	1.389(7)	C30S	C31S	1.129(18)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	W	P	175.99(12)	C10	C9	C8	119.6(4)
C18	W	C19	86.80(17)	C9	C10	C11	120.0(4)
C18	W	C20	90.99(17)	C6	C11	C10	121.0(4)
C18	W	C21	93.34(17)	C13	C12	C5	121.7(4)
C18	W	C22	88.95(17)	C17	C12	C5	120.2(4)
C19	W	P	92.25(11)	C17	C12	C13	118.0(4)
C19	W	C20	91.29(17)	C14	C13	C12	120.5(4)
C20	W	P	85.13(12)	C13	C14	C15	120.7(5)
C21	W	P	87.71(13)	C16	C15	C14	119.2(4)
C21	W	C19	178.56(17)	C15	C16	C17	120.7(5)
C21	W	C20	90.14(18)	C16	C17	C12	120.8(5)
C21	W	C22	87.49(18)	O2	C18	W	177.2(4)
C22	W	P	94.97(12)	O3	C19	W	177.3(4)
C22	W	C19	91.08(16)	O4	C20	W	179.0(4)
C22	W	C20	177.62(17)	O5	C21	W	178.4(4)
C1	S1	C3	92.82(19)	O6	C22	W	176.6(4)
O1	P	W	117.55(12)	Cl1	C36	Cl2	112.7(3)
O1	P	C1	103.79(17)	C34	O7	C33	132.8(15)
O1	P	C5	109.02(17)	O7	C33	C32	112.6(12)

C1	P	W	111.90(13)	O7	C34	C35	124.0(16)
C1	P	C5	96.51(17)	C28	N2	C23	121.8(4)
C5	P	W	115.46(13)	C28	N2	C29	121.0(4)
C2	N1	C4	122.6(3)	C29	N2	C23	117.1(4)
C3	N1	C2	114.5(3)	C28	N3	C31	127.4(7)
C3	N1	C4	122.9(3)	C28	N3	C31S	117.6(7)
C8	C0AA	C6	121.4(4)	N2	C23	C24	113.7(4)
S1	C1	P	124.9(2)	C23	C24	C25	113.4(4)
C2	C1	S1	109.1(3)	C26	C25	C24	115.3(3)
C2	C1	P	125.5(3)	C25	C26	C27	115.0(4)
C1	C2	N1	114.9(4)	C28	C27	C26	113.9(3)
S2	C3	S1	123.4(2)	N2	C28	C27	120.6(4)
N1	C3	S1	108.7(3)	N3	C28	N2	122.0(4)
N1	C3	S2	127.9(3)	N3	C28	C27	117.4(4)
C6	C5	P	113.5(3)	N2	C29	C30S	111.6(5)
C12	C5	P	110.5(3)	C30	C29	N2	114.3(5)
C12	C5	C6	113.4(3)	C29	C30	C31	124.0(9)
C0AA	C6	C5	118.9(4)	C31S	C30S	C29	117.9(10)
C11	C6	C0AA	118.1(4)	N3	C31	C30	105.2(10)
C11	C6	C5	123.0(4)	C30S	C31S	N3	125.2(12)
C0AA	C8	C9	119.9(4)				

12.13 Crystal data and structure refinement for 16 (IB-90)



Identification code	GSTR412, IB-90 // GXray4031f	μ/mm^{-1}	0.837
Device Type	Bruker X8-KappaApexII	F(000)	464
Empirical formula	$C_{13}H_{20}Cl_2N_3PS_4$	Crystal size/mm^3	0.18 × 0.1 × 0.08
Moiety formula	C H2 Cl2, C12 H18 N3 P S4	Absorption correction	empirical
Formula weight	448.43	Tmin; Tmax	0.6462; 0.7460
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	5.526 to 51.996°
Space group	P-1	Completeness to theta	0.922
a/Å	9.6379(17)	Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 11
b/Å	9.9399(17)	Reflections collected	6890
c/Å	11.0264(18)	Independent reflections	3567 [R_{int} = 0.0312, R_{sigma} = 0.0511]
α/°	108.158(4)	Data/restraints/parameters	3567/0/212
β/°	91.978(4)	Goodness-of-fit on F^2	1.085
γ/°	100.067(4)	Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.1101
Volume/Å^3	983.8(3)	Final R indexes [all data]	R_1 = 0.0639, wR_2 = 0.1207
Z	2	Largest diff. peak/hole / e Å^{-3}	0.40/-0.55
ρ_{calc}g/cm^3	1.514		

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C13	1.758(4)	N1	C3	1.382(4)
Cl2	C13	1.764(5)	N1	C4	1.467(5)
S1	C1	1.743(3)	N2	C6	1.356(5)
S1	C2	1.743(4)	N2	C7	1.379(4)
S2	C2	1.672(3)	N2	C8	1.465(5)
S3	C5	1.752(4)	N3	C9	1.471(5)
S3	C6	1.736(4)	N3	C11	1.473(5)
S4	C6	1.667(4)	C1	C3	1.351(5)
P	N3	1.682(3)	C5	C7	1.354(5)
P	C1	1.818(4)	C9	C10	1.505(5)
P	C5	1.824(4)	C11	C12	1.531(5)
N1	C2	1.346(5)			

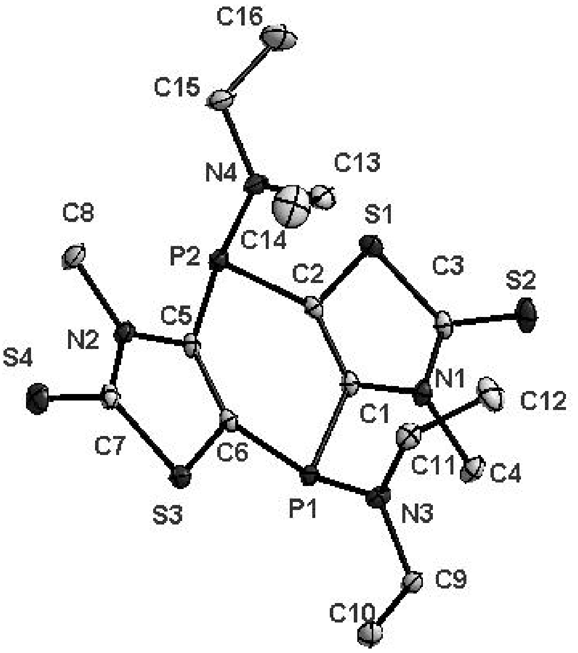
Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl1	C13	Cl2	112.0(2)	C3	C1	S1	109.0(3)
C2	S1	C1	92.72(17)	C3	C1	P	128.9(3)
C6	S3	C5	92.88(17)	S2	C2	S1	124.5(2)
N3	P	C1	100.02(16)	N1	C2	S1	108.2(2)
N3	P	C5	109.34(16)	N1	C2	S2	127.3(3)
C1	P	C5	96.77(16)	C1	C3	N1	114.2(3)
C2	N1	C3	115.9(3)	S3	C5	P	128.4(2)
C2	N1	C4	122.5(3)	C7	C5	S3	108.2(3)
C3	N1	C4	121.6(3)	C7	C5	P	123.4(3)
C6	N2	C7	114.9(3)	S4	C6	S3	124.1(2)
C6	N2	C8	121.9(3)	N2	C6	S3	108.8(2)
C7	N2	C8	123.2(3)	N2	C6	S4	127.1(3)
C9	N3	P	120.4(3)	C5	C7	N2	115.2(3)
C9	N3	C11	113.2(3)	N3	C9	C10	115.1(3)
C11	N3	P	123.3(2)	N3	C11	C12	114.5(3)
S1	C1	P	121.8(2)				

Torsion Angles

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C3	N1	-0.1(4)	C3	N1	C2	S2	179.1(3)
S3	C5	C7	N2	0.3(4)	C4	N1	C2	S1	-179.6(3)
P	N3	C9	C10	-33.6(4)	C4	N1	C2	S2	1.2(5)
P	N3	C11	C12	-106.4(4)	C4	N1	C3	C1	179.1(3)
P	C1	C3	N1	173.2(3)	C5	S3	C6	S4	-178.6(2)
P	C5	C7	N2	178.3(2)	C5	S3	C6	N2	1.1(3)
N3	P	C1	S1	-49.5(2)	C5	P	N3	C9	-110.1(3)
N3	P	C1	C3	138.0(3)	C5	P	N3	C11	48.9(3)
N3	P	C5	S3	-47.3(3)	C5	P	C1	S1	-160.5(2)
N3	P	C5	C7	135.2(3)	C5	P	C1	C3	26.9(4)
C1	S1	C2	S2	-179.4(2)	C6	S3	C5	P	-178.6(3)
C1	S1	C2	N1	1.3(3)	C6	S3	C5	C7	-0.8(3)
C1	P	N3	C9	149.0(3)	C6	N2	C7	C5	0.5(5)
C1	P	N3	C11	-52.0(3)	C7	N2	C6	S3	-1.1(4)
C1	P	C5	S3	55.9(3)	C7	N2	C6	S4	178.5(3)
C1	P	C5	C7	-121.7(3)	C8	N2	C6	S3	176.1(3)
C2	S1	C1	P	-174.6(2)	C8	N2	C6	S4	-4.3(5)
C2	S1	C1	C3	-0.7(3)	C8	N2	C7	C5	-176.6(3)
C2	N1	C3	C1	1.2(5)	C9	N3	C11	C12	53.9(4)
C3	N1	C2	S1	-1.6(4)	C11	N3	C9	C10	165.5(3)

12.14 Crystal data and structure refinement for 17a (IB-79).



Identification code	GSTR411, IB-79 // GXray4016f	μ/mm^{-1}	0.595
Device Type	Bruker X8-KappaApex II	F(000)	488
Empirical formula	$C_{16}H_{26}N_4P_2S_4$	Crystal size/mm^3	0.180 × 0.160 × 0.040
Moiety formula	C16 H26 N4 P2 S4	Absorption correction	Multi-Scan
Formula weight	464.59	Tmin; Tmax	0.6627; 0.7460
Temperature/K	100(2)	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	4.082 to 59.964°
Space group	P-1	Completeness to theta	0.995
a/Å	10.2641(5)	Index ranges	$-14 \le h \le 14$, $-13 \le k \le 14$, $-15 \le l \le 14$
b/Å	10.6501(5)	Reflections collected	18814
c/Å	11.1884(5)	Independent reflections	6192 [R_{int} = 0.0243, R_{sigma} = 0.0290]
α/°	84.638(2)	Data/restraints/parameters	6192/3/241
β/°	63.293(2)	Goodness-of-fit on F^2	1.038
γ/°	84.173(2)	Final R indexes [I>=2σ (I)]	R_1 = 0.0264, wR_2 = 0.0621
Volume/Å^3	1085.35(9)	Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0657
Z	2	Largest diff. peak/hole / e Å^{-3}	0.41/-0.26

ρ_{calc}g/cm^3 1.422

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C3	1.7371(12)	N1	C4	1.4651(15)
S1	C2	1.7499(12)	N2	C7	1.3637(16)
S2	C3	1.6659(12)	N2	C5	1.4066(14)
S3	C7	1.7356(12)	N2	C8	1.4609(15)
S3	C6	1.7455(12)	N3	C9	1.4681(15)
S4	C7	1.6706(12)	N3	C11	1.4696(15)
P1	N3	1.6743(10)	N4	C15	1.4667(16)
P1	C6	1.8158(11)	N4	C13	1.4699(16)
P1	C1	1.8344(12)	C1	C2	1.3564(16)
P2	N4	1.6729(11)	C5	C6	1.3542(16)
P2	C2	1.8137(12)	C9	C10	1.5247(17)
P2	C5	1.8326(12)	C11	C12	1.5211(18)
N1	C3	1.3631(15)	C13	C14	1.518(2)
N1	C1	1.4082(14)	C15	C16	1.5152(19)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	S1	C2	92.40(6)	C2	C1	P1	128.36(9)
C7	S3	C6	92.54(6)	N1	C1	P1	118.60(8)
N3	P1	C6	101.67(5)	C1	C2	S1	110.54(8)
N3	P1	C1	106.44(5)	C1	C2	P2	133.56(9)
C6	P1	C1	96.60(5)	S1	C2	P2	115.83(7)
N4	P2	C2	102.12(5)	N1	C3	S2	127.55(9)
N4	P2	C5	104.12(5)	N1	C3	S1	108.94(8)
C2	P2	C5	96.86(5)	S2	C3	S1	123.50(7)
C3	N1	C1	115.59(10)	C6	C5	N2	112.55(10)
C3	N1	C4	120.81(9)	C6	C5	P2	128.99(9)
C1	N1	C4	123.60(10)	N2	C5	P2	118.46(8)
C7	N2	C5	115.59(10)	C5	C6	S3	110.53(8)
C7	N2	C8	120.62(10)	C5	C6	P1	132.88(9)
C5	N2	C8	123.76(10)	S3	C6	P1	116.40(6)

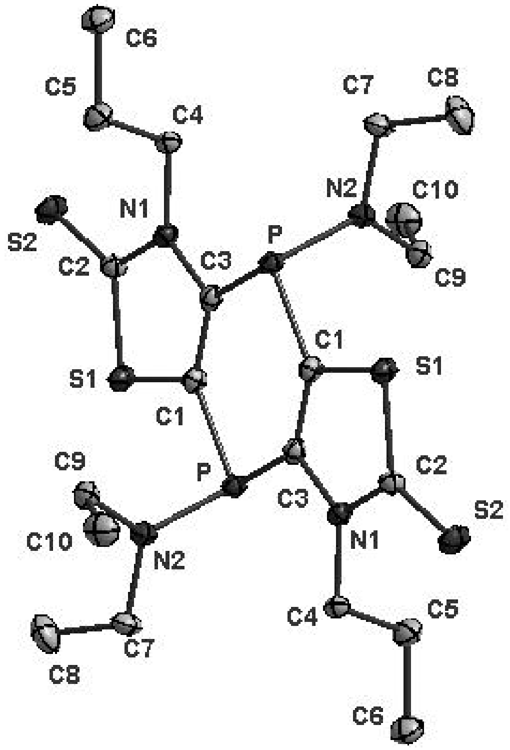
C9	N3	C11	116.60(9)	N2	C7	S4	126.76(9)
C9	N3	P1	118.82(8)	N2	C7	S3	108.75(8)
C11	N3	P1	124.58(8)	S4	C7	S3	124.48(8)
C15	N4	C13	116.76(10)	N3	C9	C10	112.83(10)
C15	N4	P2	119.50(9)	N3	C11	C12	113.25(10)
C13	N4	P2	123.75(8)	N4	C13	C14	113.70(11)
C2	C1	N1	112.52(10)	N4	C15	C16	113.45(11)

Torsion Angles

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	P1	N3	C9	132.06(9)	C7	N2	C5	C6	2.30(15)
C1	P1	N3	C9	-127.38(9)	C8	N2	C5	C6	-79.44(11)
C6	P1	N3	C11	-47.27(10)	C7	N2	C5	P2	-177.27(8)
C1	P1	N3	C11	53.29(10)	C8	N2	C5	P2	0.99(15)
C2	P2	N4	C15	132.55(10)	N4	P2	C5	C6	-11.10(11)
C5	P2	N4	C15	-27.09(10)	C2	P2	C5	C6	-6.71(12)
C2	P2	N4	C13	-47.84(11)	N4	P2	C5	N2	68.39(10)
C5	P2	N4	C13	52.53(11)	C2	P2	C5	N2	172.78(9)
C3	N1	C1	C2	1.49(14)	N2	C5	C6	S3	-1.42(12)
C4	N1	C1	C2	-79.13(10)	P2	C5	C6	S3	178.10(7)
C3	N1	C1	P1	173.88(8)	N2	C5	C6	P1	173.27(9)
C4	N1	C1	P1	-6.74(15)	P2	C5	C6	P1	-7.22(18)
N3	P1	C1	C2	-19.42(11)	C7	S3	C6	C5	0.26(9)
C6	P1	C1	C2	-15.16(12)	C7	S3	C6	P1	-175.39(7)
N3	P1	C1	N1	69.55(10)	N3	P1	C6	C5	125.44(12)
C6	P1	C1	N1	173.82(9)	C1	P1	C6	C5	17.10(13)
N1	C1	C2	S1	-1.03(12)	N3	P1	C6	S3	-60.12(7)
P1	C1	C2	S1	-172.51(7)	C1	P1	C6	S3	-168.46(6)
N1	C1	C2	P2	175.78(9)	C5	N2	C7	S4	176.96(9)
P1	C1	C2	P2	4.30(18)	C8	N2	C7	S4	-1.36(16)
C3	S1	C2	C1	0.32(9)	C5	N2	C7	S3	-2.01(12)
C3	S1	C2	P2	-177.11(7)	C8	N2	C7	S3	179.67(9)
N4	P2	C2	C1	114.14(12)	C6	S3	C7	N2	0.98(9)
C5	P2	C2	C1	8.05(13)	C6	S3	C7	S4	-178.02(8)
N4	P2	C2	S1	-69.18(7)	C11	N3	C9	C10	78.86(13)
C5	P2	C2	S1	-175.26(7)	P1	N3	C9	C10	-00.53(11)

C1	N1	C3	S2	179.52(9)	C9	N3	C11	C12	85.08(13)
C4	N1	C3	S2	0.12(16)	P1	N3	C11	C12	-95.58(12)
C1	N1	C3	S1	-1.19(12)	C15	N4	C13	C14	79.06(15)
C4	N1	C3	S1	179.41(8)	P2	N4	C13	C14	-00.56(13)
C2	S1	C3	N1	0.48(9)	C13	N4	C15	C16	73.38(15)
C2	S1	C3	S2	179.81(8)	P2	N4	C15	C16	-06.99(12)

