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Phosphorane iminato complexes of main group elements

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Contents

Abstract

A review on syntheses, chemical reactions, structures and bonding of phosphorane iminato complexes of main group elements is given. The ligand group $[(:N:)=PR_3]^-$ is not known in the ionic state. Among others, it is isoelectronic with the ligand groups OPR_3,

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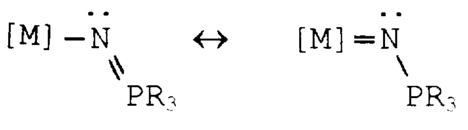
$[OSiR_3]^-$, $[NSiR_3]^{2-}$, $[CSiR_3]^{3-}$ and forms covalent bonds of the monofunctional and the μ_2-N-bridge type with many main group elements:



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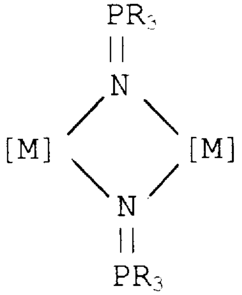

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In complexes of type **1**, surprisingly short MN bonds are often observed — they are interpreted as covalent σ bonds which are strengthened by polar bond shares.

Keywords: Phosphorane iminato complexes; Metal–nitrogen bonds

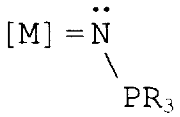
1. Introduction

Phosphorane iminato complexes contain the ligand $[(:N:)=PR_3]^-$, which is not known as an ionic species, and are mostly bonded in covalent fashion to an atom M or a complex fragment [M]. Whereas the complexes with transition metals are well developed [1], the chemistry of the derivatives with main group elements has found vivid interest only in the last few years, although the parent aminophosphonium azaylide $HN=PR_3$ was reported by Staudinger and Meyer in 1919 [2]. It was not until very much later that the aminophosphonium phosphonioazaylides $[R_3PNPR_3]^+$ [3] ('PNP cations') attracted attention on account of their good crystallizing properties. The bis(aminophosphonium azaylides) [4] soon followed. The lithium derivatives of these NH compounds [5–7] proved to be very productive in preparative respects, and their application in organic synthesis has lately been comprehensively reviewed [8].

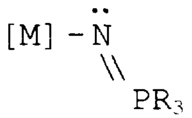
The ligand group $[NPR_3]^-$ is isoelectronic with, among others, the corresponding triorganophosphane oxides OPR_3 and with the triorgano siloxi groups $[OSiR_3]^-$. This frequently leads to striking similarities in structure and bonding between complex types $[M]–NPR_3$ and $[M]–OSiR_3$.

The bonding of the phosphorane iminato ligand and the complex fragment [M] of a main group element can be outlined by the schematic formulae **1a** and **1b**.

Actually, numerous structure determinations show M–N and N–P bond lengths coming close to double bonds. Ab initio calculations on selected examples with the atomic sequence SNP show that the bonding is best described with covalent single bonds and an overlaying share of polar bonding (see Section 6). In contrast,



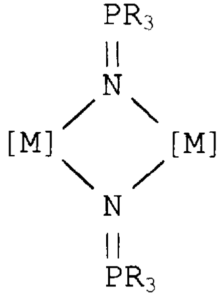
1a



1b

($p_\pi p_\pi$) or ($d_\pi p_\pi$) bonding seems to play a minor role in contrast to phosphorane iminato complexes of transition metals [1]. The MNP bond angles for main group elements M range from 150° to 120°, whereas they lie between 180° and 130° for transition metals M. A linear arrangement PNP was observed in some $[Ph_3PNPPh_3]^+$ salts only.

When the coordination conditions at the complex fragment [M] with main group elements permit, the free electron pair at the nitrogen atom gives rise to dimerization according to formula **2**:



2

The μ_3-N linkage, which is apt to lead to cluster formation in transition metal compounds, has not yet been observed with main group elements. All structural investigations on dimeric complexes of the type **2** yielded planar M_2N_2 rings. The MN bond lengths in these four-membered rings are dependent on the rest of the ligand sphere at the atoms M. With two or four identical ligands, equal or almost equal M–N distances are observed; different or odd-numbered equal ligands result in M–N distances of significantly different length.

2. Phosphorane iminato derivatives of Group I elements (H, Li)

2.1. Hydrogen compounds

The triorganophosphorane imines R_3PNH can be prepared in good yields by acid-catalysed reactions of the *N*-silylized phosphorane imines $R_3PNSiMe_3$ (see Section 5) with i-propanol or methanol [9,10]:

$$R_3PNSiMe_3 + MeOH \rightarrow R_3PNH + MeOSiMe_3 \qquad (1)$$

Known derivatives are those with R = Ph, Me, Et, ^{n}Pr and ^{n}Bu. Whereas the phenyl derivative crystallizes well, the alkyl derivatives, with the exception of the methyl compound [6], form oils. The phosphorane imines are thermally sensitive; with water they react forming the corresponding phosphorane oxides.

Phosphorane imines are also obtained by deprotonation of the corresponding aminophosphonium salts (see below) with the aid of sodium amide [11–15]:

$$[R_3PNH_2]Cl + NaNH_2 \rightarrow R_3PNH + NaCl + NH_3 \tag{2}$$

According to a crystal structure investigation on the phenyl derivative Ph_3PNH [16], which crystallizes in the space group $P2_1/c$ with four formula units in the unit cell, the compound has a definitely monomeric molecular structure without intermolecular N–H···N contacts. The PN bond length (152.4 pm) is significantly shorter than the expected value of a double bond (155–164 pm [17,18]). As the H atom bound to the N atom could not be located, linearity of P=N–H can only be speculated.

A derivative is the donor acceptor complex $[Ph_3PNH \cdot BF_3] \cdot THF$ (Fig. 1) [19], which is accessible from $Ph_3PNSiMe_3$ (see Section 5) and $BF_3 \cdot OEt_2$ in THF. The adduct formation brings about an elongation of the PN bond length to 161.2 pm which is in accordance with a double bond. A significantly different situation is observed in the tantalum complex $[Ph_3PNH \cdot TaF_4(\eta^5\text{-}C_5H_5)]$ [20], where the long PN bond of 184.2 pm corresponds to a single bond. This is explained by the assumption of a dipolar bond character $^{\oplus}P\text{–}\ddot{N}(H)\text{–}Ta^{\ominus}$. Normal PN double bond lengths are also found in the cobalt complex of the trimethylphosphorane imine $[CoCl_2(Me_3PNH)_2]$ [21].

Closely related to the donor acceptor complexes of the phosphorane imines are the aminophosphonium salts $[R_3PNH_2]^+X^-$. The first example was prepared by Staudinger and Hauser in 1921 [22]. They found that triphenyl phosphane reacts with excess hydrazoic acid according to Eq. (3):

$$PPh_3 + 2HN_3 \rightarrow [Ph_3PNH_2]N_3 + N_2 \tag{3}$$

The nonexplosive azide is stable in aqueous solution. Only upon addition of strong acids does rapid hydrolysis occur with formation of Ph_3PO. With triphenyl phosphane the azide reacts at 180–200 °C as shown by Eq. (4) forming the phosphorane imine [12]:

$$[Ph_3PNH_2]N_3 + PPh_3 \rightarrow 2Ph_3PNH + N_2 \tag{4}$$

The aminophosphonium chloride which is not resistant to water can also be prepared by reaction of PPh_3 with chlorine amine [11]:

$$PPh_3 + NH_2Cl \rightarrow [Ph_3PNH_2]Cl \tag{5}$$

Real preparative importance, however, is only attributed to the synthesis found later on which starts from triphenyl phosphane, carbon tetrachloride and ammonia,

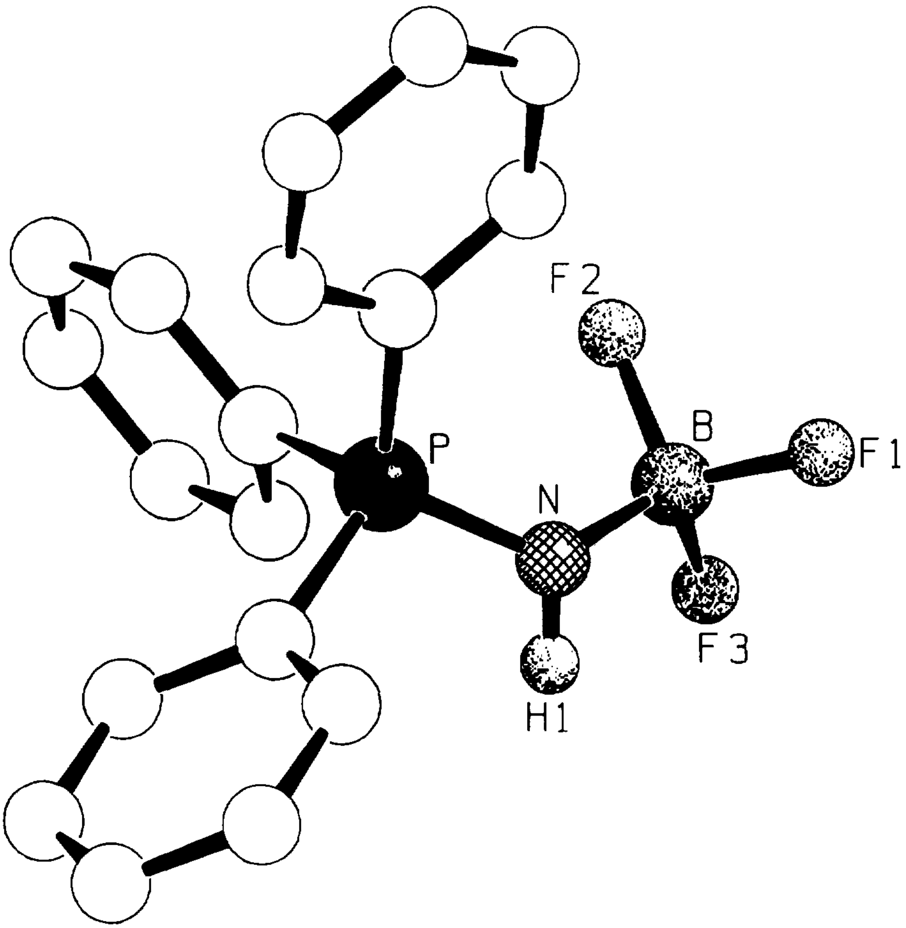


Fig. 1. Molecular structure of $[Ph_3PNH \cdot BF_3]$.

and which is easily transposed to other amines [23]:

$$PPh_3 + CCl_4 + NH_3 \rightarrow [Ph_3PNH_2]Cl + HCCl_3 \qquad (6)$$

In addition, some formation reactions of compounds with the $[Ph_3PNH_2]^+$ ion are known, which are preparatively unimportant. Among these are the hydrolysis of phosphorane iminato complexes of transition metals [24,25]

$$Cl–[M]{=}N{=}PPh_3 + H_2O \rightarrow [M]{=}O + [Ph_3PNH_2]Cl \qquad (7)$$

and reactions of triphenyl phosphane with thiazyl chloride, $(NSCl)_3$, in THF [15].

Salts with the $Ph_3PNH_2^+$ ion were characterized by crystal structure analysis repeatedly [15,25–28]. In all cases the observed PN distance (159 to 164 pm) corresponds to a double bond. As far as the positions of the N-bound hydrogen atoms could be localized, the environment of the N atom is vastly planar. More or less

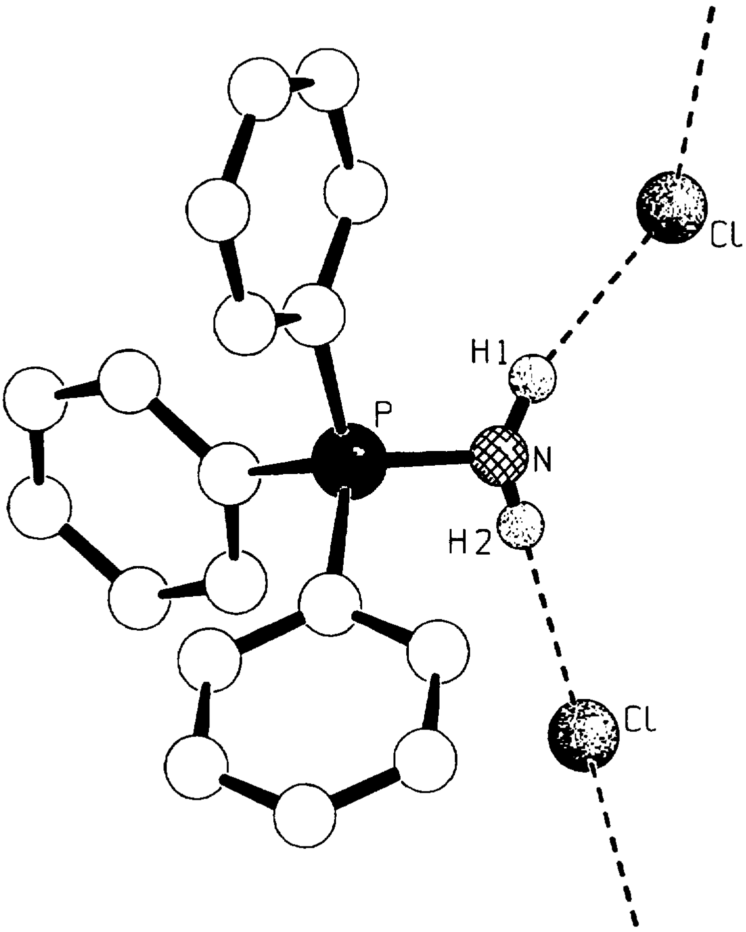


Fig. 2. Structure of $[Ph_3PNH_2]^+Cl^-$ with N–HCl hydrogen bridges.

stable interionic hydrogen bridges N–H···X are formed. A typical example is shown in Fig. 2; here the chloride ion has a bridging function so that a chain structure is afforded [25]. An analogous structure is found in the methyl derivative $[Me_3PNH_2]Cl$ [29].

2.2. Lithium compounds

The *N*-lithiated phosphorane imines $R_3P{=}N{-}Li$ with R = Me, Et, ⁿBu and Ph according to Schmidbaur and Jonas [6] are accessible by reaction of the phosphorane imines with methyl lithium in ether:

$$R_3P{=}NH + LiCH_3 \rightarrow R_3PNLi + CH_4 \qquad (8)$$

The phenyl derivative is also obtained by double deprotonation of aminophosphonium salts with *n*-butyl lithium in THF [30,31]:

$$[Ph_3PNH_2]Br + 2^nBuLi \rightarrow Ph_3PNLi + LiBr + 2^nBuH \qquad (9)$$

Their reactions with various organic chlorides, esters and carbonates were lately reported in a comprehensive paper [8].

3. Phosphorane iminato complexes of Group XIII elements (B, Al, Ga, In)

3.1. Boron compounds

Phosphorane iminato complexes of these elements are obtained by the most frequently used method, which is the reaction of the anhydrous halides with *N*-trimethylsilyl-substituted phosphorane imines (see Section 4). So, boron trifluoride etherate reacts smoothly under substitution [19]:

$$BF_3 \cdot OEt_2 + Me_3SiNPPh_3 \rightarrow BF_2(NPPh_3) + FSiMe_3 + OEt_2 \qquad (10)$$

The structure of the boron complex is as yet unknown. Quite recently the boron complexes $[BCl_2(NPPh_3)]_2$ and $[B_2Cl_3(NPEt_3)_2]^+BCl_4^-$ could be prepared and characterized by crystal structure determinations [32].

3.2. Aluminium, gallium and indium compounds

In the reaction of silylated phosphorane imines with Lewis acid metal halides, in many cases well-defined donor–acceptor complexes can be isolated as primary products. Thus, the trihalides MX_3 with X = Cl, Br, I of aluminium, gallium and indium form stable (1 : 1) adducts with $Me_3SiNPMe_3$ [33]. Moreover, the organometallic donor–acceptor complexes $[Me_3SiNPPh_3 \cdot AlMe_3]$ [34] and $[Me_3SiNPPh_3 \cdot MPh_3]$ with M = Al and Ga have been reported [35]. By thermolysis at 215 °C $[Me_3SiNPMe_3 \cdot AlBr_3]$ can be converted into the dimeric phosphorane iminato complex $[Br_2Al(NPMe_3)]_2$ eliminating $BrSiMe_3$ [33]. In contrast, the trichlorides of aluminium and gallium were induced to cleave off trimethyl chlorosilane at 50–80 °C in acetonitrile solution according to Eq. (11) [19]:

$$2MCl_3 + 2Me_3SiNPPh_3 \rightarrow [Cl_2M(NPPh_3)]_2 + 2ClSiMe_3 \qquad (11)$$

$$(M = Al, Ga)$$

Both phosphorane iminato complexes have been characterized crystallographically [19]. The two isotypic complexes form centrosymmetric dimeric molecules, in which the metal atoms are linked by the N atoms of the phosphorane iminato ligands in an almost square arrangement. Fig. 3 shows the structure of the aluminium complex.

The M–N bond lengths are only slightly different: their mean values, being 185.9 pm for M = Al and 190.8 pm for M = Ga, are very short. The M–N distances in the complexes $[Me_2M(N{=}CMe_2)]_2$ [36,37] for example, in which the N atoms

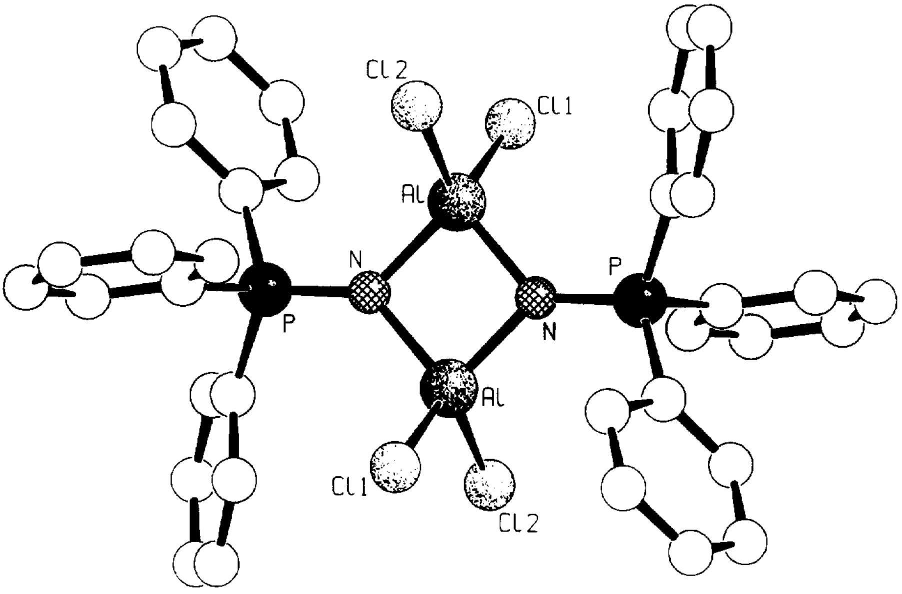


Fig. 3. Molecular structure of $[Cl_2Al(NPPh_3)]_2$.

are sp^2 hybridized as in the phosphorane iminato complexes, are 192.8 pm for M = Al and 201.3 pm for M = Ga on the average. An even shorter Al–N bond than in $[Cl_2Al(NPPh_3)]_2$, i.e. 178 pm, has only been found in $\{Al[N(SiMe_3)_2]_3\}$ [38] with coordination number (CN) three at the aluminium atom. The short M–N bonds in $[Cl_2M(NPPh_3)]_2$ are accounted for with the inductive effect of the chloro ligands [19]. Together with the small MNM bond angles (91.4° for M = Al and 93.7° for M = Ga) they effect very short M···M distances of 266.0 pm and 278.7 pm respectively, which is little more than the sum of the covalent radii of aluminium and gallium.

Indium trichloride also reacts with $Me_3SiNPPh_3$ according to Eq. (11) in boiling acetonitrile giving the insoluble $Cl_2In(NPPh_3)$, which with dimethyl formamide is readily converted to the solvate $[Cl_2In(NPPh_3)(DMF)]_2$ [39]. According to the crystal structure analysis (Fig. 4) the In atoms are linked to a centrosymmetric In_2N_2 four-membered ring by the N atoms of the $NPPh_3^-$ ligands.

The In atoms are embedded in a distorted trigonal bipyramidal surrounding, the O atoms of the DMF molecules occupying the axial positions. On account of its axiality the trans-positioned In–N bond with 217.9 pm is slightly longer than the distance $In{-}N_{eq}$, which is 211.2 pm. The intramolecular distance In···In, amounting to 323.3 pm, is significantly longer than the sum of the covalent radii (300 pm). This may be ascribed to the CN, which is increased to five in contrast to the aluminium and gallium complexes.

The organometallic-substituted phosphorane iminato complexes $[Me_2M(NPR_3)]_2$ with M = Al, Ga, In and R = Me, Et are obtained by thermolysis of the corresponding donor–acceptor complexes $[Me_3M(HNPR_3)]$ at 50 °C [40].

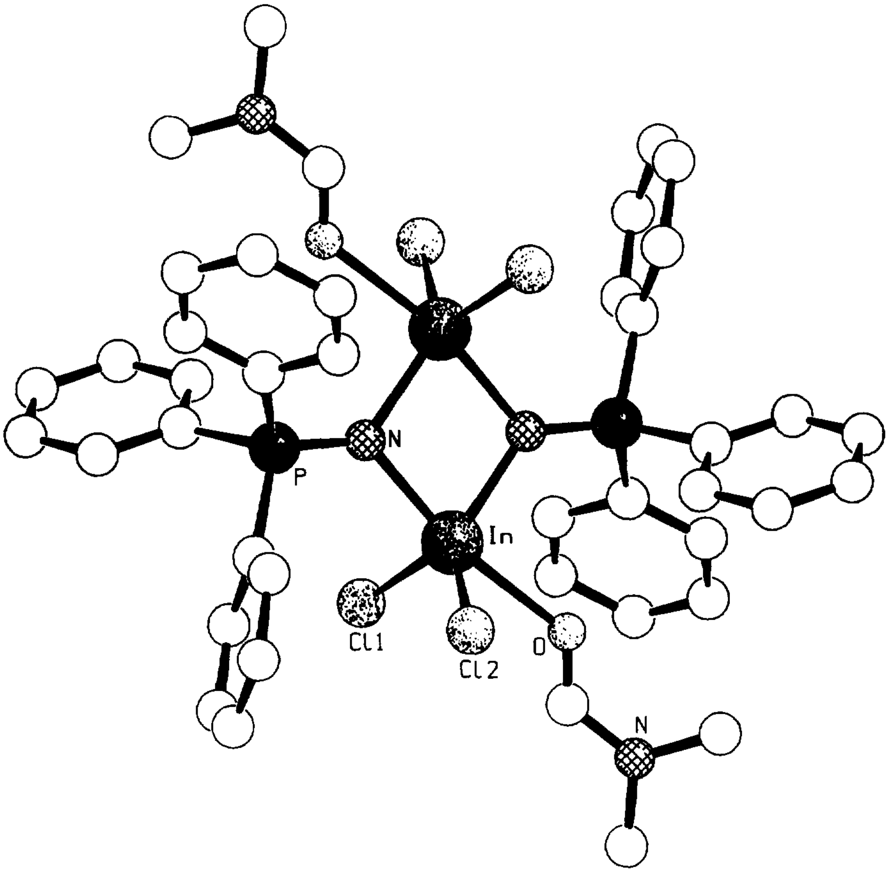


Fig. 4. Molecular structure of $[Cl_2In(NPPh_3)(DMF)]_2$.

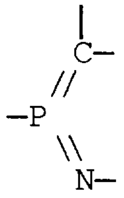
4. Phosphorane iminato complexes of Group XIV elements (C, Si, Ge, Sn)

4.1. Carbon compounds

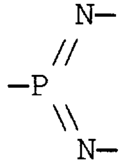
The imino phosphoranes $R_3P{=}N{-}R'$ with R' = organic substituent are dealt with here in a marginal way. Their chemistry is well developed [41,42]; additionally spectroscopic investigations [43,44] and some structural analyses [45–49] are available. They are accessible by the general synthetic procedure from triorgano phosphanes and organic azides [50].

A representative example is $Ph_3P{=}NPh$, in which a P–N bond length of 160.2 pm is found indicating a double bond. The PNC bond angle is 130.4° [48]. The N atom can be protonated; in the structure of $[Ph_3PN(H)Ph]^+AuI_2^-$ [48] the P–N distance exhibits elongation to 162.4 pm, whereas the bond angle PNC is just slightly decreased to 129.3°.

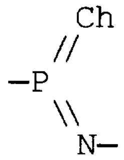
It must be noted that a series of compounds which are closely related to the phosphorane iminato complexes have recently been comprehensively reviewed [51–53]. Among them are the methylene(imino)phosphoranes [51]:



the bis(imino)phosphoranes [52]:



and the imino(chalcogeno)phosphoranes [53] (Ch = O, S, Se):



4.2. Silicon compounds

Vast preparative importance can be ascribed to the imino phosphoranes $R_3P{=}N{-}SiMe_3$ with a trimethylsilyl substituent. Generally, they react in an unproblematic way with many element halides under elimination of trimethyl silyl halide and formation of the corresponding phosphorane iminato derivatives in the fashion of the reaction in Eq. (11).

