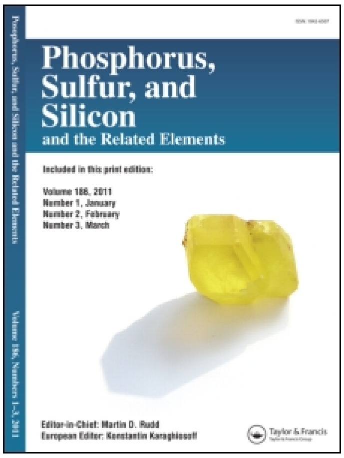

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THE CHEMISTRY OF PHOSPHINIMINES

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THE CHEMISTRY OF PHOSPHINIMINES

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The synthesis, reactions and physical properties of phosphinimines and some related species are reviewed. Particular emphasis is placed upon recent developments in the field including their organometallic and coordination chemistry.

CONTENTS

1 INTRODUCTION

Phosphinimines may be regarded as monomeric compounds containing a phosphorus-nitrogen double bond. Until recently such compounds were solely derivatives of 4-coordinate phosphorus (V), $R_3P{=}NR'$, but now the subject has been extended to include compounds of 3-coordinate phosphorus (V) and 2-coordinate phosphorus (III). This review covers the literature up to the end of 1978.

The nomenclature of monomeric compounds containing a P=N double bond has been the subject of considerable debate, but despite this no firm agreement appears to have been reached. Other authors have used the names phosphazenes, phosphinimides and iminphosphoranes to describe such compounds. It seems, however, that the most widely used name remains phosphinimines (indeed the name first proposed), thus phosphinimines will be used in this review.

Phosphimines were first prepared by Staudinger and Meyer[1] in 1919; subsequent work continued at a steady rate, but it was the isolation of organometallic phosphimines that enabled the field of phosphinimine chemistry to develop rapidly to its present state.

Although the early work on organometallic derivatives has been covered by Schmidbaur[2] in his excellent review of organometallic isoelectronic species, the two previous reviews on phosphinimines[3,4] were published before the organometallic compounds had made such a great impact. Several authors have included phosphinimines under works of a more general nature concerning organophosphorus chemistry.[5–8]

Cyclic compounds containing P=N double bonds (cyclophosphazenes) are not included in this review since they and their precursors, the halo-phosphinimines, are very fully covered in recent works.[9–12]

2 SYNTHESIS

Since the general syntheses of phosphinimines are well covered in previous reviews, an outline only of synthetic methods is described here.

i) General Methods

One of the earliest methods used for the preparation of phosphinimines, which was introduced by Mann and Chaplin,[13] involved the reaction of a tertiary phosphine and sodio-N-chlorotoluene-*p*-sulphnoamide (chloramine-T), giving crytalline products in good yield.

$$R_3P + [(p)CH_3\cdot C_6H_4\cdot SO_2NCl]^-Na^+ \longrightarrow R_3P{=}NSO_2\cdot C_6H_4\cdot CH_3(p) + NcCl \quad (1)$$

$$R = Ph,\ o\text{-},\ m\text{-},\ p\text{-}X\cdot C_6H_4;\ X = CH_3,\ OCH_3,\ Cl$$

A later development of this type of reaction was due to Appel *et al.*[14,15] who showed that triphenylphosphine and hydroxylamine-O-sulphonic acid gave a phosphonium salt which could be deprotonated in liquid ammonia to give the parent phosphinimine (**1**).

$$Ph_3P + H_2NOSO_3H \longrightarrow [Ph_3P{-}NH_2]^+[HSO_4]^- \xrightarrow{NH_3(l)} \underset{(\mathbf{1})}{Ph_3P{=}NH} + (NH_4)_2SO_4 \quad (2)$$

Attempts to deprotonate

$$[Ph_3P{-}NH_2]^+[HSO_4]^-$$

with sodium methoxide in methanol gave triphenylphosphine oxide.

Triphenylphosphinimine (**1**) was also prepared from triphenylphosphine-iminium chloride (**2**) by dehydrohalogenation with sodamide[16,17] or magnesium hydride.[18]

$$Ph_3P + H_2NCl \longrightarrow \underset{(\mathbf{2})}{[Ph_3P{-}NH_2]^+Cl^-} \xrightarrow{base} Ph_3P{=}NH \quad (3)$$

N-Substituted triphenylphosphinimines can be prepared in good yield by the action of acid chlorides upon triphenylphosphine-iminium salts in the presence of triethylamine.[19]

$$[Ph_3P{-}NH_2]^+Br^- + R'Cl \xrightarrow{Et_3N} Ph_3P{=}NR' \quad (4)$$

$$R'{=}PhCO,\ MeCO,\ (p)CH_3C_6H_4SO_2$$

The method most widely applicable to the preparation of phosphinimines however, was developed by Horner and Oediger,[20] and involves reaction of primary arylamines with dibromotriphenylphosphorane in the presence of two moles of triethylamine. The reaction probably proceeds by attack of the nitrogen on phosphorus, followed by deprotonation.

$$Ph_3PBr_2 + ArNH_2 \longrightarrow [Ph_3P{-}NHAr]^+Br^- + HBr \xrightarrow{Et_3N} Ph_3P{=}NAr \quad (5)$$

Zimmer and Singh[21] demonstrated that N-alkyl phosphinimines can be prepared in the same way, using sodamide as the base.

$$Ph_3PBr_2 + R'NH_2 \xrightarrow[NH_3(l)]{NaNH} Ph_3P{=}NR' \quad (6)$$

$R'{=}Me$, Et, n-Pr, i-Pr, i-Bu, t-Bu

Similarly[21] Ph_3PBr_2 and hydrazine give N-aminotriphenylphosphinimine, whilst the bis-iimine (**3**)[22] was formed using two moles of the phosphorane.

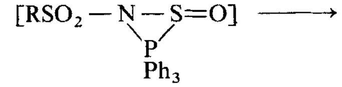
$$Ph_3PBr_2 + N_2H_4 \longrightarrow Ph_3P{=}N\cdot NH_2 \quad (7)$$

$$2Ph_3PBr_2 + N_2H_4 \longrightarrow Ph_3P{=}N{-}N{=}PPh_3 \quad (8)$$

(**3**)

A novel synthesis of methane-sulphonyl triphenylphosphinimine and p-toluene-sulphonyl triphenylphosphinimine uses the corresponding N-sulphinylamides.[23,24]

$$Ph_3P + RSO_2N{-}S{=}O \longrightarrow$$



$$\longrightarrow Ph_3P{=}NSO_2R + SO \quad (9)$$

$R = Me, (p)CH_3\cdot C_6H_4$

These phosphinimines are also formed from the reaction of N-sulphinylamides and triphenylphosphine sulphide.[23,24]

The oldest method for the production of phosphinimines is that of Staudinger and Meyer,[1] which involves reaction of a tertiary phosphine with an organic azide.

$$R_3P + R'N_3 \longrightarrow R_3P{=}NR' + N_2 \quad (10)$$

Trialkylphosphines[25] and trialkylphosphites[26] may also be used. The application of this method is limited by the explosive nature of organic azides.

The isolation of trimethylsilyl azide[27] and other organometallic azides led to the preparation of organometallic phosphinimines. In contrast to organic azides, these organometallic azides have proved to be remarkably thermally stable, and the ease of preparation of organometallic phosphinimines has led to them being extensively studied, (see Ref. 2).

Reactions of triorganosilyl azides with tertiary phosphines give evolution of nitrogen and the corresponding phosphinimine in good yield.

$$R_3P + R'_3SiN_3 \longrightarrow R_3P{=}NSiR'_3 + N_2 \quad (11)$$

In this way, a large number of triorganosilyl phosphinimines have been synthesized.[25,28–36]

N-(Trimethylsilyl)triphenylphosphinimine affords a simple preparation of triphenylphosphininime.[29]

$$Ph_3P{=}NSiMe_3 \xrightarrow[i\text{-}PrOH]{H_2SO_4} Ph_3P{=}NH + i\text{-}PrOSiMe_3 \quad (12)$$

In a similar fashion two authors[37,38] have recently reported the preparation of $(t\text{-}Bu)_3P{=}NH$ which is stable up to 200°C, and is chemically rather inert, presumably due to extensive steric hindrance.

Reaction of trimethylstannyl azide with tertiary phosphines does not give the corresponding organostannylphosphinimines[39] due to a disproportionation reaction to tetramethyltin and the diazide, $Me_2Sn(N_3)_2$, which reacts to give $(Me_2(N_3)SnN{=}PR_3$, which in turn reacts with another mole of phosphine.