12.15 Crystal data and structure refinement for 17b (IB-264).



Identification code	GSTR555, IB-264 // GXray5084f	ρ_{calc}g/cm^3	1.351
Crystal Habitus	clear colourless plate	µ/mm^{-1}	0.512
Device Type	Bruker X8-KappaApexII	F(000)	276
Empirical formula	$C_{20}H_{34}N_4P_2S_4$	Crystal size/mm^3	0.13 × 0.09 × 0.04
Moiety formula	C20 H34 N4 P2 S4	Absorption correction	empirical
Formula weight	520.69	Tmin; Tmax	0.6036; 0.7460
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	5.296 to 55.984°
Space group	P-1	Completeness to theta	0.998

a/Å	7.9498(4)	Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-14 \leq l \leq 14$
b/Å	9.0267(5)	Reflections collected	17142
c/Å	10.7417(6)	Independent reflections	3091 [R_{int} = 0.0495, R_{sigma} = 0.0369]
α/°	107.368(2)	Data/restraints/parameters	3091/0/139
β/°	100.629(2)	Goodness-of-fit on F^2	1.102
γ/°	112.392(2)	Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0743
Volume/$Å^3$	640.21(6)	Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.0794
Z	1	Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.32

Bond Lengths

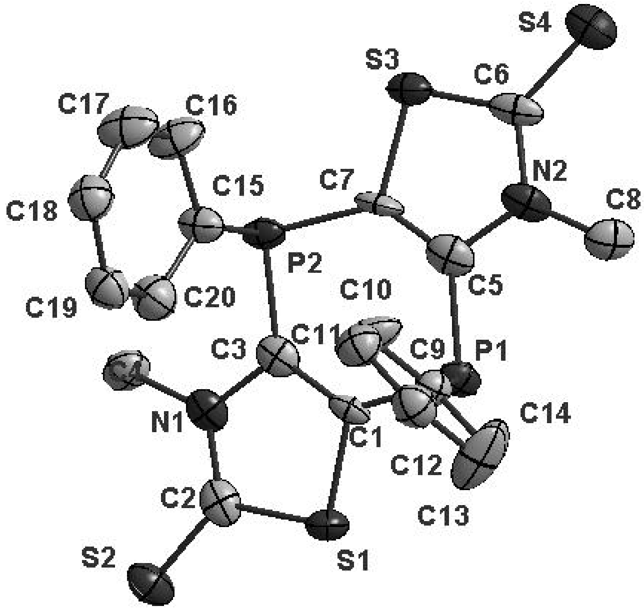
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.7454(17)	N2	C7	1.470(2)
S1	C2	1.7331(17)	N2	C9	1.466(2)
S2	C2	1.6632(18)	C1	C3	1.358(2)
P	N2	1.6684(15)	C3	P^1	1.8339(17)
P	C1	1.8105(17)	C4	C5	1.517(2)
P	$C3^1$	1.8339(17)	C5	C6	1.523(2)
N1	C2	1.361(2)	C7	C8	1.514(3)
N1	C3	1.401(2)	C9	C10	1.518(3)
N1	C4	1.468(2)			

Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	92.75(8)	C3	C1	P	134.35(13)
N2	P	C1	101.88(8)	S2	C2	S1	123.97(10)
N2	P	$C3^1$	106.71(8)	N1	C2	S1	108.55(12)
C1	P	$C3^1$	96.79(7)	N1	C2	S2	127.48(13)
C2	N1	C3	115.95(14)	N1	C3	P^1	118.66(12)
C2	N1	C4	120.68(14)	C1	C3	P^1	128.34(13)
C3	N1	C4	123.23(14)	C1	C3	N1	112.58(15)
C7	N2	P	118.84(12)	N1	C4	C5	111.66(14)
C9	N2	P	123.60(12)	C4	C5	C6	111.47(16)
C9	N2	C7	117.00(15)	N2	C7	C8	113.19(16)

S1	C1	P	115.46(9)	N2	C9	C10	113.25(15)
C3	C1	S1	110.17(12)				

12.16 Crystal data and structure refinement for 17c (IB-202).



Identification code	GSTR562, IB-202 // GXray5086_1m0	ρ_{calc}g/cm^3	1.483
Crystal Habitus	clear colourless plate	μ/mm^{-1}	0.607
Device Type	Bruker X8-KappaApexII	F(000)	976
Empirical formula	$C_{20}H_{16}N_2P_2S_4$	Crystal size/mm^3	0.26 × 0.15 × 0.1
Moiety formula	C20 H16 N2 P2 S4	Absorption correction	empirical
Formula weight	474.53	Tmin; Tmax	0.396302; 0.745909
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	monoclinic	2Θ range for data collection/°	3.828 to 55.992°
Space group	$P2_1/n$	Completeness to theta	0.996
a/Å	11.595(3)	Index ranges	$-15 \leq h \leq 15, 0 \leq k \leq 13, 0 \leq l \leq 24$
b/Å	9.879(3)	Reflections collected	5089
c/Å	18.893(5)	Independent reflections	5089 [R_{int} = 0.1508, R_{sigma} = 0.0935]
α/°	90	Data/restraints/parameters	5089/93/315
β/°	100.872(9)	Goodness-of-fit on F^2	1.431

γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.1191, wR_2 = 0.3681
Volume/Å^3	2125.3(10)	Final R indexes [all data]	R_1 = 0.1776, wR_2 = 0.3998
Z	4	Largest diff. peak/hole / e Å^{-3}	1.20/-1.10

Bond Lengths

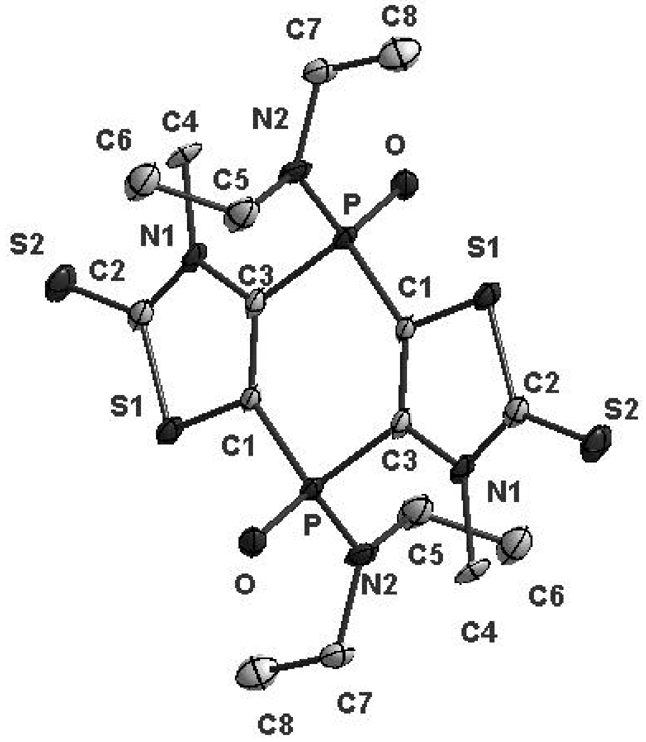
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.754(7)	C9	C14	1.39
S1	C2	1.742(8)	C10	C11	1.39
S2	C2	1.679(8)	C11	C12	1.39
S3	C6	1.733(9)	C12	C13	1.39
S3	C7	1.761(7)	C13	C14	1.39
S4	C6	1.687(8)	C9S	C10S	1.39
P1	C1	1.827(7)	C9S	C14S	1.39
P1	C5	1.834(9)	C10S	C11S	1.39
P1	C9	1.940(7)	C11S	C12S	1.39
P1	C9S	1.763(10)	C12S	C13S	1.39
P2	C3	1.820(8)	C13S	C14S	1.39
P2	C7	1.829(8)	C15	C16	1.396(8)
P2	C15	1.861(7)	C15	C20	1.412(18)
N1	C2	1.377(10)	C15	C20S	1.436(17)
N1	C3	1.424(9)	C16	C17	1.401(7)
N1	C4	1.445(10)	C17	C18	1.32(2)
N2	C5	1.409(10)	C17	C18S	1.395(9)
N2	C6	1.387(10)	C18	C19	1.398(10)
N2	C8	1.450(10)	C19	C20	1.41(2)
C1	C3	1.384(11)	C18S	C19S	1.44(2)
C5	C7	1.360(12)	C19S	C20S	1.397(9)
C9	C10	1.39			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C1	92.7(4)	C5	C7	S3	110.6(6)
C6	S3	C7	92.6(4)	C5	C7	P2	132.3(6)
C1	P1	C5	98.7(4)	C10	C9	P1	125.4(5)

C1	P1	C9	100.8(4)	C10	C9	C14	120
C5	P1	C9	97.5(4)	C14	C9	P1	114.5(5)
C9S	P1	C1	103.2(6)	C11	C10	C9	120
C9S	P1	C5	104.6(6)	C10	C11	C12	120
C3	P2	C7	97.9(4)	C13	C12	C11	120
C3	P2	C15	98.6(3)	C14	C13	C12	120
C7	P2	C15	102.0(3)	C13	C14	C9	120
C2	N1	C3	116.0(7)	C10S	C9S	P1	121.6(9)
C2	N1	C4	121.9(7)	C10S	C9S	C14S	120
C3	N1	C4	122.1(7)	C14S	C9S	P1	118.4(9)
C5	N2	C8	123.9(7)	C11S	C10S	C9S	120
C6	N2	C5	115.4(7)	C10S	C11S	C12S	120
C6	N2	C8	120.7(7)	C13S	C12S	C11S	120
S1	C1	P1	118.0(4)	C14S	C13S	C12S	120
C3	C1	S1	111.0(5)	C13S	C14S	C9S	120
C3	C1	P1	131.0(6)	C16	C15	P2	118.1(6)
S2	C2	S1	123.3(5)	C16	C15	C20	115.7(9)
N1	C2	S1	109.0(5)	C16	C15	C20S	116.2(8)
N1	C2	S2	127.8(6)	C20	C15	P2	123.5(8)
N1	C3	P2	118.8(6)	C20S	C15	P2	122.1(7)
C1	C3	P2	130.0(6)	C15	C16	C17	120.5(8)
C1	C3	N1	111.2(7)	C18	C17	C16	120.3(11)
N2	C5	P1	118.3(6)	C18S	C17	C16	121.3(12)
C7	C5	P1	129.1(6)	C17	C18	C19	122.6(16)
C7	C5	N2	112.6(7)	C18	C19	C20	116.2(16)
S4	C6	S3	123.1(5)	C15	C20	C19	121.5(15)
N2	C6	S3	108.8(6)	C17	C18S	C19S	118.1(15)
N2	C6	S4	128.0(6)	C20S	C19S	C18S	119.7(16)
S3	C7	P2	117.0(5)	C19S	C20S	C15	120.8(14)

12.17 Crystal data and structure refinement for 18 (IB-94).



Identification code	GSTR469, IB-94 // GXraycu_4499f	ρ_{calc}g/cm^3	1.472
Crystal Habitus	clear yellow plank	μ/mm^{-1}	5.427
Device Type	Bruker D8-Venture	F(000)	1040
Empirical formula	$C_{16}H_{26}N_4O_2P_2S_4$	Crystal size/mm^3	0.25 × 0.14 × 0.12
Moiety formula	C16 H26 N4 O2 P2 S4	Absorption correction	empirical
Formula weight	496.59	Tmin; Tmax	0.3240; 0.7536
Temperature/K	123	Radiation	CuKα (λ = 1.54178)
Crystal system	monoclinic	2Θ range for data collection/°	8.88 to 135.454°
Space group	C2/c	Completeness to theta	0.998
a/Å	20.1720(11)	Index ranges	$-24 \leq h \leq 24$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
b/Å	10.2030(5)	Reflections collected	22312
c/Å	11.0256(5)	Independent reflections	2024 [R_{int} = 0.1138, R_{sigma} = 0.0475]
α/°	90	Data/restraints/parameters	2024/0/130
β/°	99.162(3)	Goodness-of-fit on F^2	1.104
γ/°	90	Final R indexes [I>=2σ	R_1 = 0.0627, wR_2 = 0.1762

		(I)]	
Volume/Å^3	2240.3(2)	Final R indexes [all data]	R_1 = 0.0646, wR_2 = 0.1795
Z	4	Largest diff. peak/hole / e Å^{-3}	0.54/-0.89

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.734(3)	N1	C4	1.471(4)
S1	C2	1.737(3)	N2	C5	1.478(4)
S2	C2	1.652(3)	N2	C7	1.479(4)
P	O	1.479(2)	C1	C3^1	1.358(4)
P	N2	1.633(3)	C2	N1^1	1.359(4)
P	C1	1.795(3)	C3	C1^1	1.358(4)
P	C3	1.811(3)	C5	C6	1.492(5)
N1	C2^1	1.360(4)	C7	C8	1.506(5)
N1	C3	1.395(4)			

Bond Angles

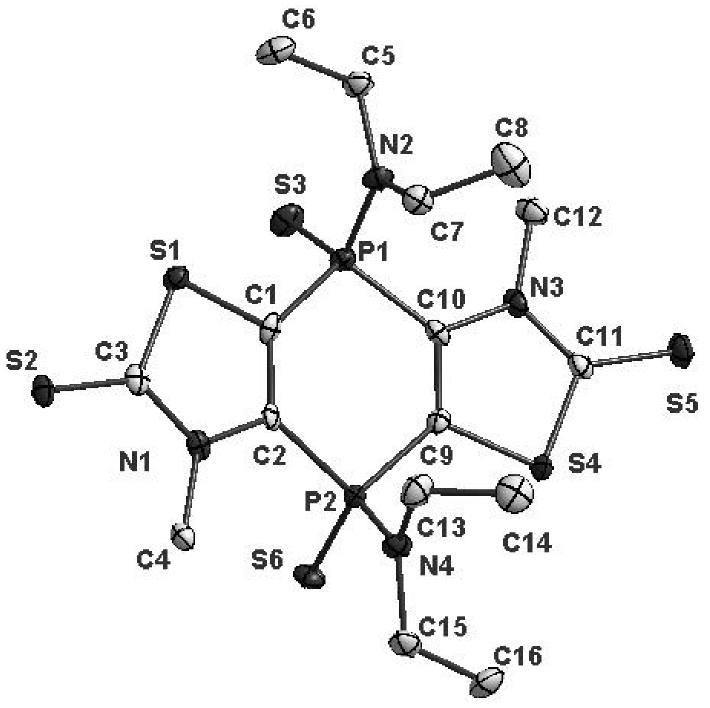
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	S1	C2	92.60(15)	C7	N2	P	120.3(2)
O	P	N2	113.49(14)	S1	C1	P	118.36(18)
O	P	C1	114.41(13)	C3^1	C1	S1	110.3(2)
O	P	C3	110.62(14)	C3^1	C1	P	131.4(3)
N2	P	C1	106.32(15)	S2	C2	S1	124.1(2)
N2	P	C3	109.19(14)	N1^1	C2	S1	108.7(2)
C1	P	C3	102.10(14)	N1^1	C2	S2	127.2(2)
C2^1	N1	C3	115.4(3)	N1	C3	P	120.4(2)
C2^1	N1	C4	120.3(3)	C1^1	C3	P	125.6(2)
C3	N1	C4	124.3(3)	C1^1	C3	N1	113.0(3)
C5	N2	P	120.2(2)	N2	C5	C6	113.8(3)
C5	N2	C7	118.1(3)	N2	C7	C8	112.9(3)

Torsion Angles

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P	N2	C5	C6	123.3(3)	C1	P	N2	C7	-119.0(3)

P	N2	C7	C8	91.1(3)	C1	P	C3	N1	177.8(2)
O	P	N2	C5	173.9(2)	C1	P	C3	C1^{1}	9.9(3)
O	P	N2	C7	7.6(3)	C2	S1	C1	P	178.24(18)
O	P	C1	S1	-70.1(2)	C2	S1	C1	C3^{1}	-0.9(2)
O	P	C1	C3^{1}	108.8(3)	C2^{1}	N1	C3	P	-169.5(2)
O	P	C3	N1	55.6(3)	C2^{1}	N1	C3	C1^{1}	-0.2(4)
O	P	C3	C1^{1}	-112.3(3)	C3	P	N2	C5	-62.2(3)
N2	P	C1	S1	56.0(2)	C3	P	N2	C7	131.5(3)
N2	P	C1	C3^{1}	-125.1(3)	C3	P	C1	S1	170.37(16)
N2	P	C3	N1	-70.0(3)	C3	P	C1	C3^{1}	-10.7(4)
N2	P	C3	C1^{1}	122.1(3)	C4	N1	C3	P	11.4(4)
C1	S1	C2	S2	-179.1(2)	C4	N1	C3	C1^{1}	-179.2(3)
C1	S1	C2	N1^{1}	1.0(2)	C5	N2	C7	C8	-75.5(4)
C1	P	N2	C5	47.3(3)	C7	N2	C5	C6	-70.1(4)

12.18 Crystal data and structure refinement for 19 (IB-152).



Identification code	GSTR524, IB-152 // GXray4890f	μ/mm^{-1}	0.724

Crystal Habitus	clear colourless block	F(000)	1104
Device Type	Bruker X8-KappaApexII	Crystal size/mm^3	0.09 × 0.08 × 0.05
Empirical formula	$C_{16}H_{26}N_4P_2S_6$	Absorption correction	empirical
Moiety formula	C16 H26 N4 P2 S6	Tmin; Tmax	0.5973; 0.7459
Formula weight	528.71	Radiation	MoKα (λ = 0.71073)
Temperature/K	100	2Θ range for data collection/°	5.95 to 55.998°
Crystal system	orthorhombic	Completeness to theta	0.995
Space group	$Pca2_1$	Index ranges	$-10 \leq h \leq 8$, $-20 \leq k \leq 18$, $-26 \leq l \leq 24$
a/Å	7.5980(7)	Reflections collected	9063
b/Å	15.8071(13)	Independent reflections	5034 [R_{int} = 0.0490, R_{sigma} = 0.0793]
c/Å	19.728(3)	Data/restraints/parameters	5034/37/260
α/°	90	Goodness-of-fit on F^2	1.079
β/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1087
γ/°	90	Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.1142
Volume/Å^3	2369.3(4)	Largest diff. peak/hole / e Å^{-3}	0.68/-0.48
Z	4	Flack parameter	0.12(17)
ρ_{calc}g/cm^3	1.482		