The chemistry of the silylated phosphorane imines has been developed especially by the investigations of Wolfsberger. Many of these compounds are accessible by the Staudinger reaction from triorganophosphane and trimethylsilyl azide [34,54]. In the same manner, bis(phosphorane iminato) derivatives are produced from the easily handled diorgano diazides of silicon [55,56]:

$$R'_2Si(N_3)_2 + 2PR_3 \rightarrow R'_2Si(NPR_3)_2 + 2N_2 \tag{12}$$

An alternative route consists in the reaction of lithiated phosphorane imines with diorganodichloro silane [57]:

$$2R_3PNLi + R'_2SiCl_2 \rightarrow R'_2Si(NPR_3)_2 + 2LiCl \tag{13}$$

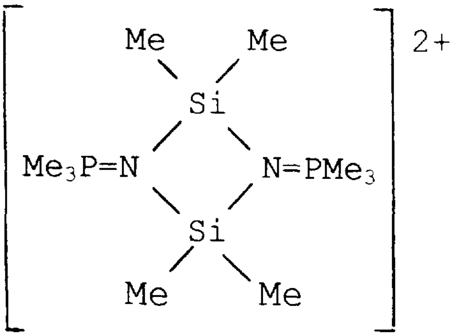
The synthesis of phosphorane imines possessing a silicon function is effected by trans-silylation of *N*-trimethylsilyl-substituted compounds with (organo)halogen silanes [58]:

$$Et_3P{=}N{-}SiMe_3 + Me_2SiCl_2 \rightarrow Me_3SiCl + Et_3P{=}N{-}SiMe_2Cl \qquad (14)$$

Compounds of this type are obtained by application of bis(triorganophosphorane imino) dimethyl silane [57,58]:

$$Me_2Si(NPR_3)_2 + Me_2SiCl_2 \rightarrow [Me_2Si(NPR_3)]_2Cl_2 \qquad (15)$$

Whereas the ethyl derivative, prepared by the reaction in Eq. (14) forms monomeric molecules, the methyl compound obtained by Eq. (15) is formulated as an ionic dimer [59]:



Reactions analogous to Eq. (15) are also observed for SiF_4, $RSiCl_3$ (R = Me, Et), $SiCl_4$, $SiBr_4$, Et_3SiCl, Me_2SiBr_2 and Me_2SiI_2, whereas Me_2SiF_2 and Me_2SiCl_2 react according to Eq. (14) forming monomeric molecules [57,60].

A series of elementary silylated phosphorane imines were characterized by crystal structure analyses. Amongst them are $Me_3SiNPMe_3$ [61], $Me_3SiNPPh_3$ [62], $Me_3SiNPPh_2{-}CH_2{-}PPh_2$ [63], $Me_3SiNPPh_2{-}CH_2{-}CH_2{-}PPh_2NSiMe_3$ [62] and $F_3SiNPMe_3$ [64], which forms dimeric molecules. Moreover, the crystal structures of some derivatives carrying functional groups at the phosphorus atom were determined [65–68].

Fig. 5 shows the molecular structure of the phenyl derivative [62], which is frequently used as a starting material in the synthesis of phosphorane iminato complexes.

As an example for a bis(phosphoraneiminato) derivative, Fig. 6 shows the structure of $Me_3SiNPPh_2{-}CH_2{-}CH_2{-}PPh_2NSiMe_3$ [62], in which the PNSi-groups are oriented in a cisoidic configuration.

In all investigated examples, the PN bond lengths ranging from 153 to 162 pm essentially correspond to double bonds, and the SiN distances amounting to 165 to 173 pm can be classified as single bonds. The SiNP bond angles with values of 128° to 150° are relatively variable, presumably they react in a flexible manner to the requirements of packing. The differences in the structure of $Me_3SiNPMe_3$ in the solid [61] and in the gas phase [69] are in favour of this assumption. Whereas the PN distance in the solid is 162 pm, with an SiNP bond angle of 128°, in the gas

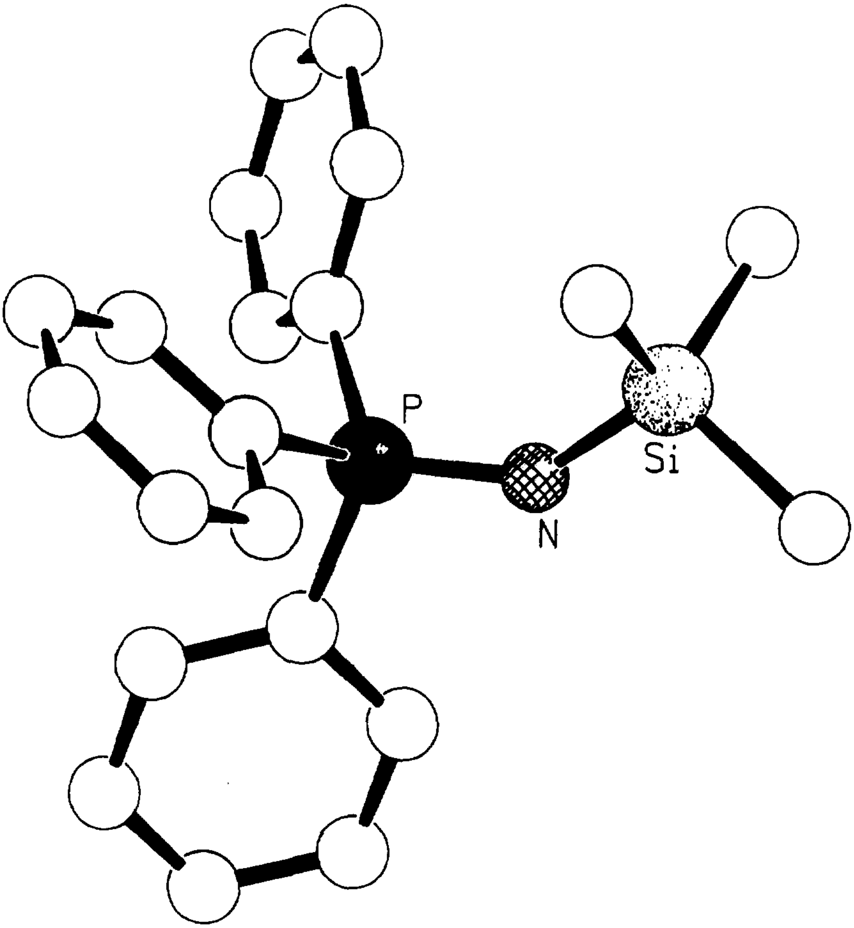


Fig. 5. Molecular structure of $Me_3SiNPPh_3$.

phase, according to electron diffraction measurements, values of 154.2 pm and 144.6° are found [69].

The silylated phosphorane imines can be protonated at the N atom. Crystal structures are available for the complexes $[Me_3SiN(H)PPh_3]_2HfCl_6$ [70] and $[Me_3SiN(H)PPh_3]_2ZrCl_6 \cdot CH_3CN$ [71]. Fig. 7 depicts the structure of the $[Me_3SiN(H)PPh_3]^+$ ion. Compared with $Me_3SiNPPh_3$ [62] the bonds Si–N and P–N are elongated from 168.6 pm and 154.2 pm to 177.7 pm and 162.4 pm respectively, whereas protonation causes the bond angle SiNP to decrease from 140.2° to 135.8° [71].

Some interest must be devoted to the differences in molecular structures for the monomeric $Me_3SiNPMe_3$ and the fluoro derivative $[F_3SiNPMe_3]_2$ [64], which forms centrosymmetric dimers with trigonal bipyramidal environment of the silicon atoms (Fig. 8). The consequence of the association is two SiN distances of different length:

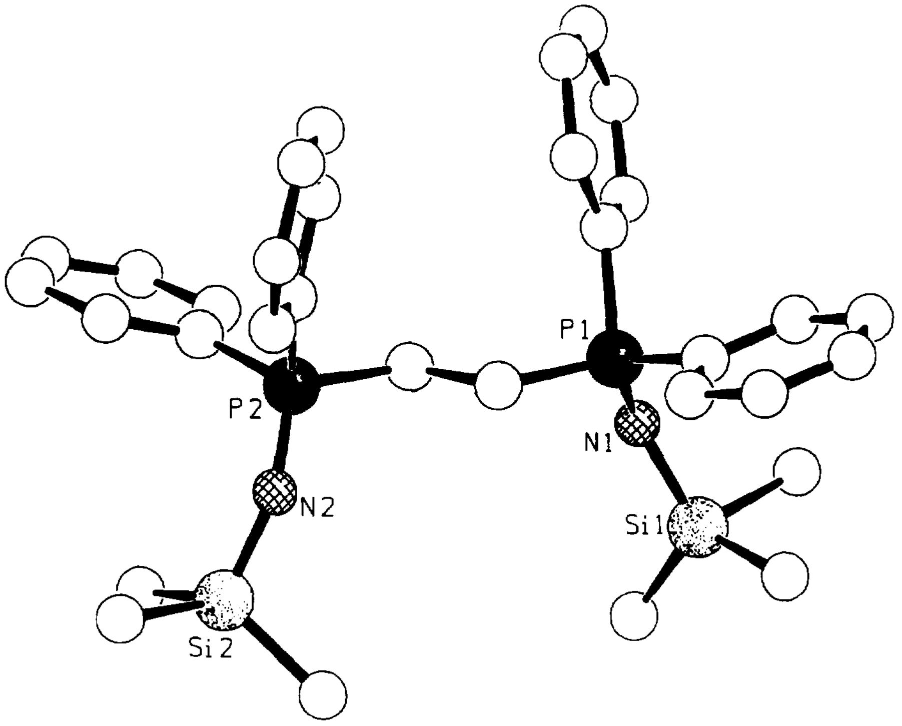


Fig. 6. Molecular structure of $Me_3SiNPPh_2–CH_2–CH_2–PPh_2NSiMe_3$.

173.6 pm equatorial and 185.7 pm in the axial position. In contrast, the PN bonds and the SiNP bond angles amounting 162.3 pm and 128.9° and 130.4° respectively, rather resemble those of the methyl derivative [61]. It may be noted that according to ^{19}F NMR spectra at 30 °C the derivatives F_3SiNPR_3 with more bulky organic substituents like $R = Et$ and n-C_3H_7 form monomeric molecules tending to dimerize only upon cooling to 0 °C [64].

Special interest has to be paid to the lithiated phosphorane imines on account of their preparative potential [6,72] and because of their attractive coordination chemistry. They result from the reaction of methyl and *n*-butyl lithium with silylated phosphoranes in hexane solution in the manner of the reaction of Eq. (16) [6]:

$$Me_3SiNP(CH_3)_3 + LiCH_3 \rightarrow Me_3SiNP(CH_3)_2CH_2Li + CH_4 \quad (16)$$

According to the crystal structure analysis [73] (Fig. 9) the product from Eq. (16) forms an Li_4 tetrahedron, the planes of which are capped by the CH_2 carbon atoms with mean Li–C distances of 233 and 251 pm, whereas the N atoms are joined to the corners of the Li_4 tetrahedron [73]. Passing to the i-propyl derivative $[Me_3SiNP(C_3H_7)_2(C_3H_6Li)]_2$ the result is a dimeric molecule [73] (Fig. 10) in which the Li atoms, besides one Li–N bond each, only operate two Li–C bonds [73].

An impressive example for the control of reactions by different inductive effects

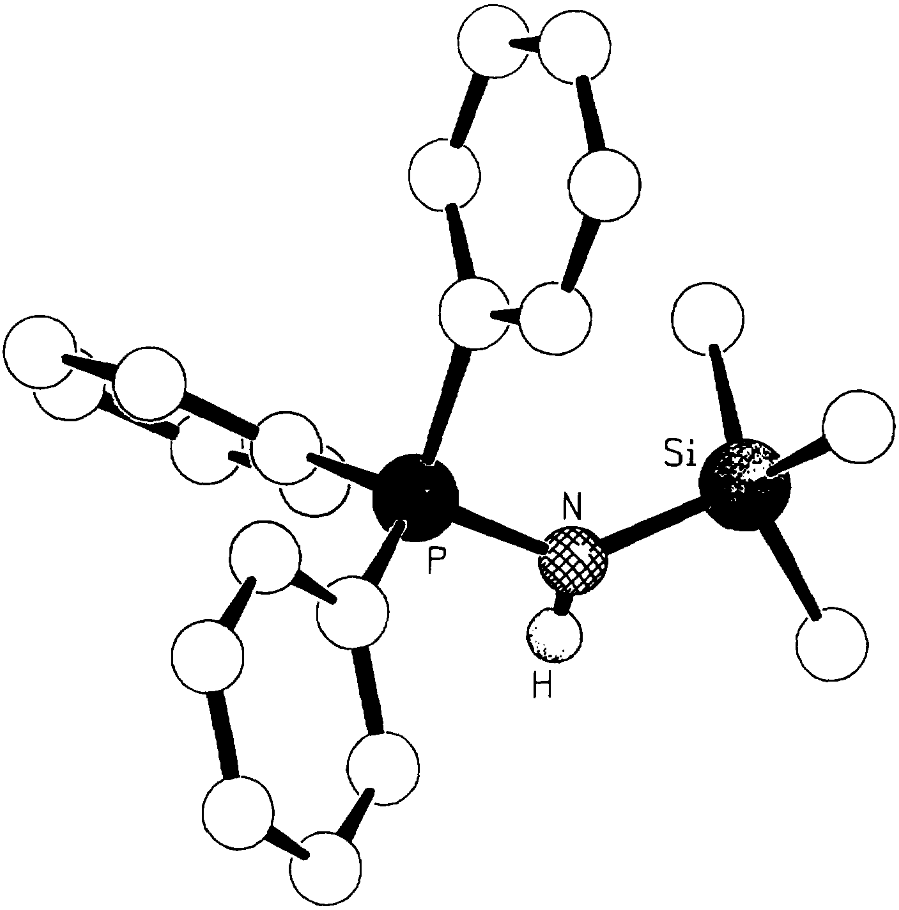


Fig. 7. View of the $[Me_3SiN(H)PPh_3]^+$ ion in the structure of $[Me_3SiN(H)PPh_3]_2ZrCl_6 \cdot CH_3CN$.

of the substituents at the phosphorus atom of silylated phosphorane imines has just recently been reported [74]. Whereas $Py_3P{=}N{-}SiMe_3$ (Py = 2-pyridyl) reacts with methyl lithium in diethyl ether at −78 °C giving $[(2,2'\text{-dipy})Li(Me_3SiNP(Me)Py)]$ with four-coordinated lithium atoms, the phenyl derivative $Ph_3P{=}N{-}SiMe_3$ under the same conditions forms $[(Et_2O)Li_2(Me_3SiNP(Ph_2)C_6H_4)_2]$ with threefold and fourfold coordinated lithium atoms [74].

4.3. Germanium compounds

In the case of the germanium complex $GeCl_3(NPMe_3)$ [75] the structures of the monomeric and dimeric molecules could be determined simultaneously in a crystal obtained from the gas phase (Fig. 11 and Fig. 12). Naturally, the Ge–N, Ge–Cl and P–N bond lengths in the monomeric molecule (173.7, 214 and 157.2 pm) are significantly shorter than in the dimer with five-coordinated germanium atoms. In

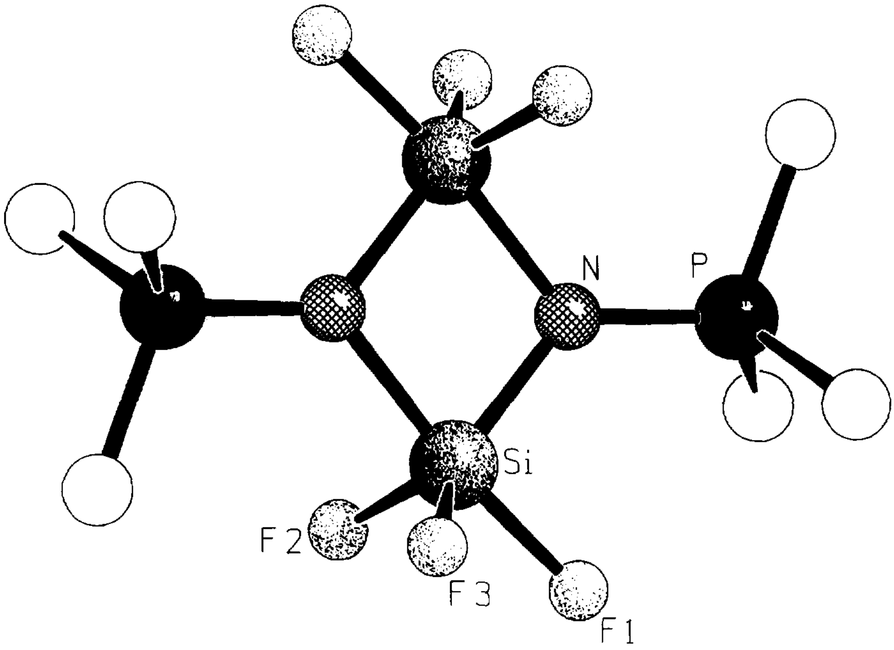


Fig. 8. Molecular structure of $[F_3Si(NPMe_3)]_2$.

these, as in $[SiF_3(NPMe_3)]_2$, the coordination polyhedron of the central atom is trigonal bipyramidal with consequently different Ge–N distances of 197.2 pm in the axial and 183.7 pm in the equatorial positions. The same holds for the Ge–Cl_{ax} distances (234.5 pm) and Ge–Cl_{eq} distances (217.3 pm). The two P–N bonds of different length in the monomer (157.2 pm) and in the dimer (163.8 pm) give rise to two clearly different PN stretching modes of 1152 cm^{-1} and 1060 cm^{-1} in the IR spectrum [75].

4.4. Tin compounds

A trigonal bipyramidal environment is also found with the Sn(IV) atom in the mixed valent dimeric tin compound $[SnCl_2(NPPh_3)]_2$ [39], which was prepared by partial oxidation of tin(II) chloride according to Eq. (17):

$$2SnCl_2 + 2Me_3SiNPPh_3 \rightarrow [SnCl_2(NPPh_3)]_2 + Si_2Me_6 \tag{17}$$

Hence the Sn–N_{ax} distances (209.2 pm) and the Sn–N_{eq} distances (204 pm) differ significantly, whereas the Sn–N bonds originating from the tin atom with oxidation state +II (218.5 pm) are equidistant within the standard deviation (Fig. 13).

An unexpected redox reaction yielded the interesting tetrakis(phosphorane iminato) complex $Sn(NPPh_3)_4$ with tetravalent tin [76]:

$$Me_2Si(N\text{-}^tBu)_2Sn + 4Ph_3PNH \rightarrow Me_2Si(NH\text{-}^tBu)_2 + Sn(NPPh_3)_4 + \ldots \tag{18}$$

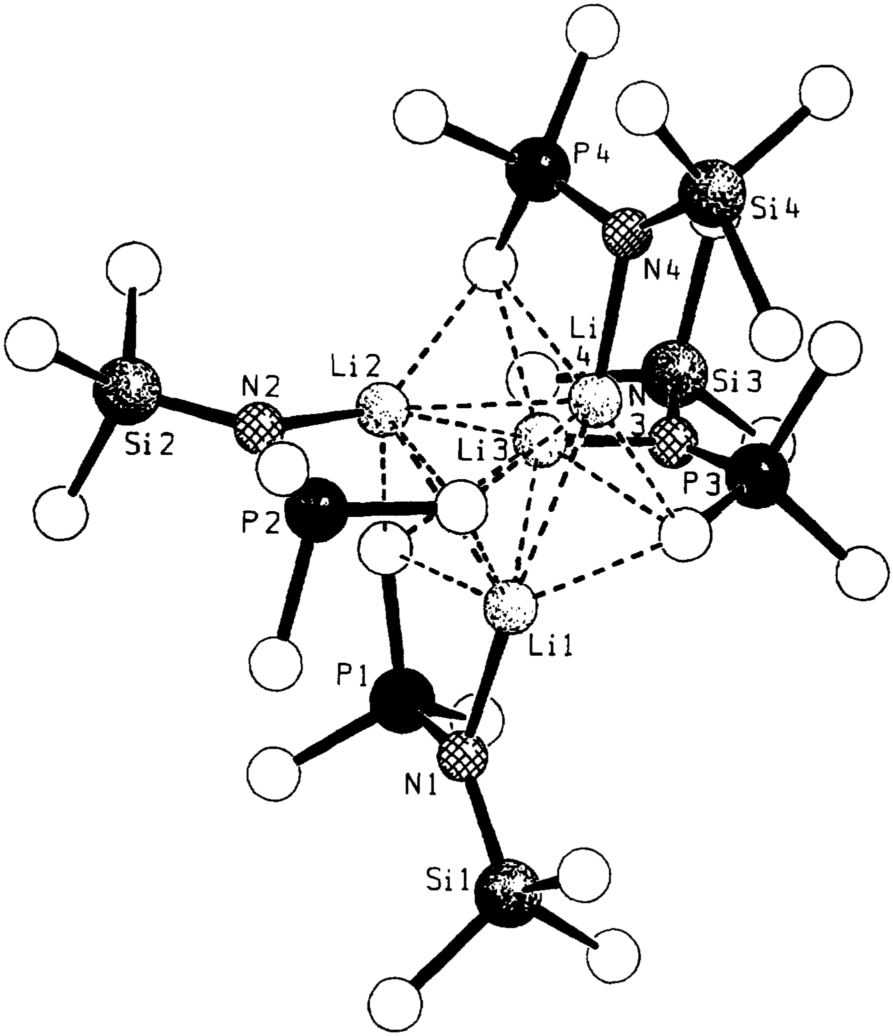


Fig. 9. Molecular structure of $[Me_3SiNPMe_2CH_2Li]_4$.

According to the crystal structure analysis, $Sn(NPPh_3)_4$ has C_2 symmetry; however, the deviations from tetrahedral symmetry are small [76] (Fig. 14). The Sn–N distances lie in the narrow range of 197–199 pm, which is clearly shorter than in $Sn(NMe_2)_4$ (205 pm [77]), possibly a result of the different hybridization of $[Sn]\text{–}\ddot{N}Me_2$ (sp^3) and $[Sn]\text{–}\ddot{N}{=}PR_3$ (sp^2). The PN bonds (156 pm) are also comparatively short, being accompanied by large mean SnNP bond angles of 138°. A quite similar situation is found in the isoelectronic ion $[Sb(NPPh_3)_4]^+$ (see Section 5).

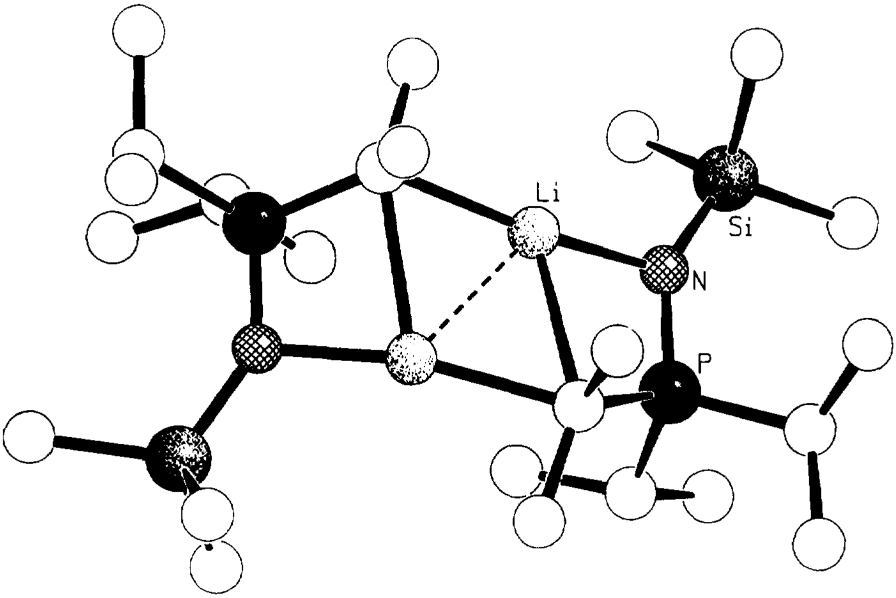


Fig. 10. Molecular structure of $[Me_3SiNP(^iPr)_2C_3H_6Li]_2$.

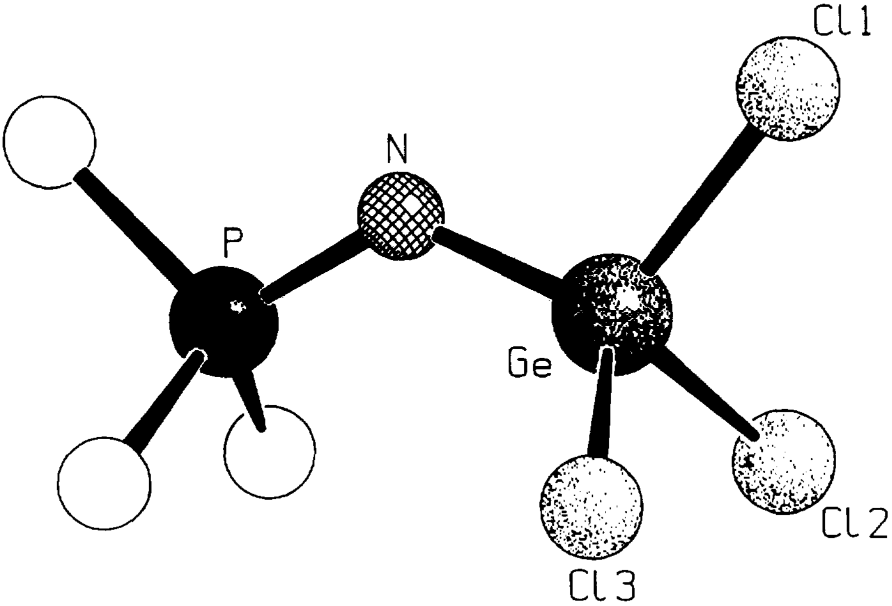


Fig. 11. Molecular structure of $[Cl_3Ge(NPMe_3)]$.

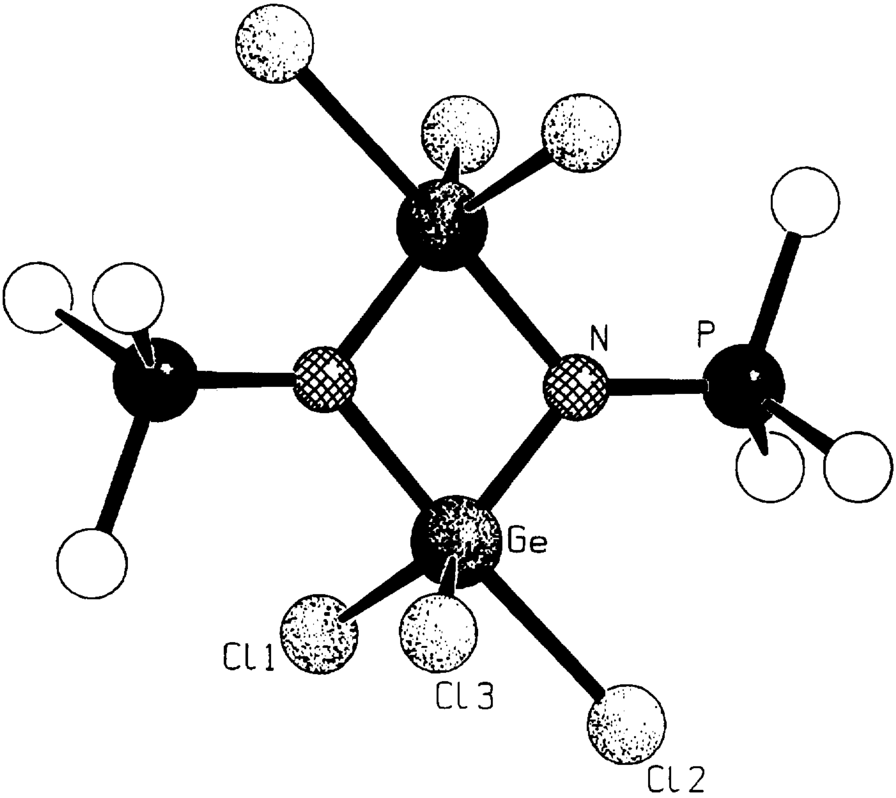


Fig. 12. Molecular structure of $[Cl_3Ge(NPMe_3)]_2$.