Trimethylgermanyl azide and dimethylgermanyldiazide did react with tertiary phosphines to give the corresponding germanylphosphinimines.[39]

$$R_3P + Me_3GeN_3 \longrightarrow R_3P{=}NGeMe_3 + N_2 \quad (13)$$

$$2R_3P + Me_2Ge(N_3)_2 \longrightarrow (R_3P{=}N)_2GeMe_2 + 2N_2 \quad (14)$$

Although both West and Thayer[27] and Reichle[30] had previously reported that triphenylstannyl azide does not react with triphenylphosphine, Lehn[32] showed that at elevated temperatures triphenylstannyl azide does indeed react with tertiary phosphines.

$$R_3P + Ph_3SnN_3 \longrightarrow R_3P{=}NSnPh_3 + N_2 \quad (15)$$

$R{=}Ph$, $n\text{-}C_8H_{17}$, n-Bu

Although trichlorotellurium azide does react with triphenylphosphine,[40] the corresponding phosphinimine is not formed, due to a disproportionation reaction.

$$4Ph_3P + Cl_3TeN_3 \longrightarrow 2[Ph_3P{=}N{=}PPh_3]^+TeCl_6^{2-} + Te + 2N_2 \quad (16)$$

[i.e. Te(II) → Te(IV) + Te(O)]

Organometallic phosphinimines can also be prepared by using metallated phosphinimines and organometallic halides.[32,41]

$$R_3P{=}NLi + R'_3SiX \longrightarrow R_3P{=}NSiR'_3 + LiX \quad (17)$$

Kabachnik *et al.*[42] have described the synthesis of the bis-phosphinimine $CH_2(Ph_2P{=}NPh)_2$, and also the synthesis of some asymmetric bis-phosphinimines.[43]

$$(Ph_2P)_2CH_2 + PhN_3 \longrightarrow PhN{=}P(Ph_2)CH_2{-}PPh_2 \xrightarrow{ArN_3} PhN{=}P(Ph_2){-}CH_2{-}P(Ph_2){=}NAr \quad (18)$$

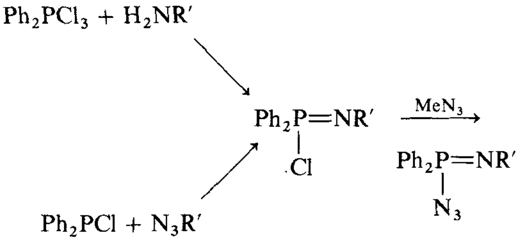
Ar = (*m*)-, (*p*)-$CH_3 \cdot C_6H_4$, (*m*)$Cl \cdot C_6H_4$

Appel and Ruppert[44] have prepared some bis-silylphosphinimines and studied some of their chemistry.[45]

$$Ph_2P(CH_2)_nPPh_2 + 2Me_3SiN_3 \longrightarrow Me_3SiN{=}PPh_2(CH_2)_nPh_2P{=}NSiMe_3 + 2N_2 \quad (19)$$

$n = 1, 2, 3.$

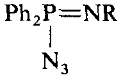
The novel phosphinimines $Ph_2(N_3)P{=}NR'$ have been synthesised by Bock and Wiegräbe.[46]



(20)

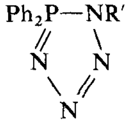
R' = Ph, (*p*)$CH_3 \cdot C_6H_4 \cdot SO_2$

It was shown that these compounds exist only in the open chain azide form (**4**) and not as phosphorus analogues of the tetrazoles (**5**).



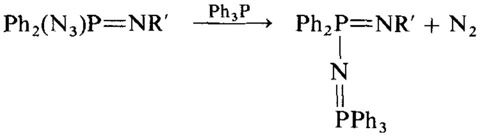
$Ph_2P(N_3){=}NR'$

(**4**)



(**5**)

$$Ph_2(N_3)P{=}NR' \xrightarrow{H_2O} Ph_2P(O)NHR' + HN_3 \quad (21)$$



$$Ph_2(N_3)P{=}NR' \xrightarrow{Ph_3P} Ph_2P(N{=}PPh_3){=}NR' + N_2 \quad (22)$$

ii) *Mechanism of the Staudinger and Meyer Reaction*

The reaction between tertiary phosphines and azides is thought to proceed via nucleophilic attack by the phosphine on the azide nitrogen,[47] although the actual position of attack is unknown.

The question of the structure of the intermediate in the reaction between tertiary phosphines and azides has been a matter of some controversy.

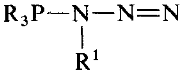
$$R_3P + R^1N_3 \longrightarrow \underset{(6)}{R_3PN_3R^1} \longrightarrow R_3P{=}NR^1 + N_2 \quad (23)$$

Intermediates of the type (**6**) were referred to as phosphazides by Staudinger and Meyer[1] who depicted them has having a linear structure (**7**).

$R_3P{=}N{-}N{=}NR^1$

(**7**)

Horner,[47] however, preferred the branched structure (**8**).



$R_3P{-}N(R^1){-}N{=}N$

(**8**)

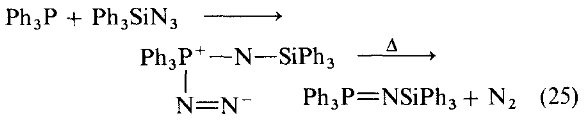
The intermediate phosphazides for some reactions have been isolated. Bergmann[48] reported that the reaction between triphenylmethyl azide and triphenylphosphine in ether gave an adduct (**9**) which retained *all three nitrogen atoms.*

$$Ph_3P + Ph_3CN_3 \longrightarrow \underset{(9)}{Ph_3P{=}N{-}N{=}N{-}CPh_3} \xrightarrow{\Delta} Ph_3P{=}NCPh_3 + N_2 \quad (24)$$

Nitrogen was eliminated on heating the adduct forming the phosphinimine, which was not itself characterised, but its expected product from reaction with ketene was identified.

Leffler *et al.*[49] later confirmed the formation of (**9**), and formulated it as a linear molecule on the basis of the absence of an asymmetric azide absorption near 2100 cm^{-1}. The adduct appears to dissociate in solution, since this absorption slowly appeared.

Thayer and West[50] isolated the adduct of Ph_3P and Ph_3SiN_3, this they formulated as a branched molecule **(10)** since it showed asymmetric azide absorption at 2018 cm^{-1} in the solid and in solution.



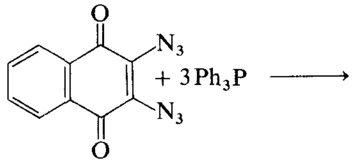
$$Ph_3P + Ph_3SiN_3 \longrightarrow \underset{\substack{|\\ N=N^-}}{Ph_3P^+{-}N{-}SiPh_3} \xrightarrow{\Delta} Ph_3P{=}NSiPh_3 + N_2 \quad (25)$$

(10)

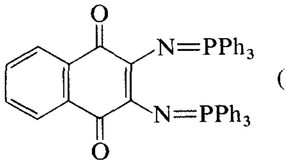
The adduct **(10)** readily decomposed to give the corresponding phosphinimine.

Other groups[51,52] have claimed isolation of linear intermediates from sulphonyl azides and triphenylphosphine, in both cases the intermediate showed no asymmetric azide absorption, and could be thermally decomposed into the corresponding phosphinimine.

Chemical evidence for the linear structure of phosphazides has come from some elegant work by Mosby and Silva.[53] Reaction of 2,3-bisazidonaphthaquinone **(11)** with two moles of Ph_3P yields the expected bis-phosphinimine **(12)**, and a phosphiniminyl derivative of naphtho (2,3-*d*)triazoledione **(13)**.

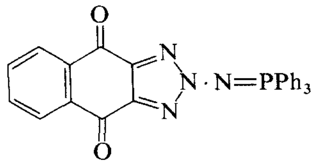


(11)



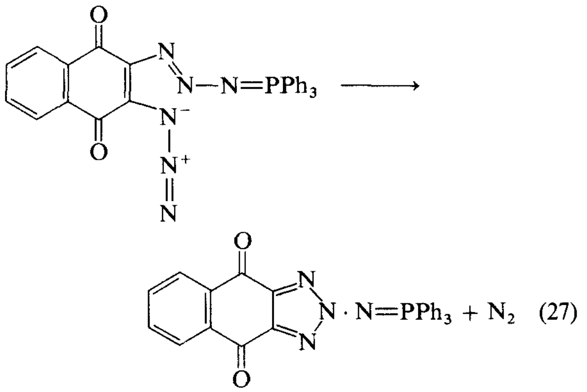
(26)

(12)



(13)

Formation of the latter can only be rationalised by considering a linear structure for the intermediate phosphazide.

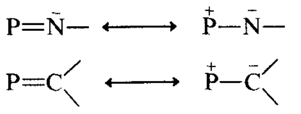


(27)

The formation of the branched adduct **(10)** with triphenylsilyl azide and triphenylphosphine may have been facilitated by some delocalisation of the lone pair of electrons on nitrogen to the 3*d* orbitals of both phosphorus and silicon.