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.740(6)	N1	C3	1.378(8)
S1	C3	1.745(8)	N1	C4	1.452(9)
S2	C3	1.651(7)	N2	C5	1.467(9)
S3	P1	1.935(2)	N2	C7	1.479(8)
S4	C9	1.750(6)	N3	C10	1.395(8)
S4	C11	1.745(8)	N3	C11	1.362(8)
S5	C11	1.656(7)	N3	C12	1.462(9)
S6	P2	1.938(2)	N4	C13	1.516(9)
P1	N2	1.635(6)	N4	C15	1.478(9)
P1	C1	1.800(7)	C1	C2	1.345(10)
P1	C10	1.806(7)	C5	C6	1.507(9)
P2	N4	1.636(5)	C7	C8	1.491(11)
P2	C2	1.820(6)	C9	C10	1.361(9)

P2	C9	1.793(7)	C13	C14	1.495(10)
N1	C2	1.390(8)	C15	C16	1.511(9)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	S1	C3	92.1(3)	C15	N4	P2	123.2(5)
C11	S4	C9	92.4(3)	C15	N4	C13	117.0(5)
N2	P1	S3	114.6(2)	S1	C1	P1	117.4(4)
N2	P1	C1	106.9(3)	C2	C1	S1	110.9(5)
N2	P1	C10	106.1(3)	C2	C1	P1	131.6(5)
C1	P1	S3	112.8(2)	N1	C2	P2	120.7(5)
C1	P1	C10	101.7(3)	C1	C2	P2	125.8(5)
C10	P1	S3	113.7(2)	C1	C2	N1	113.5(6)
N4	P2	S6	114.6(2)	S2	C3	S1	124.1(4)
N4	P2	C2	107.5(3)	N1	C3	S1	108.5(5)
N4	P2	C9	107.3(3)	N1	C3	S2	127.4(6)
C2	P2	S6	113.1(2)	N2	C5	C6	113.3(6)
C9	P2	S6	112.6(2)	N2	C7	C8	113.1(6)
C9	P2	C2	100.7(3)	S4	C9	P2	117.3(4)
C2	N1	C4	125.3(5)	C10	C9	S4	109.9(5)
C3	N1	C2	115.0(6)	C10	C9	P2	132.6(5)
C3	N1	C4	119.7(5)	N3	C10	P1	121.8(5)
C5	N2	P1	122.6(4)	C9	C10	P1	124.7(5)
C5	N2	C7	117.0(6)	C9	C10	N3	113.3(6)
C7	N2	P1	119.5(5)	S5	C11	S4	124.6(4)
C10	N3	C12	124.9(6)	N3	C11	S4	108.8(5)
C11	N3	C10	115.6(6)	N3	C11	S5	126.7(6)
C11	N3	C12	119.5(6)	C14	C13	N4	111.7(6)
C13	N4	P2	119.2(5)	N4	C15	C16	114.2(6)

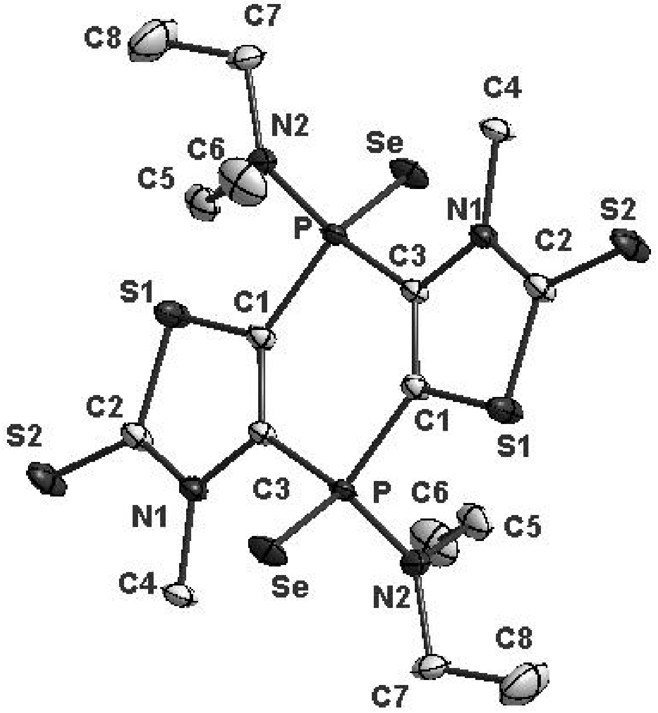
Torsion Angles

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C2	P2	-177.3(3)	C2	P2	N4	C13	41.0(6)
S1	C1	C2	N1	0.0(7)	C2	P2	N4	C15	-130.0(5)

S3	P1	N2	C5	-8.1(6)	C2	P2	C9	S4	-170.7(4)
S3	P1	N2	C7	-177.3(4)	C2	P2	C9	C10	14.4(7)
S3	P1	C1	S1	67.2(4)	C2	N1	C3	S1	2.1(6)
S3	P1	C1	C2	-108.2(6)	C2	N1	C3	S2	-179.1(5)
S3	P1	C10	N3	-65.0(5)	C3	S1	C1	P1	-175.2(4)
S3	P1	C10	C9	110.0(5)	C3	S1	C1	C2	1.1(5)
S4	C9	C10	P1	-177.6(3)	C3	N1	C2	P2	176.0(4)
S4	C9	C10	N3	-2.2(7)	C3	N1	C2	C1	-1.4(7)
S6	P2	N4	C13	167.5(4)	C4	N1	C2	P2	-3.1(8)
S6	P2	N4	C15	-3.4(6)	C4	N1	C2	C1	179.5(5)
S6	P2	C2	N1	-68.6(5)	C4	N1	C3	S1	-178.7(4)
S6	P2	C2	C1	108.5(5)	C4	N1	C3	S2	0.1(8)
S6	P2	C9	S4	68.6(4)	C5	N2	C7	C8	67.9(8)
S6	P2	C9	C10	-106.3(6)	C7	N2	C5	C6	75.7(8)
P1	N2	C5	C6	-93.8(6)	C9	S4	C11	S5	179.8(4)
P1	N2	C7	C8	-122.3(6)	C9	S4	C11	N3	0.2(5)
P1	C1	C2	P2	-1.7(9)	C9	P2	N4	C13	-66.7(6)
P1	C1	C2	N1	175.6(5)	C9	P2	N4	C15	122.4(5)
P2	N4	C13	C14	119.5(6)	C9	P2	C2	N1	171.0(5)
P2	N4	C15	C16	-82.2(7)	C9	P2	C2	C1	-11.9(6)
P2	C9	C10	P1	-2.4(9)	C10	P1	N2	C5	-134.4(5)
P2	C9	C10	N3	173.0(5)	C10	P1	N2	C7	56.4(6)
N2	P1	C1	S1	-59.6(4)	C10	P1	C1	S1	-170.7(3)
N2	P1	C1	C2	125.0(6)	C10	P1	C1	C2	14.0(7)
N2	P1	C10	N3	61.9(5)	C10	N3	C11	S4	-1.5(7)
N2	P1	C10	C9	-123.2(6)	C10	N3	C11	S5	178.9(5)
N4	P2	C2	N1	58.8(6)	C11	S4	C9	P2	-174.8(4)
N4	P2	C2	C1	-124.1(6)	C11	S4	C9	C10	1.2(5)
N4	P2	C9	S4	-58.4(4)	C11	N3	C10	P1	178.0(5)

N4	P2	C9	C10	126.7(6)	C11	N3	C10	C9	2.5(8)
C1	S1	C3	S2	179.4(4)	C12	N3	C10	P1	-3.4(9)
C1	S1	C3	N1	-1.8(4)	C12	N3	C10	C9	-178.9(6)
C1	P1	N2	C5	117.6(5)	C12	N3	C11	S4	179.8(5)
C1	P1	N2	C7	-51.6(6)	C12	N3	C11	S5	0.2(9)
C1	P1	C10	N3	173.5(5)	C13	N4	C15	C16	106.6(7)
C1	P1	C10	C9	-11.6(6)	C15	N4	C13	C14	-69.0(8)

12.19 Crystal data and structure refinement for 20 (IB-154).



Identification code	GSTR482, IB-154 // GXraymo_4560f	ρ_{calc}g/cm^3	1.525
Crystal Habitus	clear yellow block	μ/mm^{-1}	2.767
Device Type	Bruker D8-Venture	F(000)	362
Empirical formula	$C_{23}H_{34}N_4P_2S_4Se_2$	Crystal size/mm^3	0.22 × 0.1 × 0.08
Moiety formula	C16 H26 N4 P2 S4 Se2, C7 H8	Absorption correction	empirical
Formula weight	714.64	Tmin; Tmax	0.5154; 0.7459
Temperature/K	123	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data	5.28 to 55.99°

		collection/°	
Space group	P-1	Completeness to theta	0.999
a/Å	8.0145(5)	Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
b/Å	10.0354(7)	Reflections collected	29818
c/Å	10.7141(7)	Independent reflections	3764 [R_{int} = 0.0545, R_{sigma} = 0.0283]
α/°	74.652(3)	Data/restraints/parameters	3764/93/170
β/°	75.681(3)	Goodness-of-fit on F^2	1.046
γ/°	72.251(2)	Final R indexes [I>=2σ (I)]	R_1 = 0.0321, wR_2 = 0.0750
Volume/Å^3	778.30(9)	Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0801
Z	1	Largest diff. peak/hole / e Å^{-3}	1.00/-0.58

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Se	P	2.0850(6)	C3	N1^1	1.399(3)
S1	C2	1.733(2)	C3	C1^1	1.356(3)
S1	C1	1.739(2)	C1	C3^1	1.356(3)
S2	C2	1.669(2)	C5	C6	1.514(4)
P	N2	1.638(2)	C7	C8	1.518(4)
P	C3	1.813(2)	C9	C10	1.39
P	C1	1.795(2)	C9	C14	1.39
N1	C3^1	1.399(3)	C9	C15	1.4902(10)
N1	C2	1.364(3)	C10	C11	1.39
N1	C4	1.464(3)	C11	C12	1.39
N2	C5	1.483(3)	C12	C13	1.39
N2	C7	1.469(3)	C13	C14	1.39

Bond Angles

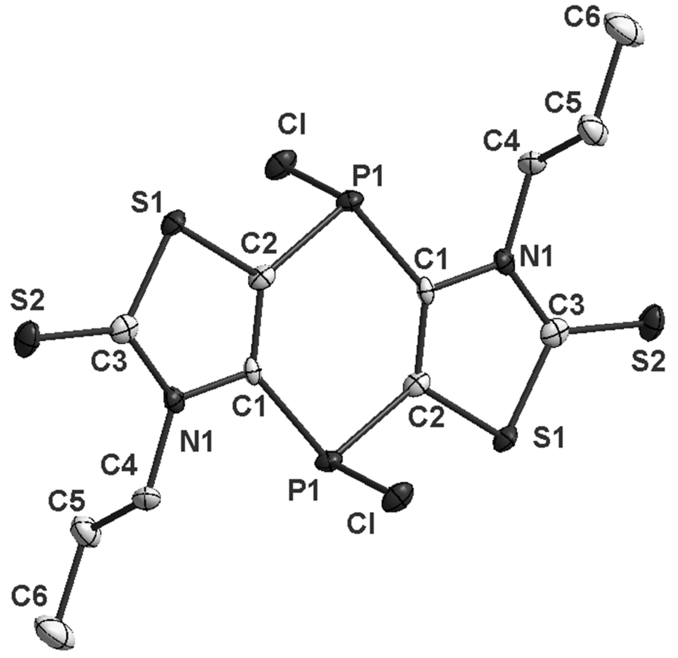
Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	92.04(11)	S2	C2	S1	123.29(15)
N2	P	Se	117.25(8)	N1	C2	S1	109.57(17)
N2	P	C3	105.83(11)	N1	C2	S2	127.14(18)
N2	P	C1	106.78(11)	S1	C1	P	116.83(13)
C3	P	Se	113.37(8)	C3^1	C1	S1	110.71(17)

C1	P	Se	110.87(8)	C3^1	C1	P	132.40(18)
C1	P	C3	101.34(10)	N2	C5	C6	114.0(2)
C3^1	N1	C4	124.5(2)	N2	C7	C8	112.6(2)
C2	N1	C3^1	114.73(19)	C10	C9	C14	120
C2	N1	C4	120.8(2)	C10	C9	C15	113.8(3)
C5	N2	P	118.91(17)	C14	C9	C15	126.2(3)
C7	N2	P	123.82(18)	C9	C10	C11	120
C7	N2	C5	117.1(2)	C12	C11	C10	120
N1^1	C3	P	120.84(17)	C11	C12	C13	120
C1^1	C3	P	126.22(17)	C14	C13	C12	120
C1^1	C3	N1^1	112.9(2)	C13	C14	C9	120

Torsion Angles

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Se	P	N2	C5	-76.25(17)	C2	S1	C1	C3^1	-0.8(2)
Se	P	N2	C7	-0.9(2)	C1	S1	C2	S2	-78.61(18)
Se	P	C3	N1^1	-63.27(19)	C1	S1	C2	N1	1.18(19)
Se	P	C3	C1^1	116.9(2)	C1	P	N2	C5	-51.2(2)
Se	P	C1	S1	58.51(15)	C1	P	N2	C7	124.1(2)
Se	P	C1	C3^1	-118.5(2)	C1	P	C3	N1^1	177.88(18)
P	N2	C5	C6	-102.5(3)	C1	P	C3	C1^1	-2.0(3)
P	N2	C7	C8	-97.9(3)	C4	N1	C2	S1	178.77(18)
N2	P	C3	N1^1	66.6(2)	C4	N1	C2	S2	-1.5(3)
N2	P	C3	C1^1	-113.3(2)	C5	N2	C7	C8	77.5(3)
N2	P	C1	S1	-70.31(16)	C7	N2	C5	C6	81.9(3)
N2	P	C1	C3^1	112.7(3)	C9	C10	C11	C12	0
C3	P	N2	C5	56.2(2)	C10	C9	C14	C13	0
C3	P	N2	C7	-128.5(2)	C10	C11	C12	C13	0
C3	P	C1	S1	179.13(13)	C11	C12	C13	C14	0
C3	P	C1	C3^1	2.2(3)	C12	C13	C14	C9	0
C3^1	N1	C2	S1	-1.3(3)	C14	C9	C10	C11	0
C3^1	N1	C2	S2	178.43(19)	C15	C9	C10	C11	179.6(6)
C2	S1	C1	P	-78.36(15)	C15	C9	C14	C13	-179.5(6)

12.20 Crystal data and structure refinement for 24b (IB-266 (P-Cl)).



Identification code	IB-266 // GXray5379_twin1_hklf4	ρ_{calc}g/cm^3	1.602
Crystal Habitus	clear yellow plank	μ/mm^{-1}	0.968
Device Type	STOE IPDS 2T	F(000)	228
Empirical formula	$C_{12}H_{14}Cl_2N_2P_2S_4$	Crystal size/mm^3	0.3 × 0.16 × 0.15
Moiety formula	C12 H14 Cl2 N2 P2 S4	Absorption correction	multi-scan
Formula weight	447.33	Tmin; Tmax	0.85066; 1.00000
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	6.194 to 51.976°
Space group	P-1	Completeness to theta	0.982
a/Å	6.5353(5)	Index ranges	$-8 \le h \le 8$, $-8 \le k \le 8$, $-13 \le l \le 13$
b/Å	6.6119(4)	Reflections collected	3033
c/Å	10.7915(9)	Independent reflections	3033 [R_{int} = 0.0234, R_{sigma} = 0.0636]
α/°	84.231(6)	Data/restraints/parameters	3033/0/102
β/°	88.651(6)	Goodness-of-fit on F^2	1.046
γ/°	88.674(6)	Final R indexes [I>=2σ (I)]	R_1 = 0.0329, wR_2 = 0.1072
Volume/Å^3	463.72(6)	Final R indexes [all data]	R_1 = 0.0459, wR_2 = 0.1225

Z	1	Largest diff. peak/hole / e Å^{-3}	0.57/-0.61

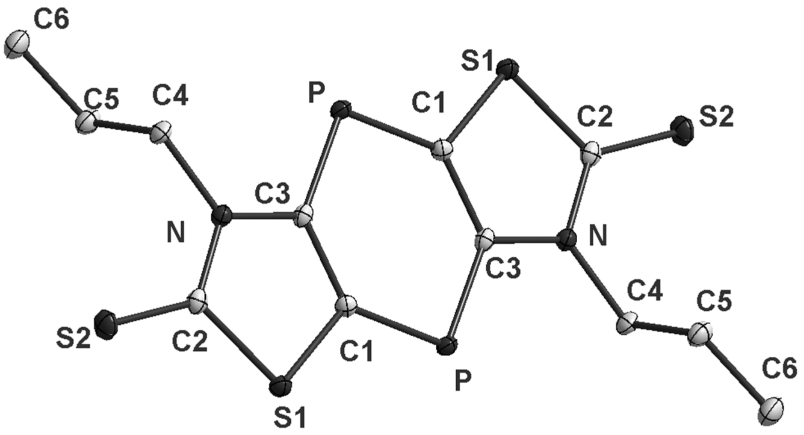
Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	P1	2.0973(13)	N1	C3	1.359(5)
S1	C2	1.735(4)	N1	C4	1.470(5)
S1	C3	1.723(4)	C1	C2	1.350(5)
S2	C3	1.679(4)	C2	P1^{1}	1.817(4)
P1	C1	1.828(4)	C4	C5	1.524(6)
P1	C2^{1}	1.817(4)	C5	C6	1.523(6)
N1	C1	1.394(4)			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	S1	C2	91.63(19)	C2	C1	N1	112.8(4)
C1	P1	Cl1	97.47(12)	S1	C2	P1^{1}	116.1(2)
C2^{1}	P1	Cl1	99.08(13)	C1	C2	S1	111.0(3)
C2^{1}	P1	C1	98.32(17)	C1	C2	P1^{1}	132.8(3)
C1	N1	C4	123.7(3)	S2	C3	S1	123.2(3)
C3	N1	C1	114.4(3)	N1	C3	S1	110.1(3)
C3	N1	C4	121.9(3)	N1	C3	S2	126.7(3)
N1	C1	P1	118.3(3)	N1	C4	C5	111.7(3)
C2	C1	P1	128.9(3)	C6	C5	C4	111.2(3)