5. Phosphorane iminato complexes of Group XV elements (N, P, As, Sb)

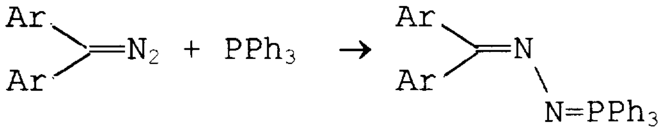
5.1. Nitrogen compounds

The phosphorane iminato compounds of nitrogen can mostly be regarded as hydrazone derivatives. They are obtained by a standard synthesis [78] from triorgano dibromides and the corresponding hydrazines in the presence of triethyl amine:

$$R_3PBr_2 + H_2N\text{-}NR'_2 + 2Et_3N \rightarrow R_3P{=}N\text{-}NR'_2 + 2[Et_3NH]Br \qquad (19)$$

The bis(hydrazone) derivatives $R_3P{=}N\text{-}N{=}CR'_2$ decompose in vacuum thermolysis forming sterically hindered alkenes [79]. Crystal structure analyses are available for some of these compounds [80,81], and the fluorenone derivative [80] is represented in Fig. 15.

An alternative synthesis is the reaction of diazodiaryl methanes with triphenyl phosphane [82,83]:



(20)

It seems to be an elementary biphilic reaction in which each reactant behaves simultaneously as both electrophile and nucleophile.

Some hydrazone derivatives can be generated at a transition metal complex. So, for example, the pentacarbonyl hydrazide $(CO)_5W{=}N{-}NMe_2$ reacts with tetraphenyl diphosphinomethane according to Eq. (21), the resulting phosphino hydrazone being fixed at the metal centre as a chelate [84]:

$$(CO)_5W{=}N{-}NMe_2 + Ph_2PCH_2PPh_2 \xrightarrow[-CO]{} (CO)_4\overline{W[PPh_2CH_2PPh_2N}NMe_2] \quad (21)$$

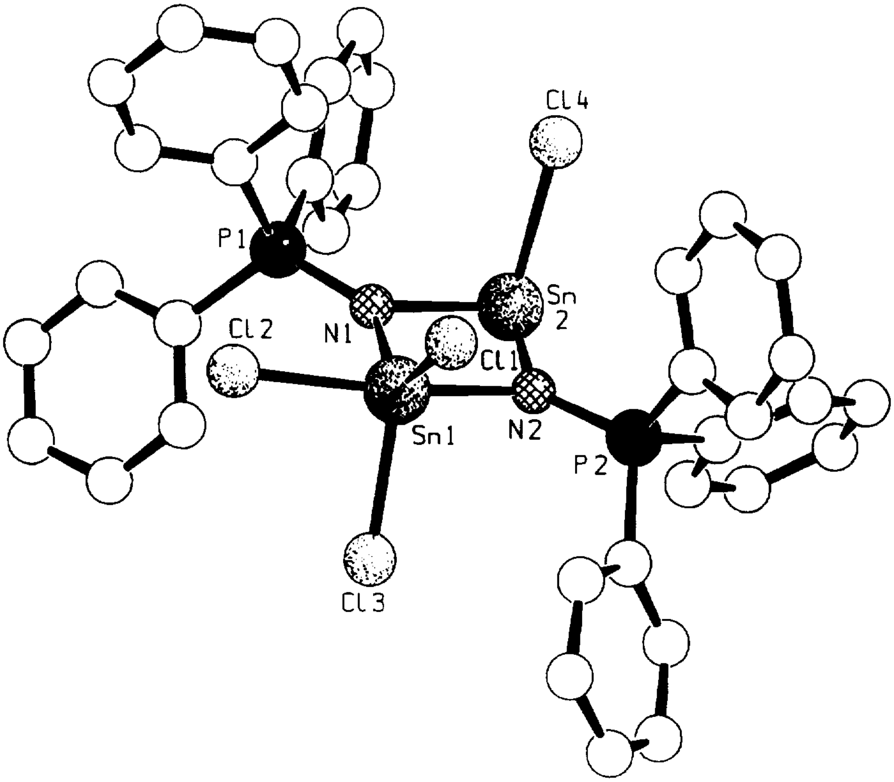


Fig. 13. Molecular structure of the mixed-valenced complex $[SnCl_2(NPPh_3)]_2$.

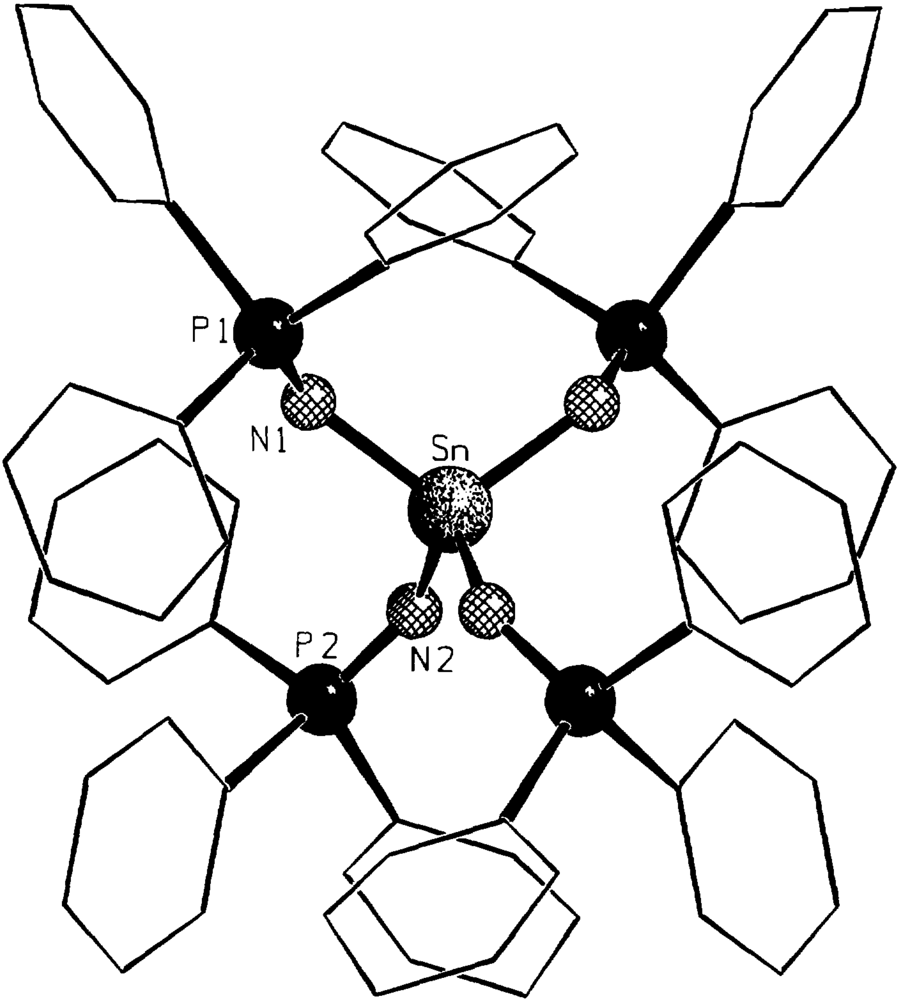


Fig. 14. Molecular structure of $Sn(NPPh_3)_4$.

Whereas the PN bond length of 160.7 pm corresponds to a double bond, the long WN distance of 228.2 pm can be understood as a typical donor–acceptor bond.

Also belonging to the phosphorane iminato derivatives of nitrogen are the phosphazides $R_3P{=}N{-}N{=}N{-}R'$, which are formed as intermediates in the Staudinger reaction from azides $R'{-}N_3$ and triorgano phosphanes PR_3. Commonly they are unstable; however, some representative compounds could be produced in which the substituent R′ is strongly electron withdrawing, or when R and R′ are sterically imposing [85,86].

N-(*p*-Tolyl-triphenylphosphoranylidene)triazene $Ph_3P{=}N{-}N{=}N{-}tol$ could be fixed at the tungsten–dibromo-tricarbonyl fragment $[W]{=}WBr_2(CO)_3$ as a chelate and was characterized crystallographically [87].

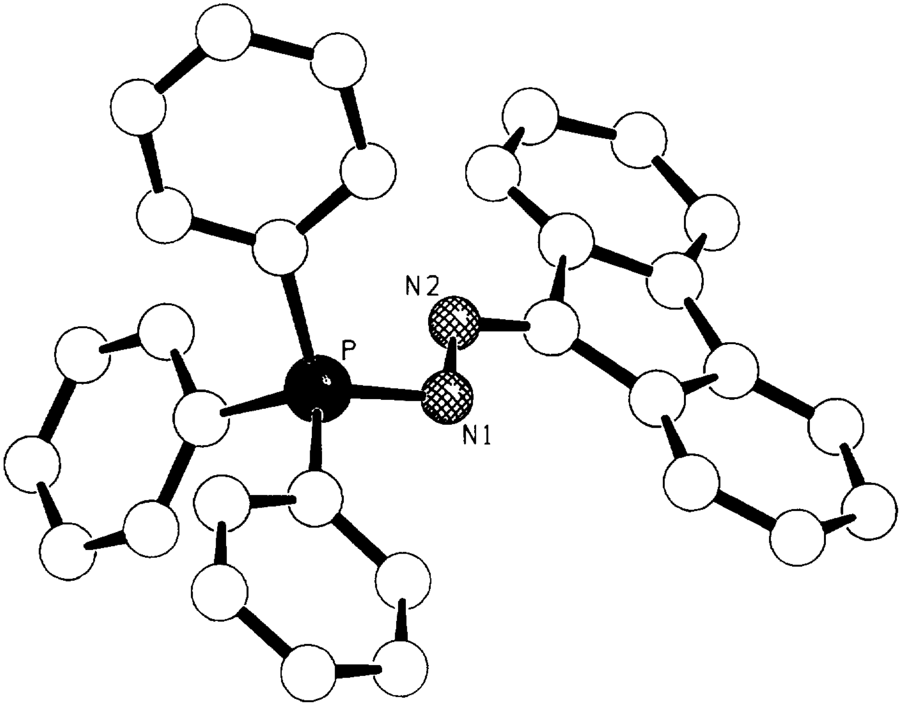
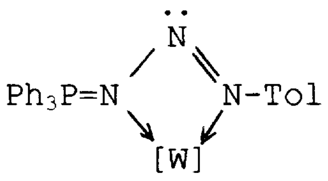
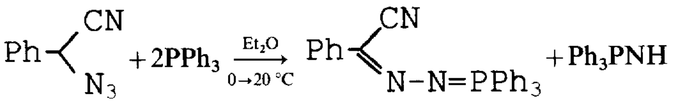


Fig. 15. Molecular structure of the fluorenone complex $Ph_3PN_2C_{13}H_8$.



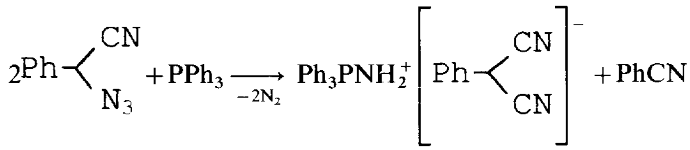
The PN distance (167.2 pm) is slightly longer than the expected value of a double bond. The two NN bonds, 136.4 pm and 127.9 pm, correspond to single and double bonds respectively, whereas the WN bonds (222.0 pm and 216.3 pm) represent a typical donor–acceptor bond.

A reaction deviating from the typical Staudinger process occurs between triphenyl phosphane and α-azido phenylacetonitrile [88]:



$$\mathrm{Ph}\!-\!\!<^{\mathrm{CN}}_{\mathrm{N_3}} + 2PPh_3 \xrightarrow[0\to 20\,^{\circ}\mathrm{C}]{Et_2O} \mathrm{Ph}\!-\!\!<^{\mathrm{CN}}_{\mathrm{N{-}N{=}PPh_3}} + Ph_3PNH \qquad (22)$$

When PPh_3 is deficient, formation of the amino triphenylphosphonium salt of phenyl malonitrile is preferred [88]:



(23)

5.2. Phosphorus compounds

Comprehensive coverage of the phosphorane iminato derivatives of phosphorus is beyond the scope of this review; however, some characteristic representatives shall be dealt with.

The compounds derived from pentavalent phosphorus were mainly developed in the fundamental work of Becke-Goehring. The synthesis of $(PNCl_2)_n$ from PCl_5 and NH_4Cl gave intermediates of the type $[Cl_3PNPCl_3]^+PCl_6^-$ [89] and $[PCl_2(NPCl_3)_2]^+PCl_6^-$ [90] which were isolated and later on were followed by the parent chloride $[Cl_3PNPCl_3]^+Cl^-$ [91,92]. Of all the organic derivatives, the cation of the phenyl compound $[Ph_3PNPPh_3]Cl$ [11,93,94] '$[PNP]^+$' has proved useful on account of its good crystallizing properties as a counter ion in numerous complex ionic compounds, the number of crystal structure analyses amounting to more than 500.

The methyl derivative $[Me_3PNPMe_3]^+$ was used less frequently as a counter ion. Well known are the crystal structures of $[Me_3PNPMe_3]Br \cdot H_2O$ [95] and $[Me_3PNPMe_3]Cl$ [96], in which PN distances of 158.2 pm in the bromide and 159.1 pm in the chloride along with PNP bond angles of 137.0° and 132.4° were measured. It is of some interest that the $[Me_3PNPMe_3]^+$ ion can be protonated to the dication $[Me_3PN(H)PMe_3]^{2+}$ (Fig. 16), which is not known of the phenyl derivative. In the structure of $[Me_3PN(H)PMe_3][ICl_2]_2$ [97] only a slight change of the PNP bond angle (134.4°) is observed, but a significant elongation of the PN distances to 165.9 pm [97] occurs, which is somewhat more than the value expected for a double bond. This effect is accounted for by the equinomial charges of the dication.

Related to the PNP^+ ions are the cations of a series of bis(phosphoraneiminato) derivatives, for which various synthetic pathways were developed [98,99]:

$$2[R_3P{=}N{-}PPh_2-PPh_2]Cl \xrightarrow{200\,^\circ C}$$

$$[R_3P{=}N{-}PPh_2{-}N{=}PPh_3]Cl + Ph_2P{-}PPh_2 + ClPPh_2 \qquad (24)$$

$$(R = Et, Ph)$$

$$Na[Me_3Si{-}N{=}PPh_2{=}N{-}SiMe_3] + 2Me_3PCl_2 \xrightarrow{THF}$$

$$[Me_3P{=}N{-}PPh_2{-}N{=}PMe_3]Cl + NaCl + 2ClSiMe_3 \qquad (25)$$

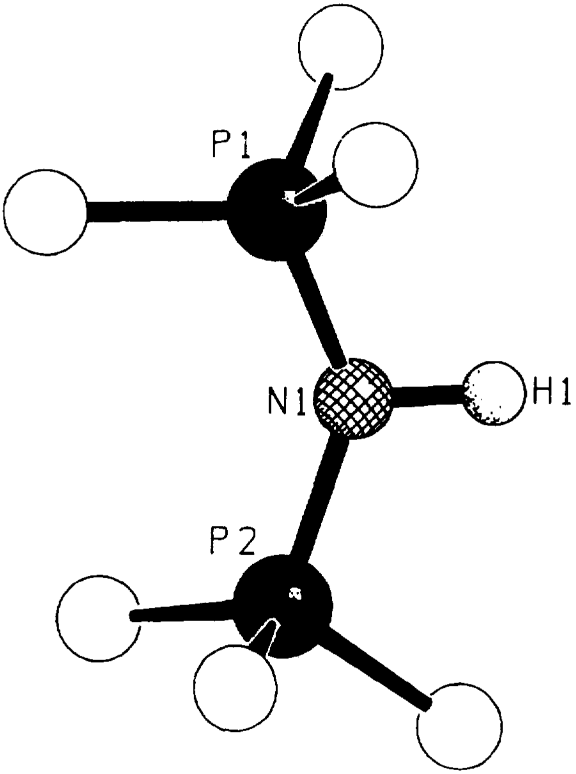


Fig. 16. View of the dication $[Me_3PN(H)PMe_3]^{2+}$ in the structure of $[Me_3PN(H)PMe_3][ICl_2]_2$.

Fluorinated derivatives of bis(phosphoraneiminato) complexes of phosphorus can be produced under very mild conditions from silylated phosphorane imines with various fluorides of pentavalent phosphorus [100,101]:

$$2Me_3SiNPR_3 + 2Me_2PF_3 \rightarrow [Me_2P(N{=}PR_3)_2]^+[Me_2PF_4]^- + 2FSiMe_3 \quad (26)$$

$(R_3 = Me_3, Me_2Ph, {}^iPr_3)$

$$2Me_3SiNPPh_3 + 2RPF_4 \rightarrow [RFP(N{=}PPh_3)_2]^+[RPF_5]^- + 2FSiMe_3 \quad (27)$$

$(R = F, Ph)$

Reaction with the diethyletherate of phosphorus pentafluoride gives mainly the monosubstituted derivative [102]:

$$Me_3SiNPR_3 + 2PF_5 \cdot OEt_2 \rightarrow [R_3PNPF_3]^+PF_6^- + 2OEt_2 + FSiMe_3 \quad (28)$$

The only tris(phosphoraneiminato) derivative of phosphorus is formed at high temperatures by the action of $Me_3SiNPMe_3$ on the bis(phosphoraneiminato) complex prepared according to Eq. (27) [102]:

$$[F_2P(NPMe_3)_2]^+PF_6^- + Me_3SiNPMe_3 \rightarrow [FP(NPMe_3)_3]^+PF_6^- + FSiMe_3 \quad (29)$$

$[Ph_3PNP(O)Cl_2]$ [103] and $[Ph_3PNP(O)Ph_2]$ [104] are representative examples of phosphorane iminato complexes of pentavalent phosphorus. The former is accessible by hydrolysis of $[Ph_3PNPCl_3]Br$, and the latter is prepared from PPh_3 and $Ph_2P(O)N_3$ by a Staudinger reaction. Their structures are shown in Figs. 17 and 18 respectively. In the structure of $[Ph_3PNP(O)Cl_2]$ [105] the PN bonds (158.2 and 155.7 pm) are very short, while the PN bond at the $P(O)Ph_2$ group in the structure of $[Ph_3PNP(O)Ph_2]$ [105] is elongated to 160.5 pm. This effect, as well as the opening of the PNP bond angle from 139.7° in $[Ph_3PNP(O)Cl_2]$ to 146.0°, are due to the steric influence of the two phenyl groups.

Other structural reports are quoted in Ref. [105]; cf. also the review [106].

The tetra(organo)dithioimido diphosphinates $[R_2(S)PNP(S)R_2]^-$, which are obtained from the corresponding bis(thiophosphinyl)amines $R_2(S)PN(H)P(S)R_2$ and strong bases, are interesting for their chelating properties [107–109]. Crystal structure analyses reveal bent PNP bridges with anti-orientation of the sulphur atoms as well in the amino derivatives [110], as in the dithio phosphinates [111]. Lately, a linear PNP bridge was observed in the anion of $[PNP]^+[Ph_2(S)PNP(S)Ph_2]^-$ with extremely short PN distances of 155.4 pm [112]. The synthesis and some complexing characteristics of the corresponding seleno

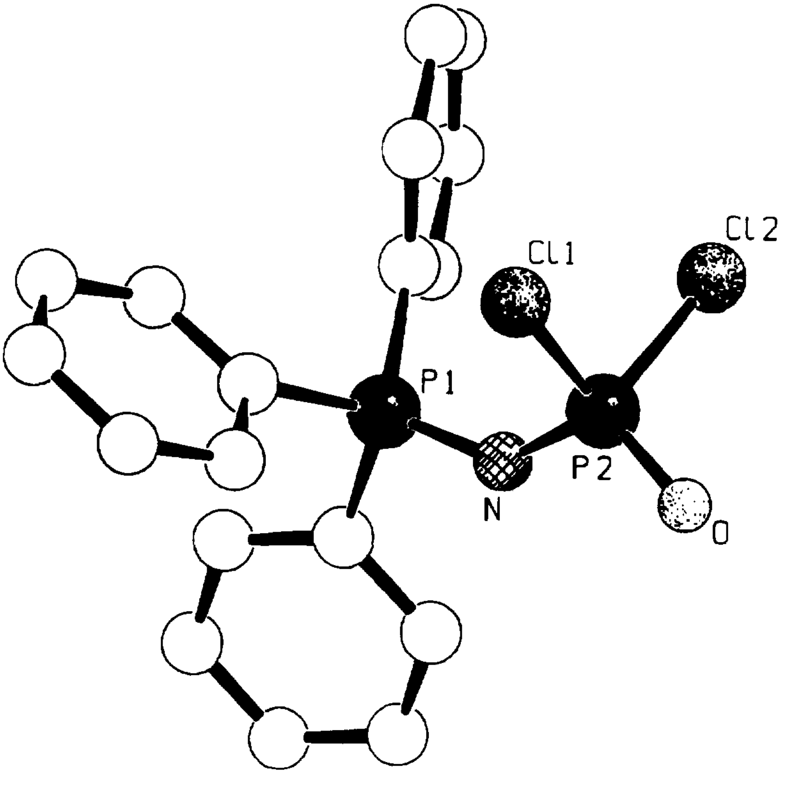


Fig. 17. Molecular structure of $Ph_3PNP(O)Cl_2$.

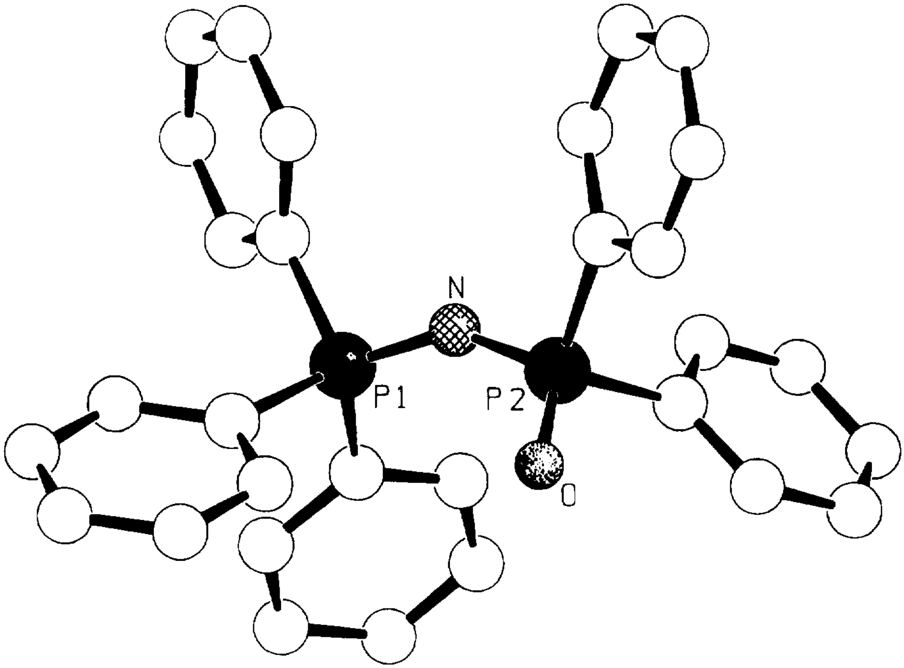


Fig. 18. Molecular structure of $Ph_3PNP(O)Ph_2$.

derivatives $Ph_2(Se)PN(H)P(Se)Ph_2$ and $K[N(SePPh_2)_2]$ have recently been reported [113].

Phosphorane iminato complexes of trivalent phosphorus were first prepared by Schmidbaur and Jonas [40]:

$$Me_3PNLi + ClPMe_2 \rightarrow Me_3P{=}N{-}PMe_2 + LiCl \qquad (30)$$

This method was applied later on to a series of other derivatives [114,115]. An approach to the phenyl derivative $Ph_3P{=}N{-}PPh_2$ is also possible by the successive reactions Eq. (31) [116]:

$$Ph_3PNSiMe_3 + 2Ph_2PCl \xrightarrow[-ClSiMe_3]{} [Ph_3PN{-}PPh_2{-}PPh_2]Cl \xrightarrow{210\,^\circ C}$$
$$Ph_3P{=}N{-}PPh_2 + Ph_2PCl \qquad (31)$$

Derivatives with a functional group at the phosphorus(III) atom are attained by reaction of phosphites [117]:

$$R_3P{=}N{-}SiMe_3 + P(OR')_3 \rightarrow R_3P{=}N{-}P(OR')_2 + R'OSiMe_3 \qquad (32)$$

$(R = Me, Ph, NMe_2;\ R' = Ph, CH_2{-}CF_3)$

With astonishing ease, the $[Cl_3PNPCl_3]^+$ ion is reduced by 2-chloro acrylonitrile in

PCl_3 solution under catalysis of aluminium trichloride [118]:

$$[Cl_3PNPCl_3]Cl + H_2C{=}C(Cl){-}CN \rightarrow Cl_3P{=}N{-}PCl_2 + ClH_2C{-}CCl_2CN \qquad (33)$$

The phosphorane iminato derivatives of trivalent phosphorus are readily oxidized by oxidizing agents like sulphur or chlorine giving the corresponding derivatives of phosphorus(V), thus achieving an additional variety of products [116,118].