3 CHEMISTRY

The phosphinimines are isoelectronic with the phosphorus ylids, and to a large extent their chemical properties are very similar.



i) Hydrolysis

Phosphinimines are susceptible to hydrolysis, the ease of hydrolysis being related to the basicity of the imine. Triphenylphosphinimine is very readily hydrolysed to ammonia and triphenylphosphine oxide.[16] N-Alkyltriphenylphosphinimines are also readily hydrolysed to $Ph_3P{=}O$ and the corresponding alkylamine.[1,54]

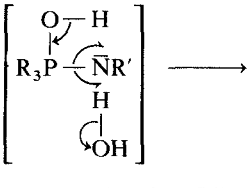
$$R_3P{=}NR' + H_2O \longrightarrow Ph_3P{=}O + H_2NR' \quad (28)$$

N-Aryltriphenylphosphinimines are usually stable in the atmosphere, but are rapidly hydrolysed in dilute acids.[1]

$$Ph_3P{=}NAr \xrightarrow[H_2O]{H^+} Ph_3P{=}O + ArNH_2 \quad (29)$$

Base hydrolysis of phosphinimines is thought to proceed by initial attack of OH^- on the phosphorus atom, followed by elimination of the amine and formation of $Ph_3P{=}O$.[4]

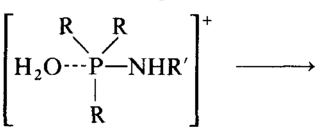
$$R_3P{=}NR' + OH^- \xrightarrow{H_2O}$$



$$R_3P{=}O + R'NH_2 + OH^- \quad (30)$$

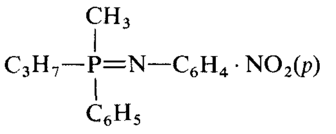
Acid hydrolysis involves initial protonation of the nitrogen followed by attack of oxygen on the phosphorus atom.[4]

$$R_3P{=}NR' + H^+ \longrightarrow R_3\overset{+}{P}NHR' \xrightarrow{H_2O}$$



$$R_3P{=}O + R'NH_2 + H^+ \quad (31)$$

By studying the hydrolysis of the optically active phosphinimine (**14**), Horner and Winkler[55] have shown this mechanism to be correct since the reaction proceeded to give predominantly the inverted phosphine oxide.



$$C_3H_7{-}\underset{C_6H_5}{\overset{CH_3}{P}}{=}N{-}C_6H_4\cdot NO_2(p)$$

(**14**)

ii) Reaction with HX and RX

Hydrogen halides readily protonate phosphinimines to yield the corresponding phosphonium salts.[47,56,57]

$$R_3P{=}NR' + HX \longrightarrow [R_3P{-}NHR']^+[X]^- \quad (32)$$

X = Cl, Br, I

Phosphinimines react with alkyl, acyl and aroyl halides[22,47,54,57] to give the corresponding phosphonium salts.

$$R_3P{=}NR' + R^2X \longrightarrow [R_3P{-}NR'R^2]^+[X]^- \quad (33)$$

The higher alkyl halides tend to undergo HX elimination during such reactions.[54]

$$Ph_3P{=}NR' + RI \longrightarrow [Ph_3PNHR']^+I^- + \text{Olefin}$$

R' = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu, *t*-Bu;

R(I) = Pr, *i*-Pr, *i*-Bu, *t*-Bu (34)

Reaction of $Ph_3P{=}NH$ with alkyl halides[57] resulted in a N-alkylimine which could be further alkylated.

$$2Ph_3P{=}NH + 2EtI \longrightarrow [Ph_3P{-}NEt_2]^+I^- + [Ph_3P{-}NH_2]^+I^- \quad (35)$$

With bulky alkylating agents the second alkylation did not occur, thus reaction of $Ph_3P{=}NH$ with trityl chloride afforded N-trityltriphenylphosphinimine.[58]

$$2Ph_3P{=}NH + Ph_3CCl \longrightarrow Ph_3P{=}N{-}CPh_3 + [Ph_3P{-}NH_2]^+Cl^- \quad (36)$$

iii) Reaction with X_2

Halogenation of phosphinimines gives the N-halo derivative, thus reaction of $Ph_3P{=}NH$ with chlorine, bromine or iodine gives the corresponding N-halotriphenylphosphinimines as crystalline products.[57,59]

$$Ph_3P{=}NH + X_2 \longrightarrow [Ph_3PNHX]^+X^- \xrightarrow{Ph_3P=NH} Ph_3P{=}NX + [Ph_3P{-}NH_2]^+X^- \quad (37)$$

X = Cl, Br, I.

The fact that the reaction proceeds via initial nucleophilic attack of the phosphinimine on the halogen was demonstrated by the action of iodine monochloride on $Ph_3P{=}NH$.[57,59]

$$2Ph_3P{=}NH + I{-}Cl \longrightarrow Ph_3P{=}NI + [Ph_3P{-}NH_2]^+Cl^- \quad (38)$$

iv) Reaction with Carbonyl Compounds

Like phosphorus ylids, phosphinimines undergo Wittig-type reactions with carbonyl compounds.[7,60] This sort of reaction was first reported by Staudinger and Meyer[1] in their original work on phosphinimines. N-Phenyltriphenylphosphinimine reacted with diphenylketene to afford triphenylketenimine and triphenylphosphine oxide.

$$Ph_3P{=}NPh + Ph_2C{=}C{=}O \longrightarrow Ph_2C{=}C{=}NPh + Ph_3P{=}O \quad (39)$$

This type of reaction was extended[56] to include reaction with benzophenone, benzaldehyde, phenylisocyanate, carbon dioxide, carbon disulphide and sulphur dioxide.

$$Ph_3P{=}NPh + Ph_2CO \longrightarrow Ph_2C{=}NPh + Ph_3P{=}O \quad (40)$$

$$Ph_3P{=}NPh + PhCHO \longrightarrow PhCH{=}NPh + Ph_3P{=}O \quad (41)$$

$$Ph_3P{=}NPh + PhNCO \longrightarrow PhN{=}C{=}NPh + Ph_3P{=}O \quad (42)$$

$$Ph_3P{=}NPh + CO_2 \longrightarrow PhN{=}C{=}O + Ph_3P{=}O \quad (43)$$

$$Ph_3P{=}NPh + CS_2 \longrightarrow PhN{=}C{=}S + Ph_3P{=}S \quad (44)$$

$$Ph_3P{=}NPh + SO_2 \longrightarrow PhN{=}S{=}O + Ph_3P{=}0 \quad (45)$$

N-Phenyltriethylphosphinimine reacted with carbon dioxide and carbon disulphide to give N,N-diphenylcarbodiimide,[56] the isocyanate initially formed undergoing further reaction with unreacted phosphinimine.

$$Et_3P{=}NPh + CO_2 \longrightarrow Et_3P{=}O + PhN{=}C{=}O \xrightarrow{Et_3P=NPh} Et_3P{=}O + PhN{=}C{=}NPh \quad (46)$$

Triphenylphosphinimine also reacts with a variety of carbonyl compounds[17,57] to yield the corresponding imino compounds and triphenylphosphine oxide. N-Substituted-triphenylphosphinimines have also been shown to undergo analogous reactions.[22,47,48]

N-Aminotriarylphosphinimines react with aldehydes and ketones to give either phosphazines under strictly anhydrous conditions[61] or the phosphine oxide and the corresponding hydrazone.[22]

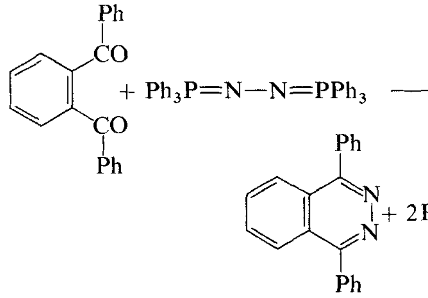
$$Ph_3P{=}N\cdot NH_2 + O{=}CR_2 \longrightarrow Ph_3P{=}N{-}N{=}CR_2 + H_2O \quad (47)$$

$$Ph_3P{=}N\cdot NH_2 + O{=}CR_2 \xrightarrow{H_2O} Ph_3P{=}O + H_2N{-}N{=}CR_2 \quad (48)$$

Recently Appel and Volz[62] have shown that bisphosphinimines of the type

$Ph_3P{=}N(CH_2)_nN{=}PPh_3$ (n = 0, 2)

undergo Wittig-type reactions with 1,2- and 1,4-diketones to give triphenylphosphine oxide and N-heterocycles.

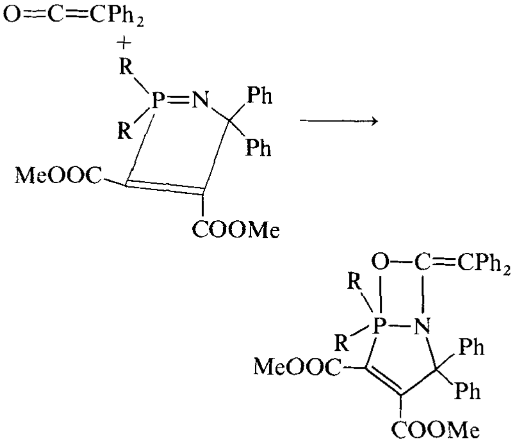

(49)

Triphenylphosphinimine has been reported to react with some isocyanates to give the corresponding carbamate derivatives[63] rather than the Wittig-type of product.

$$Ph_3P{=}NH + R^1NCO \longrightarrow Ph_3P{=}NCONHR^1 \quad (50)$$

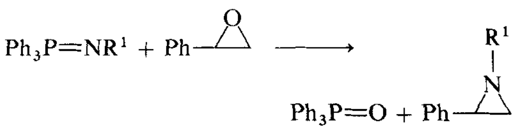
$R^1 = C_6H_5CO, Cl_2P(O), Me_3Si$

The P=N bond in azaphospholes does not undergo a Wittig-type reaction with diphenylketene, but an addition reaction occurs giving a bridgehead phosphorane.[64]

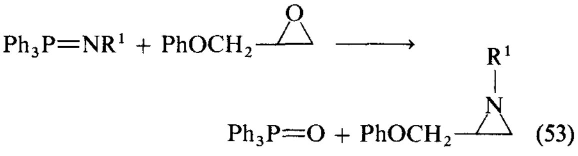

(51)

R=Me, Ph

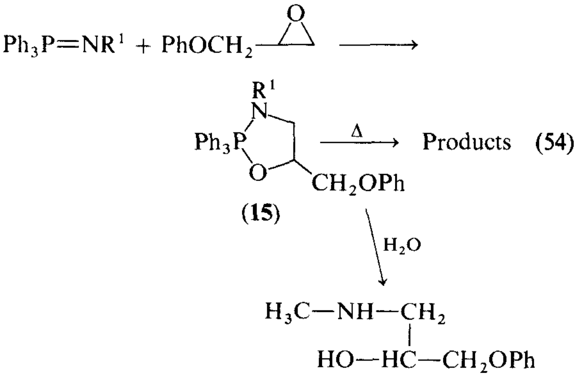
A novel synthesis of N-substituted aziridines[65] has employed Wittig-type reactions of N-substituted phosphinimines.