12.21 Crystal data and structure refinement for 25 (IB-266).



Identification code	GSTR595, IB-266 // GXray5379	ρ_{calc}g/cm^3	1.602
Crystal Habitus	clear yellow plank	μ/mm^{-1}	0.97
Device Type	STOE IPDS-2T	F(000)	682
Empirical formula	$C_{18}H_{20}Cl_3N_3P_3S_6$	Crystal size/mm^3	0.3 × 0.16 × 0.15
Moiety formula	C12 H13 Cl2 N2 P2 S4, C6 H7 Cl N P S2	Absorption correction	integration
Formula weight	669.99	Tmin; Tmax	0.5612; 0.8133
Temperature/K	123	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	6.2 to 53.996°
Space group	P-1	Completeness to theta	0.977
a/Å	6.5339(6)	Index ranges	$-8 \leq h \leq 7$, $-8 \leq k \leq 8$, $-41 \leq l \leq 41$
b/Å	6.6068(6)	Reflections collected	9565
c/Å	32.349(3)	Independent reflections	5625 [R_{int} = 0.0807, R_{sigma} = 0.0580]
α/°	84.230(8)	Data/restraints/parameters	5625/222/302
β/°	88.655(8)	Goodness-of-fit on F^2	2.699
γ/°	88.734(8)	Final R indexes [I>=2σ (I)]	R_1 = 0.0978, wR_2 = 0.4728
Volume/Å^3	1388.7(2)	Final R indexes [all data]	R_1 = 0.1847, wR_2 = 0.4942
Z	2	Largest diff. peak/hole / e Å^{-3}	0.78/-0.68

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å

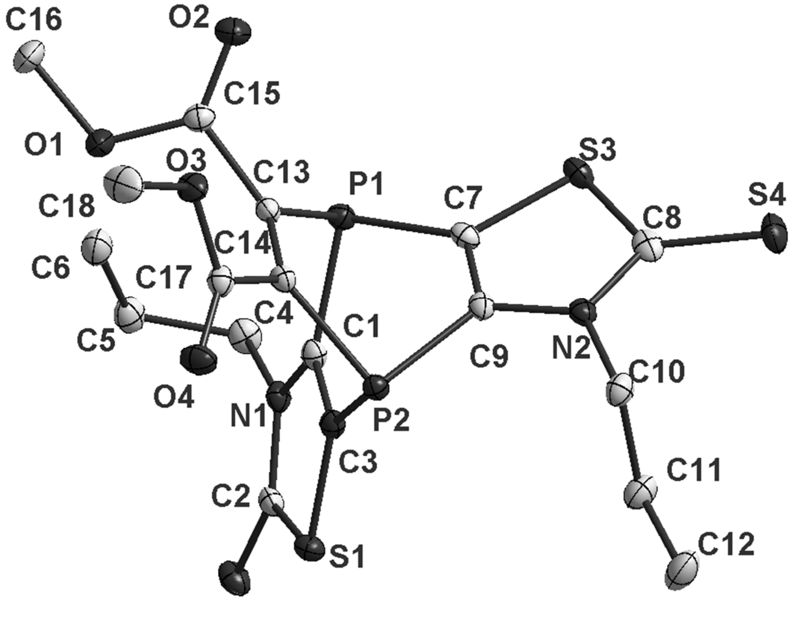
Cl1	P1	2.102(6)	C4	C5	1.56(2)
Cl2	P2	2.076(5)	C5	C6	1.36(3)
S1	C2	1.725(18)	C7	C8	1.36(2)
S1	C3	1.689(18)	C10	C11	1.49(2)
S2	C3	1.678(19)	C11	C12	1.56(3)
S3	C7	1.734(17)	Cl1'	P1'	2.120(5)
S3	C9	1.714(17)	S1'	C1'	1.762(18)
S4	C9	1.683(18)	S1'	C2'	1.794(18)
P1	C1	1.824(18)	S2'	C2'	1.64(2)
P1	C7	1.797(18)	P1'	C1'	1.767(18)
P2	C2	1.841(18)	P1'	C6'	1.820(16)
P2	C8	1.839(17)	N1'	C2'	1.37(2)
N1	C1	1.39(2)	N1'	C3'	1.43(2)
N1	C3	1.39(2)	N1'	C6'^{1}	1.43(2)
N1	C4	1.51(2)	C1'	C6'^{1}	1.34(2)
N2	C8	1.37(2)	C3'	C4'	1.53(3)
N2	C9	1.33(2)	C4'	C5'	1.65(3)
N2	C10	1.47(2)	C6'	N1'^{1}	1.43(2)
C1	C2	1.36(2)	C6'	C1'^{1}	1.34(2)

Bond Angles

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C3	S1	C2	91.9(9)	C8	C7	P1	133.8(13)
C9	S3	C7	92.4(8)	N2	C8	P2	118.9(12)
C1	P1	Cl1	97.2(6)	C7	C8	P2	127.7(14)
C7	P1	Cl1	97.6(5)	C7	C8	N2	113.5(15)
C7	P1	C1	98.9(8)	S4	C9	S3	123.0(10)
C2	P2	Cl2	99.3(5)	N2	C9	S3	109.6(13)
C8	P2	Cl2	97.3(5)	N2	C9	S4	127.2(13)
C8	P2	C2	98.7(8)	N2	C10	C11	114.4(13)
C1	N1	C3	114.6(15)	C10	C11	C12	113.2(15)
C1	N1	C4	121.2(15)	C1'	S1'	C2'	92.4(8)
C3	N1	C4	124.1(16)	C1'	P1'	Cl1'	100.7(5)
C8	N2	C10	123.6(14)	C1'	P1'	C6'	97.2(7)
C9	N2	C8	115.7(14)	C6'	P1'	Cl1'	97.3(5)
C9	N2	C10	120.7(15)	C2'	N1'	C3'	119.1(16)

N1	C1	P1	120.1(13)	C2'	N1'	C6'^{1}	113.8(14)
C2	C1	P1	128.8(15)	C6'^{1}	N1'	C3'	126.9(15)
C2	C1	N1	111.1(16)	S1'	C1'	P1'	116.4(9)
S1	C2	P2	115.8(9)	C6'^{1}	C1'	S1'	109.4(13)
C1	C2	S1	112.2(14)	C6'^{1}	C1'	P1'	134.1(14)
C1	C2	P2	132.0(14)	S2'	C2'	S1'	121.1(10)
S2	C3	S1	125.6(11)	N1'	C2'	S1'	108.4(14)
N1	C3	S1	110.2(14)	N1'	C2'	S2'	130.3(14)
N1	C3	S2	124.3(14)	N1'	C3'	C4'	111.5(14)
N1	C4	C5	109.8(13)	C3'	C4'	C5'	104.5(14)
C6	C5	C4	114.8(16)	N1'^{1}	C6'	P1'	115.3(11)
S3	C7	P1	116.9(9)	C1'^{1}	C6'	P1'	128.6(13)
C8	C7	S3	108.7(13)	C1'^{1}	C6'	N1'^{1}	116.0(15)

12.22 Crystal data and structure refinement for 26 (IB-282).



Identification code	GSTR581, IB-282 // GXray5246f	ρ_{calc}g/cm^3	1.495
Crystal Habitus	clear yellow plate	μ/mm^{-1}	0.579
Device Type	Bruker X8-KappaApexII	F(000)	536
Empirical formula	$C_{18}H_{20}N_2O_4P_2S_4$	Crystal size/mm^3	0.24 × 0.14 × 0.08
Moiety formula	C18 H20 N2 O4 P2 S4	Absorption correction	empirical
Formula weight	518.54	Tmin; Tmax	0.6499; 0.7460

Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	4.168 to 56°
Space group	P-1	Completeness to theta	0.996
a/Å	10.1125(6)	Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$
b/Å	10.1260(6)	Reflections collected	29215
c/Å	11.9070(7)	Independent reflections	5556 [R_{int} = 0.0723, R_{sigma} = 0.0597]
α/°	77.826(3)	Data/restraints/parameters	5556/0/275
β/°	75.301(3)	Goodness-of-fit on F^2	1.061
γ/°	89.011(3)	Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1003
Volume/Å^3	1151.99(12)	Final R indexes [all data]	R_1 = 0.0710, wR_2 = 0.1105
Z	2	Largest diff. peak/hole / e Å^{-3}	0.54/-0.44

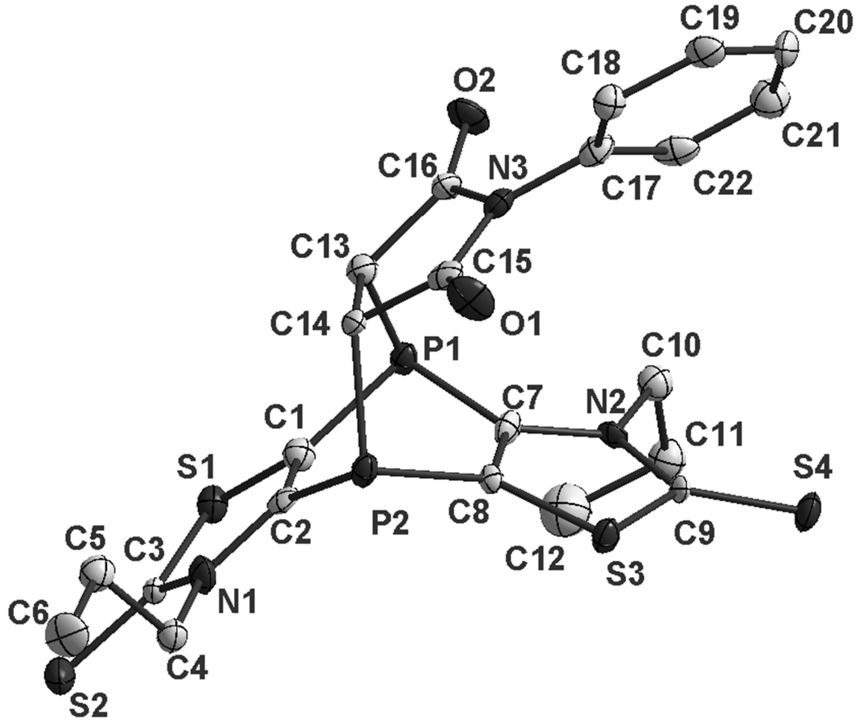
Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C2	1.741(3)	O4	C17	1.209(3)
S1	C3	1.737(3)	N1	C1	1.381(4)
S2	C2	1.663(3)	N1	C2	1.369(4)
S3	C7	1.732(3)	N1	C4	1.479(4)
S3	C8	1.735(3)	N2	C8	1.373(4)
S4	C8	1.670(3)	N2	C9	1.381(4)
P1	C1	1.846(3)	N2	C10	1.474(4)
P1	C7	1.818(3)	C1	C3	1.348(4)
P1	C13	1.870(3)	C4	C5	1.529(4)
P2	C3	1.826(3)	C5	C6	1.523(4)
P2	C9	1.845(3)	C7	C9	1.350(4)
P2	C14	1.871(3)	C10	C11	1.520(4)
O1	C15	1.330(4)	C11	C12	1.526(4)
O1	C16	1.454(4)	C13	C14	1.336(4)
O2	C15	1.203(4)	C13	C15	1.495(4)
O3	C17	1.331(4)	C14	C17	1.493(4)
O3	C18	1.451(3)			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	S1	C2	91.97(14)	N1	C4	C5	110.9(2)
C7	S3	C8	91.83(14)	C6	C5	C4	114.0(3)
C1	P1	C13	93.48(12)	S3	C7	P1	125.92(17)
C7	P1	C1	95.63(13)	C9	C7	S3	110.8(2)
C7	P1	C13	94.77(13)	C9	C7	P1	123.2(2)
C3	P2	C9	93.88(13)	S4	C8	S3	123.84(18)
C3	P2	C14	94.79(13)	N2	C8	S3	109.2(2)
C9	P2	C14	94.61(13)	N2	C8	S4	126.9(2)
C15	O1	C16	115.2(2)	N2	C9	P2	125.3(2)
C17	O3	C18	115.2(2)	C7	C9	P2	121.1(2)
C1	N1	C4	124.4(2)	C7	C9	N2	113.5(3)
C2	N1	C1	114.3(2)	N2	C10	C11	111.4(2)
C2	N1	C4	121.3(2)	C10	C11	C12	110.2(3)
C8	N2	C9	114.5(3)	C14	C13	P1	121.1(2)
C8	N2	C10	122.3(3)	C14	C13	C15	125.6(3)
C9	N2	C10	122.9(2)	C15	C13	P1	113.1(2)
N1	C1	P1	124.3(2)	C13	C14	P2	122.2(2)
C3	C1	P1	121.2(2)	C13	C14	C17	123.1(3)
C3	C1	N1	114.4(3)	C17	C14	P2	114.5(2)
S2	C2	S1	123.47(18)	O1	C15	C13	112.5(2)
N1	C2	S1	109.2(2)	O2	C15	O1	125.6(3)
N1	C2	S2	127.3(2)	O2	C15	C13	121.8(3)
S1	C3	P2	127.01(17)	O3	C17	C14	112.3(2)
C1	C3	S1	110.1(2)	O4	C17	O3	125.0(3)
C1	C3	P2	122.9(2)	O4	C17	C14	122.7(3)

12.23 Crystal data and structure refinement for 27 (IB-305).



Identification code	GSTR630, IB-305 // GXraycu_5685g	μ/mm^{-1}	5.167
Crystal Habitus	clear colourless plate	F(000)	2272
Device Type	Bruker D8-Venture	Crystal size/mm^3	0.16 × 0.07 × 0.02
Empirical formula	$C_{22}H_{21}N_3O_2P_2S_4$	Absorption correction	empirical
Moiety formula	C22 H21 N3 O2 P2 S4	Tmin; Tmax	0.3233; 0.7536
Formula weight	549.6	Radiation	CuKα (λ = 1.54178)
Temperature/K	150	2Θ range for data collection/°	6.48 to 135.442°
Crystal system	orthorhombic	Completeness to theta	1
Space group	$Pna2_1$	Index ranges	$-18 \leq h \leq 18$, $-13 \leq k \leq 13$, $-32 \leq l \leq 32$
a/Å	15.3334(4)	Reflections collected	76930
b/Å	11.3840(3)	Independent reflections	8617 [R_{int} = 0.3257, R_{sigma} = 0.1444]
c/Å	27.2807(6)	Data/restraints/parameters	8617/121/599
α/°	90	Goodness-of-fit on F^2	1.022
β/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0954, wR_2 = 0.2203
γ/°	90	Final R indexes [all data]	R_1 = 0.1461, wR_2 = 0.2659

Volume/Å^3	4762.0(2)	Largest diff. peak/hole / e Å^{-3}	0.64/-1.15
Z	8	Flack parameter	0.45(5)
ρ_{calc}g/cm^3	1.533		

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.708(19)	S1'	C1'	1.739(19)
S1	C3	1.743(17)	S1'	C3'	1.744(18)
S2	C3	1.655(18)	S2'	C3'	1.667(18)
S3	C8	1.723(16)	S3'	C8'	1.734(16)
S3	C9	1.741(17)	S3'	C9'	1.722(18)
S4	C9	1.657(16)	S4'	C9'	1.669(18)
P1	C1	1.82(2)	P1'	C1'	1.824(19)
P1	C7	1.839(18)	P1'	C7'	1.848(18)
P1	C13	1.892(18)	P1'	C13'	1.877(19)
P2	C2	1.833(19)	P2'	C2'	1.807(19)
P2	C8	1.819(16)	P2'	C8'	1.813(16)
P2	C14	1.880(18)	P2'	C14'	1.896(18)
O1	C15	1.21(2)	O1'	C15'	1.20(2)
O2	C16	1.22(2)	O2'	C16'	1.20(2)
N1	C2	1.38(2)	N1'	C2'	1.40(2)
N1	C3	1.37(3)	N1'	C3'	1.38(2)
N1	C4	1.48(2)	N1'	C4'	1.47(2)
N2	C7	1.40(2)	N2'	C7'	1.42(2)
N2	C9	1.37(2)	N2'	C9'	1.38(2)
N2	C10	1.50(2)	N2'	C10'	1.46(2)
N3	C15	1.40(2)	N3'	C15'	1.39(2)
N3	C16	1.37(2)	N3'	C16'	1.41(2)
N3	C17	1.43(2)	N3'	C17'	1.44(2)
C1	C2	1.36(3)	C1'	C2'	1.36(3)
C4	C5	1.52(3)	C4'	C5'	1.52(3)
C5	C6	1.50(3)	C5'	C6'	1.55(3)
C7	C8	1.34(2)	C7'	C8'	1.35(2)
C10	C11	1.50(3)	C10'	C11'	1.52(3)
C11	C12	1.50(3)	C11'	C12'	1.52(3)
C13	C14	1.53(2)	C13'	C14'	1.55(2)