Last, but not least, in some cases the synthesis of phosphorane iminato complexes of trivalent phosphorus is achieved by applying the Staudinger reaction [119]:

$$(CF_3)_2PN_3 + PPh_3 \rightarrow Ph_3P{=}N{-}P(CF_3)_2 + N_2 \qquad (34)$$

The reaction in Eq. (34) proceeds in dichloromethane solution at 20 °C within 4 days. The crystal structure analysis [119] shows that the P^V–N bond length (157.6 pm) and P^{III}–N bond length (161.2 pm) do not differ very much. In the iron carbonyl complex $\{(CO)_4Fe[Ph_3PNP(CF_3)_2]\}$ [119], prepared by the reaction in Eq. (35),

$$Ph_3PNP(CF_3)_2 + Fe_2(CO)_9 \xrightarrow{20\,^{\circ}C,\ Hexane} [Fe(CO)_4(Ph_3PNP(CF_3)_2)] + Fe(CO)_5 \qquad (35)$$

in which the P^{III} atom is tied to the Fe atom, the distances P^V–N (156.0 pm) and P^{III}–N (156.8 pm) are even more similar. This effect is explained with a vast delocalization of the π bonds in the PNP bridge. At the same time, the bond angle PNP is opened to 151.8° in the iron complex [119] compared with 130.7° in $Ph_3PNP(CF_3)_2$.

5.3. *Arsenic compounds*

The first phosphorane iminato complexes of arsenic, which were compounds of the formula $[Me_2As(NPR_3)]$ with R = Me, Et, were prepared in 1968 by reactions analogous to Eq. (30) from the diorganoarsane chlorides R_2AsCl [40]. Whereas the dichloro derivative $[Cl_2As(NPPh_3)]$, which is accessible from arsenic trichloride and $Me_3SiNPPh_3$, has a dimeric molecular structure with linkage via the N atoms, the trifluoromethyl compound [120] is a monomeric molecule (Fig. 19). The PN bond (156.4 pm) corresponds to a double bond; at the same time, the AsN bond (178.3 pm) is significantly shorter than the value expected for an AsN single bond (187 pm) so that the AsNP bridge can be described by partially delocalized π bonds. Coordination of the As atom in the osmium complexes $Os_3(CO)_{11}[(CF_3)_2AsNPPh_3]$ and $Os_3(\mu\text{-}H_2)(CO)_9[(CF_3)_2AsNPPh_3]$ [120] results in an additional shortening of the As–N distance to 171.6 and 173.9 pm, along with little change in the PN distances and an enhancement of the AsNP bond angle from 126.7° to 135.4° and 133.0° respectively.

In contrast to the dimeric molecular structure of the phenyl derivative $[Cl_2As(NPPh_3)]_2$ [121], the methyl compound, which is produced from arsenic

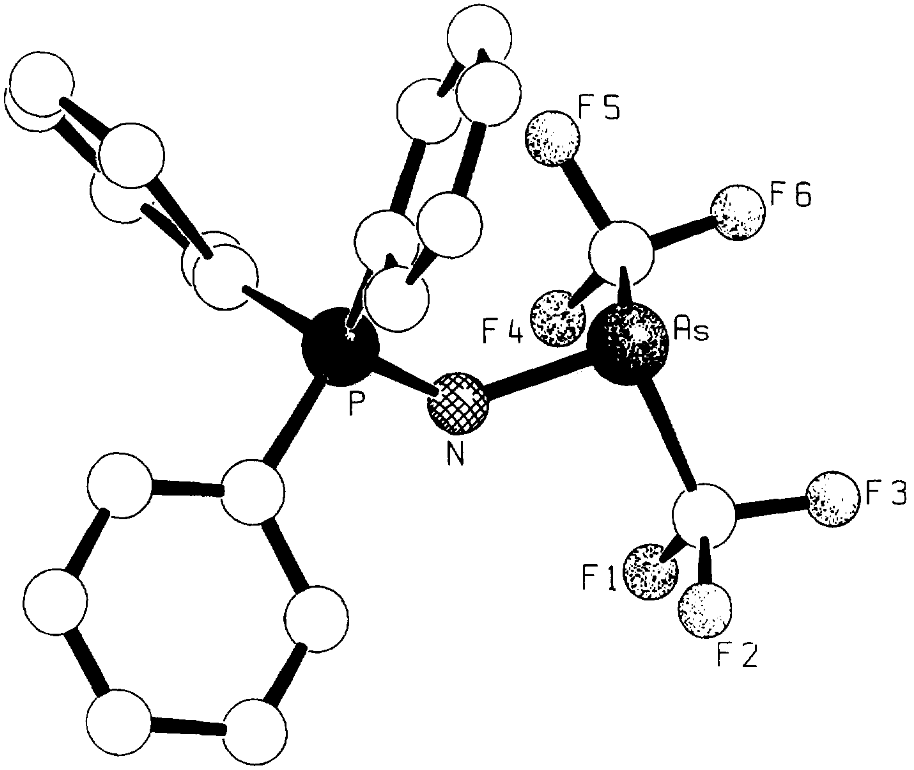


Fig. 19. Molecular structure of $(CF_3)_2As(NPPh_3)$.

trichloride and $Me_3SiNPMe_3$, forms complex ions which can be formulated as $[ClAs(NPMe_3)]_2^{2+}2Cl^-$ [122] (Fig. 20).

This description follows from the two remarkably long distances As2···Cl2 of 251.1 pm and As1···Cl4 of 291.4 pm, whereas the distances As1–Cl1 and As2–Cl3 with 225.7 and 222.4 pm are in accordance with normal covalent bonds. In fact the compound may well be regarded as a triple ion. The AsN bonds with their values of 182.3 pm to 206.8 pm are, on account of the μ_2-bridging function, clearly longer than in the monomeric $[(CF_3)_2As(NPPh_3)]$ (171.6 pm) [120]. In the reaction with zirconium tetrachloride, hexachloro zirconate is formed [122], confirming the ionic structure of the methyl compound:

$$[ClAs(NPMe_3)]_2Cl_2 + ZrCl_4 \rightarrow [ClAs(NPMe_3)]_2ZrCl_6 \tag{36}$$

In contrast, with the Lewis acid antimony pentachloride, arsenic trichloride is surprisingly cleaved off [122]:

$$[ClAs(NPMe_3)]_2Cl_2 + 2SbCl_5 \rightarrow [ClAs(NPMe_3)_2SbCl_4]^+SbCl_6^- + AsCl_3 \tag{37}$$

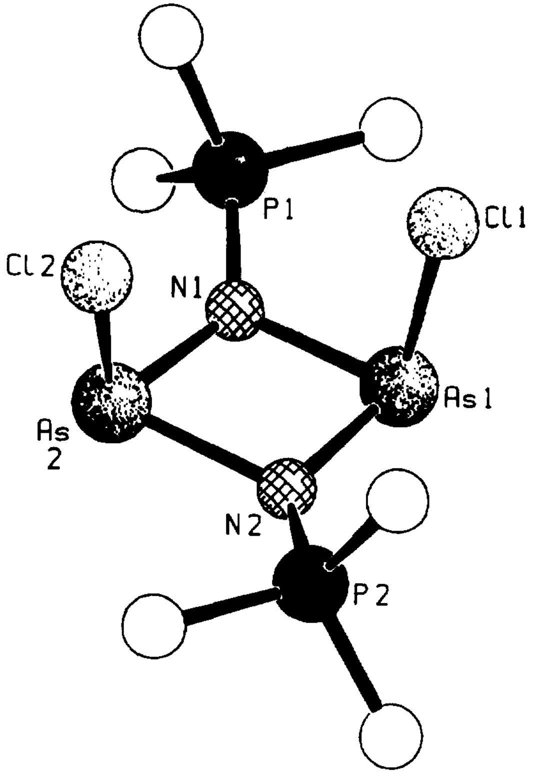


Fig. 20. View of one of the two symmetry-independent dications $[ClAs(NPMe_3)]_2^{2+}$ in the structure of $[ClAs(NPMe_3)]_2Cl_2$.

According to the crystal structure analysis the cation of this compound can be interpreted as the $SbCl_4^+$ ion, which is coordinated in a chelate manner by the N atoms of the $AsCl(NPMe_3)_2$ molecule [122] (Fig. 21). Taking into account now the stereochemically active lone pair, the arsenic atoms achieve φ-tetrahedral environment, whereas in $[ClAs(NPMe_3)]_2Cl_2$ a φ-trigonal bipyramidal geometry is realized. A reaction analogous to Eq. (37) takes place with tin tetrachloride leading to the molecule $[ClAs(NPMe_3)_2SnCl_4]$ which is isoelectronic to the ion $[ClAs(NPMe_3)_2SbCl_4]^+$ [122] (Fig. 22):

$$[ClAs(NPMe_3)]_2Cl_2 + SnCl_4 \rightarrow [ClAs(NPMe_3)_2SnCl_4] + AsCl_3 \qquad (38)$$

5.4. Antimony compounds

Phosphorane iminato complexes of pentavalent antimony with organic substituents of the $R_3Sb(NPPh_3)_2$ type can be obtained by reaction of the triorganic dibromides with $Me_3SiNPPh_3$ in methanol solution in the presence of triethyl amine

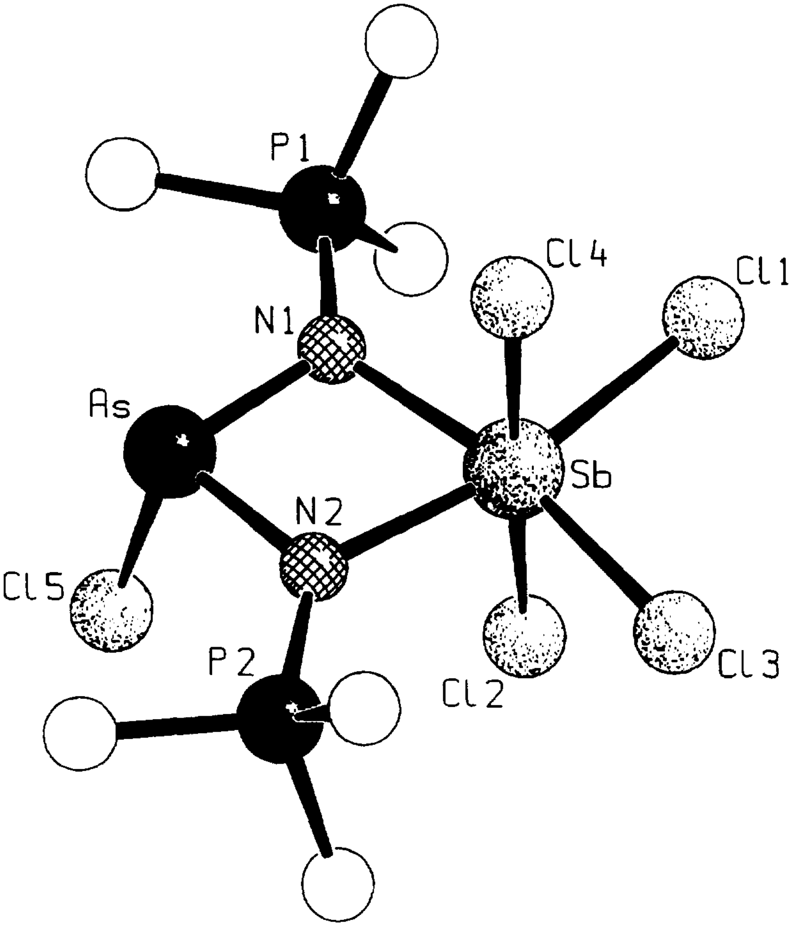


Fig. 21. View of the cation $[ClAs(NPMe_3)_2SbCl_4]^+$ in the structure of $[ClAs(NPMe_3)_2SbCl_4]SbCl_6$.

[123]:

$$R_3SbBr_2 + 2Me_3SiNPPh_3 + 2CH_3OH + 2NEt_3 \rightarrow$$
$$R_3Sb(NPPh_3)_2 + 2CH_3OSiMe_3 + 2[HNEt_3]Br \qquad (39)$$
$$(R = Ph, Tol, c\text{-}C_6H_{11})$$

Whereas the structures of the triorgano antimony derivatives are unknown, the trichloro complexes of antimony(V) which are produced according to Eq. (40) are characterized crystallographically [124]:

$$2SbX_5 + 4Me_3SiNPPh_3 \xrightarrow[(X=F,\,Cl)]{CH_3CN} [Sb(NPPh_3)_4]^+[SbX_6]^- + 4XSiMe_3 \qquad (40)$$

Surprisingly, the products have a complex ionic structure (Fig. 23). The Sb atom

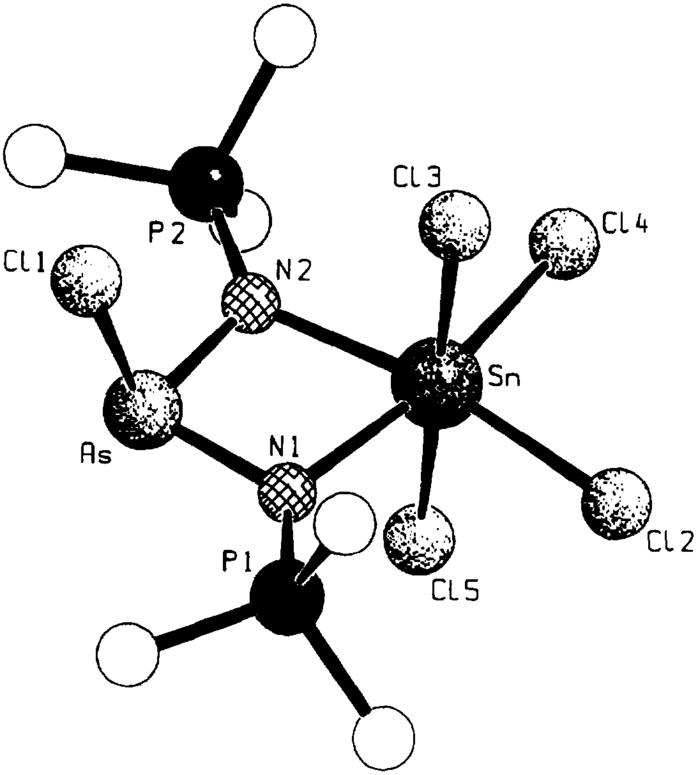


Fig. 22. Molecular structure of $ClAs(NPMe_3)_2SnCl_4$.

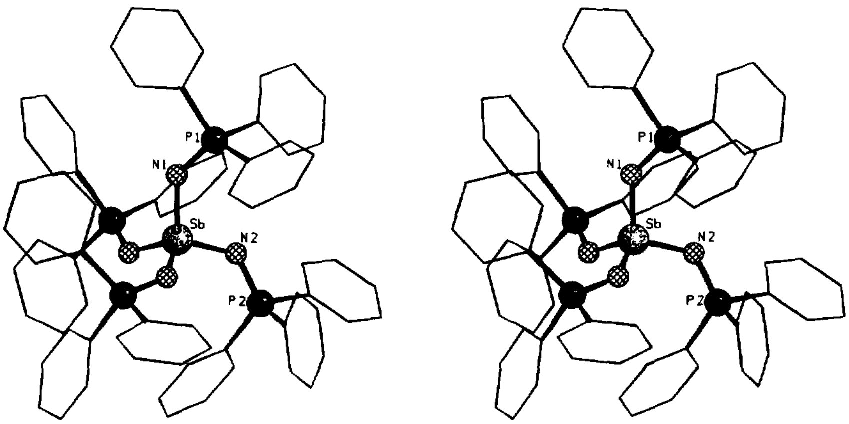


Fig. 23. Stereoscopic representation of the cation $[Sb(NPPh_3)_4]^+$ in the structure of $[Sb(NPPh_3)_4]SbF_6$.

in the $[Sb(NPPh_3)_4]^+$ ion as well as the Sn atom in the isoelectronic tin compound $[Sn(NPPh_3)_4]$ (see Section 4) are surrounded tetrahedrally by the four N atoms of the phosphorane iminato ligands. The SbNP bond angles are 136.0° and 128.3° and are accompanied by extremely short SbN bond lengths of 192.8 pm. However, the SbN bonds presumably do not contain any π bonding, as in the ^{121}Sb Mössbauer spectra the values of isomer shift $\delta_{IS} = -2.4$ mm s^{-1} (X = F) and $\delta_{IS} = -3.0$ mm s^{-1} (X = Cl) are of the same order of magnitude as in $[SbMe_4]^+F^-$ ($\delta_{IS} = -4.6$ mm s^{-1} [125]), and in the cation of $[SbCl_4]^+[Sb_2F_9Cl_2]^-$ ($\delta_{IS} = -4.3$ mm s^{-1} [125]), where no π bonding is suggested.

Phosphorane iminato complexes of trivalent antimony are known in a somewhat greater variety. Reacting antimony trichloride with $Me_3SiNPMe_3$ in a dichloromethane solution, gives, in a first step, the donor–acceptor complex $[SbCl_3(Me_3SiNPMe_3)]$ which was isolated [126] and characterized by IR spec-

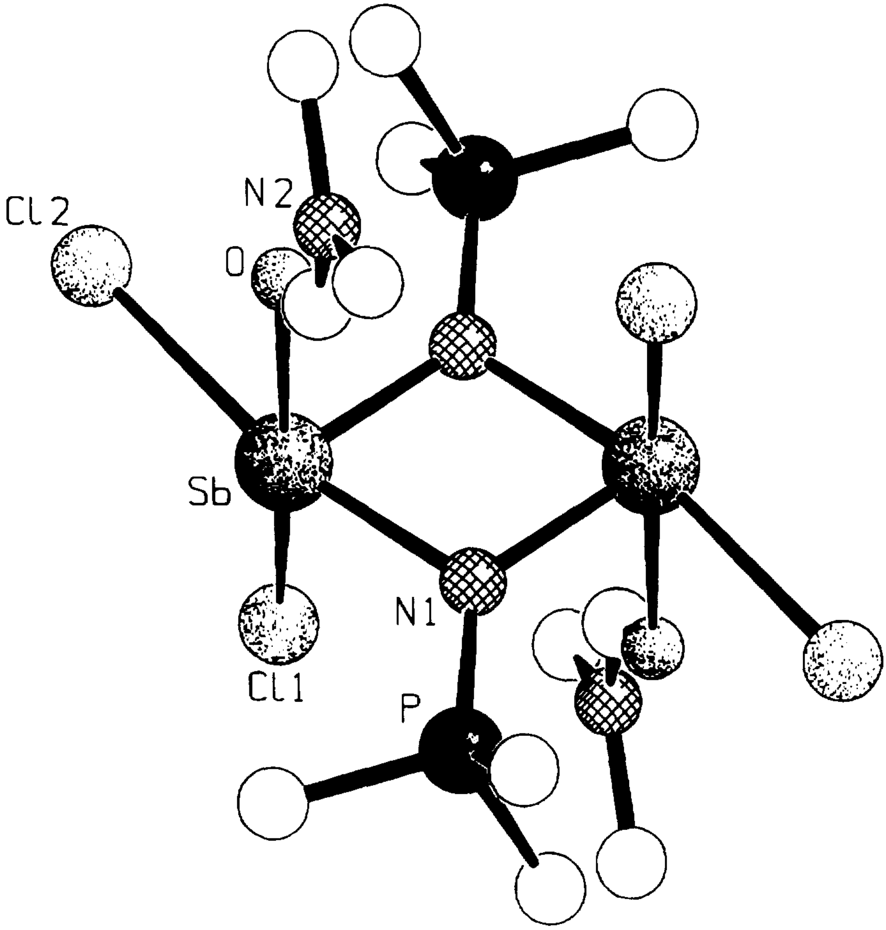


Fig. 24. Molecular structure of $[Cl_2Sb(NPMe_3)DMF]_2$.

troscopy. Heating in acetonitrile cleaves off $ClSiMe_3$, and the dimeric complex $[SbCl_2(NPMe_3)]_2$ is obtained, which can be recrystallized from DMF forming the solvated $[SbCl_2(NPMe_3)(DMF)]_2$ [19]. The compound consists of centrosymmetric molecules in which the antimony atoms are linked via μ_2-N bridges and attain φ-octahedral coordination with consideration of the stereochemically active lone pair [19] (Fig. 24). The N atom which is located in trans-position to the free electron pair realizes a short SbN bond of 203.6 pm, whereas the second SbN bond of the four-membered ring Sb_2N_2 has a length of 221.3 pm. In contrast, the corresponding fluoro derivative $[SbF_2(NPMe_3)]_2$ is isolated from dichloromethane as a solvate-free product [127]. Here, the antimony atoms are φ-trigonal bipyramidal, the bond lengths SbN_{ax} (224.8 pm) and SbF_{ax} (203.4 pm) being significantly longer than the equatorial distances SbN_{eq} (200.9 pm) and SbF_{eq} (192.5 pm) [127] (Fig. 25).

A reaction analogous to Eq. (37) is observed for antimony pentachloride with $[SbCl_2(NPMe_3)]_2$ in acetonitrile solution. Antimony trichloride is eliminated and the mixed valent ionic Sb^{III}–Sb^{V} complex $[Sb_2Cl_5(NPMe_3)_2]^+$ is formed [128]:

$$[SbCl_2(NPMe_3)]_2 + 2SbCl_5 \xrightarrow{CH_3CN}$$

$$[ClSb(NPMe_3)_2SbCl_4(CH_3CN)]SbCl_6 + SbCl_3 \tag{41}$$

The structure of the cation can be interpreted as $SbCl_4^+$ ion which is chelated by

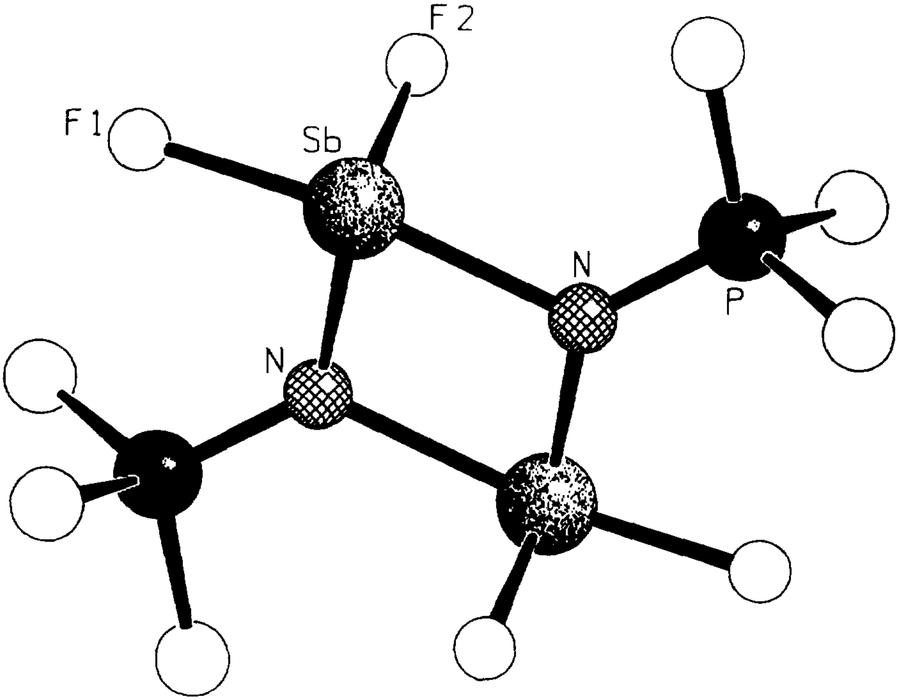


Fig. 25. Molecular structure of $[F_2Sb(NPMe_3)]_2$.

$ClSb(NPMe_3)_2$ (Fig. 26). In contrast to the $[ClAs(NPMe_3)_2SbCl_4]^+$ ion, the Sb^{III} atom is additionally coordinated by an acetonitrile molecule.

The phenyl derivative reacts with antimony pentachloride to produce the centrosymmetric dimeric dication $[SbCl(NPPh_3)]_2^{2+}$. Here the antimony atoms are solvated by two acetonitrile molecules each, which results in a distorted φ-octahedral environment [128] (Fig. 27):

$$[SbCl_2(NPPh_3)]_2 + 2SbCl_5 \xrightarrow{CH_3CN} [ClSb(NPPh_3)(CH_3CN)_2]_2[SbCl_6]_2 \cdot 2CH_3CN \quad (42)$$

The SbN distances of the Sb_2N_2 four-membered ring (213.1 pm and 207.1 pm) are slightly different. The geometry of the two Sb^{III}–Sb^V complexes is reproduced in

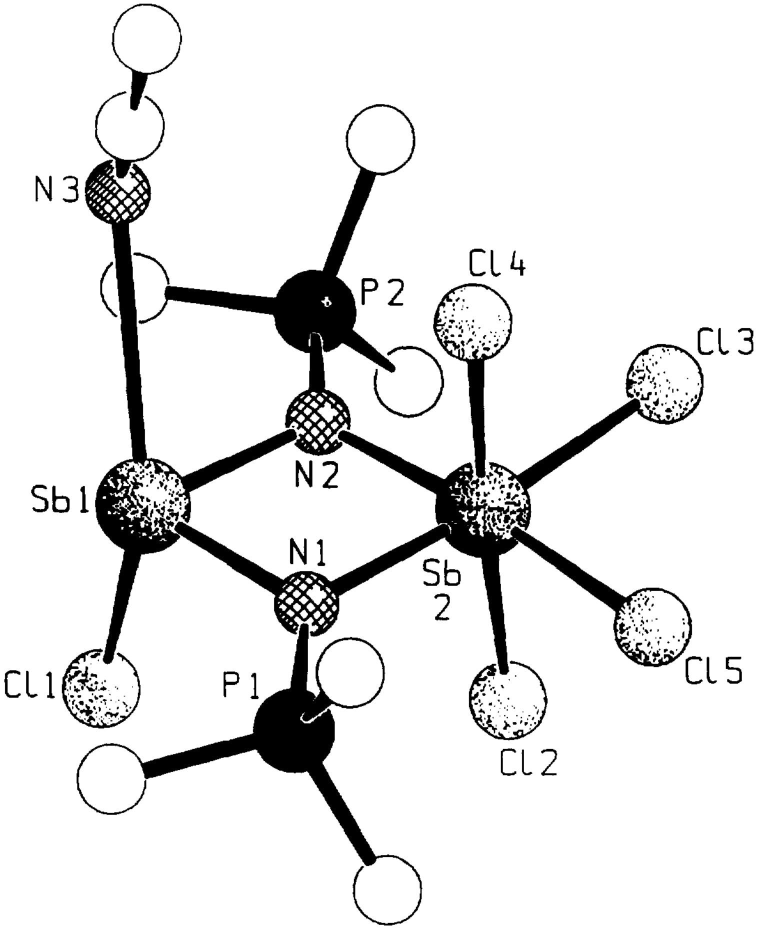


Fig. 26. View of the cation $[ClSb(NPMe_3)_2SbCl_4(CH_3CN)]^+$ in the structure of $[ClSb(NPMe_3)_2SbCl_4(CH_3CN)]SbCl_6$.