(52)

R^1=Me, Et, i-Pr, Ph



The latter reaction was shown to proceed via a cyclic adduct (**15**).

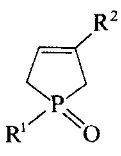


A similar aziridine synthesis[66] involves reaction of NaN_3 with an epoxide followed by treatment with a tertiary phosphine.

v) Mechanism of the Reaction with Carbonyl Compounds

There were no mechanistic studies carried out on the reaction of phosphinimines with carbonyl compounds until the mid-1960's. Earlier Monagle *et al.*[67,68] had suggested that phosphinimines were intermediates in the reaction of phenyl isocyanate with phospholene oxides (**16**) to form diphenylcarbodiimide and carbon dioxide, regenerating the phospholene oxide.

$$2PhN{=}C{=}O \xrightarrow{(16)} PhN{=}C{=}NPh + CO_2 \quad (55)$$



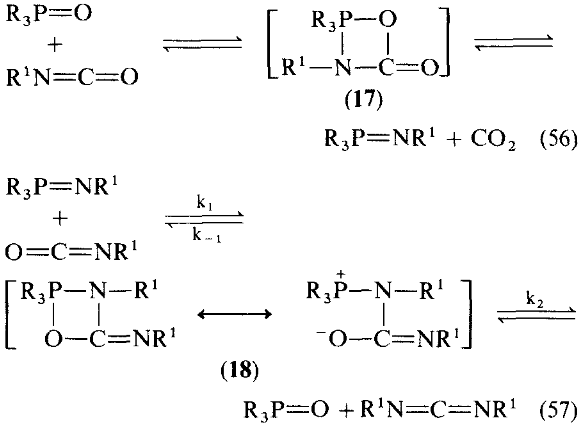
$R^1{=}Et; R^2{=}Me$

$R^1{=}Ph; R^2{=}Me$

(**16**)

This was later extended to cover other tertiary phosphine oxides.[69]

It was assumed that the mechanism paralleled that established for the reaction of phosphorus ylids with carbonyl compounds. The carbonyl carbon atom undergoing attack by the phosphinimine nitrogen to give a betaine intermediate, followed by oxyanion attack on phosphorus to give the products, the second step being faster than the first, i.e. $k_2 > k_1$.



Scheme I

Johnson and Wong[70] studied the kinetics of the reaction of a large, series of N-substituted triphenylphosphinimines and N-phenyl tri(substitutedphenyl)phosphinimines with *p*-nitrobenzaldehyde.

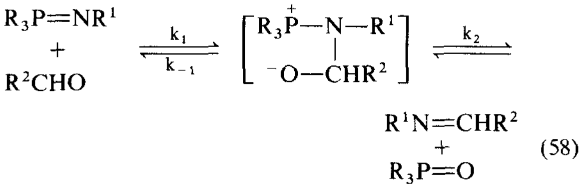
$X{-}C_6H_4N{=}PPh_3$

$X{=}H, (p)NO_2, (m)NO_2, (m)Cl, (p)Cl, (p)CH_3, (p)CH_3O$

$C_6H_5N{=}PR_3$

$R = (m)CH_3 \cdot C_6H_4, Ph, (p)Br \cdot C_6H_4, (p)Cl \cdot C_6H_4$

They observed a substantial solvent effect, the reaction being 30 times as fast in ethanol as in benzene, they noted that this was consistent with a betaine intermediate having a considerable degree of localised charge.



From their observations they concluded that the structure of the phosphinimine affects k_1 by altering the nucleophilicity of the imine. Electron withdrawing substituents on the P-phenyl or on the N-phenyl decrease electron density on the P and N atoms reducing the nucleophilic character of the nitrogen and thus lowering k_1. At the same time the phosphorus atom is more susceptible to oxyanion attack, increasing k_2. Thus k_1 remains the rate determining step and this is reflected in k_{obs}.

Electron donating substituents on the P-phenyl or on the N-phenyl increase the electron density on both P and N. Thus the nitrogen atom becomes more nucleophilic, increasing k_1, but the phosphorus atom becomes less susceptible to oxyanion attack and k_2 is lowered. Hence k_2 then becomes rate determining.

This change of rate determining step was later shown not to be restricted to the specific case above, but to be, in general, true of the reaction between phosphinimines with aldehydes.[71]

Aksnes and Frøyen[72] showed that phosphinimines reacted 10^5–10^7 times faster with phenyl isocyanate than the corresponding phosphine oxides. In contrast to phosphine oxide-phenyl isocyanate reactions the activation energy for the reactions of phosphinimines and phenyl isocyanate was found to be independent of the substituents on phosphorus. This was inconsistent with Scheme I since two very similar intermediates (**17**) and (**18**) are postulated as rate determining.

Thus they suggested a modification of Scheme I to include both a betaine intermediate and a 4-membered pentacovalent phosphorus intermediate, (Scheme II).

Phosphorus has a greater affinity for oxygen than nitrogen, thus in the first step of Scheme II, (**19**) will revert to reactants faster than it will form (**17**), i.e. the latter stage of the reaction is rate determining. Similarly in the second step, (**20**) will form (**18**) faster than it will revert to the reactants, i.e. the first stage of reaction is rate determining.

Recently Frøyen[73] has pointed out some facts inconsistent with the proposed mechanism. Electron donating substituents on the N-phenyl group lower the nucleophilicity of the phosphinimine and slow the reaction by reducing k_2. Electron releasing substituents on phosphorus, such as Et, however, do not slow the reaction.

Although intermediates for the Wittig reaction have been detected and isolated, there is no experimental proof for the existence of intermediates in the reaction between phosphinimines and carbonyl compounds.

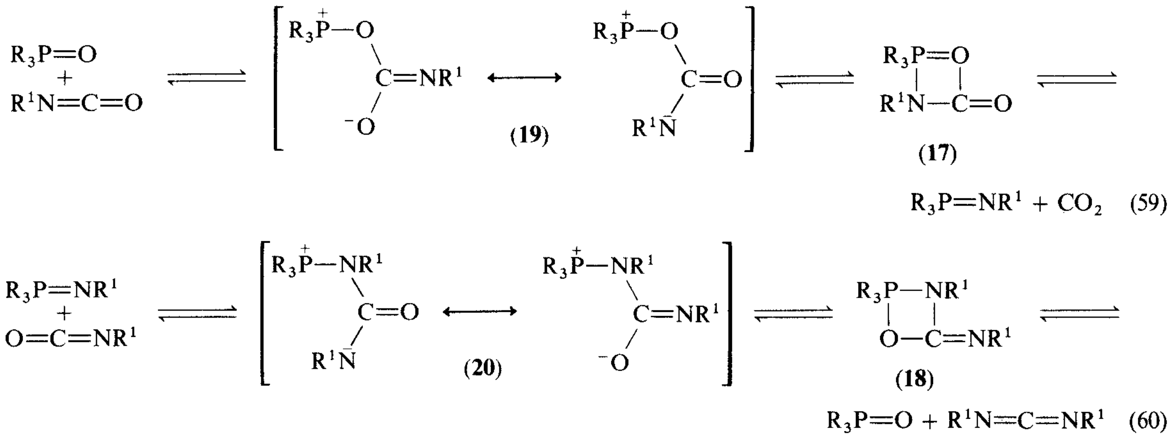
The experimental observations can be explained[73] in terms of a concerted mechanism involving a pentacovalent 4-membered transition state without formation of a betaine.

Frøyen[73] also showed that the rate of reaction in benzene was similar to that in polar solvents such as acetone and dimethylformamide, i.e. solvents which are not capable of hydrogen bonding. Previously[70] the faster rate of reaction in polar solvents was used as evidence to support the existence of a betaine intermediate. In fact the reaction is only accelerated by solvents with hydrogen atoms capable of hydrogen bonding, the catalytic effect being approximately related to the hydrogen bonding ability of the solvent and not to its acid strength.

At this time the precise mechanism of the reaction between phosphinimines and carbonyl compounds remains unresolved.