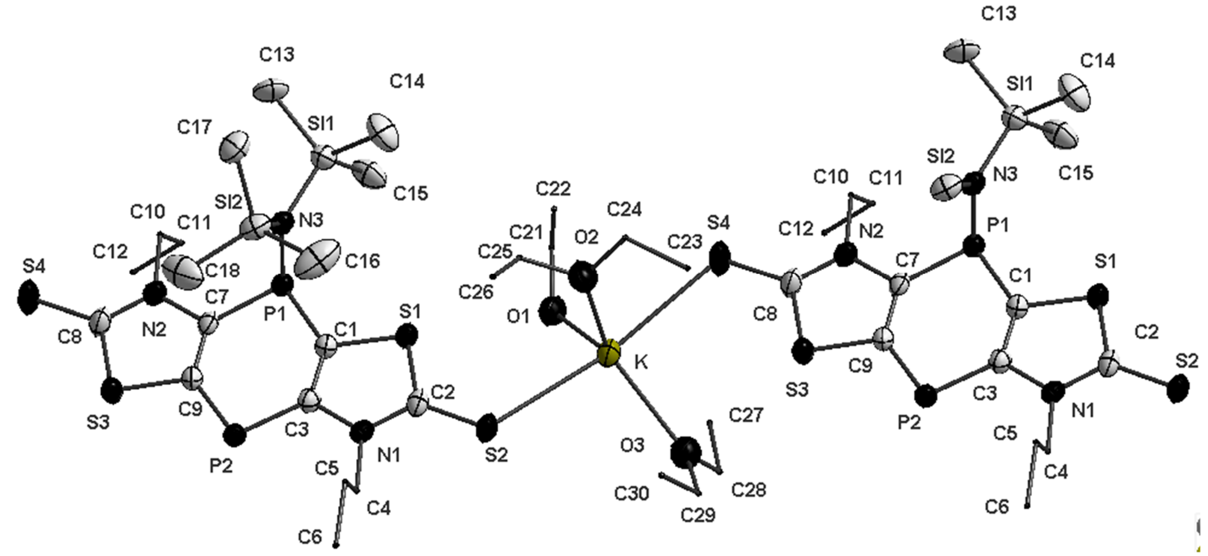
C13	C16	1.51(2)	C13'	C16'	1.52(3)
C14	C15	1.52(3)	C14'	C15'	1.52(2)
C17	C18	1.41(3)	C17'	C18'	1.40(3)
C17	C22	1.37(3)	C17'	C22'	1.40(3)
C18	C19	1.39(3)	C18'	C19'	1.36(3)
C19	C20	1.39(3)	C19'	C20'	1.39(3)
C20	C21	1.41(3)	C20'	C21'	1.39(3)
C21	C22	1.37(3)	C21'	C22'	1.37(3)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	S1	C3	93.0(9)	C1'	S1'	C3'	92.2(9)
C8	S3	C9	92.6(8)	C9'	S3'	C8'	92.4(8)
C1	P1	C7	96.9(9)	C1'	P1'	C7'	95.8(8)
C1	P1	C13	94.3(8)	C1'	P1'	C13'	93.3(8)
C7	P1	C13	95.2(8)	C7'	P1'	C13'	95.3(8)
C2	P2	C14	95.9(8)	C2'	P2'	C8'	96.0(8)
C8	P2	C2	95.8(8)	C2'	P2'	C14'	96.2(8)
C8	P2	C14	94.8(8)	C8'	P2'	C14'	93.2(8)
C2	N1	C4	122.0(16)	C2'	N1'	C4'	122.8(16)
C3	N1	C2	116.0(15)	C3'	N1'	C2'	115.3(14)
C3	N1	C4	121.9(15)	C3'	N1'	C4'	122.0(15)
C7	N2	C10	124.7(15)	C7'	N2'	C10'	124.9(14)
C9	N2	C7	114.9(14)	C9'	N2'	C7'	112.5(14)
C9	N2	C10	120.3(14)	C9'	N2'	C10'	122.6(14)
C15	N3	C17	126.2(16)	C15'	N3'	C16'	112.3(15)
C16	N3	C15	112.4(16)	C15'	N3'	C17'	124.6(15)
C16	N3	C17	121.5(15)	C16'	N3'	C17'	123.1(15)
S1	C1	P1	127.2(11)	S1'	C1'	P1'	125.2(11)
C2	C1	S1	110.6(14)	C2'	C1'	S1'	111.2(14)
C2	C1	P1	122.1(15)	C2'	C1'	P1'	123.5(14)
N1	C2	P2	124.6(13)	N1'	C2'	P2'	124.9(13)
C1	C2	P2	122.7(15)	C1'	C2'	P2'	122.7(14)
C1	C2	N1	112.7(17)	C1'	C2'	N1'	112.4(16)
S2	C3	S1	123.4(11)	S2'	C3'	S1'	123.3(11)
N1	C3	S1	107.6(12)	N1'	C3'	S1'	108.9(12)

N1	C3	S2	129.0(14)	N1'	C3'	S2'	127.9(14)
N1	C4	C5	111.7(15)	N1'	C4'	C5'	110.8(14)
C6	C5	C4	111.7(17)	C4'	C5'	C6'	108.7(17)
N2	C7	P1	122.9(13)	N2'	C7'	P1'	122.4(13)
C8	C7	P1	124.1(13)	C8'	C7'	P1'	123.8(13)
C8	C7	N2	113.0(15)	C8'	C7'	N2'	113.7(15)
S3	C8	P2	126.9(9)	S3'	C8'	P2'	126.6(9)
C7	C8	S3	111.3(12)	C7'	C8'	S3'	110.9(12)
C7	C8	P2	121.3(13)	C7'	C8'	P2'	122.4(13)
S4	C9	S3	124.6(11)	S4'	C9'	S3'	125.0(11)
N2	C9	S3	108.1(11)	N2'	C9'	S3'	110.4(13)
N2	C9	S4	127.2(13)	N2'	C9'	S4'	124.6(14)
N2	C10	C11	112.9(16)	N2'	C10'	C11'	112.2(15)
C12	C11	C10	114.4(19)	C10'	C11'	C12'	113.5(17)
C14	C13	P1	116.4(12)	C14'	C13'	P1'	116.9(13)
C16	C13	P1	107.4(13)	C16'	C13'	P1'	106.0(13)
C16	C13	C14	104.6(14)	C16'	C13'	C14'	103.9(15)
C13	C14	P2	119.9(13)	C13'	C14'	P2'	119.7(13)
C15	C14	P2	106.7(12)	C15'	C14'	P2'	106.8(12)
C15	C14	C13	104.6(14)	C15'	C14'	C13'	105.5(15)
O1	C15	N3	125.4(19)	O1'	C15'	N3'	125.9(17)
O1	C15	C14	126.8(17)	O1'	C15'	C14'	125.5(16)
N3	C15	C14	107.8(16)	N3'	C15'	C14'	108.5(15)
O2	C16	N3	124.6(17)	O2'	C16'	N3'	124.1(18)
O2	C16	C13	126.4(17)	O2'	C16'	C13'	127.0(18)
N3	C16	C13	109.0(15)	N3'	C16'	C13'	108.8(15)
C18	C17	N3	119.4(17)	C18'	C17'	N3'	122.7(18)
C22	C17	N3	119.5(18)	C18'	C17'	C22'	118.5(19)
C22	C17	C18	121.1(19)	C22'	C17'	N3'	118.7(18)
C19	C18	C17	117(2)	C19'	C18'	C17'	121(2)
C20	C19	C18	123(2)	C18'	C19'	C20'	121(2)
C19	C20	C21	118.5(18)	C19'	C20'	C21'	118(2)
C22	C21	C20	119.4(19)	C22'	C21'	C20'	122(2)
C17	C22	C21	121(2)	C21'	C22'	C17'	120(2)

12.24 Crystal data and structure refinement for 29b (IB-365).



Identification code	GSTR607, IB-365 // GXray5545	ρ_{calc}g/cm^3	1.205
Crystal Habitus	clear yellow plate	μ/mm^{-1}	0.469
Device Type	STOE IPDS-2T	F(000)	856
Empirical formula	$C_{30}H_{62}KN_3O_3P_2S_4Si_2$	Crystal size/mm^3	0.27 × 0.12 × 0.1
Moiety formula	C30 H62 K N3 O3 P2 S4 Si2	Absorption correction	integration
Formula weight	798.28	Tmin; Tmax	0.7658; 0.9471
Temperature/K	123	Radiation	MoKα (λ = 0.71073)
Crystal system	triclinic	2Θ range for data collection/°	5.352 to 50.498°
Space group	P-1	Completeness to theta	0.975
a/Å	8.9737(6)	Index ranges	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$
b/Å	14.8907(9)	Reflections collected	14534
c/Å	16.9261(11)	Independent reflections	7756 [R_{int} = 0.0955, R_{sigma} = 0.1279]
α/°	77.937(5)	Data/restraints/parameters	7756/56/468
β/°	83.960(5)	Goodness-of-fit on F^2	0.859
γ/°	88.797(5)	Final R indexes [I>=2σ (I)]	R_1 = 0.0609, wR_2 = 0.1395
Volume/Å^3	2199.5(2)	Final R indexes [all data]	R_1 = 0.1095, wR_2 = 0.1544
Z	2	Largest diff. peak/hole / e Å^{-3}	0.45/-0.37

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
K	S2	3.2492(16)	O1	C21	1.416(7)
K	S4[1]	3.2715(17)	O2	C24	1.424(8)
K	O1	2.733(3)	O2	C25	1.435(6)
K	O2	2.746(4)	O3	C28	1.372(14)
K	O3	2.708(9)	O3	C29	1.396(8)
K	O3S	2.774(8)	N1	C2	1.353(6)
S1	C1	1.748(4)	N1	C3	1.418(5)
S1	C2	1.729(4)	N1	C4	1.465(5)
S2	C2	1.675(4)	N2	C7	1.438(5)
S3	C8	1.739(5)	N2	C8	1.330(6)
S3	C9	1.746(4)	N2	C10	1.477(5)
S4	K[2]	3.2715(17)	C1	C3	1.376(6)
S4	C8	1.691(4)	C4	C5	1.505(7)
P1	N3	1.744(4)	C5	C6	1.540(6)
P1	C1	1.807(4)	C7	C9	1.373(6)
P1	C7	1.805(4)	C10	C11	1.516(7)
P2	C3	1.776(4)	C11	C12	1.513(8)
P2	C9	1.777(4)	C19	C20	1.425(8)
Si1	N3	1.760(4)	C21	C22	1.435(9)
Si1	C13	1.865(5)	C23	C24	1.481(10)
Si1	C14	1.866(6)	C25	C26	1.497(8)
Si1	C15	1.856(6)	C27	C28	1.532(15)
Si2	N3	1.765(4)	C29	C30	1.534(16)
Si2	C16	1.872(6)	C28S	O3S	1.43(2)
Si2	C17	1.862(5)	C28S	C27S	1.56(2)
Si2	C18	1.849(6)	C30S	C29S	1.52(2)
O1	C20	1.430(8)	C29S	O3S	1.376(9)

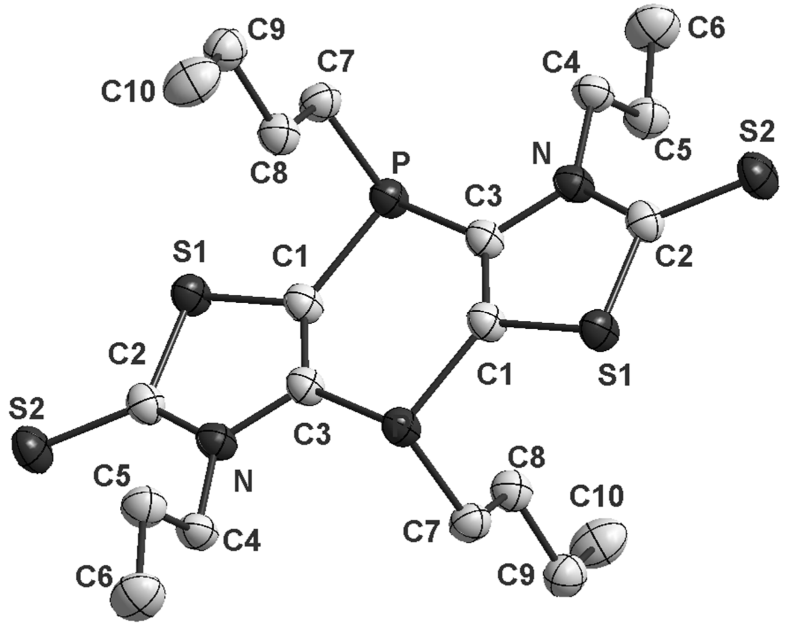
Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S2	K	S4[1]	170.98(5)	C2	N1	C3	116.4(3)
O1	K	S2	94.90(8)	C2	N1	C4	121.5(4)
O1	K	S4[1]	82.89(8)	C3	N1	C4	122.1(3)

O1	K	O2	111.01(11)	C7	N2	C10	121.8(4)
O1	K	O3S	130.8(3)	C8	N2	C7	116.1(4)
O2	K	S2	82.97(8)	C8	N2	C10	122.1(4)
O2	K	S4^1	89.64(9)	P1	N3	Si1	114.0(2)
O2	K	O3S	118.2(3)	P1	N3	Si2	125.2(2)
O3	K	S2	97.21(19)	Si1	N3	Si2	120.0(2)
O3	K	S4^1	91.54(19)	S1	C1	P1	115.9(2)
O3	K	O1	117.9(2)	C3	C1	S1	110.3(3)
O3	K	O2	130.8(2)	C3	C1	P1	133.7(3)
O3S	K	S2	89.7(2)	S2	C2	S1	124.4(3)
O3S	K	S4^1	98.4(2)	N1	C2	S1	109.0(3)
C2	S1	C1	93.0(2)	N1	C2	S2	126.6(3)
C2	S2	K	116.42(16)	N1	C3	P2	118.6(3)
C8	S3	C9	93.2(2)	C1	C3	P2	130.0(3)
C8	S4	K^2	112.82(17)	C1	C3	N1	111.3(4)
N3	P1	C1	105.81(19)	N1	C4	C5	112.7(4)
N3	P1	C7	107.76(19)	C4	C5	C6	110.2(4)
C7	P1	C1	95.24(19)	N2	C7	P1	118.2(3)
C3	P2	C9	96.6(2)	C9	C7	P1	130.1(3)
N3	Si1	C13	111.6(2)	C9	C7	N2	111.6(4)
N3	Si1	C14	111.1(2)	S4	C8	S3	122.5(3)
N3	Si1	C15	111.7(2)	N2	C8	S3	109.3(3)
C13	Si1	C14	109.7(3)	N2	C8	S4	128.2(4)
C15	Si1	C13	107.5(3)	S3	C9	P2	116.2(2)
C15	Si1	C14	105.0(3)	C7	C9	S3	109.8(3)
N3	Si2	C16	110.6(2)	C7	C9	P2	133.9(3)
N3	Si2	C17	109.3(2)	N2	C10	C11	113.5(4)
N3	Si2	C18	114.3(3)	C12	C11	C10	114.1(4)
C17	Si2	C16	109.3(3)	C19	C20	O1	112.4(5)
C18	Si2	C16	109.1(4)	O1	C21	C22	111.6(5)
C18	Si2	C17	104.0(3)	O2	C24	C23	108.8(6)
C20	O1	K	121.4(3)	O2	C25	C26	114.0(5)
C21	O1	K	121.2(4)	O3	C28	C27	106.7(9)
C21	O1	C20	114.4(4)	O3	C29	C30	111.2(9)
C24	O2	K	127.2(4)	O3S	C28S	C27S	106.3(13)
C24	O2	C25	111.6(5)	O3S	C29S	C30S	110.8(11)
C25	O2	K	118.2(3)	C28S	O3S	K	128.9(9)

C28	O3	K	128.1(7)	C29S	O3S	K	123.3(8)
C28	O3	C29	108.3(9)	C29S	O3S	C28S	107.7(12)
C29	O3	K	123.6(6)				

12.25 Crystal data and structure refinement for 30a (IB-409).



Identification code	GSTR628, IB-409 // GXraycu_5684f	ρ_{calc}g/cm^3	1.314
Crystal Habitus	clear colourless block	μ/mm^{-1}	4.806
Device Type	Bruker D8-Venture	F(000)	260
Empirical formula	$C_{20}H_{32}N_2P_2S_4$	Crystal size/mm^3	0.21 × 0.14 × 0.12
Moiety formula	C20 H32 N2 P2 S4	Absorption correction	empirical
Formula weight	490.65	Tmin; Tmax	0.3564; 0.7536
Temperature/K	150	Radiation	CuKα (λ = 1.54178)
Crystal system	triclinic	2Θ range for data collection/°	11.064 to 135.498°
Space group	P-1	Completeness to theta	0.996
a/Å	9.1069(8)	Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-11 \leq l \leq 10$
b/Å	9.3073(8)	Reflections collected	18123
c/Å	9.3134(8)	Independent reflections	2230 [R_{int} = 0.0668, R_{sigma} = 0.0329]
α/°	113.126(4)	Data/restraints/parameters	2230/0/129

β/°	113.896(4)	Goodness-of-fit on F^2	1.127
γ/°	98.092(4)	Final R indexes [I>=2σ (I)]	R_1 = 0.0612, wR_2 = 0.1651
Volume/Å^3	620.10(10)	Final R indexes [all data]	R_1 = 0.0680, wR_2 = 0.1709
Z	1	Largest diff. peak/hole / e Å^{-3}	0.50/-0.52