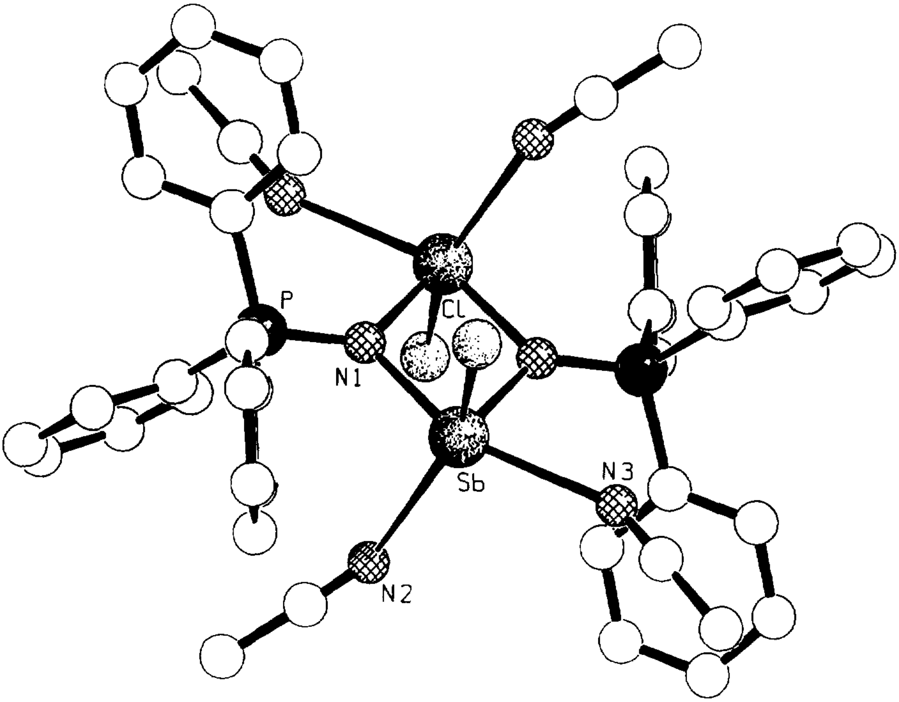


Fig. 27. View of the dication $[ClSb(NPPh_3)(CH_3CN)_2]_2^{2+}$ in the structure of $[ClSb(NPPh_3)_2(CH_3CN)]_2[SbCl_6]_22CH_3CN$.

the ^{121}Sb Mössbauer spectra [128], in which the Sb^{III} positions induced by the stereochemical activity of the lone pair give rise to quadrupole splittings of 16.6 mm s^{-1} for $[ClSb(NPMe_3)_2SbCl_4(CH_3CN)]SbCl_6$ and 13.3 mm s^{-1} for $[ClSb(NPPh_3)(CH_3CN)_2]_2[SbCl_6]_2 \cdot 2CH_3CN$ [128].

6. Phosphorane iminato complexes of Group XVI elements (S, Se, Te)

6.1. Sulphur compounds

An especially large number of examples are derived from sulphur, where syntheses not only start from sulphur halides, but take into account oxides, oxohalides, nitrides and nitride halides as well, so that a great variety of partly unusual results were obtained.

The first well-defined derivative came from the reaction of triphenyl phosphane with tetrasulphur tetranitride according to Eq. (43) [129]. The synthesis of this material

$$2PPh_3 + S_4N_4 \rightarrow Ph_3P{=}N{-}S_3N_3 + Ph_3PS \qquad (43)$$

forming red crystals, runs even better when triphenylmethylene ylide is used Eq. (44), giving trithio formaldehyde as a side-product [129].

$$Ph_3PCH_2 + S_4N_4 \rightarrow Ph_3P{=}N{-}S_3N_3 + \tfrac{1}{3}(CH_2S)_3 \qquad (44)$$

According to the crystal structure (Fig. 28) [130], five of the six ring atoms lie in a plane — all but the tricoordinate sulphur atom S1. The SN distances of this atom to the N atoms in the ring (168 pm) are significantly longer than all other SN bonds (approximately 161 pm), which therefore contain a degree of π bonding. The PN bond with its value of 164.5 pm is relatively long, and delocalized π bonds are assumed for the PNS bridge. The PNS bond angle (121.0°) is slightly larger than in the triphenyl arsane derivative $Ph_3As{-}N{=}S_3N_3$ (116.9°) [131], whose AsN bond of 183.7 pm corresponds to a single bond and the exocyclic SN distance of 155.4 pm implies a double bond. Very similar structures are found in the 2-pyridyl derivative $Ph_2(2\text{-}Py)P{=}N{-}S_3N_3$ [132] and in the tris(piperidino) complex $(C_5H_{10}N)_3P{=}N{-}S_3N_3$ [133]. The tris(pyrrolidino) and the tris(morpholino) derivatives have also been reported, all of which are accessible from the corresponding amidophosphoranes and S_4N_4 [133].

$Ph_3P{=}N{-}S_3N_3$ exhibits interesting subsequent reactions. In boiling dichloromethane it adds norbornadiene (NBD) smoothly to two S atoms of the S_3N_3 ring [134].

$$Ph_3P{=}N{-}S_3N_3 + NBD \rightarrow Ph_3P{=}N{-}S_3N_3 \cdot NBD \qquad (45)$$

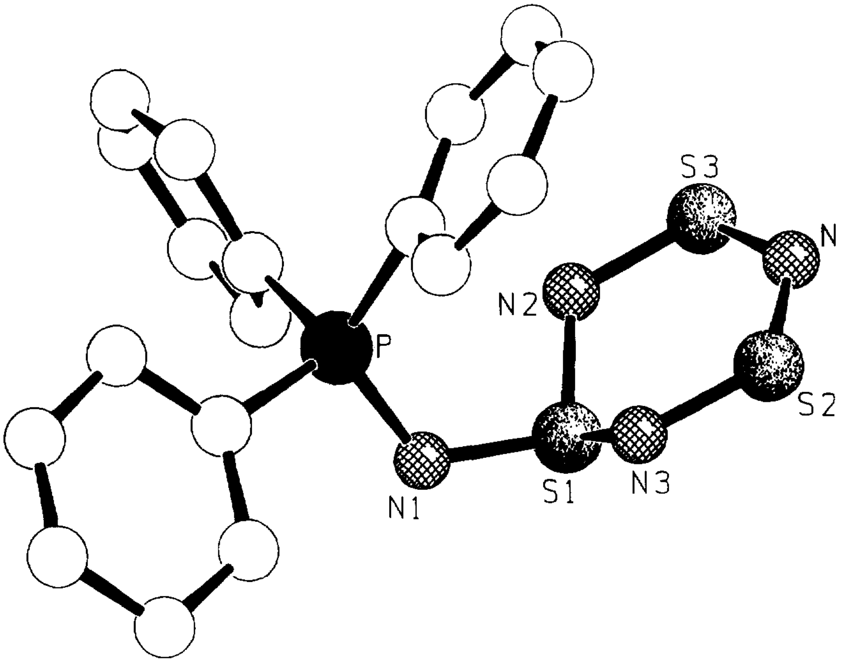
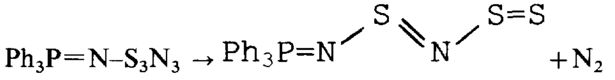


Fig. 28. Molecular structure of $Ph_3PN(S_3N_3)$.

The crystal structure shows the addition to have occurred in exo fashion (Fig. 29). The PN bond is 6 pm shorter in the adduct, and the PNS bond angle is opened by 6.6° [134]. A likewise remarkable reaction is the thermolysis, which in boiling acetonitrile leads to loss of dinitrogen [135]:



$$Ph_3P{=}N{-}S_3N_3 \rightarrow Ph_3P{=}N{-}S{=}N{-}S{=}S + N_2 \qquad (46)$$

The product has a very short SS bond of 190.8 pm. The NSNSS chain forms an almost planar cis–trans conformation with NS distances between 160.7 pm and 158.7 pm [135] (Fig. 30).

The reaction of S_4N_4 and PPh_3 has a strong solvent dependence. Whereas in benzene solution $[S(NPPh_3)_3]^+S_4N_5^-$ is preferentially formed (see below), in acetonitrile the preferred product is 1,5-bis(triphenylphosphinimino)cyclotetrathiazene [136] (Fig. 31). This compound has the structure of a partially opened S_4N_4 cage in which the remaining transannular SS bond has a bond length of 245.2 pm, distinctly shorter than the transannular SS distances in S_4N_4 (259–260 pm [137]). The two exocyclic $NPPh_3$ groups are in axial and equatorial configuration [136].

Other sulphur–nitrogen rings are also subject to nucleophilic attack by PPh_3.

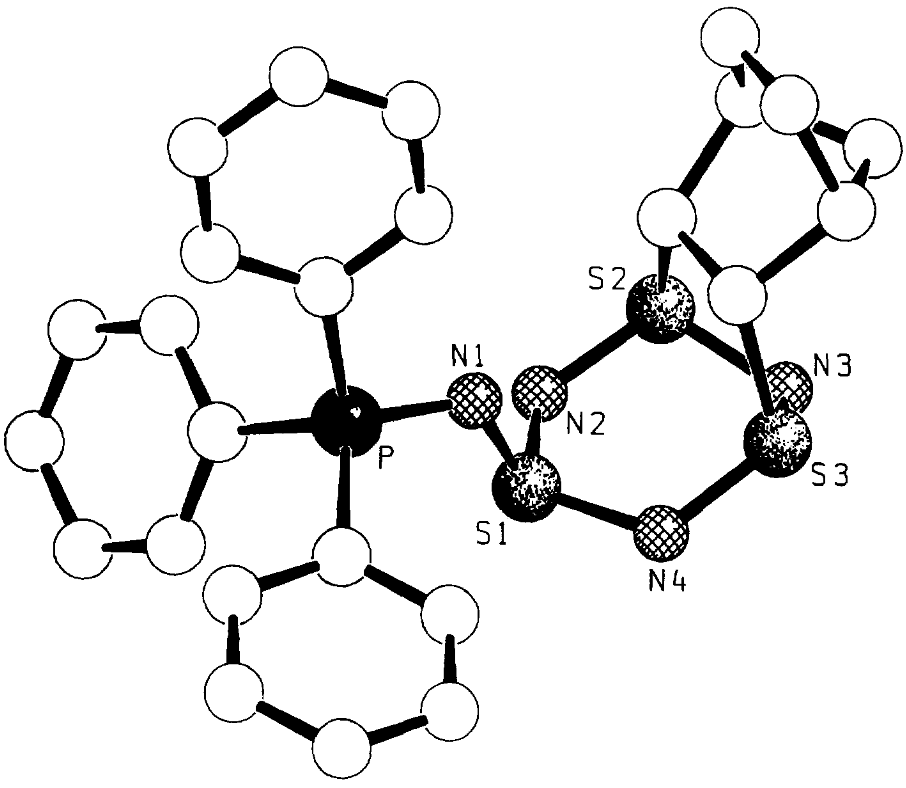


Fig. 29. Molecular structure of the norbornadiene complex $Ph_3PN{-}S_3N_3NBD$.

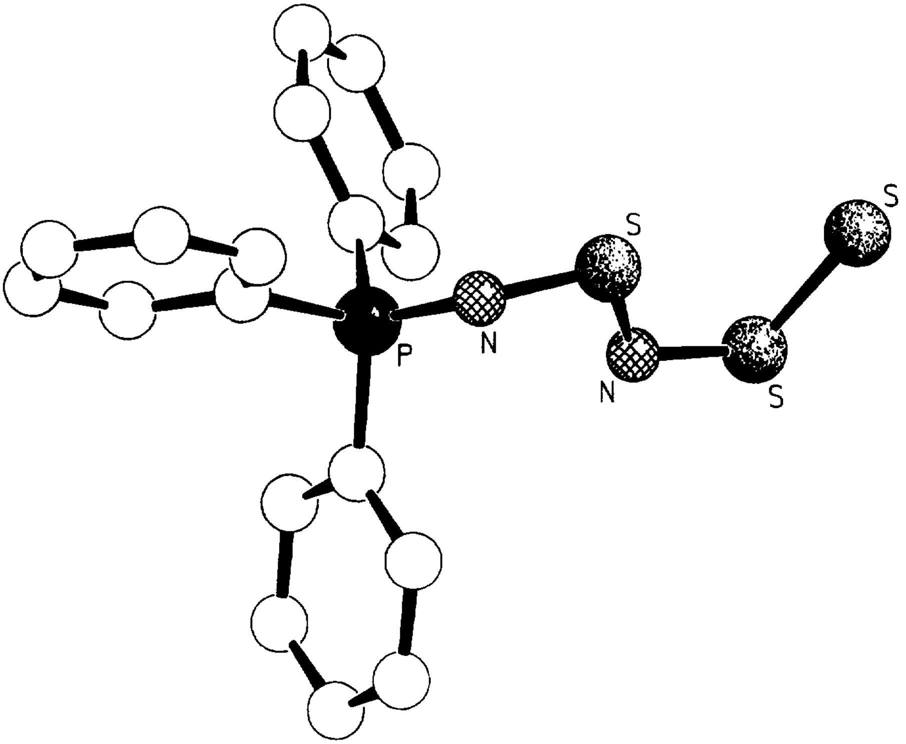


Fig. 30. Molecular structure of $Ph_3PNSNSS$.

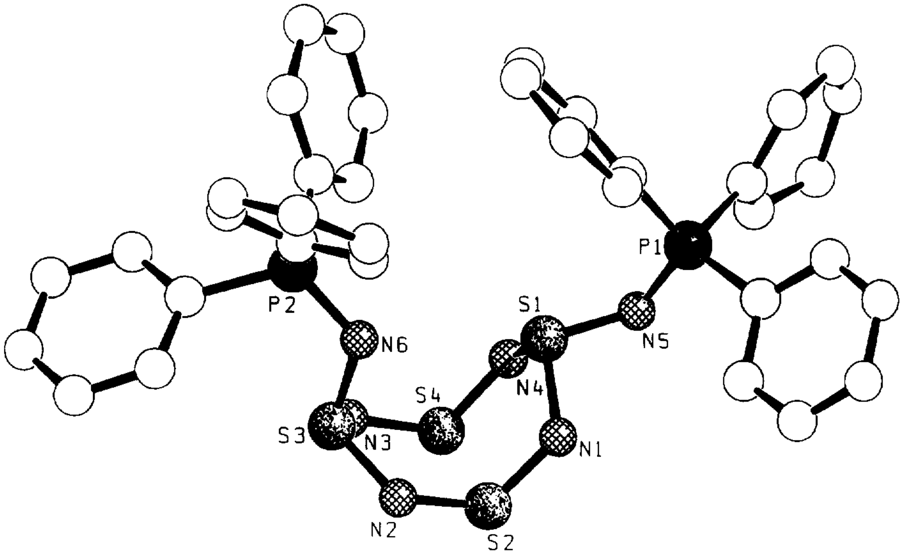


Fig. 31. Molecular structure of $(Ph_3PN)_2S_4N_4$.

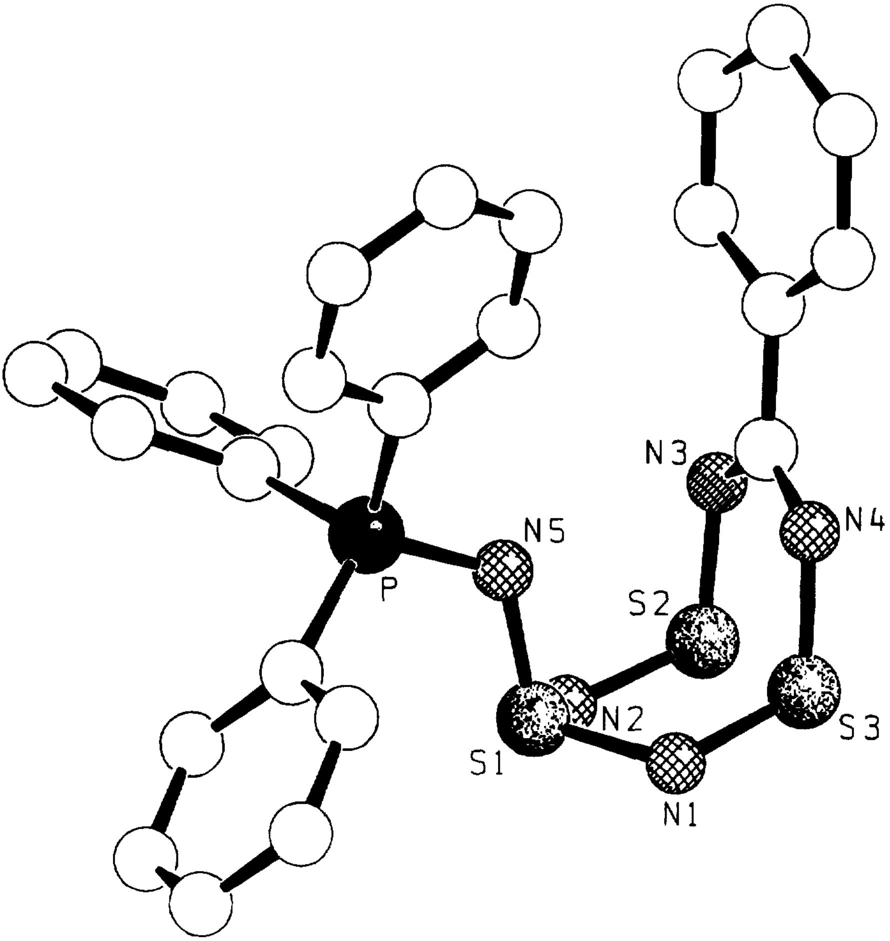
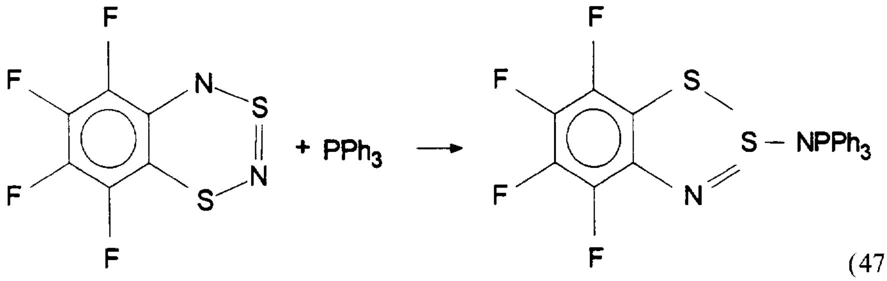


Fig. 32. Molecular structure of $PhC(S_3N_4)NPPh_3$.

The bicyclic derivative $PhC(S_3N_5)$ [138], which is obtained from $\{Ph–C(NSiMe_3)[N(SiMe_3)_2]\}$ and trithiazyl chloride, gives trithiatetrazocine $[PhC(S_3N_4)NPPh_3]$, in which the $NPPh_3$ group is in endo conformation [139] (Fig. 32). Again, the transannular SS bond is relatively short (241.0 pm). In a similar way, the diphenylphosphino derivative $Ph_2P(S_3N_5)$ reacts with triphenyl phosphane in acetonitrile forming $[Ph_2P(S_3N_4)NPPh_3]$ in which the $NPPh_3$ group now takes the exo-position [140] (Fig. 33). Now the transannular SS bond is 253.2 pm, which is not much shorter than in S_4N_4 [137]. It is interesting that in solution the endo-isomer can also be detected by ^{31}P NMR spectroscopy [140]. A detailed ^{15}N NMR study can be found in Ref. [141].

The reaction of PPh_3 with tetrafluoro benzodithiadiazine (Eq. (47)) [142] gives a non-planar five-membered heterocycle.



(47)

The site of the S atom connected with the $NPPh_3$ group lies 39.6 pm above the C_2NS plane (Fig. 34). A special feature of the structure is the very short PN bond length of 149.4 pm, which to our knowledge is the shortest found in a phosphorane iminato complex.

In one case PPh_3 has been introduced from the ligand sphere of a transition metal complex. *trans*-$[IrCl(CO)_2(PPh_3)_2]$ reacted with the 2,4-dinitrobenzenesulphene amide of 1,4-dihydro-1,4-iminonaphthalene in boiling toluene forming the red 2,4-dinitrobenzenesulphenylimino (triphenyl)-phosphane [143] (Fig. 35). The PN bond of 155.6 pm is relatively short; the NS bond of 166.8 pm is relatively long, so that bonding scheme **1b** can be applied. A similar situation is met in the thiocyanato derivative $Ph_3P{=}N{-}SCN$, which can easily be prepared by a redox reaction with the aid of Cu(II) thiocyanate (Eq. (48)) [144] (Fig. 36).

$$2Cu(SCN)_2 + 2Me_3SiNPPh_3 \rightarrow Ph_3P{=}N{-}SCN + 2CuSCN + Me_3SiSCN \quad (48)$$

The crystal structure analysis shows it to form monomeric molecules with a PN bond length of 160.4 pm, an SN bond length of 167.9 pm, and PNS and NSC bond angles of 117.4° and 101.8° respectively. Redox reactions participate in the reaction

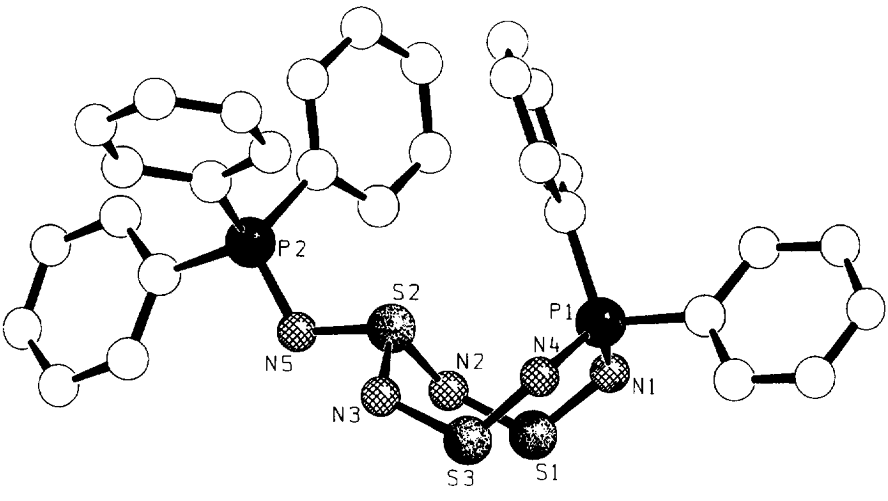


Fig. 33. Molecular structure of $Ph_2P(S_3N_4)NPPh_3$.

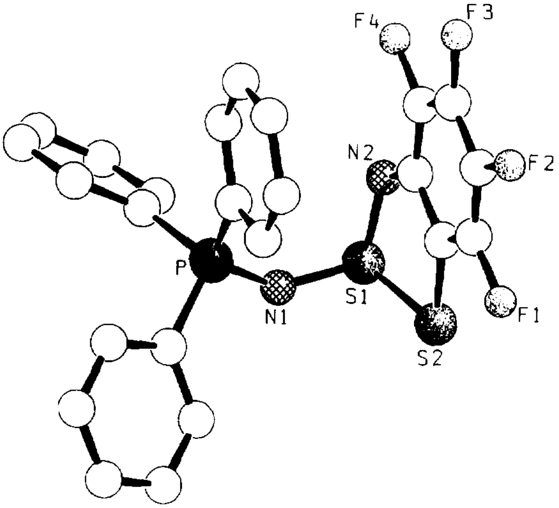


Fig. 34. Molecular structure of $Ph_3PN(S_2NC_6F_4)$.

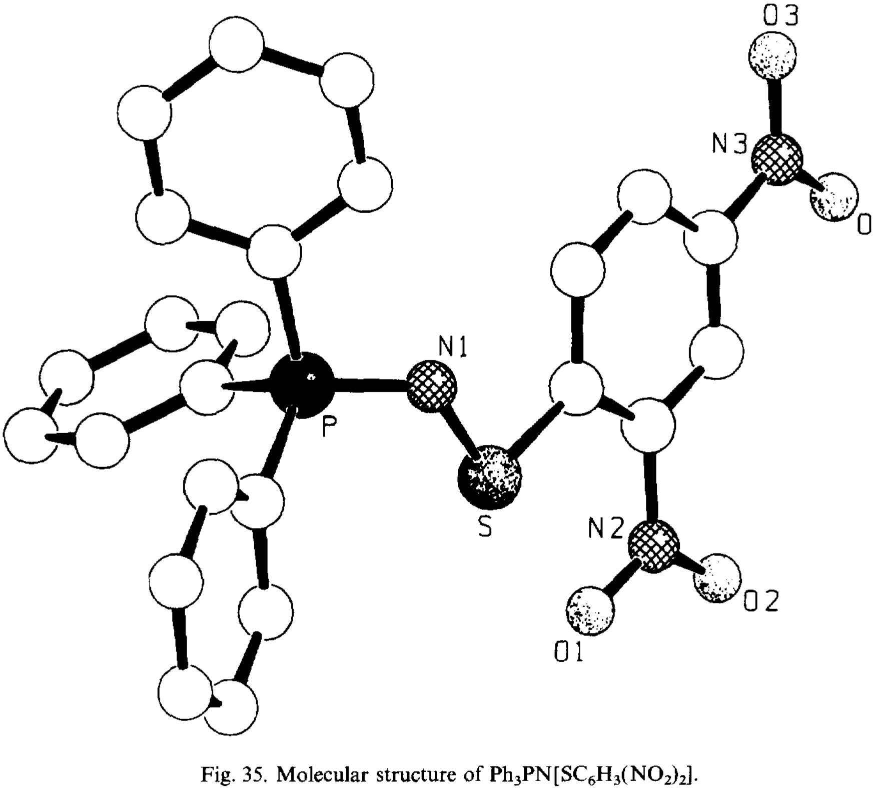


Fig. 35. Molecular structure of $Ph_3PN[SC_6H_3(NO_2)_2]$.