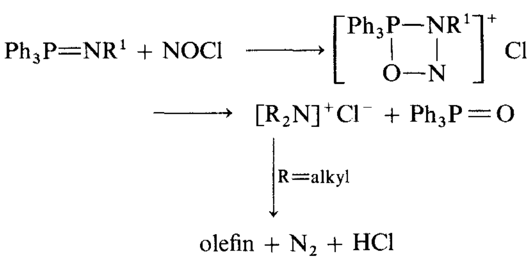
vi) *Reactions with Inorganic Reagents*

Triphenylphosphinimines react with nitrosyl chloride[74] under anhydrous conditions to give triphenylphosphine oxide and a diazonium chloride,



Scheme II

which in the case of alkyl diazonium salts decompose to give an olefin, nitrogen and HCl.



$$Ph_3P{=}NR^1 + NOCl \longrightarrow \left[\begin{matrix} Ph_3P{-}NR^1 \\ | \quad\; | \\ O{-}N \end{matrix}\right]^+ Cl^- \longrightarrow [R_2N]^+Cl^- + Ph_3P{=}O \quad (61)$$

$$\xrightarrow{R=\text{alkyl}} \text{olefin} + N_2 + HCl$$

Triphenylphosphinimine reacts with sulphuryl chloride,[75] the product depending on the reactant proportions.

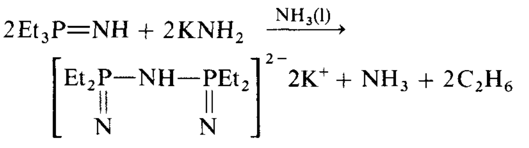
$$4Ph_3P{=}NH + SO_2Cl_2 \longrightarrow 2[Ph_3PNH_2]Cl + (Ph_3P{=}N)_2SO_2 \quad (62)$$

$$2Ph_3P{=}NH + SO_2Cl_2 \longrightarrow [Ph_3PNH_2]Cl + Ph_3P{=}NSO_2Cl \quad (63)$$

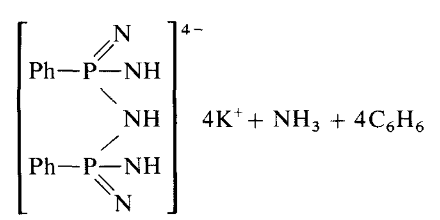
$Ph_3P{=}NSO_2Cl$ is readily hydrolysed to triphenylphosphazosulphuric acid (**21**), a monobasic acid, cleaved by hot H_2O.

$$Ph_3P{=}NSO_2Cl \xrightarrow{H_2O} \underset{(\mathbf{21})}{Ph_3P{=}NSO_3H} \xrightarrow{\text{hot } H_2O} Ph_3P{=}O + H_2SO_4 \quad (64)$$

Ross[76–78] has studied the ammonolysis of some phosphinimines, the products being the aza-analogues of the phosphorus oxo-acids.



$$2Et_3P{=}NH + 2KNH_2 \xrightarrow{NH_3(l)} \left[\begin{matrix} Et_2P{-}NH{-}PEt_2 \\ \| \qquad\qquad \| \\ N \qquad\qquad N \end{matrix}\right]^{2-} 2K^+ + NH_3 + 2C_2H_6 \quad (65)$$



$$2Ph_3P{=}NH + 4KNH_2 \xrightarrow{NH_3(l)} \left[\begin{matrix} Ph{-}P({=}N){-}NH \\ \backslash \\ NH \\ / \\ Ph{-}P({=}N){-}NH \end{matrix}\right]^{4-} 4K^+ + NH_3 + 4C_6H_6 \quad (66)$$

Triarylphosphinimines react with aryl lithium[79,80] to give pentaarylphosphoranes.

$$Ph_3P{=}NR^1 + 2PhLi \longrightarrow Ph_5P + R^1_2NLi \quad (67)$$

$(R^1 = SO_2 \cdot C_6H_4 \cdot CH_3\text{-}p)$

vii) Photochemistry

Homolytic fission of multiple phosphorus-nitrogen bonds are a possible source of nitrene species.

$$R_3P{=}NR' \xrightarrow{h\nu} R_3P\!: + :\ddot{N}R' \quad (68)$$

Zimmer and Jayawant[81] studied the irradiation of $Ph_3P{=}Nt\text{-}Bu$ in cyclohexene from which

Ph_3P, $Ph_3P{=}O$, $t\text{-}BuNH_2$, $(t\text{-}Bu)_2NH$, $t\text{-}BuN(C_6H_9)H$, C_6H_6, N_2, H_2

and 3,3′-bicyclohexenyl were isolated. These products were considered to be derived from the competing fission of P—N and C—N bonds, (Scheme III). $Ph_3P{=}O$ is produced from hydrolysis.

Irradiation of N-aryltriphenylphosphinimines in inert solvents leads to efficient production of Ph_3P and the diaryl-azo compound derived from the N-aryl substituent.[32]

$$Ph_3P{=}NR \xrightarrow{h\nu} Ph_3P + RN{=}NR \quad (69)$$

$R{=}Ph$, $(p)Br \cdot C_6H_4$, $(p)NO_2 \cdot C_6H_4$, $(o)CH_3 \cdot C_6H_4$, $(p)CH_3 \cdot C_6H_4$, (p)anisyl

Triphenylphosphinimines with N-substituents capable of strong delocalisation of the lone pair on nitrogen

$(Ph_3P{=}NR;\ R{=}SO_2 \cdot C_6H_5, CO \cdot C_6H_5, COOCH_3,$ *cis*-$PhC{=}CHPh)$

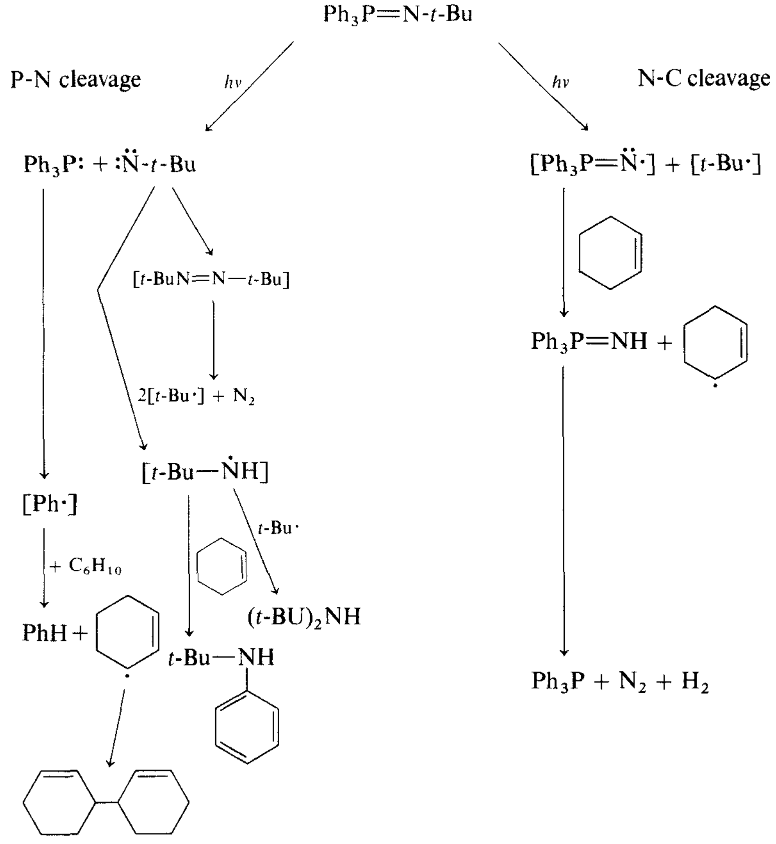
are photostable and are recovered unchanged after irradiation.[82] These phosphinimines have less reactive P=N bonds than other phosphinimines.[7]

Photolysis of N-alkyltriphenylphosphinimines leads to products derived from both P—N and C—N bond cleavage,[82] these reactions are analogous to those observed for photolysis of the corresponding azides.[83,84]

All attempts to trap nitrene intermediates in the above reactions[82] failed, and the reactions are considered to proceed via an excited ylid intermediate rather than P=N bond fission.

$$\rangle P{=}\ddot{N}{-} \rightleftharpoons \rangle\dot{P}{-}\dot{\ddot{N}}{-} \longrightarrow \text{products} \quad (70)$$

$$\rangle P{=}\ddot{N}{-} \rightleftharpoons \rangle P\!: + :\ddot{N}{-} \longrightarrow \text{products} \quad (71)$$



Scheme III

viii) Phosphorimidates

Reaction of trialkyl- or triarylphosphites with organic[85,86] or organometallic azides[87] gives phosphorimidates, $(RO)_3P{=}NR^1$.