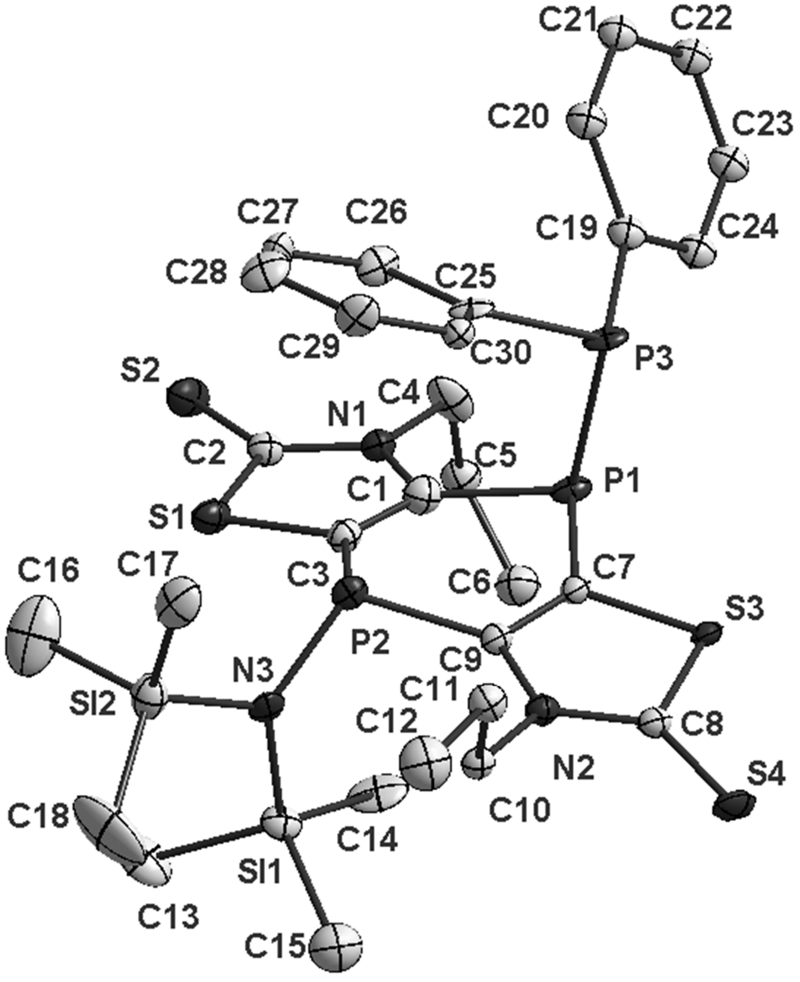
Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.743(4)	N	C4	1.472(5)
S1	C2	1.740(5)	C1	C3	1.351(6)
S2	C2	1.662(4)	C3	P^1	1.822(4)
P	C1	1.821(4)	C4	C5	1.519(6)
P	C3^1	1.822(4)	C5	C6	1.519(7)
P	C7	1.864(5)	C7	C8	1.522(6)
N	C2	1.355(6)	C8	C9	1.525(6)
N	C3	1.403(5)	C9	C10	1.528(7)

Table 3 Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C1	92.3(2)	N	C2	S1	108.6(3)
C1	P	C3^1	98.27(19)	N	C2	S2	128.2(4)
C1	P	C7	99.3(2)	N	C3	P^1	118.6(3)
C3^1	P	C7	101.9(2)	C1	C3	P^1	128.8(3)
C2	N	C3	116.0(4)	C1	C3	N	112.4(4)
C2	N	C4	120.8(4)	N	C4	C5	111.9(4)
C3	N	C4	123.1(4)	C4	C5	C6	112.4(4)
S1	C1	P	116.2(2)	C8	C7	P	117.5(3)
C3	C1	S1	110.7(3)	C7	C8	C9	113.0(4)
C3	C1	P	132.9(3)	C8	C9	C10	111.7(4)
S2	C2	S1	123.2(3)				

12.26 Crystal data and structure refinement for 30b (IB-370).



Identification code	GSTR610, IB-370 // GXraycu_5544f	μ/mm^{-1}	4.44
Crystal Habitus	clear light yellow plate	F(000)	3040
Device Type	Bruker D8-Venture	Crystal size/mm^3	0.21 × 0.18 × 0.03
Empirical formula	$C_{30}H_{42}N_3Si_2P_3S_4$	Absorption correction	empirical
Moiety formula	C30 H42 N3 P3 S4 Si2	Tmin; Tmax	0.3855; 0.7536
Formula weight	721.99	Radiation	CuKα (λ = 1.54178)
Temperature/K	100.02	2Θ range for data collection/°	7.512 to 135.498°
Crystal system	orthorhombic	Completeness to theta	0.999
Space group	$Pca2_1$	Index ranges	$-22 \leq h \leq 22$, $-14 \leq k \leq 14$, $-40 \leq l \leq 40$
a/Å	18.7088(7)	Reflections collected	189014

b/Å	11.7664(4)	Independent reflections	13271 [R_{int} = 0.1718, R_{sigma} = 0.0576]
c/Å	33.3168(12)	Data/restraints/parameters	13271/391/774
α/°	90	Goodness-of-fit on F^2	1.131
β/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.1158, wR_2 = 0.2750
γ/°	90	Final R indexes [all data]	R_1 = 0.1247, wR_2 = 0.2804
Volume/$Å^3$	7334.2(5)	Largest diff. peak/hole / e $Å^{-3}$	2.32/-1.10
Z	8	Flack parameter	0.58(7)
ρ_{calc}g/cm^3	1.308		

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C2	1.74(2)	S1'	C2'	1.709(19)
S1	C3	1.748(19)	S1'	C3'	1.741(18)
S2	C2	1.66(2)	S2'	C2'	1.682(19)
S3	C7	1.729(19)	S3'	C7'	1.747(18)
S3	C8	1.74(2)	S3'	C8'	1.72(2)
S4	C8	1.653(19)	S4'	C8'	1.66(2)
P1	P3	2.246(6)	P1'	P3'	2.260(6)
P1	C1	1.81(2)	P1'	C1'	1.813(19)
P1	C7	1.813(19)	P1'	C7'	1.826(18)
P2	N3	1.691(16)	P2'	N3'	1.731(16)
P2	C3	1.856(19)	P2'	C3'	1.810(19)
P2	C9	1.845(19)	P2'	C9'	1.82(2)
P3	C19	1.81(2)	P3'	C19'	1.845(19)
P3	C25	1.806(19)	P3'	C25'	1.822(19)
Si1	N3	1.791(17)	Si1'	N3'	1.797(16)
Si1	C13	1.87(2)	Si1'	C13'	1.87(2)
Si1	C14	1.85(2)	Si1'	C14'	1.84(2)
Si1	C15	1.86(2)	Si1'	C15'	1.87(2)
Si2	N3	1.778(17)	Si2'	N3'	1.750(16)
Si2	C16	1.83(3)	Si2'	C16'	1.88(2)
Si2	C17	1.87(2)	Si2'	C17'	1.85(2)
Si2	C18	1.83(3)	Si2'	C18'	1.83(2)
N1	C1	1.47(3)	N1'	C1'	1.43(2)

N1	C2	1.36(2)	N1'	C2'	1.33(2)
N1	C4	1.46(3)	N1'	C4'	1.50(2)
N2	C8	1.35(2)	N2'	C8'	1.37(2)
N2	C9	1.38(2)	N2'	C9'	1.44(3)
N2	C10	1.50(2)	N2'	C10'	1.47(2)
C1	C3	1.28(3)	C1'	C3'	1.35(3)
C4	C5	1.51(3)	C4'	C5'	1.49(3)
C5	C6	1.50(3)	C5'	C6'	1.54(3)
C7	C9	1.36(3)	C7'	C9'	1.36(3)
C10	C11	1.46(3)	C10'	C11'	1.56(3)
C11	C12	1.56(3)	C11'	C12'	1.50(3)
C19	C20	1.45(3)	C19'	C20'	1.40(2)
C19	C24	1.37(3)	C19'	C24'	1.38(2)
C20	C21	1.39(3)	C20'	C21'	1.39(3)
C21	C22	1.44(3)	C21'	C22'	1.38(3)
C22	C23	1.36(3)	C22'	C23'	1.38(3)
C23	C24	1.39(3)	C23'	C24'	1.40(3)
C25	C26	1.40(3)	C25'	C26'	1.39(3)
C25	C30	1.41(2)	C25'	C30'	1.38(3)
C26	C27	1.35(3)	C26'	C27'	1.38(3)
C27	C28	1.36(3)	C27'	C28'	1.44(3)
C28	C29	1.41(3)	C28'	C29'	1.40(3)
C29	C30	1.37(3)	C29'	C30'	1.41(3)

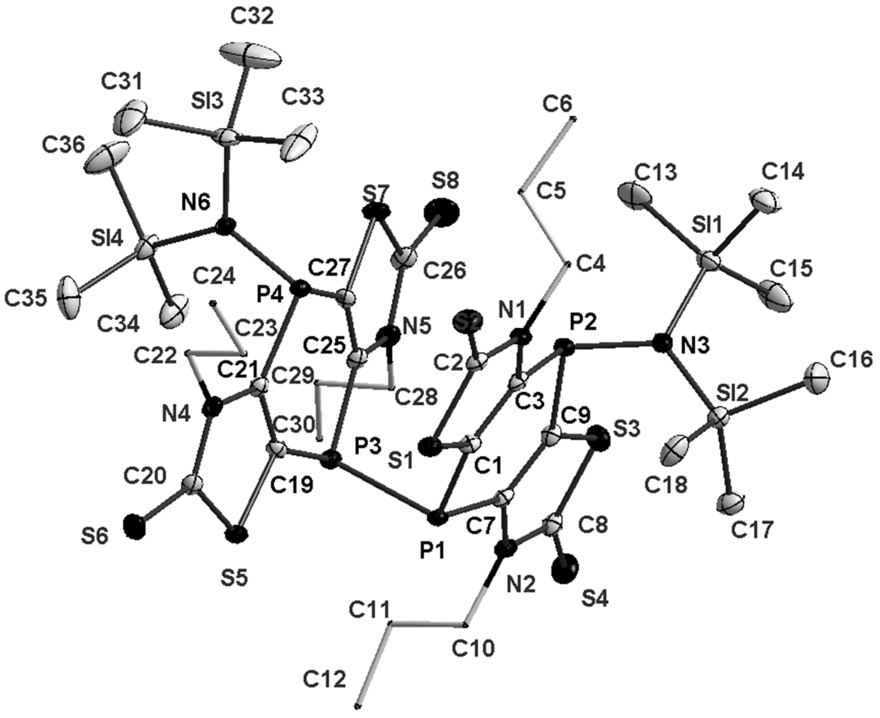
Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C3	91.5(9)	C2'	S1'	C3'	92.4(9)
C7	S3	C8	92.7(9)	C8'	S3'	C7'	92.2(9)
C1	P1	P3	106.6(7)	C1'	P1'	P3'	104.9(6)
C1	P1	C7	96.2(9)	C1'	P1'	C7'	96.6(8)
C7	P1	P3	95.5(6)	C7'	P1'	P3'	93.7(6)
N3	P2	C3	104.6(8)	N3'	P2'	C3'	101.7(8)
N3	P2	C9	108.6(8)	N3'	P2'	C9'	109.2(8)
C9	P2	C3	96.4(8)	C3'	P2'	C9'	96.1(9)
C19	P3	P1	101.1(6)	C19'	P3'	P1'	103.3(6)
C19	P3	C25	105.6(9)	C25'	P3'	P1'	101.9(6)

C25	P3	P1	103.1(6)	C25'	P3'	C19'	104.9(8)
N3	Si1	C13	111.0(10)	N3'	Si1'	C13'	110.7(9)
N3	Si1	C14	112.4(9)	N3'	Si1'	C14'	110.3(10)
N3	Si1	C15	111.2(9)	N3'	Si1'	C15'	109.7(9)
C14	Si1	C13	106.4(11)	C14'	Si1'	C13'	106.8(11)
C14	Si1	C15	107.2(11)	C14'	Si1'	C15'	110.8(10)
C15	Si1	C13	108.3(11)	C15'	Si1'	C13'	108.5(10)
N3	Si2	C16	108.6(10)	N3'	Si2'	C16'	112.8(8)
N3	Si2	C17	111.1(9)	N3'	Si2'	C17'	108.8(8)
N3	Si2	C18	112.1(13)	N3'	Si2'	C18'	108.9(9)
C16	Si2	C17	107.8(12)	C17'	Si2'	C16'	107.7(9)
C18	Si2	C16	111.1(16)	C18'	Si2'	C16'	109.4(10)
C18	Si2	C17	106.0(13)	C18'	Si2'	C17'	109.3(10)
C2	N1	C1	114.1(16)	C1'	N1'	C4'	123.1(15)
C2	N1	C4	123.3(16)	C2'	N1'	C1'	114.9(16)
C4	N1	C1	122.5(16)	C2'	N1'	C4'	121.8(16)
C8	N2	C9	116.7(16)	C8'	N2'	C9'	114.8(16)
C8	N2	C10	118.5(15)	C8'	N2'	C10'	121.8(16)
C9	N2	C10	124.4(15)	C9'	N2'	C10'	123.2(16)
P2	N3	Si1	126.2(10)	P2'	N3'	Si1'	112.5(8)
P2	N3	Si2	113.0(9)	P2'	N3'	Si2'	125.7(9)
Si2	N3	Si1	120.5(9)	Si2'	N3'	Si1'	121.6(9)
N1	C1	P1	117.2(14)	N1'	C1'	P1'	120.0(13)
C3	C1	P1	131.0(17)	C3'	C1'	P1'	128.2(15)
C3	C1	N1	111.8(18)	C3'	C1'	N1'	111.8(16)
S2	C2	S1	123.9(12)	S2'	C2'	S1'	123.5(11)
N1	C2	S1	109.1(14)	N1'	C2'	S1'	110.4(14)
N1	C2	S2	127.0(15)	N1'	C2'	S2'	126.0(15)
S1	C3	P2	115.8(10)	S1'	C3'	P2'	115.9(10)
C1	C3	S1	113.4(16)	C1'	C3'	S1'	110.5(14)
C1	C3	P2	130.2(16)	C1'	C3'	P2'	133.0(15)
N1	C4	C5	112.3(19)	C5'	C4'	N1'	116.0(17)
C6	C5	C4	114.6(18)	C4'	C5'	C6'	113.8(18)
S3	C7	P1	115.4(10)	S3'	C7'	P1'	114.3(10)
C9	C7	S3	110.3(14)	C9'	C7'	S3'	111.7(14)
C9	C7	P1	134.2(15)	C9'	C7'	P1'	134.0(15)
S4	C8	S3	123.3(12)	S4'	C8'	S3'	123.2(12)

N2	C8	S3	107.9(13)	N2'	C8'	S3'	110.0(14)
N2	C8	S4	128.8(15)	N2'	C8'	S4'	126.8(16)
N2	C9	P2	122.8(14)	N2'	C9'	P2'	121.1(14)
C7	C9	P2	123.7(15)	C7'	C9'	P2'	126.1(16)
C7	C9	N2	112.3(16)	C7'	C9'	N2'	111.3(17)
C11	C10	N2	113.7(15)	N2'	C10'	C11'	110.5(16)
C10	C11	C12	112.0(17)	C12'	C11'	C10'	110.2(18)
C20	C19	P3	118.6(14)	C20'	C19'	P3'	118.9(14)
C24	C19	P3	121.0(15)	C24'	C19'	P3'	120.9(13)
C24	C19	C20	119.2(18)	C24'	C19'	C20'	118.9(17)
C21	C20	C19	119.6(18)	C21'	C20'	C19'	119.7(18)
C20	C21	C22	119.0(18)	C22'	C21'	C20'	120.5(19)
C23	C22	C21	119.9(18)	C21'	C22'	C23'	120.9(19)
C22	C23	C24	121.4(19)	C22'	C23'	C24'	118.3(17)
C19	C24	C23	120.9(19)	C19'	C24'	C23'	121.7(17)
C26	C25	P3	126.8(14)	C26'	C25'	P3'	124.1(15)
C26	C25	C30	116.2(17)	C30'	C25'	P3'	115.9(14)
C30	C25	P3	117.0(14)	C30'	C25'	C26'	119.9(18)
C27	C26	C25	123.1(19)	C27'	C26'	C25'	121.2(18)
C26	C27	C28	121(2)	C26'	C27'	C28'	118.2(18)
C27	C28	C29	118.1(19)	C29'	C28'	C27'	121.5(18)
C30	C29	C28	121.3(18)	C28'	C29'	C30'	116.8(18)
C29	C30	C25	120.2(17)	C25'	C30'	C29'	122.2(18)

12.27 Crystal data and structure refinement for 31 (IB-371).



Identification code	GSTR618, IB-371 // GXraycu_5546f	ρ_{calc}g/cm^3	1.219
Crystal Habitus	clear yellow block	μ/mm^{-1}	4.887
Device Type	Bruker D8-Venture	F(000)	2264
Empirical formula	$C_{36}H_{64}N_6P_4S_8Si_4$	Crystal size/mm^3	0.24 × 0.13 × 0.12
Moiety formula	C36 H64 N6 P4 S8 Si4	Absorption correction	empirical
Formula weight	1073.65	Tmin; Tmax	0.3114; 0.7536
Temperature/K	99.99	Radiation	CuKα (λ = 1.54178)
Crystal system	monoclinic	2Θ range for data collection/°	7.146 to 135.498°
Space group	$P2_1/c$	Completeness to theta	0.999
a/Å	12.0838(2)	Index ranges	$-14 \leq h \leq 14$, $-23 \leq k \leq 23$, $-29 \leq l \leq 29$
b/Å	19.5676(4)	Reflections collected	106752
c/Å	24.8575(5)	Independent reflections	10602 [R_{int} = 0.0628, R_{sigma} = 0.0289]
α/°	90	Data/restraints/parameters	10602/0/539
β/°	95.5499(9)	Goodness-of-fit on F^2	1.038
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0938

Volume/Å^3	5850.03(19)	Final R indexes [all data]	$R_1 = 0.0395$, $wR_2 = 0.0960$
Z	4	Largest diff. peak/hole / e Å^{-3}	0.97/-0.51

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.749(2)	Si3	C31	1.873(3)
S1	C2	1.732(2)	Si3	C32	1.847(3)
S2	C2	1.657(2)	Si3	C33	1.843(3)
S3	C8	1.740(2)	Si4	N6	1.7825(18)
S3	C9	1.742(2)	Si4	C34	1.860(3)
S4	C8	1.656(2)	Si4	C35	1.863(3)
S5	C19	1.742(2)	Si4	C36	1.849(3)
S5	C20	1.732(2)	N1	C2	1.367(3)
S6	C20	1.658(2)	N1	C3	1.400(3)
S7	C26	1.735(2)	N1	C4	1.474(3)
S7	C27	1.739(2)	N2	C7	1.408(2)
S8	C26	1.657(2)	N2	C8	1.366(3)
P1	P3	2.2893(7)	N2	C10	1.480(3)
P1	C1	1.793(2)	N4	C20	1.366(3)
P1	C7	1.811(2)	N4	C21	1.404(3)
P2	N3	1.7048(18)	N4	C22	1.478(3)
P2	C3	1.831(2)	N5	C25	1.405(3)
P2	C9	1.824(2)	N5	C26	1.367(3)
P3	C19	1.796(2)	N5	C28	1.468(3)
P3	C25	1.802(2)	C1	C3	1.364(3)
P4	N6	1.7026(17)	C4	C5	1.514(3)
P4	C21	1.832(2)	C5	C6	1.528(3)
P4	C27	1.816(2)	C7	C9	1.359(3)
Si1	N3	1.7845(18)	C10	C11	1.518(3)
Si1	C13	1.866(3)	C11	C12	1.526(3)
Si1	C14	1.868(3)	C19	C21	1.358(3)
Si1	C15	1.861(3)	C22	C23	1.519(3)
Si2	N3	1.7928(19)	C23	C24	1.532(3)
Si2	C16	1.869(3)	C25	C27	1.362(3)
Si2	C17	1.856(2)	C28	C29	1.521(3)
Si2	C18	1.860(2)	C29	C30	1.524(3)