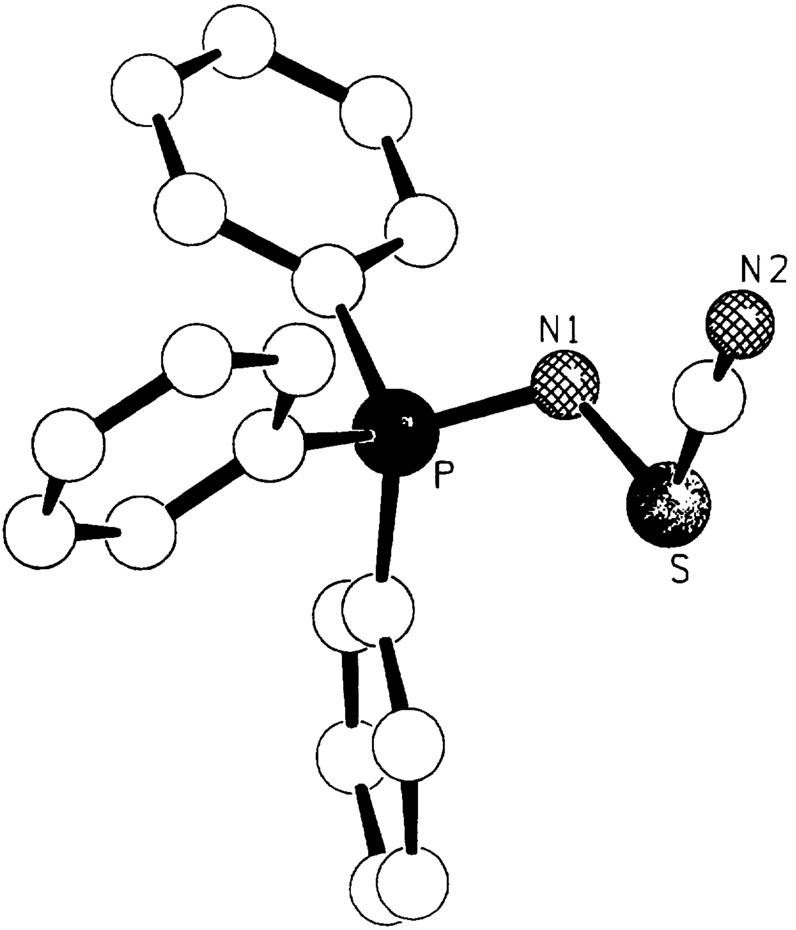
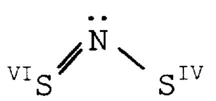


Fig. 36. Molecular structure of $Ph_3PN(SCN)$.

of trithiazylchloride with $Me_3SiNPMe_3$ in acetonitrile, which surprisingly leads to a mixed valent phosphorane iminato dication containing a nitrido bridge [145]:

$$(NSCl)_3 + Me_3SiNPMe_3 \rightarrow [(Me_3PN)_2SNS(NPMe_3)_3]Cl_2 + ClSiMe_3 + \ldots \quad (49)$$

The assignment of the oxidation numbers +IV to the atom S1 and +VI to S2 is consistent with the geometrical array, as S1 has a pyramidal environment owing to the stereochemical activity of the lone pair [145] (Fig. 37). At the same time, the SN distances of the SNS bridge are of different length (157.0 pm at S^{VI} and 167.1 pm at S^{IV}) as expressed in the formulation



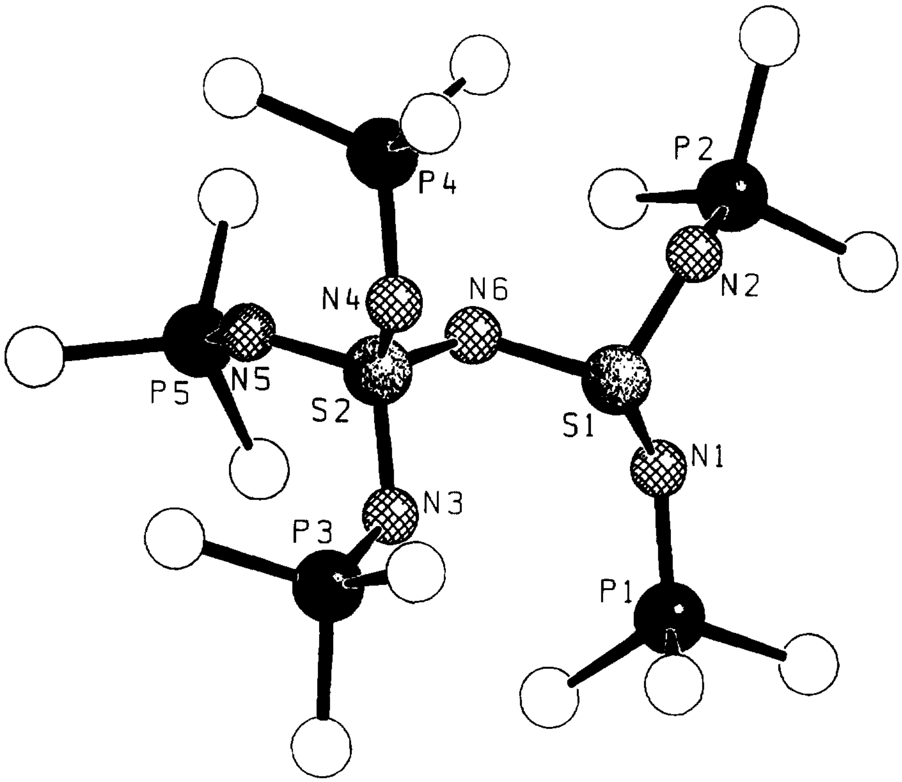


Fig. 37. View of the dication $[(Me_3PN)_2SNS(NPMe_3)_3]^{2+}$ in the structure of $[(Me_3PN)_2SNS(NPMe_3)_3]Cl_2$.

Table 1
Calculated structure data and results of the NBO analysis of $S(NPH_3)_4^{2+}$

Quantity[a]	Variable	(S_4)
r	N-S	156.7
r	N-P	163.7
ϑ	N-S-N	109.5
ϑ	S-N-P	122.6
q	S	+2.64
q	N	−1.47
q	P	+1.27
%N	N-S	64.2
Hybr. (N)	N-S	$sp^{2.20}d^{0.01}$
Hybr. (S)	N-S	$sp^{2.91}d^{0.09}$
%N	N-P	71.0
Hybr. (N)	N-P	$sp^{2.11}d^{0.01}$
Hybr. (P)	N-P	$sp^{2.76}d^{0.07}$

[a] Interatomic distances r (pm); bond angles ϑ (deg); partial charges q; %N, orbital share of the N-S and N-P bonds; hybridization of the bonding orbitals of N, S, and P in the N-S and N-P bonds.

Last, but not least, the SN bonds of the $NPMe_3$ groups at the S^{IV} atom (S1) (160.6 pm) are somewhat longer than at the S^{VI} atom (S2) (156.7 pm) (average values). A similar situation is found in the dication of hexavalent sulphur $[S(NPMe_3)_4]^{2+}$, which is obtained as the chloride salt from disulphur dichloride and the silylated phosphorane imine $Me_3SiNPMe_3$ in boiling acetonitrile forming colourless needles (Eq. (50)) [146].

$$3S_2Cl_2 + 4Me_3SiNPMe_3 \rightarrow [S(NPMe_3)_4]Cl_2 + \tfrac{5}{8}S_8 + 4ClSiMe_3 \qquad (50)$$

From the crystal structure analysis [146] the dication is known to have S_4 symmetry (Fig. 38). The S atom is tetrahedrally surrounded by the N atoms of the $NPMe_3$ groups with SN distances of 156.5 pm, which about correspond to double bonds. The PN bonds with distances of 162.1 pm can also be understood as approximate double bonds; the SNP bond angles of 122.3° go with sp^2 hybridization. The

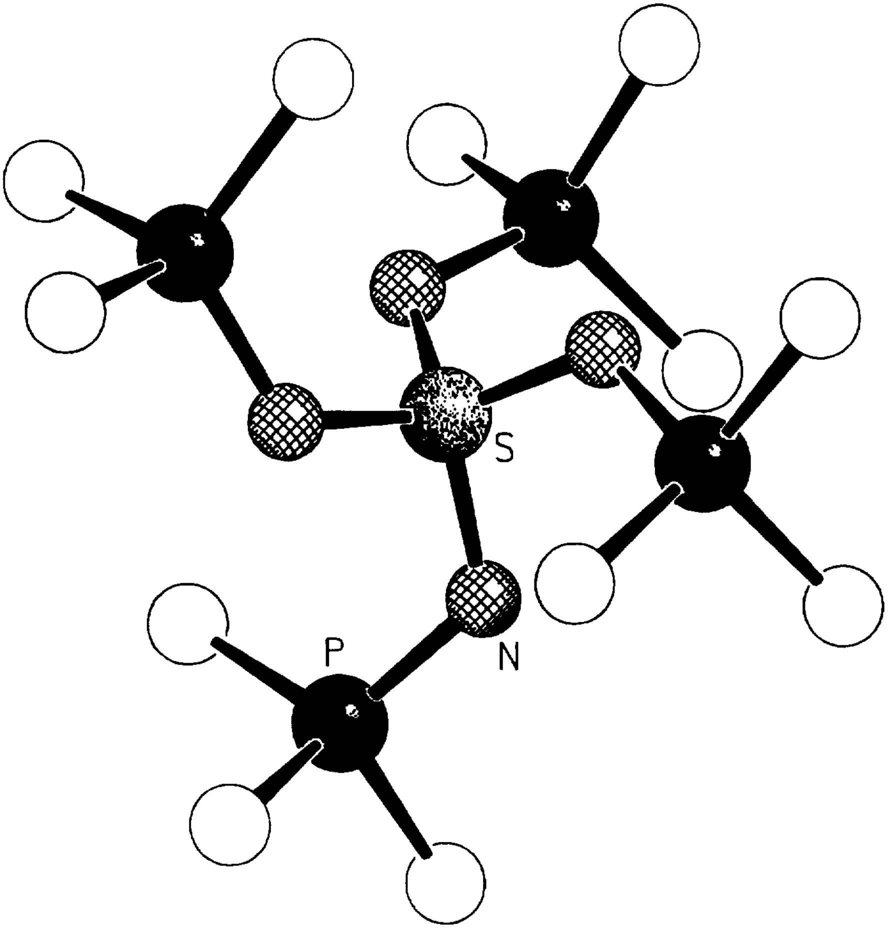


Fig. 38. View of the dication $[S(NPMe_3)_4]^{2+}$ in the structure of $[S(NPMe_3)_4]Cl_2 \cdot 4CH_3CN$.

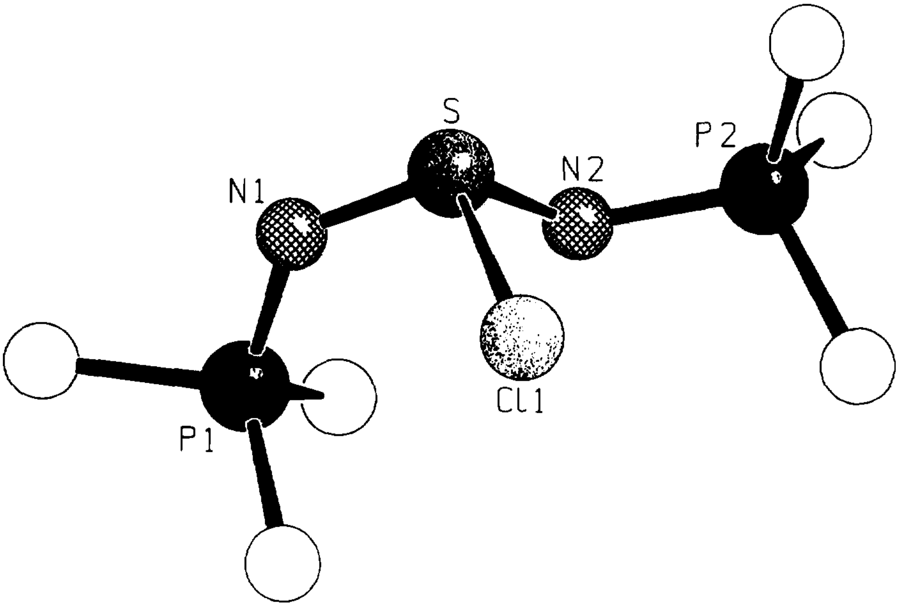


Fig. 39. View of the cation $[SCl(NPMe_3)_2]^+$ in the structure of $[SCl(NPMe_3)_2]Cl$.

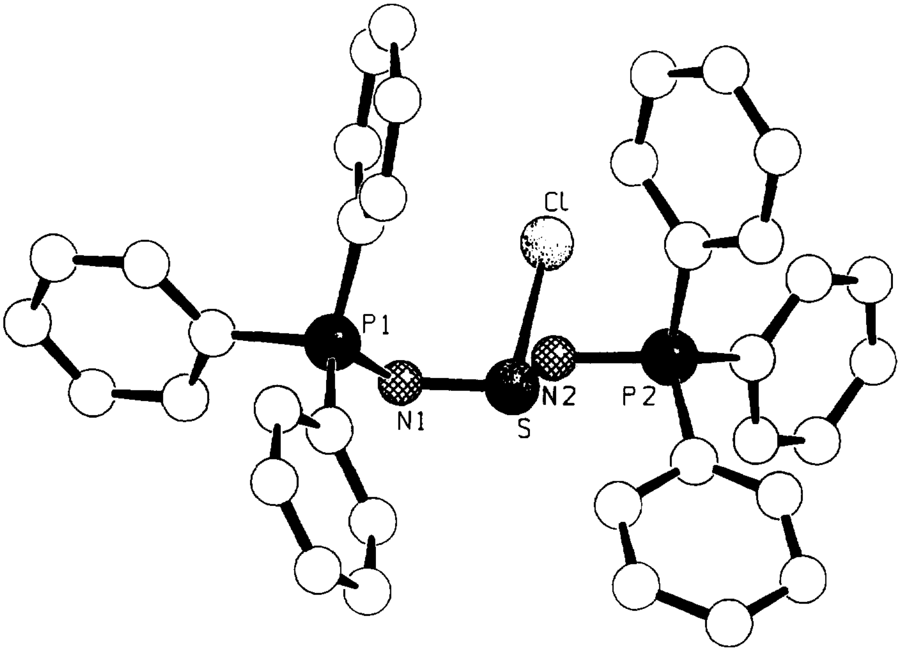


Fig. 40. View of the cation $[SCl(NPPh_3)_2]^+$ in the structure of $[SCl(NPPh_3)_2]Cl$.

geometric data determined experimentally at the $[S(NPMe_3)_4]^{2+}$ ion are in good agreement with those of the hypothetical ion $[S(NPH_3)_4]^{2+}$ known from ab initio calculations [146] (Table 1). The analysis of bonding with the NBO method yielded a strongly positive partial charge at the S atom (+2.64) and at the P atoms (+1.27) and a negative partial charge at the N atoms (−1.47). For the NS and NP bonds a single bond is calculated with strong polarization in the direction of the more electronegative N atom (Table 1).

Thus, bonding in the $[S(NPMe_3)_4]^{2+}$ ion can be understood as polar covalent single bonds with a tendency to double bonds owing to the strong charge attraction between the nitrogen atoms with a negative charge and the phosphorus and sulphur atoms with their positive charge. It can be assumed that this bonding model holds for the phosphorane iminato derivatives of the chalcogens as well.

In the literature, one more phosphorane iminato complex of hexavalent sulphur is mentioned: $[S(NPPh_3)_3]Cl_3$, which is one of the products in the reaction of S_4N_3Cl with PPh_3; however, no detailed information is given [136,147].

In contrast, several cationic phosphorane iminato complexes are described of tetravalent sulphur whose tendency to form SX_3^+ cations with numerous ligand groups X^- is well known [148]. The bis(phosphorane iminato) compounds $[SCl(NPR_3)_2]Cl$ with R = Me, Ph are obtained from sulphur chlorides with the corresponding silylated phosphorane imines in acetonitrile solution [149,150]:

$$3SCl_2 + 2Me_3SiNPPh_3 \rightarrow [SCl(NPPh_3)_2]Cl + 2ClSiMe_3 + S_2Cl_2 \qquad (51)$$

$$2S_2Cl_2 + 2Me_3SiNPMe_3 \rightarrow [SCl(NPMe_3)_2]Cl + 2ClSiMe_3 + \tfrac{3}{8}S_8 \qquad (52)$$

In both compounds the cations have a pyramidal structure (Figs. 39 and 40) with strikingly long SCl bond lengths of 246.9 pm (R = Me) and 248.5 pm (R = Ph) [149,150].

The anticipated substitution by a third NPR_3 group was realized by reaction of SCl_2 with excess $Me_3SiNPMe_3$ in dichloromethane solution at 0 °C [151] or the reaction with $S_3N_2Cl_2$ in dichloromethane solution [151]:

$$S_3N_2Cl_2 + Me_3SiNPMe_3 \rightarrow [S(NPMe_3)_3]Cl + ClSiMe_3 + \ldots \qquad (53)$$

The related phenyl compound $[S(NPPh_3)_3]Cl$ is obtained from sulphur dichloride and $Me_3SiNPPh_3$ in boiling dichloromethane, cf. Eq. (51); by metathesis with $n\text{-}Bu_4N^+S_4N_5^-$ it is transformed into $[S(NPPh_3)_3]S_4N_5$ [136]:

$$SCl_2 + Me_3SiNPPh_3 \rightarrow [S(NPPh_3)_3]Cl \rightarrow [S(NPPh_3)_3]S_4N_5 \qquad (54)$$

This compound is also attained directly by reaction with trithiazyl chloride in acetonitrile at 20 °C [151]:

$$(NSCl)_3 + Me_3SiNPPh_3 \rightarrow [S(NPPh_3)_3]S_4N_5 + ClSiMe_3 + \ldots \qquad (55)$$

The methyl compound as well as the phenyl compound are of the expected pyramidal structure [151] (Figs. 41 and 42). The average SN distances of 162.5 pm in the methyl derivative are significantly longer than in the $[SCl(NPMe_3)_2]^+$ ion

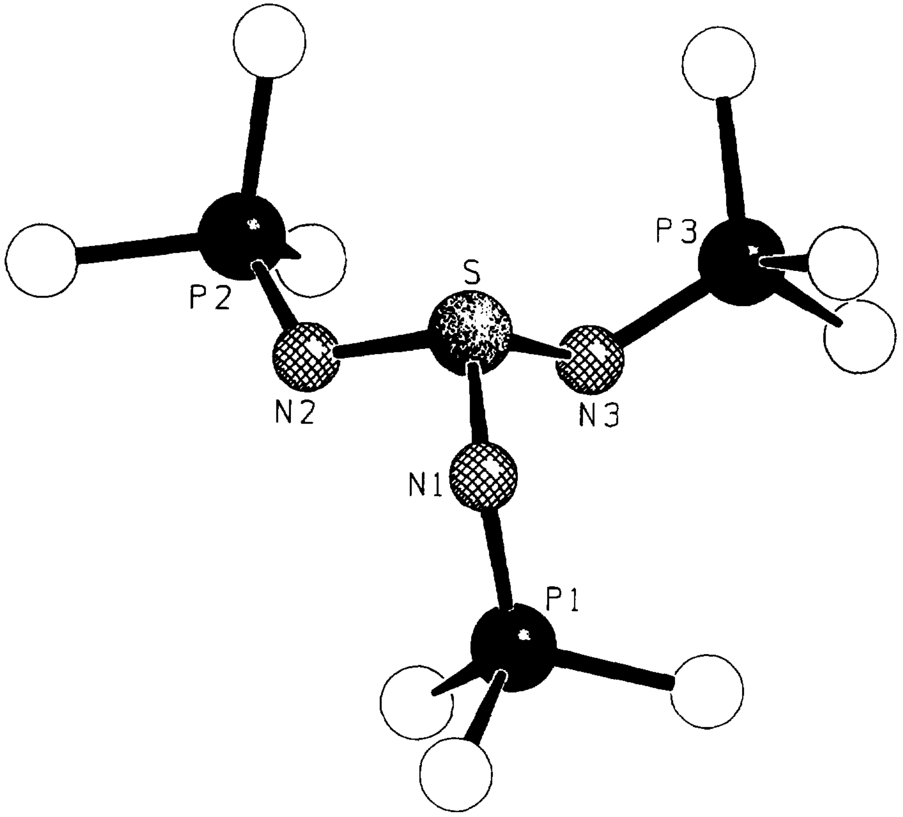


Fig. 41. View of the cation $[S(NPMe_3)_3]^+$ in the structure of $[S(NPMe_3)_3]Cl \cdot CH_2Cl_2$.

(152.5 pm, see above), the short SN distances of which are presumably made possible by the long SCl bond. The phenyl derivative $[S(NPPh_3)_3]S_4N_5^-$, however, exhibits only slight differences to $[SCl(NPPh_3)_2]Cl$ (see above). The structure determination of $[S(NPPh_3)_3]S_4N_5$ was hampered by severe disorder of the anion (cf. Ref. [136]).

In contrast to the reactions of silylated phosphorane imines with sulphur chlorides and sulphur nitrides, equivalent reactions with the oxychlorides thionyl chloride [149,150], sulphuryl chloride [149] and tosyl chloride [152] yield phosphorane iminato complexes with monomeric molecular structures. $[SO_2(Cl)(NPPh_3)]$, as well as tol–$SO_2(NPPh_3)$ [152] have a tetrahedral environment at the S atom (Fig. 43). Its SN bond of 154.5 pm is as short as that of the molecular complex $[SO(Cl)(NPPh_3)]$ [149], which is a pyramidal array at the sulphur atom, as expected (Fig. 44). A pyramidal structure, but distinctly longer SN distances of 165.5 pm, is found in the molecular complex $[SO(NPPh_3)_2]$ [150] (Fig. 45).

Worth noticing is the reaction of $Me_3SiNPPh_3$ with sulphur dioxide in acetonitrile [150]:

$$2Me_3SiNPPh_3 + 2SO_2 \rightarrow [O_3S\text{–}S(NPPh_3)_2] + O(SiMe_3)_2 \qquad (56)$$

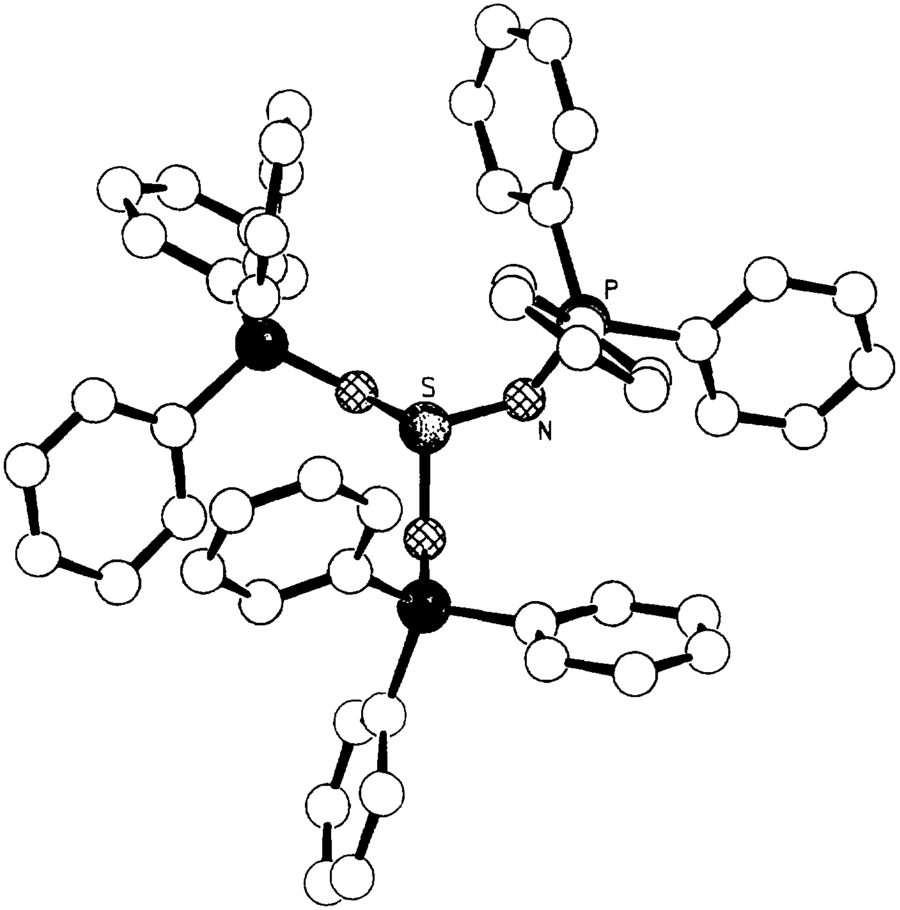
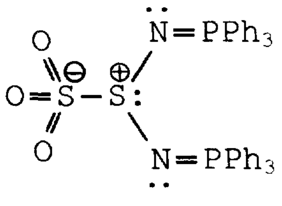


Fig. 42. View of the cation $[S(NPPh_3)_3]^+$ in the structure of $[S(NPPh_3)_3]S_4N_5$.

The compound has the molecular structure shown in Fig. 46, which can be understood as a zwitterion with the formal oxidation states +III at S1 and +V at S2 [150].