$$(RO)_3P + R^1N_3 \longrightarrow (RO)_3P{=}NR^1 + N_2 \quad (72)$$

$$(RO)_2PPh + R^1N_3 \longrightarrow (RO)_2(Ph)P{=}NR^1 + N_2 \quad (73)$$

R=Me, Et, Ph; R^1 = Me, Et

$$(RO)_3P + Me_3SiN_3 \longrightarrow (RO)_3P{=}NSiMe_3 + N_2 \quad (74)$$

R = Et, $C_2H_2F_3$, i-C_3H_7, n-C_4H_9

Methylphosphorimidates undergo thermal rearrangement to phosphoramidates. Low temperature ^{1}H-n.m.r. has shown that the barrier to rotation about the P=N bond is small, probably less than 30 kJ mol^{-1}.[85]

$$(MeO)_3P{=}NMe \xrightarrow{\Delta} (MeO)_2P(O)NMe_2 \quad (75)$$

$$Ph(MeO)_2P{=}NMe \xrightarrow{\Delta} Ph(MeO)P(O)NMe_2 \quad (76)$$

N-Benzoyl substituted phosphorimidates undergo a quasi-Arbusov reaction with HCl but do not react with MeI, EtI or Me_3MX, M=Si, Ge, Sn.[86]

$$(RO)_3P{=}NCOAr + HCl \longrightarrow (RO)_2P(O)NHCOAr + RCl \quad (77)$$

R=Me, Et; COAr=CO · C_6H_5, 3,5-$(O_2N)_2 \cdot C_6H_3 \cdot$ CO,

4 CHEMISTRY OF ORGANOMETALLIC PHOSPHINIMINES

Although the chemistry of organometallic phosphinimines closely follows that of the organic phosphinimines, they have allowed considerable expansion of the subject to include several novel aspects such as the preparation of 3-coordinate

P(V) and 2-coordinate P(III) phosphinimines, silyl group migrations and preparation of a wide variety of fluorophosphoranes. Some organic phosphinimines are susceptible to thermal decomposition[88,89] but most organosilyl phosphinimines are of very high thermal stability, usually distillable at ordinary pressures without decomposition.

i) Reactions of the Si—N *Bond*

Appel *et al.*[90] have shown that sulphur trioxide will insert into the Si—N bond of silyl phosphinimines to give the corresponding phosphinimyl sulphuric acid silylesters.

$$RR^1_2P{=}NSiMe_3 + SO_3 \longrightarrow RR^1_2P{=}N{-}SO_2{-}O{-}SiMe_3 \quad (78)$$

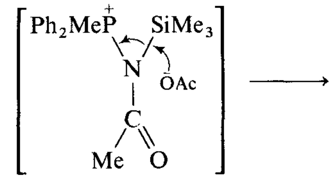
R=Ph; R^1 = Me, Ph
R=Me; R^1=Ph

The silylesters are hydrolysed to the corresponding phosphiniminylsulphuric acids.

$$RR^1_2P{=}N{-}SO_2{-}O{-}SiMe_3 \xrightarrow{H_2O} (Me_3Si)_2O + RR^1_2P{=}NSO_2\cdot OH \quad (79)$$

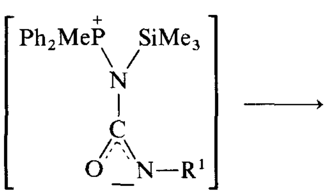
Alkyl isocyanates and acid anhydrides also cleave the Si-N bond of silylphosphinimines,[91] whereas reaction with

$$Ph_2MeP{=}NSiMe_3 + (CH_3CO)_2O \xrightarrow{0°C}$$



$$Ph_2MeP{=}NCOMe + MeCOOSiMe_3 \quad (80)$$

$$Ph_2MeP{=}NSiMe_3 + R^1N{=}C{=}O \xrightarrow{0°C}$$



$$Ph_2MeP{=}N{-}CO{-}NR^1{-}SiMe_3 \quad (81)$$

phenyl isocyanate, phenyl isothiocyanate or CS$_2$ led to Wittig-type reactions.

$$Ph_2MeP{=}NSiMe_3 + CS_2 \xrightarrow{100°C} Ph_2MeP{=}S + Me_3SiN{=}C{=}S \quad (82)$$

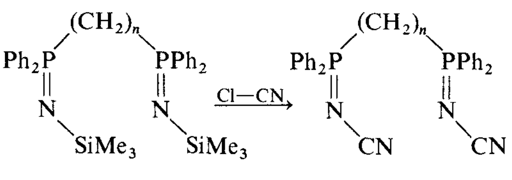
$$Ph_2MeP{=}NSiMe_3 + PhN{=}C{=}O \longrightarrow Ph_2MeP{=}O + PhN{=}C{=}N{-}SiMe_3 + PhN{=}C{=}NPh \quad (83)$$

This reaction is complicated by the strong affinity of the Me$_3$Si group for oxygen, suppressing the formation of Ph$_2$MeP=O.

Treatment of trimethylsilyphosphinimines with cyanogen chloride[92] leads to elimination of Me$_3$SiCl and formation of N-cyanophosphinimines.

$$RR_2{}^1P{=}NSiMe_3 + Cl{-}CN \longrightarrow RR_2{}^1P{=}N{-}CN + Me_3SiCl \quad (84)$$

R = Me, Ph, Me, Ph
R^1 = Me, Me, Ph, Ph



(85)

n = 2, 3, 4

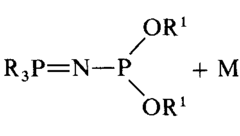
ii) Phosphinimino-phosphines and Phosphinimino-phosphonium Salts

Silylphosphinimines can be desilylated by reaction with halo-phosphines to form phosphinimino-phosphines.[93]

$$Me_3P{=}NSiMe_3 \begin{array}{l} \xrightarrow{PCl_3} (Me_3P{=}N)_3P \\ \xrightarrow{MePCl_2} (Me_3P{=}N)_2PMe \\ \xrightarrow{Me_2PCl} [Me_3P{=}N{-}(PMe_2)_2]^+Cl^- \end{array} \quad (86)$$

Reaction with esters of phosphorous acid, P(OR$^1_3$), also leads to desilylation and formation of phosphinimino-phosphites.[94]

$$R_3P{=}NSiMe_3 + P(OR^1)_3 \xrightarrow{25\text{-}100°C}$$



$$R_3P{=}N{-}P(OR^1)_2 + Me_3SiOR^1 \quad (87)$$

R=Me, NMe$_2$, Ph; R^1=CH$_2$CF$_3$, Ph.

Phosphinimino-phosphonium salts,

$[R_3P{=}N(PR^1_2)_2]^+Cl^-$,

can also be prepared from phosphinimino-phosphines and diorganochlorophosphines, a route which can be used to synthesise phosphinimino-arsonium salts.[95]

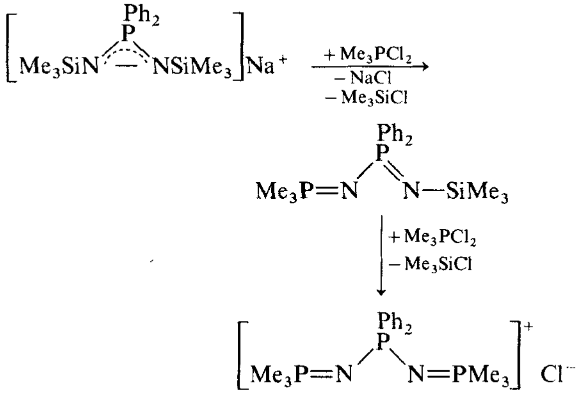
$$R_3P{=}N{-}PR^1_2 + R^2_2AsCl \longrightarrow [R_3P{=}NPR^1_2 \cdot AsR^2_2]^+Cl^- \quad (88)$$

Thermolysis of phosphinimino-phosphonium salts gives bis(phosphinimino)phosphonium salts.[96]

$$2[R_3P{=}N{-}PPh_2 \cdot PPh_2]^+Cl^- \xrightarrow{\Delta} [(R_3P{=}N)_2PPh_2]^+Cl^- + Ph_2PCl + Ph_2P{-}PPh_2 \quad (89)$$

$R = Et, Ph$

These salts can also be made by the action of Me_3PCl_2 on $[(Me_3SiN)_2PPh_2]^-Na^+$.[97,98]



(90)

iii) Reaction with HX

Silylphosphinimines form 1:1 ionic adducts with hydrogen halides,[99–102] the products being more stable with the heavier anions. No stable products are detected with HF. Further addition of hydrogen halides causes Si—N bond cleavage.[99]

$$R_3P{=}NSiR^1_3 + HX \longrightarrow [R_3PNHSiR^1_3]^+X^- \xrightarrow{HX} [R_3P{-}NH_2]^+X^- + R^1_3SiX \quad (91)$$

Addition of the highly reactive trimethyliodosilane to silylphosphinimines gives bis(triorganosilyl)-aminophosphonium iodides[99] whereas fluoro- and chlorosilanes do not react.

$$R_3P{=}NSiMe_3 + Me_3SiI \longrightarrow [R_3\overset{+}{P}{-}N(SiMe_3)_2]I^- \quad (92)$$

$R = Me, Et$

Similarly, one mole of HX reacts with N-trimethylgermanyl- and N-trimethylstannyl-substituted phosphinimines to yield 1:1 adducts whereas reaction with two moles of HX cleaves the N—E (E = Ge, Sn) bond to give aminophosphonium halides.[103]

$$R_3P{=}NEMe_3 + HX \longrightarrow [R_3P{=}NH{-}EMe_3]^+X^- \xrightarrow{HX} [R_3P{-}NH_2]^+X^- + EMe_3X \quad (93)$$

$R = Me, Et; E = Si, Ge, Sn$

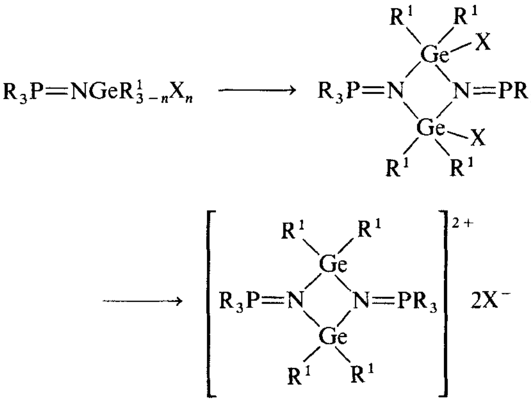
iv) Germanylphosphinimines

Germanylphosphinimines have been synthesised from silylphosphinimines[104] or stannylphosphinimines[105] by reaction with organogermanyl halides.

$$R^1_{3-n}GeX_{n+1} + R_3P{=}NEMe_3 \longrightarrow R_3P{=}NGeR^1_{3-n}X_n + Me_3EX \quad (94)$$

$R, R^1 = \text{alkyl-}; X = Cl, Br, I; n = 1, 2, 3; E = Si, Sn$

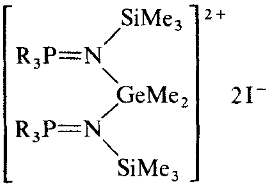
These phosphinimines tend to dimerise and isomerise to form 4-membered ring species.