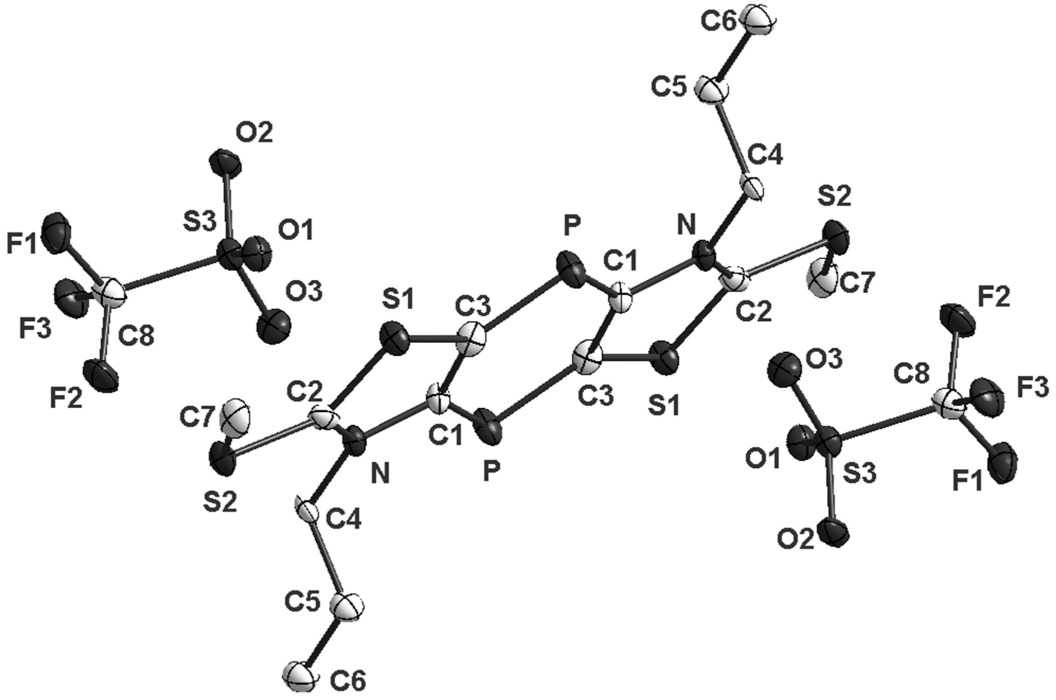
Si3	N6	1.7804(18)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C1	92.66(9)	C21	N4	C22	124.38(17)
C8	S3	C9	92.96(10)	C25	N5	C28	123.34(17)
C20	S5	C19	92.56(10)	C26	N5	C25	115.23(18)
C26	S7	C27	93.08(10)	C26	N5	C28	120.65(17)
C1	P1	P3	101.64(7)	P4	N6	Si3	115.38(10)
C1	P1	C7	99.43(9)	P4	N6	Si4	124.15(10)
C7	P1	P3	96.24(7)	Si3	N6	Si4	120.45(10)
N3	P2	C3	108.05(9)	S1	C1	P1	116.85(11)
N3	P2	C9	104.21(9)	C3	C1	S1	110.26(15)
C9	P2	C3	97.55(9)	C3	C1	P1	132.78(16)
C19	P3	P1	96.44(7)	S2	C2	S1	123.56(12)
C19	P3	C25	99.08(9)	N1	C2	S1	108.71(14)
C25	P3	P1	105.88(7)	N1	C2	S2	127.73(16)
N6	P4	C21	106.72(9)	N1	C3	P2	120.00(14)
N6	P4	C27	102.42(9)	C1	C3	P2	126.96(15)
C27	P4	C21	97.29(9)	C1	C3	N1	112.42(18)
N3	Si1	C13	110.37(10)	N1	C4	C5	112.42(18)
N3	Si1	C14	112.27(11)	C4	C5	C6	110.0(2)
N3	Si1	C15	109.25(11)	N2	C7	P1	120.02(15)
C13	Si1	C14	107.17(13)	C9	C7	P1	126.77(15)
C15	Si1	C13	107.97(15)	C9	C7	N2	113.17(18)
C15	Si1	C14	109.71(13)	S4	C8	S3	124.34(13)
N3	Si2	C16	109.69(11)	N2	C8	S3	108.59(14)
N3	Si2	C17	111.00(10)	N2	C8	S4	127.07(16)
N3	Si2	C18	112.79(10)	S3	C9	P2	116.62(12)
C17	Si2	C16	108.85(12)	C7	C9	S3	109.97(15)
C17	Si2	C18	108.61(11)	C7	C9	P2	132.79(16)
C18	Si2	C16	105.70(13)	N2	C10	C11	113.88(17)
N6	Si3	C31	110.13(11)	C10	C11	C12	110.4(2)
N6	Si3	C32	109.64(13)	S5	C19	P3	116.31(11)
N6	Si3	C33	110.37(11)	C21	C19	S5	110.62(15)
C32	Si3	C31	108.97(18)	C21	C19	P3	133.07(16)

C33	Si3	C31	106.59(16)	S6	C20	S5	123.23(13)
C33	Si3	C32	111.1(2)	N4	C20	S5	108.77(14)
N6	Si4	C34	113.83(10)	N4	C20	S6	127.99(16)
N6	Si4	C35	108.22(11)	N4	C21	P4	119.30(15)
N6	Si4	C36	111.96(12)	C19	C21	P4	127.55(16)
C34	Si4	C35	107.80(14)	C19	C21	N4	112.34(18)
C36	Si4	C34	105.33(13)	N4	C22	C23	111.66(18)
C36	Si4	C35	109.56(15)	C22	C23	C24	110.4(2)
C2	N1	C3	115.92(17)	N5	C25	P3	119.17(15)
C2	N1	C4	119.96(17)	C27	C25	P3	127.54(16)
C3	N1	C4	124.12(17)	C27	C25	N5	113.09(18)
C7	N2	C10	124.26(17)	S8	C26	S7	123.82(14)
C8	N2	C7	115.22(17)	N5	C26	S7	108.65(15)
C8	N2	C10	120.44(17)	N5	C26	S8	127.53(17)
P2	N3	Si1	113.90(10)	S7	C27	P4	116.30(11)
P2	N3	Si2	124.69(10)	C25	C27	S7	109.91(15)
Si1	N3	Si2	121.02(10)	C25	C27	P4	133.67(16)
C20	N4	C21	115.63(17)	N5	C28	C29	111.28(18)
C20	N4	C22	119.95(17)	C28	C29	C30	111.4(2)

12.28 Crystal data and structure refinement for 32 (IB-310).



Identification code	GSTR599, IB-303 // GXray5460av1_pl	ρ_{calc}g/cm^3	1.681
Crystal Habitus	clear light yellow block	μ/mm^{-1}	0.683
Device Type	Bruker APEX-II CCD	F(000)	716
Empirical formula	$C_{16}H_{20}F_6N_2O_6P_2S_6$	Crystal size/mm^3	0.09 × 0.04 × 0.03
Moiety formula	C14 H20 N2 P2 S4, 2(C F3 O3 S)	Absorption correction	empirical
Formula weight	704.64	Tmin; Tmax	0.6251; 0.7460
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	monoclinic	2Θ range for data collection/°	6.726 to 55.996°
Space group	$P2_1/c$	Completeness to theta	0.996
a/Å	7.3591(13)	Index ranges	$-8 \leq h \leq 9$, $-31 \leq k \leq 31$, $-10 \leq l \leq 10$
b/Å	23.954(4)	Reflections collected	14729
c/Å	8.2757(15)	Independent reflections	3333 [R_{int} = 0.1428, R_{sigma} = 0.1554]
α/°	90	Data/restraints/parameters	3333/0/174
β/°	107.374(7)	Goodness-of-fit on F^2	1.071
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0761, wR_2 = 0.1327

Volume/Å^3	1392.3(4)	Final R indexes [all data]	R_1 = 0.1488, wR_2 = 0.1579
Z	2	Largest diff. peak/hole / e Å^{-3}	0.78/-0.64

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C2	1.701(5)	C3	P^1	1.749(5)
S1	C3	1.750(5)	C4	C5	1.509(7)
S2	C2	1.704(5)	C5	C6	1.517(7)
S2	C7	1.799(6)	S3	O1	1.442(4)
P	C1	1.757(5)	S3	O2	1.430(4)
P	C3^1	1.749(5)	S3	O3	1.438(4)
N	C1	1.396(6)	S3	C8	1.821(5)
N	C2	1.331(7)	F1	C8	1.337(6)
N	C4	1.484(6)	F2	C8	1.331(6)
C1	C3	1.391(7)	F3	C8	1.344(6)

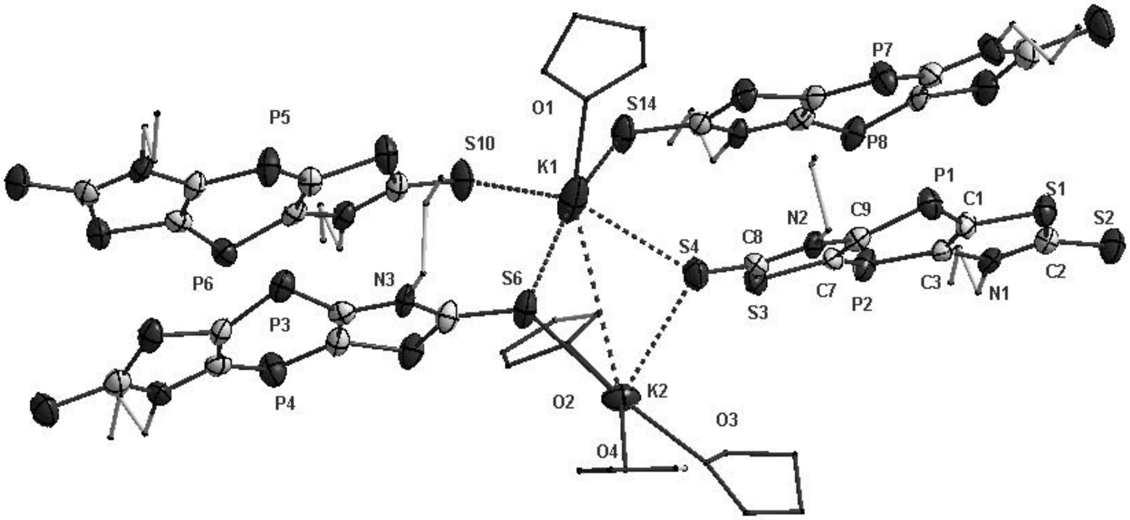
Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C3	90.9(3)	N	C4	C5	111.6(4)
C2	S2	C7	100.0(3)	C4	C5	C6	111.9(5)
C3^1	P	C1	98.5(2)	O1	S3	C8	102.4(3)
C1	N	C4	121.8(4)	O2	S3	O1	114.9(2)
C2	N	C1	114.7(4)	O2	S3	O3	115.7(2)
C2	N	C4	123.5(4)	O2	S3	C8	103.9(2)
N	C1	P	118.9(4)	O3	S3	O1	114.8(2)
C3	C1	P	129.8(4)	O3	S3	C8	102.4(2)
C3	C1	N	111.3(4)	F1	C8	S3	111.8(4)
S1	C2	S2	124.0(3)	F1	C8	F3	106.6(4)
N	C2	S1	112.7(4)	F2	C8	S3	111.8(4)
N	C2	S2	123.3(4)	F2	C8	F1	107.3(4)
P^1	C3	S1	117.8(3)	F2	C8	F3	107.3(4)
C1	C3	S1	110.4(4)	F3	C8	S3	111.7(4)
C1	C3	P^1	131.7(4)				

Torsion Angles

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P	C1	C3	S1	179.1(3)	C3^{1}	P	C1	C3	0.1(7)
P	C1	C3	P^{1}	-0.2(9)	C4	N	C1	P	-0.6(6)
N	C1	C3	S1	0.1(6)	C4	N	C1	C3	178.5(5)
N	C1	C3	P^{1}	-179.1(4)	C4	N	C2	S1	-178.9(4)
N	C4	C5	C6	177.7(4)	C4	N	C2	S2	2.9(7)
C1	N	C2	S1	-1.1(6)	C7	S2	C2	S1	12.6(4)
C1	N	C2	S2	-179.3(4)	C7	S2	C2	N	-169.4(5)
C1	N	C4	C5	-83.4(6)	O1	S3	C8	F1	61.1(4)
C2	S1	C3	P^{1}	178.7(3)	O1	S3	C8	F2	-59.2(4)
C2	S1	C3	C1	-0.6(4)	O1	S3	C8	F3	-179.5(3)
C2	N	C1	P	-178.5(4)	O2	S3	C8	F1	-58.9(5)
C2	N	C1	C3	0.6(6)	O2	S3	C8	F2	-179.2(4)
C2	N	C4	C5	94.3(6)	O2	S3	C8	F3	60.6(4)
C3	S1	C2	S2	179.2(4)	O3	S3	C8	F1	-179.7(4)
C3	S1	C2	N	1.0(4)	O3	S3	C8	F2	60.0(4)
C3^{1}	P	C1	N	179.0(4)	O3	S3	C8	F3	-60.3(4)

12.29 Crystal data and structure refinement for 33b (IB-454).



Identification code	GSTR633, IB-454 // GXraycu_5768f	ρ_{calc}g/cm^3	1.371
Crystal Habitus	clear dark brown block	μ/mm^{-1}	5.714
Device Type	Bruker D8-Venture	F(000)	4848
Empirical formula	$C_{84}H_{128}K_4N_8O_9P_8S_{16}$	Crystal size/mm^3	0.24 × 0.22 × 0.12
Moiety formula	C84 H128 K4 N8 O9 P8 S16	Absorption correction	empirical
Formula weight	2311.06	Tmin; Tmax	0.2838; 0.7536
Temperature/K	150.01	Radiation	CuKα (λ = 1.54178)
Crystal system	monoclinic	2Θ range for data collection/°	6.212 to 135.496°
Space group	$P2_1/c$	Completeness to theta	0.997
a/Å	27.6401(13)	Index ranges	$-33 \leq h \leq 32$, $-24 \leq k \leq 24$, $-25 \leq l \leq 25$
b/Å	20.4176(10)	Reflections collected	133020
c/Å	21.3228(11)	Independent reflections	20260 [R_{int} = 0.1284, R_{sigma} = 0.0718]
α/°	90	Data/restraints/parameters	20260/347/1236
β/°	111.527(3)	Goodness-of-fit on F^2	1.056
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.1206, wR_2 = 0.2908
Volume/Å^3	11194.0(10)	Final R indexes [all data]	R_1 = 0.1499, wR_2 = 0.3127

Z	4	Largest diff. peak/hole / e Å^{-3}	1.35/-1.13

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
K1	K2	4.400(4)	O5	C68	1.47(2)
K1	S4	3.191(3)	O6	C69	1.441(19)
K1	S6	3.194(4)	O6	C72	1.413(17)
K1	S10	3.164(4)	O7	C73	1.369(7)
K1	S14	3.113(3)	O7	C76	1.456(17)
K1	O1	2.678(12)	O8	C77	1.458(9)
K2	S4	3.198(3)	O8	C80	1.47(2)
K2	S6	3.363(3)	O9	C81	1.403(17)
K2	O2	2.720(10)	O9	C84	1.40(2)
K2	O3	2.635(10)	N1	C2	1.340(10)
K2	O4	2.682(14)	N1	C3	1.413(10)
K2	C61	3.480(18)	N1	C4	1.477(11)
K2	O4S	2.64(2)	N2	C8	1.362(10)
K2	C64S	3.36(3)	N2	C9	1.417(10)
K2	C78^1	3.308(16)	N2	C10	1.474(10)
K2	C79^1	3.496(19)	N3	C13	1.418(10)
K3	K4	4.618(4)	N3	C14	1.351(11)
K3	S2^2	3.206(4)	N3	C16	1.472(11)
K3	S8	3.160(4)	N4	C20	1.351(12)
K3	S12	3.148(4)	N4	C21	1.418(10)
K3	S16^2	3.091(4)	N4	C22	1.454(12)
K3	O5	2.705(16)	N5	C26	1.353(11)
K3	C65	3.46(2)	N5	C27	1.411(10)
K4	S1^2	3.770(4)	N5	C28	1.460(10)
K4	S2^2	3.314(4)	N6	C32	1.351(11)
K4	S8	3.309(4)	N6	C33	1.412(10)
K4	O6	2.694(11)	N6	C34	1.480(11)
K4	O7	2.781(13)	N7	C38	1.339(10)
K4	O8	2.771(13)	N7	C39	1.400(10)
K4	O9	2.695(10)	N7	C40	1.468(11)
K4	C69	3.531(18)	N8	C44	1.338(13)
K4	C73	3.374(16)	N8	C45	1.426(11)