The SS bond of 218.2 pm is little shorter than in $K_2S_2O_5$ (220.9 pm [153]), and not much longer than in various dithionates $S_2O_6^{2-}$ (about 215 pm [154]). The SO bonds of 143.7 pm correspond to those in $O_3S^{\oplus}-{}^{\ominus}NH_3$ (142–145 pm [155]), but the SN

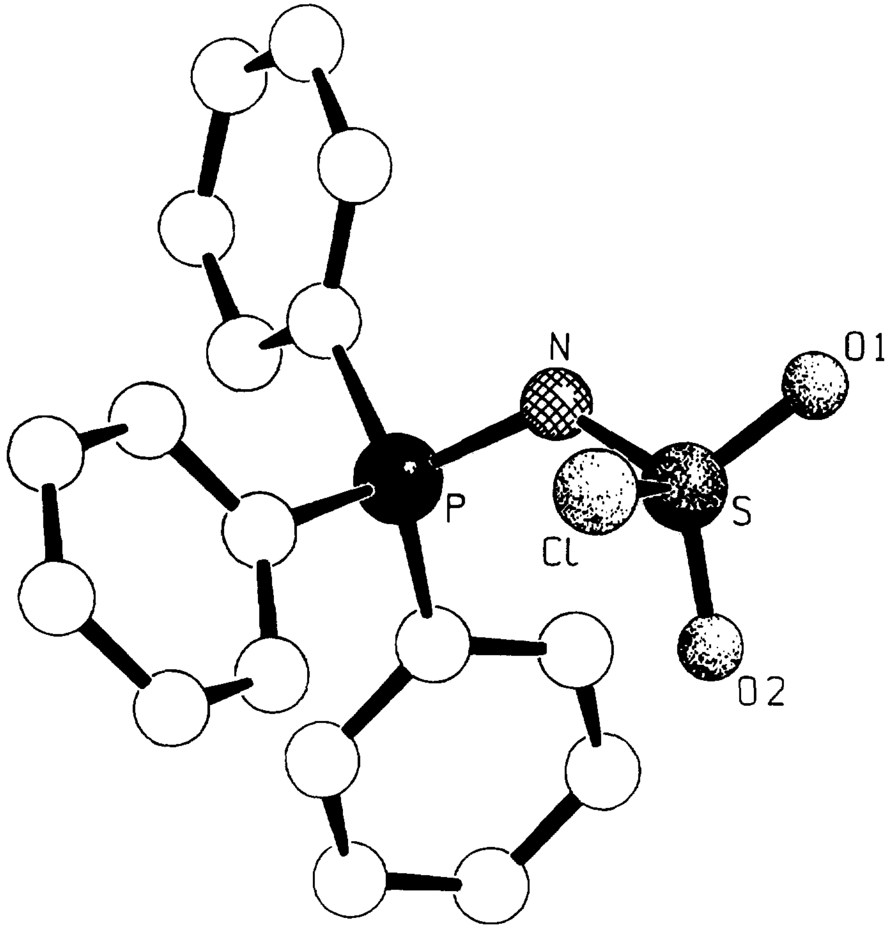


Fig. 43. Molecular structure of Ph_3PNSO_2Cl.

bonds of 161.2 pm are somewhat longer than in other phosphorane iminato complexes of sulphur(IV).

6.2. Selenium compounds

Two aspects dominate the chemistry of selenium phosphorane iminato complexes. The first is the strong solvent dependence of the synthetic procedures when applying silylated phosphorane imines on SeO_2, $SeOCl_2$ and $SeCl_4$. The second is the dependence on the inductive properties of the substituents tied to the phosphorus atom.

Thus, $Me_3SiNPPh_3$ reacts with diselenium dichloride at −78 °C in toluene yielding the molecular complex $SeCl_2(NPPh_3)_2$ [156]

$$Se_2Cl_2 + 2Me_3SiNPPh_3 \xrightarrow{\text{Toluene}} SeCl_2(NPPh_3)_2 + Se + 2ClSiMe_3 \quad (57)$$

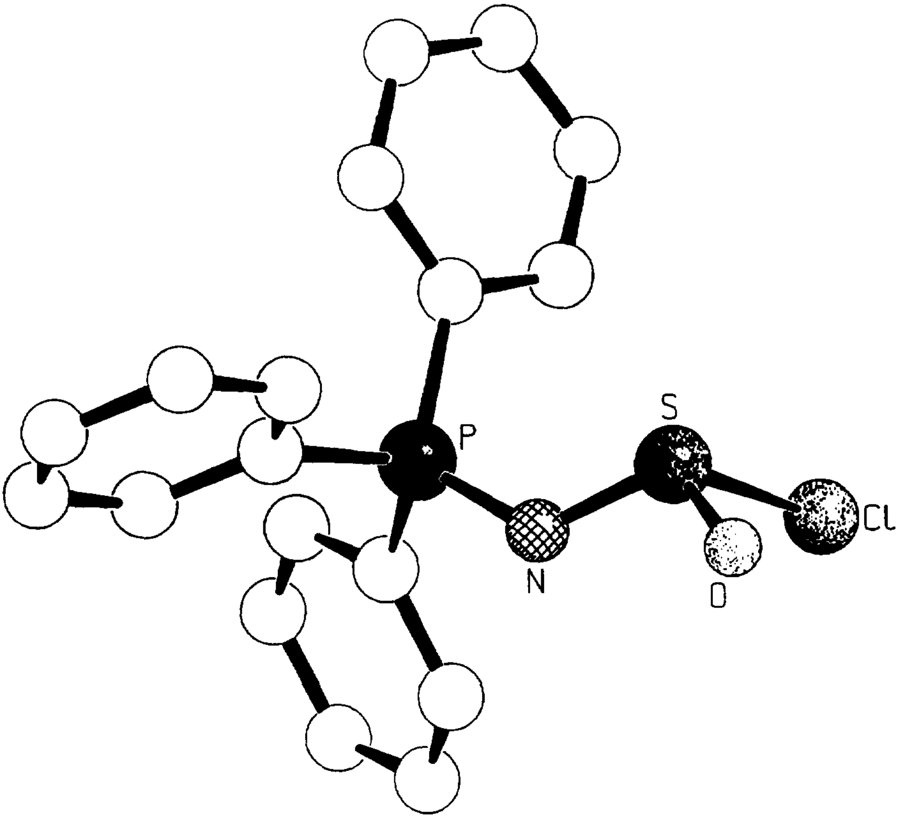


Fig. 44. Molecular structure of $Ph_3PNSOCl$.

in acetonitrile at 20 °C; however, the complex $[SeCl(NPPh_3)_2]^+SeCl_3^-$ is formed with an ionic structure (Eq. (58)) [157].

$$3Se_2Cl_2 + 2Me_3SiNPPh_3 \xrightarrow{\text{Acetonitrile}} [SeCl(NPPh_3)_2]^+SeCl_3^- + 4Se + 2ClSiMe_3 \tag{58}$$

The cation was also obtained as a hexachloro antimonate from Eq. (59) [156]:

$$SeCl_2(NPPh_3)_2 + SbCl_5 \rightarrow [SeCl(NPPh_3)_2]^+SbCl_6^- \tag{59}$$

The phosphorane iminato complexes of tetravalent selenium are also accessible directly from selenium tetrachloride in boiling toluene, with stepwise substitution [156]:

$$SeCl_4 \xrightarrow[-ClSiMe_3]{Me_3SiNPPh_3} SeCl_3(NPPh_3) \xrightarrow[-ClSiMe_3]{Me_3SiNPPh_3} SeCl_2(NPPh_3)_2 \tag{60}$$

Finally, the doubly substituted derivative is also obtained from selenyl chloride in

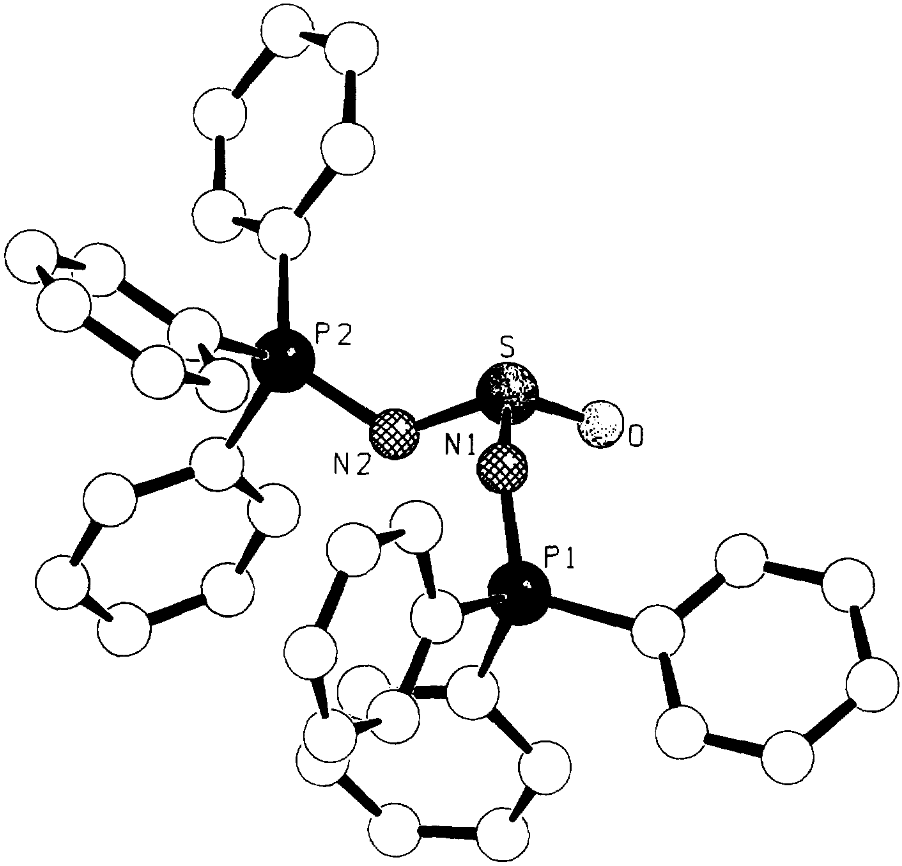


Fig. 45. Molecular structure of $(Ph_3PN)_2SO$.

toluene at 20 °C [156] according to Eq. (61):

$$SeOCl_2 + 2Me_3SiNPPh_3 \rightarrow SeCl_2(NPPh_3)_2 + O(SiMe_3)_2 \qquad (61)$$

The functionalized phosphorane iminato complex $[SeCl_2(NPPh_2NS(O)Me_2)_2]$ [158], in which a monomeric molecular structure is realized, has been produced in an analogous way. In it, the selenium atom has a φ-trigonal bipyramidal surrounded by the chlorine atoms in the axial positions [158].

Triple substitution of selenium tetrachloride is achieved with the aid of the silylated methyl derivative $Me_3SiNPMe_3$ in acetonitrile solution at 20 °C (Eq. (62)) [151]:

$$SeCl_4 + 3Me_3SiNPMe_3 \rightarrow [Se(NPMe_3)_3]Cl + 3ClSiMe_3 \qquad (62)$$

Another example of the influence of the inductive effect of the substituents at the phosphorus atom on the process of reactions can be taken from a comparison of the reactions of selenium dioxide with the silylated phosphorane imines

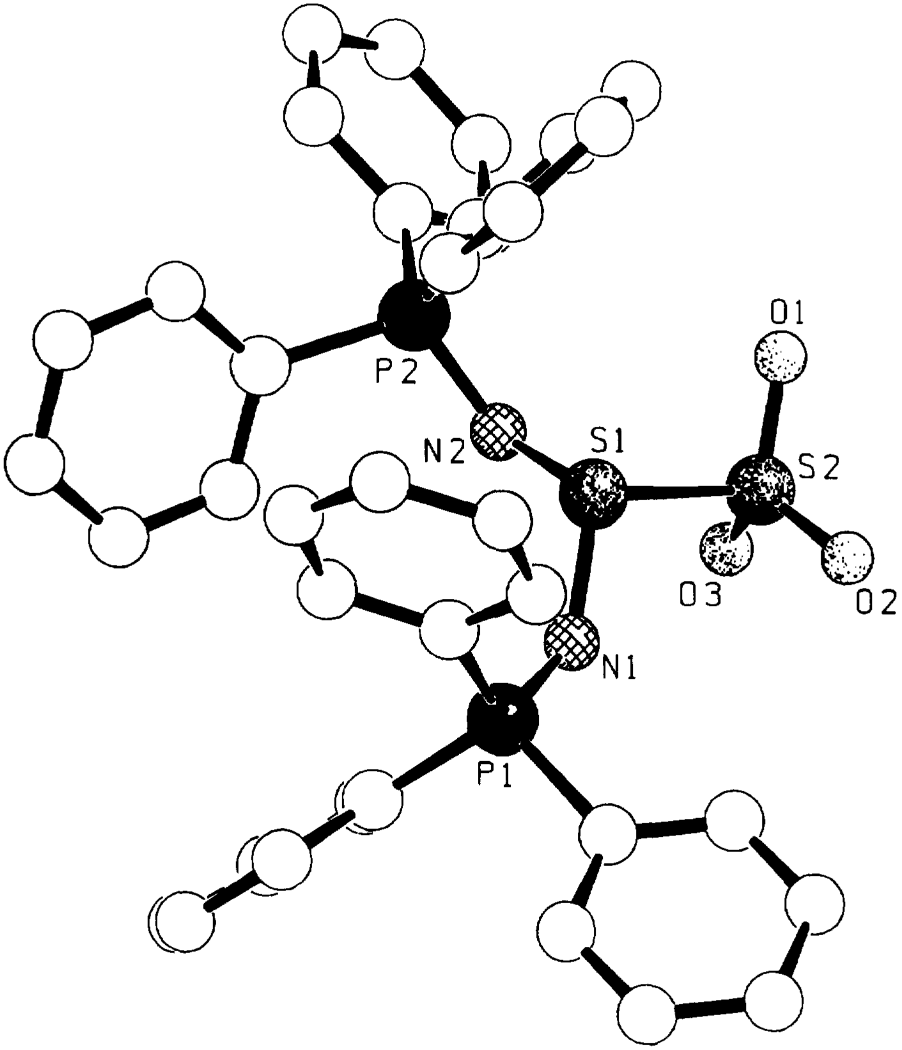


Fig. 46. Molecular structure of O_3S–$S(NPPh_3)_2$.

$Me_3SiNPPh_3$ and $Me_3SiNPMe_3$. Whereas the phenyl derivative reacts smoothly in acetonitrile suspension giving the selenyl compound in Eq. (63) [159], with

$$SeO_2 + 2Me_3SiNPPh_3 \rightarrow [SeO(NPPh_3)_2] + O(SiMe_3)_2 \qquad (63)$$

the methyl derivative tetraselenium tetranitride is formed in a slow reaction Eq. (64) [160]:

$$3SeO_2 + 4Me_3SiNPMe_3 \rightarrow \tfrac{1}{2}Se_4N_4 + Se + O(SiMe_3)_2 + 4OPMe_3 + N_2 \qquad (64)$$

The reaction in Eq. (64) is presumably a two-step process, as red selenium sepa-

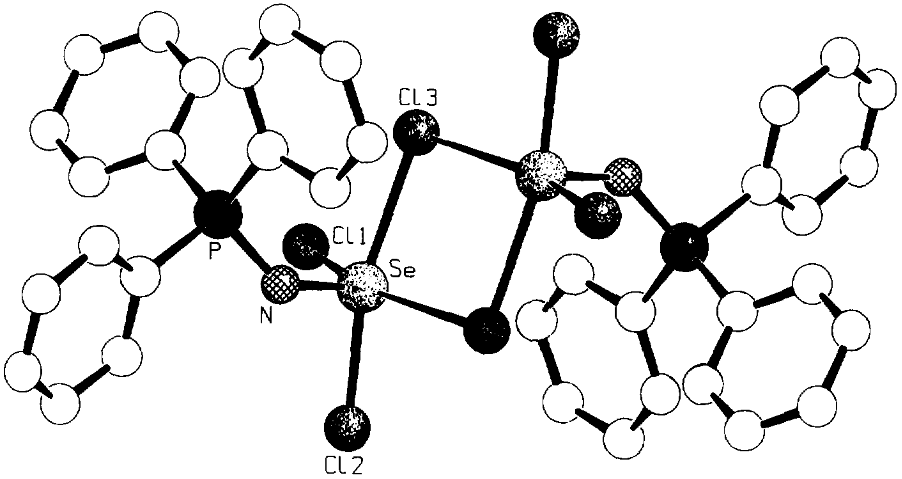


Fig. 47. Molecular structure of $[SeCl_3(NPPh_3)]_2$

rates very quickly and upon filtration of the selenium magnificent dark red single crystals of Se_4N_4 with very low solubility precipitate within a few days. The crystal structure analysis revealed a new modification [160], which is isotypic with S_4N_4 [137].

A determining feature in the structures of phosphorane iminato complexes of tetravalent selenium is the stereochemical activity of the lone pair. On the one hand, $SeCl_3(NPPh_3)$ [156] has a dimeric molecular structure associated via chloro bridges and with φ-octahedral surroundings of the selenium atoms where the $NPPh_3$ groups occupy axial positions (Fig. 47). On the other hand, $[SeCl_2(NPPh_3)_2]$ [156] exhibits, just like $[SeCl_2(NPPh_2NS(O)Me_2)_2]$ [158] mentioned above, a monomeric molecular structure with φ-trigonal bipyramidal environment and axial positions for the chlorine atoms (Fig. 48). In fact, the ClSeCl axis is severely distorted from linearity (149.9°).

A φ-tetrahedral environment of the selenium atom is found in the selenyl complex $[SeO(NPPh_3)_2]$ [159] (Fig. 49). Like in other bis(phosphorane iminato) complexes of selenium(IV) [156,158] the atoms PNSeNP are practically coplanar. A φ-tetrahedral environment is also exhibited by the selenium atoms in the ionic phosphorane iminato complexes $[SeCl(NPPh_3)_2]^+SeCl_3^-$ [157], the anion of which is the first monomeric, T-shaped $SeCl_3^-$ ion characterized crystallographically (Fig. 50), as well as in $[Se(NPMe_3)_3]^+Cl^-$ [151] (Fig. 51).

In all cases the observed SeN distances are shorter than the values expected for a covalent SeN single bond. According to Pauling [161], and considering the Schomaker–Stevenson correction [162], a value of 186 pm is calculated and a Se=N double bond should amount to 164 pm. Not much longer than this latter value expected for an SeN double bond are the SeN distances in $[SeCl_3(NPPh_3)]_2$ (168.4 pm

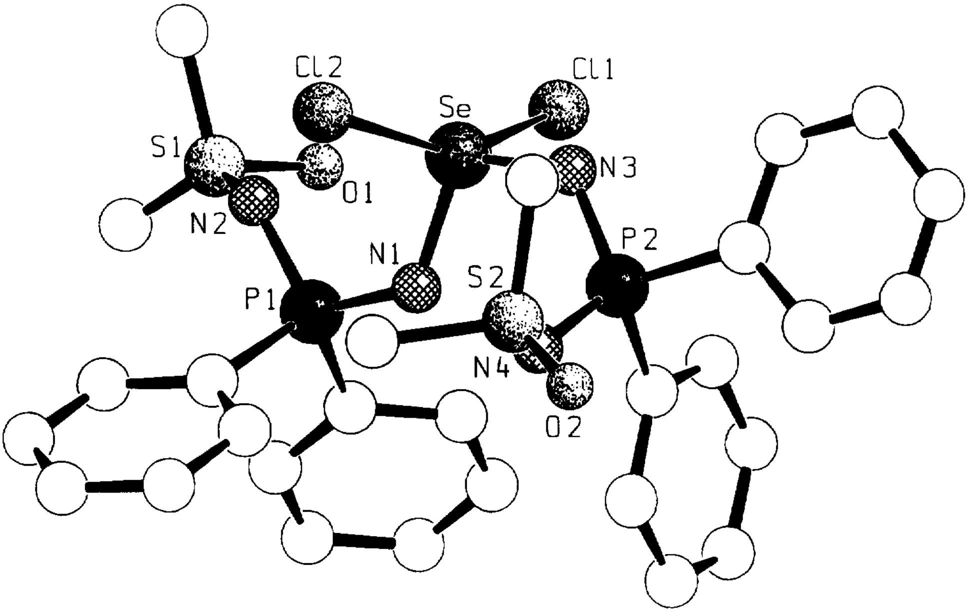


Fig. 48. Molecular structure of $SeCl_2(NPPh_2NS(O)Me_2)$.

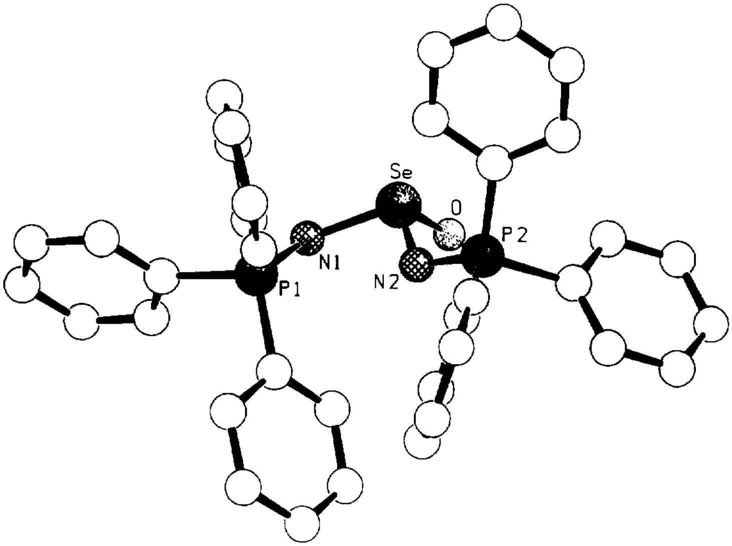


Fig. 49. Molecular structure of $SeO(NPPh_3)_2$.

[156]), in $[SeCl_2(NPPh_3)_2]$ (173.5 pm [156]) and in $[SeCl(NPPh_3)_2]SeCl_3$ (174.5 and 171.5 pm [157]), whereas they rather correspond to shortened single bonds in $[SeO(NPPh_3)_2]$ (179.9 and 181.6 pm [159]) and in $[Se(NPMe_3)_3]Cl$ (177.8 pm [151]). For the discussion of SeN and TeN bonds, see the review in Ref [163].

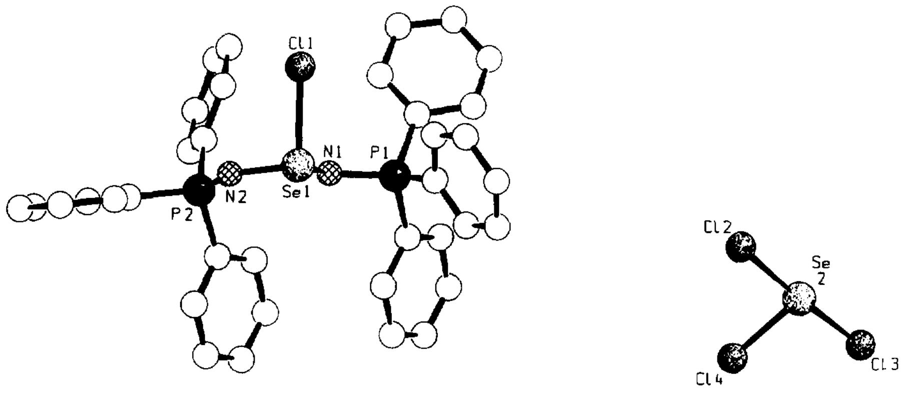


Fig. 50. Structure of $[SeCl(NPPh_3)_2]^+SeCl_3^-$.

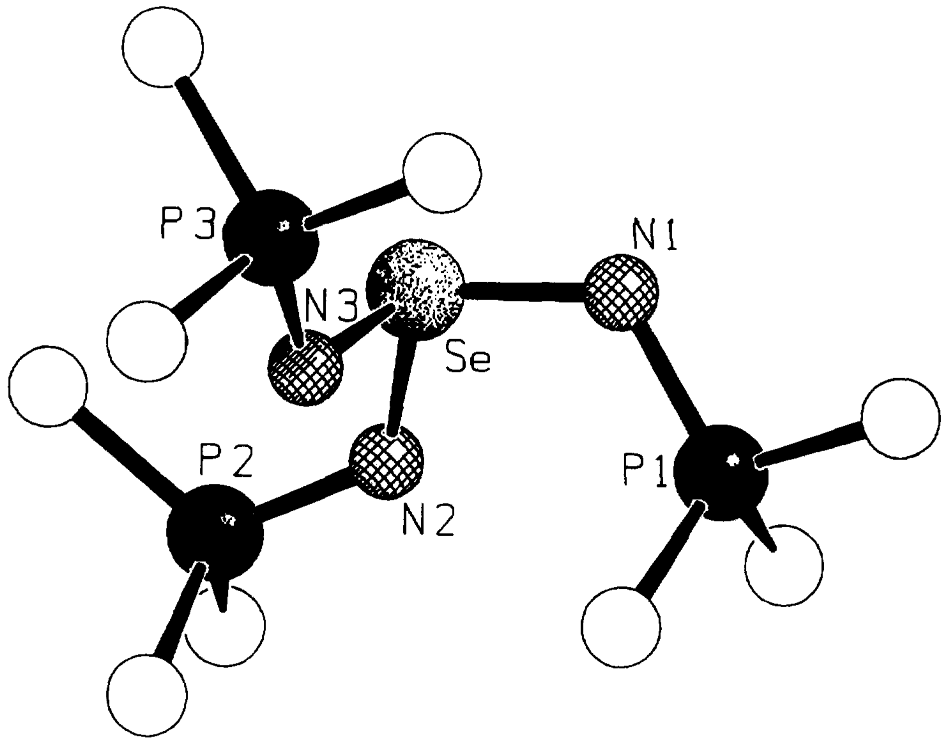


Fig. 51. View of the cation $[Se(NPMe_3)_3]^+$ in the structure of $[Se(NPMe_3)_3]Cl \cdot C_7H_8$.

6.3. Tellurium compounds

The phosphorane iminato complexes known of tellurium are derived from tellurium tetrachloride, which can be substituted step-by-step with silylated phosphorane imines. Thus, in toluene suspension $TeCl_4$ and $Me_3SiNPPh_3$ react forming the derivatives $[TeCl_3(NPPh_3)]_2$ [164] and $[TeCl_2(NPPh_3)_2]$ [165], whereas *p*-methoxyphenyl tellurium trichloride in toluene at 80 °C only yields the monosubstituted product $[MeO–C_6H_4–TeCl_2(NPPh_3)]$ [165]. $[TeCl_2(NPPh_3)_2]$ is easily recrystallized from pyridine without solvation. Its monomeric molecular structure can be understood as a distorted φ-trigonal bipyramid with the chlorine atoms in the axial positions [165] (Fig. 52).

The deviation of the ClTeCl axis from linearity is significant (162.7°). The short TeN bonds (average 191.8 pm) are noticeably shorter than the value expected for a Te–N single bond (199 pm [166]). Just as short is the TeN bond in the *p*-methoxy derivative $[MeO–C_6H_4–TeCl_2(NPPh_3)]_2$ [165], which has a centrosymmetrical structure linked via chloro bridges, the tellurium atoms being of φ-octahedral environment (Fig. 53).