(95)

Simple adducts were isolated from the reaction of N-trimethylsilylphosphinimines and Me_2GeI_2.[105]

$2R_3P{=}NSiMe_3 + Me_2GeI_2 \longrightarrow$



$$[(R_3P{=}N(SiMe_3))_2GeMe_2]^{2+}\ 2I^- \quad (96)$$

$R = Me, Et$

Trimethylsilyoxy derivatives can be prepared by reaction with $NaOSiMe_3$.[105]

$$Me_3P{=}N{-}GeMe_{3-n}Cl_n \xrightarrow[-\,nNaCl]{+\,nNaOSiMe_3} Me_3P{=}N{-}GeMe_{3-n}(OSiMe_3)_n \qquad (97)$$

$n = 2, 3$

v) Reaction with Fluorinated Compounds

Recently there has been a growing interest in the reactions of organometallic phosphinimines with fluorinated compounds, including HF, organofluorosilanes and organofluorophosphoranes.

Fluoro-silylphosphinimines[106] have been prepared by reaction of $Me_3P{=}NSiMe_3$ with organofluorosilanes.

$$Me_3P{=}NSiMe_3 + Me_2SiF_2 \longrightarrow Me_3SiF + Me_3P{=}NSiMe_2F \qquad (98)$$

$$Me_3P{=}NSiMe_3 + MeSiF_3 \longrightarrow Me_3SiF + Me_3P{=}NSiMeF_2 \qquad (99)$$

$$Me_3P{=}NSiMe_3 + SiF_4 \longrightarrow Me_3SiF + Me_3P{=}NSiF_3 \qquad (100)$$

Reaction of $R_3P{=}NSiMe_3$ with organofluorophosphoranes gives phosphinimino-phosphonium salts

$[R_nP(N{=}PR^1_3)_{4-n}]^+$ [107,108]

and elimination of Me_3SiF together with the corresponding organofluorophosphate anion.

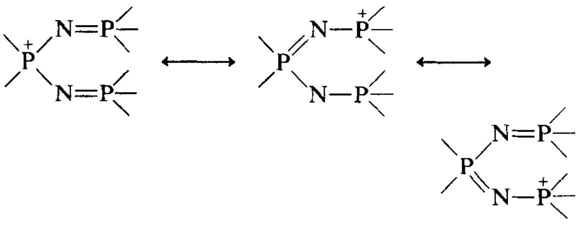
$$R_3P{=}NSiMe_3 + Me_2PF_3 \longrightarrow [Me_2P(N{=}PR_3)_2]^+[Me_2PF_4]^- + Me_3SiF \qquad (101)$$

$R_3 = Me_3, Me_2Ph, (i\text{-}Pr)_3$

$$2(i\text{-}Pr)_3P{=}NSiMe_3 + 2RPF_4 \longrightarrow [RP(F)(N{=}P(i\text{-}Pr)_3)_2]^+[RPF_5]^- + 2Me_3SiF \qquad (102)$$

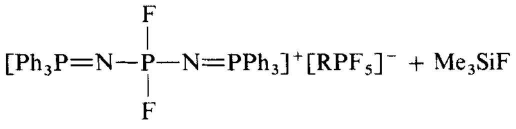
$R = Me, Ph$

The isolation of salts of the dimethyltetrafluorophosphate anion, $[Me_2PF_4]^-$[108] were the first reported and it is thought that the ability of phosphinimino-phosphonium cations to stabilise such anions is due to extensive delocalisation of the positive charge.



Phosphinimino-phosphonium salts where the cation contains two fluorine atoms have also been isolated.[109]

$$2Ph_3P{=}NSiMe_3 + 2RPF_4 \longrightarrow$$



$$[Ph_3P{=}N{-}PF_2{-}N{=}PPh_3]^+[RPF_5]^- + Me_3SiF \qquad (103)$$

$R = F, Ph$

Treatment of $R_3P{=}NSiMe_3$ with $PF_5{\cdot}Et_2O$ in 1:2 molar ratio gives elimination of Me_3SiF and formation of $[RR'_2P{=}N{-}PF_3]^+$ salts.[110]

$$RR'_2P{=}NSiMe_3 + 2PF_5\cdot Et_2O \xrightarrow[-\,Et_2O]{-\,Me_3SiF} [RR'_2P{=}N{-}PF_3]^+[PF_6]^- \qquad (104)$$

$R{=}Me, Ph; R'{=}Me, Ph$

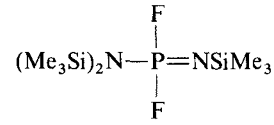
Reaction of fluorophosphoranes with

$(Me_3Si)_2N\cdot PF_2$

cleaves the Si—N bond to give phosphinimines of the type $RF_2P{=}N{-}PF_2$,[111], R=F, Ph.

Treatment of $LiN(SiMe_3)_2$ with fluorophosphoranes[112] gives elimination of LiF and Me_3SiF to yield N-trimethylsilylphosphinimines rather than bis(trimethylsilyl)aminophosphoranes.

$$PF_5 + 2LiN(SiMe_3)_2 \xrightarrow[-\,Me_3SiF]{-\,2LiF}$$



$$(Me_3Si)_2N{-}PF_2{=}NSiMe_3 \qquad (105)$$

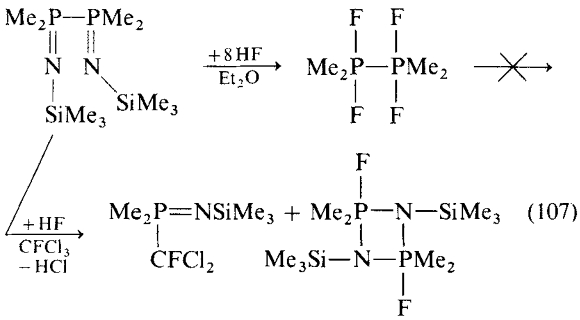
$$\not\longrightarrow (Me_3Si)_2NPF_4$$

Similarly reaction of $LiN(SiMe_3)_2$ with organophosphoranes yields the corresponding phosphinimines.

$$LiN(SiMe_3)_2 + RPF_4 \xrightarrow[-\,Me_3SiF]{-\,LiF} RF_2P{=}NSiMe_3 \qquad (106)$$

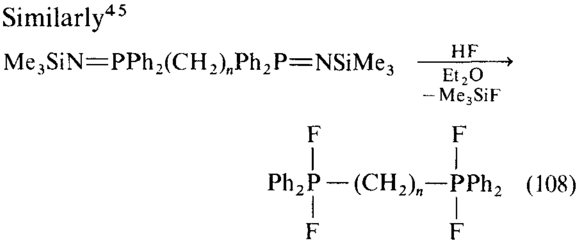
P-Fluoro-N-trimethylsilyphosphinimines undergo thermal decomposition to eliminate Me_3SiF and form cyclic phosphazenes.

The bis(phosphinimine) $(Me_2P{=}NSiMe_3)_2$ reacts with HF[113] to give the corresponding diphosphorane in ether but a diazadiphosphetidine and a phosphinimine in $CFCl_3$ solution.



(107)

Similarly[45]



$$Me_3SiN{=}PPh_2(CH_2)_nPh_2P{=}NSiMe_3 \xrightarrow[\substack{Et_2O \\ -Me_3SiF}]{HF} Ph_2\overset{F}{\underset{F}{P}}-(CH_2)_n-\overset{F}{\underset{F}{P}}Ph_2 \quad (108)$$

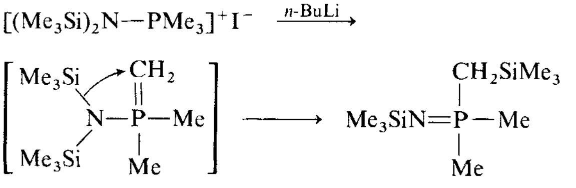
n = 1, 2, 3

vi) Trimethylsilyl Group Migrations

An aspect of phosphinimine chemistry which has only recently been explored is that of Me_3Si-group migration. Wilburn and Neilson[114] showed that dehydrohalogenation of

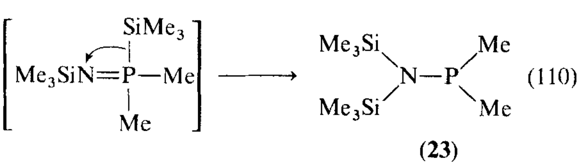
$[(Me_3Si)_2N{-}PMe_3]^+I^-$

by n-BuLi gives the phosphinimine instead of the phosphorus ylid as might be expected. The reaction is thought to proceed via the ylid (**22**) with Me_3Si-migration from N to C.