S1	K4^3	3.770(4)	N8	C46	1.37(2)
S1	C1	1.747(8)	N8	C46S	1.60(4)
S1	C2	1.710(9)	C1	C3	1.371(11)
S2	K3^3	3.206(4)	C4	C5	1.506(12)
S2	K4^3	3.314(4)	C5	C6	1.522(12)
S2	C2	1.701(9)	C7	C9	1.380(11)
S3	C7	1.752(8)	C10	C11	1.510(12)
S3	C8	1.705(9)	C11	C12	1.509(13)
S4	C8	1.689(9)	C13	C15	1.370(12)
S5	C14	1.708(9)	C16	C17	1.514(13)
S5	C15	1.744(8)	C17	C18	1.529(13)
S6	C14	1.695(9)	C19	C21	1.378(12)
S7	C19	1.739(8)	C22	C23	1.497(14)
S7	C20	1.736(10)	C23	C24	1.518(14)
S8	C20	1.680(9)	C25	C27	1.396(11)
S9	C25	1.742(8)	C28	C29	1.510(11)
S9	C26	1.714(9)	C29	C30	1.516(12)
S10	C26	1.685(8)	C31	C33	1.383(11)
S11	C31	1.746(8)	C34	C35	1.497(13)
S11	C32	1.716(10)	C35	C36	1.539(14)
S12	C32	1.679(9)	C37	C39	1.385(11)
S13	C37	1.742(8)	C40	C41	1.504(13)
S13	C38	1.738(9)	C41	C42	1.532(16)
S14	C38	1.680(8)	C43	C45	1.377(13)
S15	C43	1.756(8)	C46	C47	1.5000(10)
S15	C44	1.729(12)	C46S	C47S	1.498(10)
S16	K3^3	3.091(4)	C47	C48	1.55(2)
S16	C44	1.693(10)	C47S	C48S	1.51(5)
P1	C1	1.786(8)	C49	C50	1.498(9)
P1	C9	1.768(8)	C50	C51	1.484(19)
P2	C3	1.778(8)	C51	C52	1.47(2)
P2	C7	1.771(9)	C53	C54	1.483(9)
P3	C13	1.769(8)	C54	C55	1.36(2)
P3	C19	1.801(8)	C55	C56	1.43(2)
P4	C15	1.794(9)	C57	C58	1.492(10)
P4	C21	1.761(9)	C58	C59	1.51(2)
P5	C25	1.773(8)	C59	C60	1.45(2)

P5	C33	1.760(8)	C61S	C62S	1.52(4)
P6	C27	1.762(8)	C62S	C63S	1.58(4)
P6	C31	1.785(9)	C63S	C64S	1.5000(10)
P7	C37	1.775(9)	C65	C66	1.57(3)
P7	C45	1.775(9)	C66	C67	1.48(3)
P8	C39	1.777(8)	C67	C68	1.39(3)
P8	C43	1.758(9)	C69	C70	1.44(2)
O1	C49	1.397(15)	C70	C71	1.45(2)
O1	C52	1.44(2)	C71	C72	1.47(2)
O2	C53	1.363(17)	C73	C74	1.48(2)
O2	C56	1.43(2)	C74	C75	1.53(2)
O3	C57	1.37(2)	C75	C76	1.50(2)
O3	C60	1.46(2)	C77	C78	1.463(6)
O4	C64	1.42	C78	K2^1	3.308(16)
O4	C61	1.42	C78	C79	1.516(9)
C64	C63	1.42	C79	K2^1	3.497(19)
C63	C62	1.42	C79	C80	1.48(2)
C62	C61	1.42	C81	C82	1.47(2)
O4S	C61S	1.45(4)	C82	C83	1.47(3)
O4S	C64S	1.46(3)	C83	C84	1.54(3)
O5	C65	1.40(2)			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S4	K1	K2	46.54(7)	C62	C61	O4	108
S4	K1	S6	75.92(8)	C61S	O4S	K2	135.6(19)
S6	K1	K2	49.49(7)	C61S	O4S	C64S	102(2)
S10	K1	K2	108.08(11)	C64S	O4S	K2	106.3(16)
S10	K1	S4	147.62(13)	C65	O5	K3	110.9(13)
S10	K1	S6	103.30(10)	C65	O5	C68	108.9(17)
S14	K1	K2	111.43(9)	C68	O5	K3	118.6(13)
S14	K1	S4	97.43(9)	C69	O6	K4	113.8(8)
S14	K1	S6	158.67(14)	C72	O6	K4	136.0(10)
S14	K1	S10	71.36(8)	C72	O6	C69	106.2(12)
O1	K1	K2	138.6(2)	C73	O7	K4	103.5(10)

O1	K1	S4	100.4(3)	C73	O7	C76	101.6(12)
O1	K1	S6	106.5(2)	C76	O7	K4	139.1(12)
O1	K1	S10	110.5(3)	C77	O8	K4	118.0(9)
O1	K1	S14	94.6(2)	C77	O8	C80	102.3(13)
S4	K2	K1	46.40(6)	C80	O8	K4	139.1(10)
S4	K2	S6	73.48(8)	C81	O9	K4	127.7(9)
S4	K2	C61	89.2(3)	C84	O9	K4	119.5(10)
S4	K2	C64S	72.5(4)	C84	O9	C81	107.3(12)
S4	K2	C78^{1}	163.1(3)	C2	N1	C3	115.3(7)
S4	K2	C79^{1}	166.6(3)	C2	N1	C4	121.9(7)
S6	K2	K1	46.23(6)	C3	N1	C4	122.8(7)
S6	K2	C61	92.7(3)	C8	N2	C9	115.9(7)
S6	K2	C79^{1}	112.6(3)	C8	N2	C10	120.5(7)
O2	K2	K1	58.6(3)	C9	N2	C10	123.6(7)
O2	K2	S4	92.1(3)	C13	N3	C16	121.9(6)
O2	K2	S6	86.2(3)	C14	N3	C13	116.0(7)
O2	K2	C61	178.0(3)	C14	N3	C16	122.0(7)
O2	K2	C64S	153.9(6)	C20	N4	C21	116.0(7)
O2	K2	C78^{1}	87.8(5)	C20	N4	C22	121.9(7)
O2	K2	C79^{1}	100.1(5)	C21	N4	C22	122.0(7)
O3	K2	K1	132.5(3)	C26	N5	C27	116.2(7)
O3	K2	S4	101.3(3)	C26	N5	C28	121.4(7)
O3	K2	S6	173.6(3)	C27	N5	C28	122.4(7)
O3	K2	O2	97.9(4)	C32	N6	C33	116.7(7)
O3	K2	O4	93.5(4)	C32	N6	C34	121.4(7)
O3	K2	C61	83.3(4)	C33	N6	C34	121.9(7)
O3	K2	O4S	82.9(5)	C38	N7	C39	116.5(7)
O3	K2	C64S	105.5(6)	C38	N7	C40	120.0(7)
O3	K2	C78^{1}	95.4(4)	C39	N7	C40	123.5(6)
O3	K2	C79^{1}	71.6(4)	C44	N8	C45	115.0(8)
O4	K2	K1	125.3(3)	C44	N8	C46	122.7(14)
O4	K2	S4	106.5(3)	C44	N8	C46S	121.0(14)
O4	K2	S6	84.5(3)	C45	N8	C46S	123.8(13)
O4	K2	O2	155.9(4)	C46	N8	C45	122.4(14)
O4	K2	C61	22.2(3)	S1	C1	P1	118.4(4)
O4	K2	C78^{1}	69.9(5)	C3	C1	S1	108.9(6)

O4	K2	C79^1	63.6(4)	C3	C1	P1	132.6(6)
C61	K2	K1	121.6(3)	S2	C2	S1	123.8(5)
C61	K2	C79^1	78.8(5)	N1	C2	S1	109.9(6)
O4S	K2	K1	119.9(5)	N1	C2	S2	126.2(7)
O4S	K2	S4	86.5(5)	N1	C3	P2	118.8(6)
O4S	K2	S6	92.8(5)	C1	C3	P2	128.6(6)
O4S	K2	O2	178.5(6)	C1	C3	N1	112.5(7)
O4S	K2	C64S	24.8(7)	N1	C4	C5	112.7(7)
O4S	K2	C78^1	93.4(6)	C4	C5	C6	110.1(8)
O4S	K2	C79^1	81.4(6)	S3	C7	P2	118.0(4)
C64S	K2	K1	96.5(5)	C9	C7	S3	109.2(6)
C64S	K2	S6	69.5(5)	C9	C7	P2	132.8(6)
C64S	K2	C79^1	98.0(6)	S4	C8	S3	125.4(5)
C78^1	K2	K1	121.3(3)	N2	C8	S3	109.0(6)
C78^1	K2	S6	89.7(3)	N2	C8	S4	125.6(7)
C78^1	K2	C61	90.5(4)	N2	C9	P1	119.3(6)
C78^1	K2	C64S	101.0(5)	C7	C9	P1	128.6(6)
C78^1	K2	C79^1	25.55(19)	C7	C9	N2	111.8(7)
C79^1	K2	K1	146.3(3)	N2	C10	C11	113.6(7)
S2^2	K3	K4	45.87(7)	C12	C11	C10	109.4(8)
S2^2	K3	C65	85.6(4)	N3	C13	P3	120.2(6)
S8	K3	K4	45.77(7)	C15	C13	P3	128.8(6)
S8	K3	S2^2	71.49(9)	C15	C13	N3	110.8(7)
S8	K3	C65	97.4(4)	S6	C14	S5	124.4(5)
S12	K3	K4	115.38(10)	N3	C14	S5	109.7(6)
S12	K3	S2^2	158.66(14)	N3	C14	S6	125.8(6)
S12	K3	S8	103.00(10)	S5	C15	P4	117.1(5)
S12	K3	C65	115.7(4)	C13	C15	S5	110.7(6)
S16^2	K3	K4	101.00(12)	C13	C15	P4	132.2(6)
S16^2	K3	S2^2	100.86(11)	N3	C16	C17	113.2(7)
S16^2	K3	S8	141.03(15)	C16	C17	C18	110.0(8)
S16^2	K3	S12	70.00(9)	S7	C19	P3	117.6(5)
S16^2	K3	C65	120.5(4)	C21	C19	S7	110.8(6)
O5	K3	K4	143.5(3)	C21	C19	P3	131.6(6)
O5	K3	S2^2	102.0(3)	S8	C20	S7	123.5(6)
O5	K3	S8	116.8(3)	N4	C20	S7	109.3(6)
O5	K3	S12	98.9(3)	N4	C20	S8	127.2(7)

O5	K3	S16^2	102.2(3)	N4	C21	P4	119.3(6)
O5	K3	C65	22.3(4)	C19	C21	P4	129.1(6)
C65	K3	K4	122.1(4)	C19	C21	N4	111.3(7)
S1^2	K4	K3	68.05(7)	N4	C22	C23	111.5(7)
S2^2	K4	K3	43.97(7)	C22	C23	C24	111.4(9)
S2^2	K4	S1^2	49.77(6)	S9	C25	P5	118.8(5)
S2^2	K4	C69	148.8(3)	C27	C25	S9	109.7(6)
S2^2	K4	C73	71.2(3)	C27	C25	P5	131.4(6)
S8	K4	K3	43.17(7)	S10	C26	S9	124.5(5)
S8	K4	S1^2	109.58(9)	N5	C26	S9	109.5(6)
S8	K4	S2^2	68.32(8)	N5	C26	S10	125.9(6)
S8	K4	C69	81.3(3)	N5	C27	P6	119.9(6)
S8	K4	C73	70.5(3)	C25	C27	P6	128.9(6)
O6	K4	K3	128.6(3)	C25	C27	N5	111.2(7)
O6	K4	S1^2	148.9(3)	N5	C28	C29	112.6(7)
O6	K4	S2^2	161.2(3)	C28	C29	C30	110.7(8)
O6	K4	S8	95.3(3)	S11	C31	P6	118.7(4)
O6	K4	O7	89.3(4)	C33	C31	S11	109.4(6)
O6	K4	O8	82.6(4)	C33	C31	P6	131.9(6)
O6	K4	O9	89.4(4)	S12	C32	S11	125.2(5)
O6	K4	C69	21.9(3)	N6	C32	S11	108.7(6)
O6	K4	C73	95.1(4)	N6	C32	S12	126.1(7)
O7	K4	K3	116.2(3)	N6	C33	P5	120.0(6)
O7	K4	S1^2	106.8(3)	C31	C33	P5	128.4(6)
O7	K4	S2^2	82.7(3)	C31	C33	N6	111.4(7)
O7	K4	S8	93.5(3)	N6	C34	C35	112.2(7)
O7	K4	C69	106.9(4)	C34	C35	C36	109.3(9)
O7	K4	C73	23.2(2)	S13	C37	P7	118.9(5)
O8	K4	K3	136.5(3)	C39	C37	S13	109.0(6)
O8	K4	S1^2	71.4(3)	C39	C37	P7	132.0(6)
O8	K4	S2^2	114.3(3)	S14	C38	S13	124.0(5)
O8	K4	S8	176.0(3)	N7	C38	S13	108.8(6)
O8	K4	O7	89.9(4)	N7	C38	S14	127.2(7)
O8	K4	C69	95.7(4)	N7	C39	P8	118.5(6)
O8	K4	C73	113.0(4)	C37	C39	P8	128.9(6)
O9	K4	K3	69.1(2)	C37	C39	N7	112.4(7)
O9	K4	S1^2	71.7(2)	N7	C40	C41	112.3(8)

O9	K4	S2^{2}	100.3(2)	C40	C41	C42	109.1(10)
O9	K4	S8	92.7(2)	S15	C43	P8	118.5(5)
O9	K4	O7	173.8(3)	C45	C43	S15	108.4(6)
O9	K4	O8	83.9(3)	C45	C43	P8	133.1(6)
O9	K4	C69	73.4(4)	S16	C44	S15	123.7(7)
O9	K4	C73	162.9(3)	N8	C44	S15	109.9(7)
C69	K4	K3	107.7(2)	N8	C44	S16	126.3(9)
C69	K4	S1^{2}	143.8(3)	N8	C45	P7	117.9(7)
C73	K4	K3	95.6(2)	C43	C45	P7	128.6(7)
C73	K4	S1^{2}	110.3(3)	C43	C45	N8	113.3(8)
C73	K4	C69	105.9(4)	N8	C46	C47	121.2(12)
C1	S1	K4^{3}	148.5(3)	C47S	C46S	N8	107(3)
C2	S1	K4^{3}	81.1(3)	C46	C47	C48	117.8(19)
C2	S1	C1	93.2(4)	C46S	C47S	C48S	97(3)
K3^{3}	S2	K4^{3}	90.16(10)	O1	C49	C50	107.2(12)
C2	S2	K3^{3}	115.5(3)	C51	C50	C49	104.7(12)
C2	S2	K4^{3}	96.4(3)	C52	C51	C50	100.1(14)
C8	S3	C7	93.9(4)	O1	C52	C51	108.2(12)
K1	S4	K2	87.05(9)	O2	C53	C54	105.5(12)
C8	S4	K1	115.9(3)	C55	C54	C53	110.5(13)
C8	S4	K2	110.7(3)	C54	C55	C56	106.3(14)
C14	S5	C15	92.8(4)	C55	C56	O2	108.7(14)
K1	S6	K2	84.27(8)	O3	C57	C58	104.9(14)
C14	S6	K1	110.0(3)	C57	C58	C59	98.5(14)
C14	S6	K2	120.3(3)	C60	C59	C58	105.2(14)
C20	S7	C19	92.6(4)	C59	C60	O3	106.9(16)
K3	S8	K4	91.06(10)	O4S	C61S	C62S	108(3)
C20	S8	K3	113.0(3)	C61S	C62S	C63S	107(2)
C20	S8	K4	127.9(3)	C64S	C63S	C62S	98(2)
C26	S9	C25	93.4(4)	O4S	C64S	K2	49.0(13)
C26	S10	K1	105.8(3)	O4S	C64S	C63S	111(2)
C32	S11	C31	93.7(4)	C63S	C64S	K2	114.6(19)
C32	S12	K3	105.0(3)	O5	C65	K3	46.9(10)
C38	S13	C37	93.2(4)	O5	C65	C66	101.4(17)
C38	S14	K1	115.7(3)	C66	C65	K3	102.8(14)

C44	S15	C43	93.4(5)	C67	C66	C65	101.1(18)
C44	S16	K3[3]	111.4(4)	C68	C67	C66	111(2)
C9	P1	C1	96.8(4)	C67	C68	O5	105.0(18)
C7	P2	C3	97.0(4)	O6	C69	K4	44.3(7)
C13	P3	C19	96.7(4)	O6	C69	C70	101.9(14)
C21	P4	C15	96.7(4)	C70	C69	K4	123.9(14)
C33	P5	C25	97.6(4)	C69	C70	C71	109.9(17)
C27	P6	C31	97.6(4)	C70	C71	C72	103.2(15)
C45	P7	C37	96.9(4)	O6	C72	C71	106.9(13)
C43	P8	C39	97.1(4)	O7	C73	K4	53.3(8)
C49	O1	K1	130.3(9)	O7	C73	C74	102.7(14)
C49	O1	C52	107.0(12)	C74	C73	K4	102.1(12)
C52	O1	K1	122.6(9)	C73	C74	C75	101.4(14)
C53	O2	K2	126.6(9)	C76	C75	C74	101.7(12)
C53	O2	C56	108.9(10)	O7	C76	C75	106.2(12)
C56	O2	K2	119.9(10)	O8	C77	C78	99.5(13)
C57	O3	K2	125.9(9)	C77	C78	K2[1]	155.2(13)
C57	O3	C60	103.5(13)	C77	C78	C79	110.3(14)
C60	O3	K2	130.5(12)	C79	C78	K2[1]	84.2(9)
C64	O4	K2	124.5(9)	C78	C79	K2[1]	70.3(9)
C64	O4	C61	108	C80	C79	K2[1]	148.5(13)
C61	O4	K2	112.4(9)	C80	C79	C78	99.3(14)
C63	C64	O4	108	O8	C80	C79	108.1(14)
C62	C63	C64	108	O9	C81	C82	107.1(13)
C63	C62	C61	108	C81	C82	C83	101.7(18)
O4	C61	K2	45.4(7)	C82	C83	C84	102.4(18)
C62	C61	K2	138.1(7)	O9	C84	C83	107.0(16)

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