Very short TeN bonds of 190.1 and 192.6 pm are also observed in the methyl

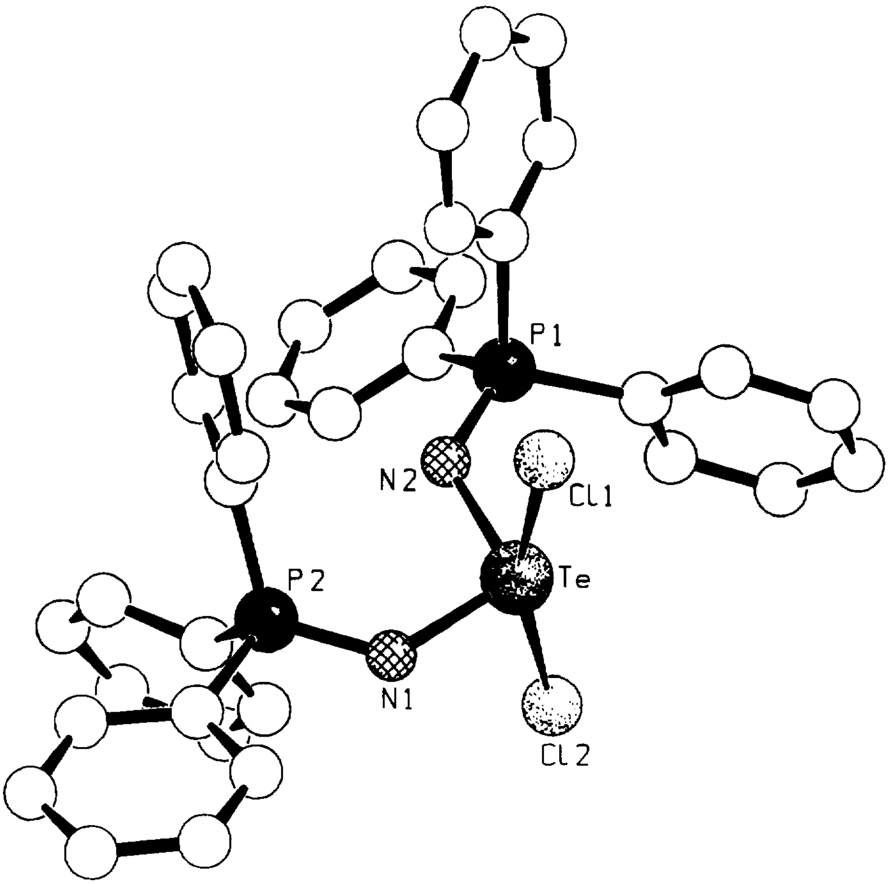


Fig. 52. Molecular structure of $TeCl_2(NPPh_3)_2$.

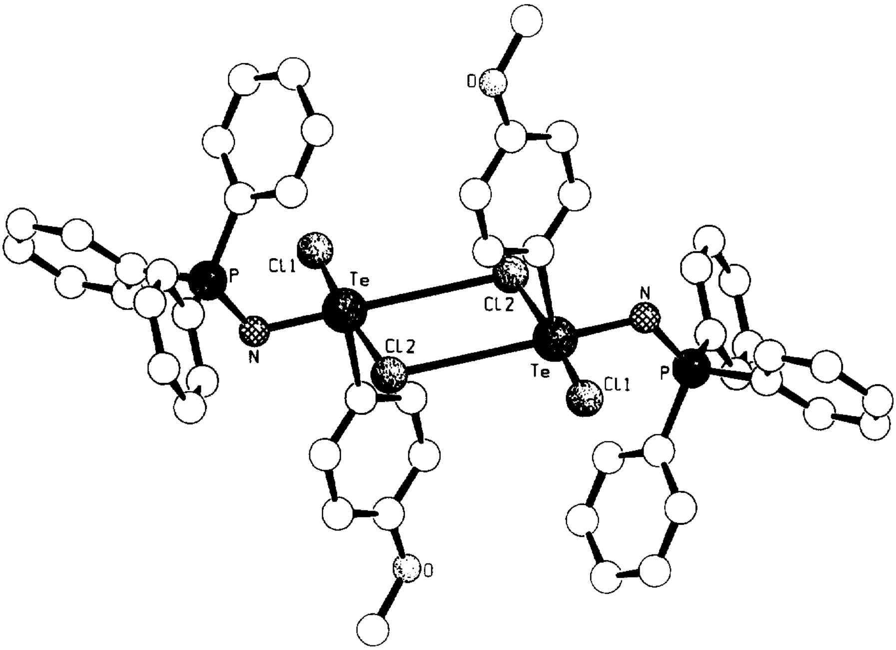


Fig. 53. Molecular structure of $[MeOC_6H_4\text{-}TeCl_2(NPPh_3)]_2$.

derivative $[TeCl_2(NPMe_3)_2]_2$ [167] which, in contrast to the monomeric phenyl compound $[TeCl_2(NPPh_3)_2]$ (see above), is linked to a centrosymmetric dimer via strongly asymmetric chloro bridges (Fig. 54). As a consequence of the stereochemically active lone pair the tellurium atoms achieve a distorted tetragonal surrounding.

In contrast, the mono(phosphorane iminato) complex $[TeCl_3(NPPh_3)]_2$ [164] is linked to a dimer via the N atoms of the $NPPh_3$ groups with TeN distances of 199.6 and 228.2 pm (Fig. 55). The shorter one of the TeN bonds is situated in trans-position to the lone pair at the tellurium atom; it is of the expected value for a covalent single bond [166]. However, the longer TeN bond of the Te_2N_2 four-membered ring must be interpreted as an interaction of the donor–acceptor type.

An interesting synthetic variation of phosphorane iminato complexes of tellurium has just recently been reported [168]. The reaction (Eq. (65)) proceeds in two steps

$$Li(THF)_2[Ph_2P(NSiMe_3)_2] \xrightarrow[-LiCl]{TeCl_4} Ph_2P(NSiMe_3)_2TeCl_3 \xrightarrow[-LiCl,\ -ClSiMe_3]{Li(THF)_2[Ph_2P(NSiMe_3)_2]}$$
$$Ph_2P(NSiMe_3)_2TeCl(NPPh_2NSiMe_3) \qquad (65)$$

first yielding the chelate complex $[Ph_2P(NSiMe_3)_2TeCl_3]_2$ (Fig. 56), in which the tellurium atom has a distorted octahedral environment [168]. The two TeN bonds of 205.6 and 218.5 pm are of distinctly different length, with the shorter bond being placed in trans-position to the lone pair. Correspondingly, the PN bonds are also different (166.2 and 160.8 pm) [168].

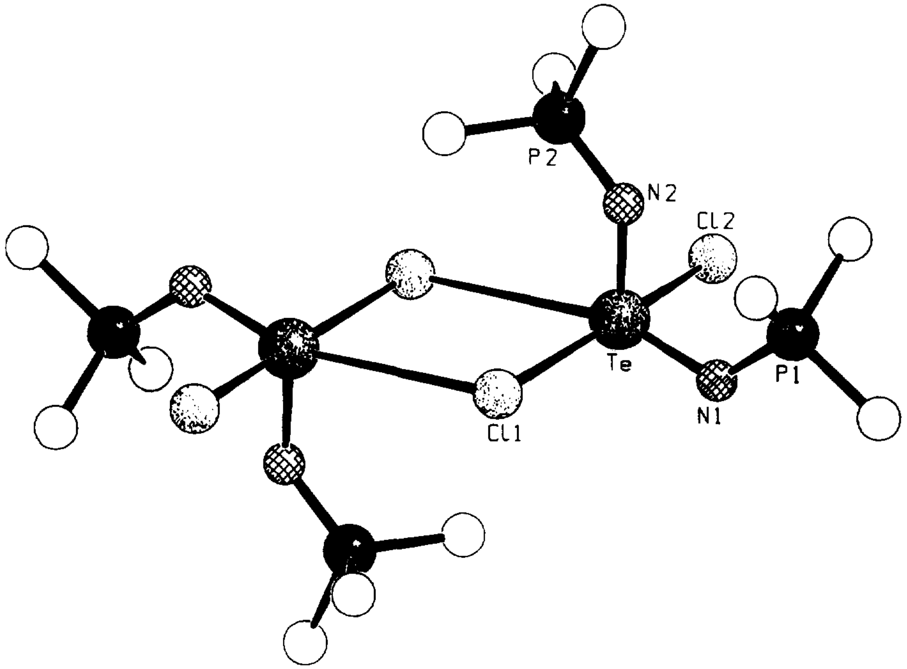


Fig. 54. Molecular structure of $[TeCl_2(NPMe_3)_2]_2$.

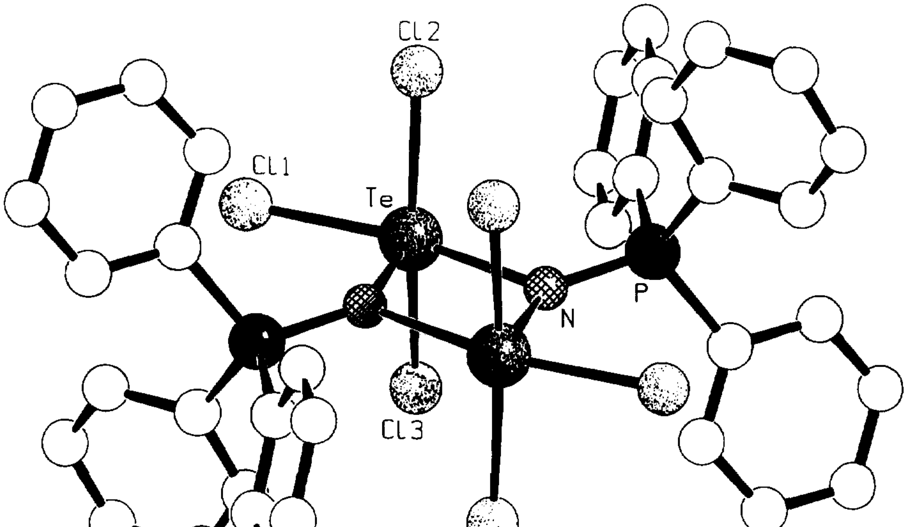


Fig. 55. Molecular structure of $[TeCl_3(NPPh_3)]_2$.

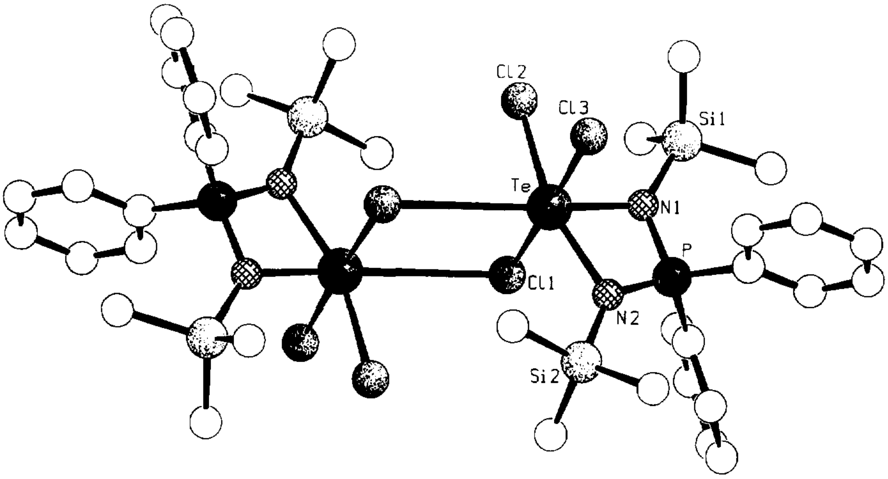


Fig. 56. Molecular structure of $[Ph_2P(NSiMe_3)_2TeCl_3]_2$.

In the second step of the reaction (Eq. (65)) two more chlorine atoms at the tellurium atom are simultaneously substituted and the monofunctionally bonded ligand $(NPPh_2NSiMe_3)^{2-}$ is introduced [168]. The tellurium atom now achieves a

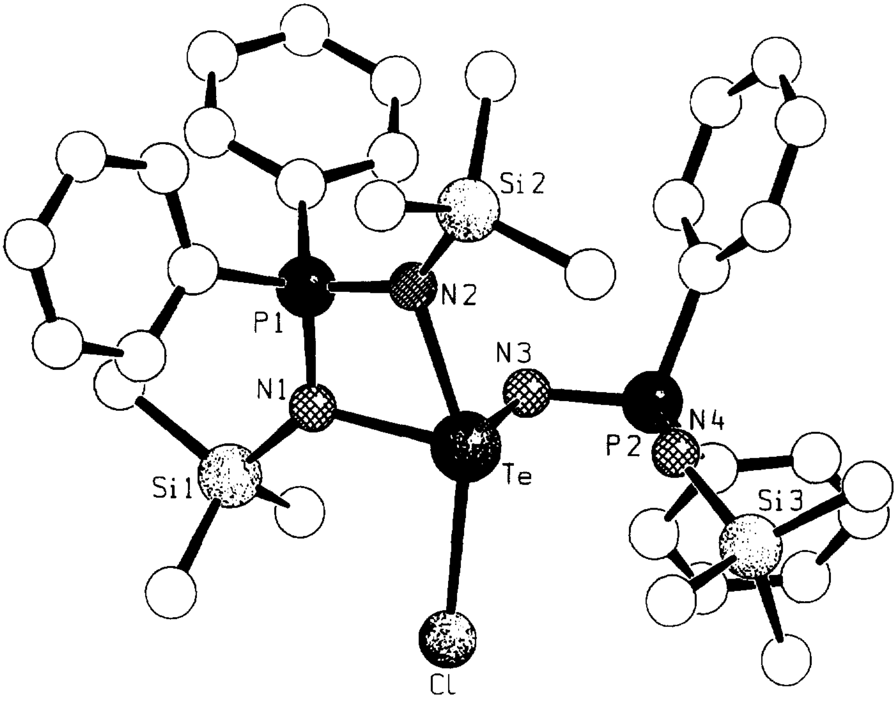


Fig. 57. Molecular structure of $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$.

distorted tetragonal surrounding (Fig. 57). The newly formed TeN bond of the $[NPPh_2NSiMe_3]^{2-}$ group with the length 192.2 pm is very short and causes an elongation of the trans-positioned TeN bond in the $PTeN_2$ four-membered ring to 227.5 pm [168].

The shortest TeN bond observed up to now (184 pm) has been found recently in the structure of $[(^tBuNH)(^tBuN)_3Te_2]Cl$ [169] and is interpreted as a double bond.

7. Phosphorane iminato complexes of Group XVII elements (Cl, Br, I)

The first records about phosphorane iminato complexes of the halogens came from the group of Appel, in which triphenylphosphorane imine was reacted with chlorine in benzene solution [103]:

$$2Ph_3P{=}NH + Cl_2 \rightarrow [Ph_3PNH_2]Cl + Ph_3P{=}NCl \qquad (66)$$

$Ph_3P{=}NCl$, which is soluble in benzene, was separated from the insoluble phosphonium salt and isolated as a yellow crystalline powder. The synthesis of the yellow bromine derivative is carried out in the same way [170], whereas for the synthesis of the orange-red iodine derivative iodine monochloride is preferred as a starting

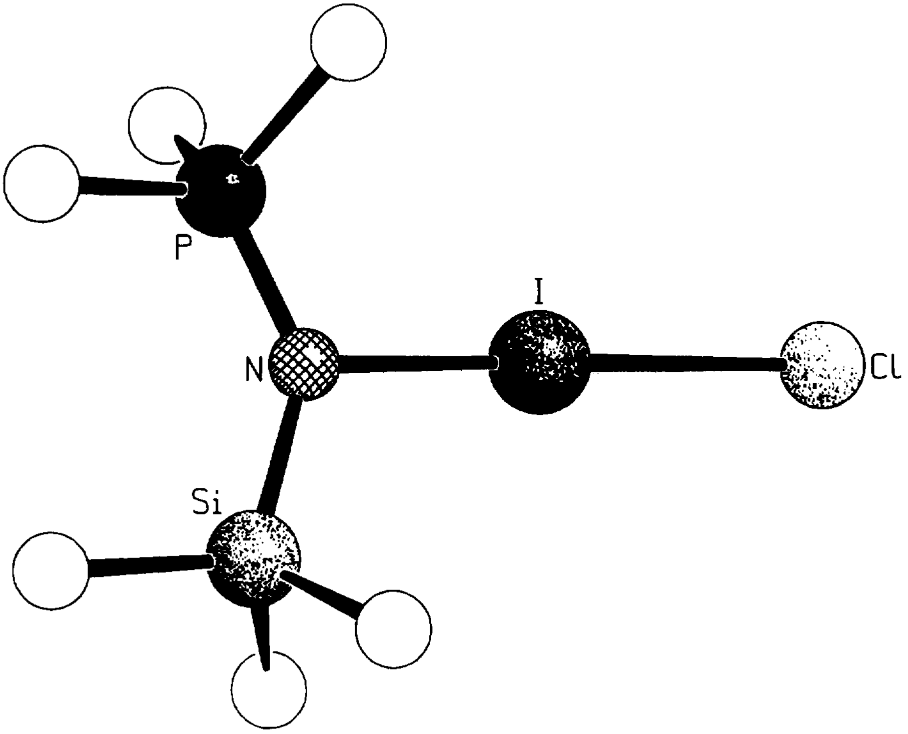


Fig. 58. Molecular structure of $Me_3PNSiMe_3 \cdot ICl$.

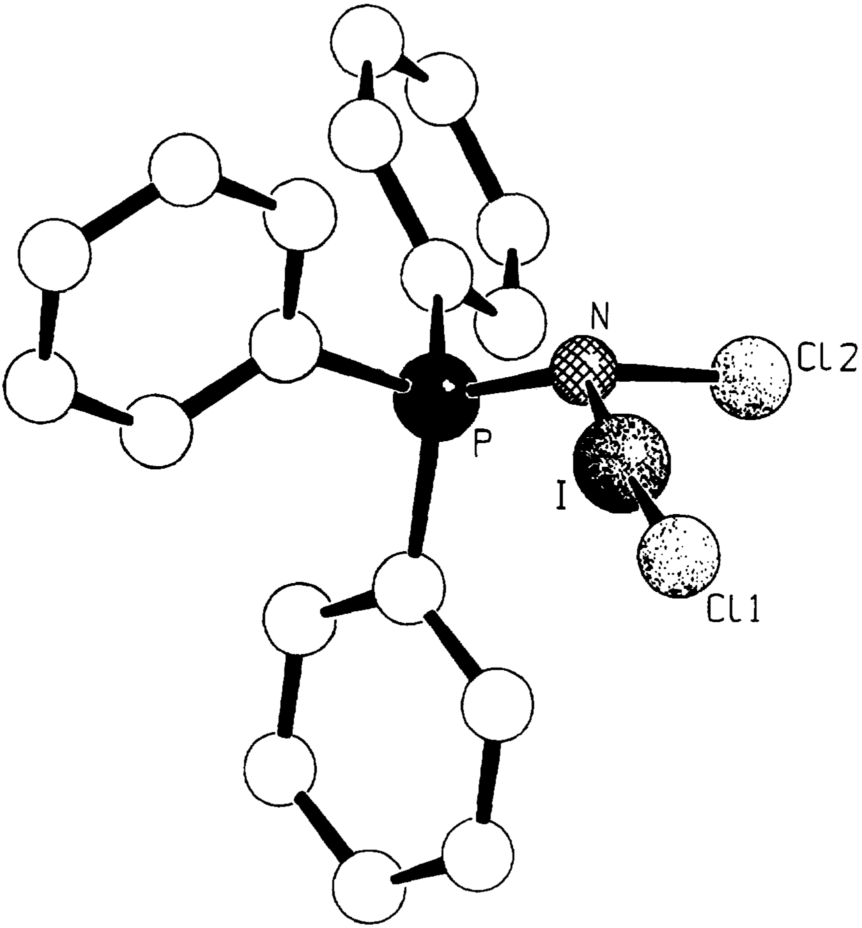


Fig. 59. Molecular structure of $Ph_3PNCl \cdot ICl$.

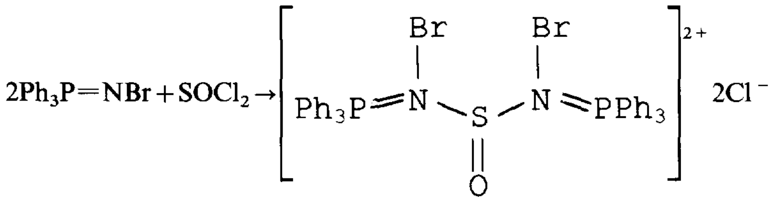
material [103]:

$$2Ph_3P{=}NH + ICl \rightarrow [Ph_3PNH_2]Cl + Ph_3P{=}NI \qquad (67)$$

The phosphorane iminato derivatives of the halogens $R_3P{=}NX$ are very reactive; however, the synthetic possibilities have been hitherto unexploited. The bromine derivative reacts smoothly with phosphorus trichloride according to Eq. (68) in a redox reaction [103]

$$Ph_3P{=}NBr + PCl_3 \rightarrow [Ph_3PNPCl_3]^+Br^- \qquad (68)$$

whereas with thionyl chloride the chloride salt of a dication linked via a sulphur atom is obtained as golden yellow crystals [103]:



$$2\mathrm{Ph_3P{=}NBr} + \mathrm{SOCl_2} \rightarrow \left[\mathrm{Ph_3P{=}}\overset{\mathrm{Br}}{\overset{|}{\mathrm{N}}}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}-\overset{\mathrm{Br}}{\overset{|}{\mathrm{N}}}\mathrm{{=}PPh_3}\right]^{2+} 2\mathrm{Cl}^-$$

(69)

Efforts to obtain $Me_3P{=}NI$ by reaction of the silylated phosphorane imine with iodine monochloride eliminating trimethylchlorosilane gave only the stable donor–acceptor complex $[Me_3P{=}N\text{–}SiMe_3 \cdot ICl]$ with the linear array N–I–Cl (bond angle 177.4°) [97] (Fig. 58).

Owing to the polarity of the ICl bond, the NI bond length of 222.7 pm is significantly shorter than in the $[Ph_3P{=}N\text{–}SiMe_3 \cdot I_2]$ which has an analogous structure, where the NI bond length is 243.2 pm [171].

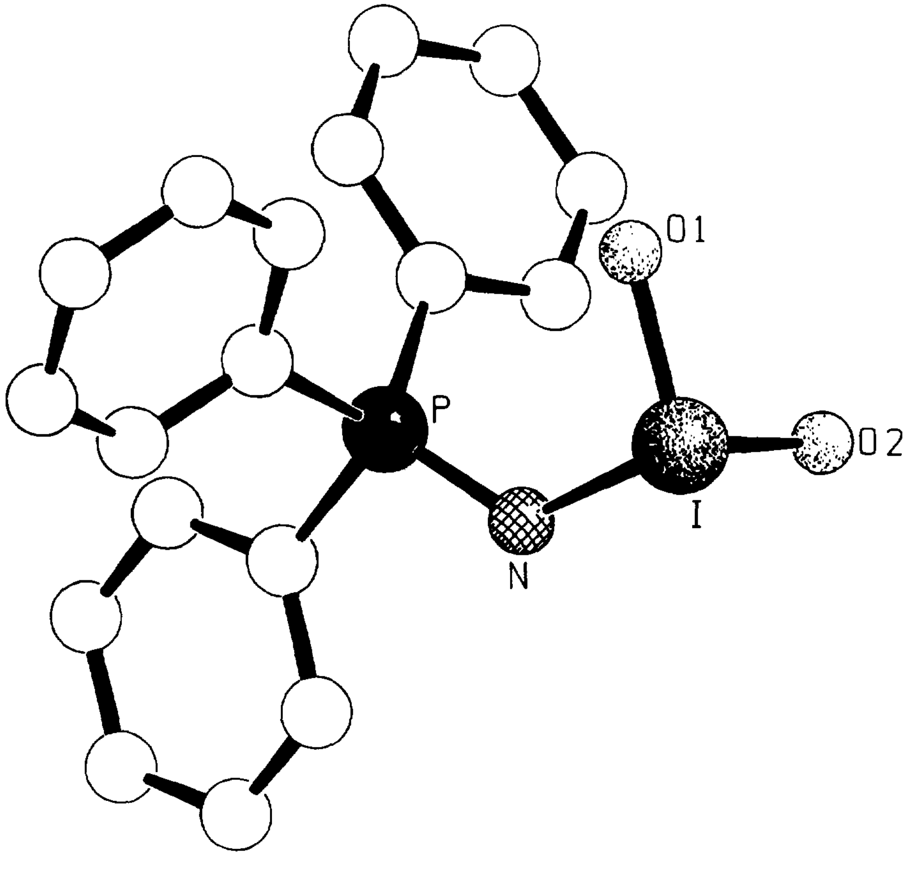


Fig. 60. Molecular structure of Ph_3PNIO_2.

A substitution of the trimethyl silyl group is achieved when the reaction with iodine trichloride is carried out in dichloromethane solution. Actually, this does not result in a phosphorane imino derivative of trivalent iodine, but $Ph_3P{=}NCl$ coordinated with ICl [97]:

$$Me_3SiNPPh_3 + ICl_3 \rightarrow [Ph_3P{=}NCl \cdot ICl] + ClSiMe_3 \tag{70}$$

The mechanism of this reaction (Eq. (70)) is understood in terms of an equilibrium between ICl_3 and ICl with Cl_2 in CH_2Cl_2, as shown by IR spectroscopy for CCl_4 solutions [172]. $[Ph_3P{=}NCl \cdot ICl]$ has the molecular structure shown in Fig. 59 [97]. The sum of the angles at the N atom is 349.4°, which corresponds to a flat pyramidal configuration. The NCl distance (174.4 pm) is comparatively long, as observed in N–Cl compounds with sp^3 hybridization at the N atom [173,174].

A phosphorane iminato complex of pentavalent iodine is obtained by reaction of $Me_3SiNPPh_3$ with diiodo pentoxide in boiling acetonitrile [171]:

$$2Me_3SiNPPh_3 + I_2O_5 \rightarrow 2Ph_3P{=}N{-}IO_2 + O(SiMe_3)_2 \tag{71}$$

The compound (Fig. 60) has a pyramidal array at the iodine atom with IO distances of 175.6 and 180.6 pm, the average of which corresponds to terminal IO bonds in I_2O_5 (177 and 178 pm [175]). The IN bond of 191.8 pm is extremely short, and far shorter than in NI compounds with terminal iodine atoms. Examples to compare with are IN_3 (213 pm, value calculated for the gas phase [176,177]) and NI_3–NH_3 (215 pm [178]). Apart from the expected shortening of the IN bond in Ph_3PNIO_2, the high oxidation state certainly implicates a component of polar IN multiple bonding.

Acknowledgements

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