(**22**) (109)

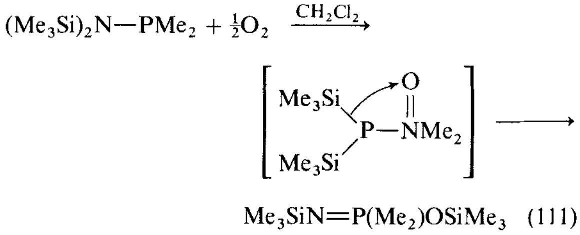
Treatment of dimethyl(trimethylsilyl)phosphine with trimethylsilyl azide does not yield the expected phosphinimine but the aminophosphine due to migration of a Me_3Si-group from P to N.[115]



(110)

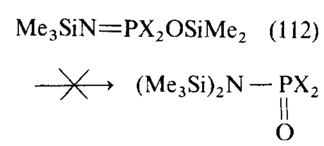
(**23**)

Reaction of (**23**) with Me_3SiN_3 yields the expected phosphinimine $(Me_3Si)_2NP(Me_2){=}NSiMe_3$, which displays only one peak for the Me_3Si groups in both ^{13}C and ^1H n.m.r. spectra, this is due to rapid 1,3 silyl group exchange.[115] Treatment of (**23**) with dry oxygen gives the siloxyphosphinimine and not the isomeric phosphine oxide because of silyl group migration from N to O.



(111)

Further examples of silyl group migration from N to O are shown by the reaction of $(Me_3Si)_2NLi$ and $ClP(O)X_2$, which yields the phosphinimines and not the isomeric phosphine oxides.[116,117]



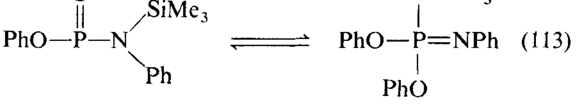
$$(Me_3Si)_2NLi + ClP(O)X_2 \longrightarrow Me_3SiN{=}PX_2OSiMe_2 \quad (112)$$

$$\not\longrightarrow (Me_3Si)_2N-\underset{\underset{O}{\|}}{P}X_2$$

X = F, Cl, Ph

Glemser *et al.*[118] reported that reaction of $(Me_3Si)_2NLi$ and $P(O)F_3$ in ether solution gave the corresponding phosphine oxide, (whereas Fluck *et al.*[119] reported Si—N bond cleavage under very similar conditions), attributing the two different Me_3Si- ^1H n.m.r. signals to the barrier to P=N rotation. In view of the work of Neilson *et al.*[116] (Eq. 112) and the usually low barrier to P=N rotation it seems probable that the product is in fact the phosphinimine and not the phosphine oxide. Glemser's work[118] agrees with Neilson's results in that reaction of $P(O)Cl_3$ with $N(SiMe_3)_3$ or $(Me_3Si)_2NLi$ yields the corresponding siloxyphosphinimine.

Reversible 1,3 Me_3Si-group migration has been demonstrated in a phosphoramidate.[120]



(113)

(89%) (11%)

5) 3-COORDINATE P(V) AND 2-COORDINATE P(III) PHOSPHINIMINES

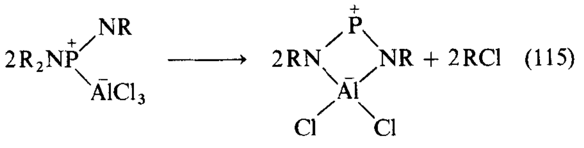
Another new area of phosphinimine chemistry brought about by use of organometallic derivatives is that of 3-coordinate phosphorus (V) and 2-coordinate P(III)phosphinimines; $RP({=}NR^1)_2$, and $RP{=}NR^1$.

Niecke and Flick[121] prepared the first tervalent phosphinimines from $(Me_3Si)_2NPF_2$ and $(Me_3Si)_2NLi$.

$$(Me_3Si)_2NPF_2 + (Me_3Si)_2NLi \longrightarrow LiF + Me_3SiF + \underset{(\mathbf{24})}{(Me_3Si)_2N{-}P{=}NSiMe_3} \quad (114)$$

(**24**) Reacts with Al_2Cl_6 to form a 4-membered heterocyclic zwitterionic compound (**25**), where the phosphorus maintains its two-fold coordination.[122]

$$2R_2N{-}P{=}NR + Al_2Cl_6 \longrightarrow$$

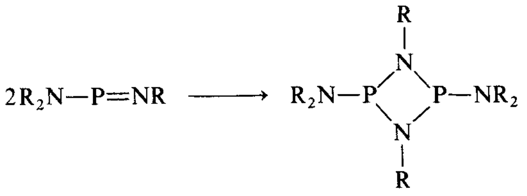


(115)

(**25**)

R = Me$_3$Si

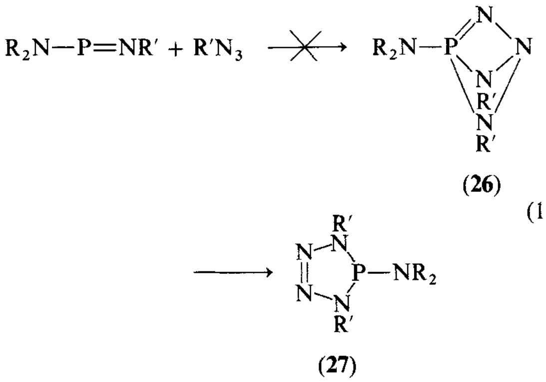
Dimerisation of (**24**) by a 2 + 2 cycloaddition process give a 4-membered heterocyclic ring compound.[123,124]



(116)

R = Me$_3$Si

Niecke and Schäfer[125] first described the reaction of $R_2N{-}P{=}NR'$ with azides as giving an imino-bridged compound (**26**), but this was later shown to be incorrect, the product being a tetraaza-λ^3-phospholine (**27**) which has an almost planar ring.[126]



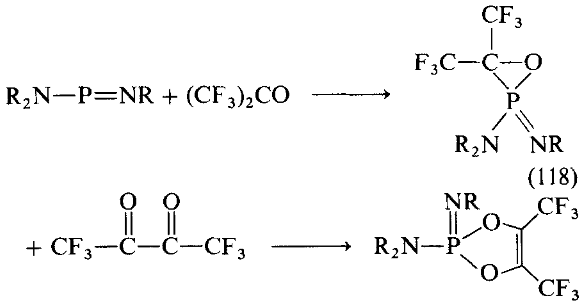
(**26**)

(117)

(**27**)

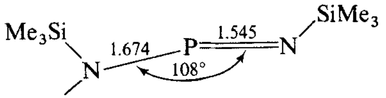
R = *i*-Pr, SiMe$_3$; R′ = *t*-Bu

Treatment of $(Me_3Si)_2N{-}P{=}NSiMe_3$ with perfluorinated ketones leads to cycloaddition products and not to Wittig-type reaction products.[127]

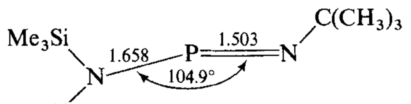


(118)

Pohl and Niecke[128] have established the structure of $(Me_3Si)_2N{-}P{=}NSiMe_3$ (**24**), and Pohl[129] has established the structure of $(Me_3Si)_2N{-}P{=}Nt{-}Bu$, (**24A**).



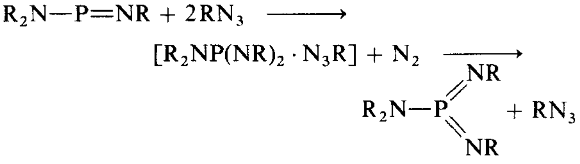
(**24**)



(**24A**)

In both cases the P—N single and double bonds can be clearly distinguished, and there are no contributions from a dipolar form because of the short P=bond lengths. The small N—P—N bond angle is due to extensive participation of *p*-orbitals in the bonds to phosphorus.

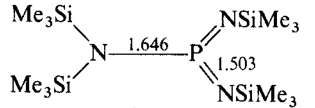
Treatment of $(Me_3Si)_2N{-}P{=}NSiMe_3$ with two moles of Me_3SiN_3 yields the 3-coordinate P(V) phosphinimine (**28**).[130,131]



$$R_2N{-}P{=}NR + 2RN_3 \longrightarrow [R_2NP(NR)_2 \cdot N_3R] + N_2 \longrightarrow R_2N{-}P({=}NR)_2 + RN_3$$

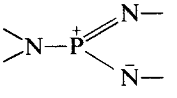
(28)

R = Me$_3$Si (119)

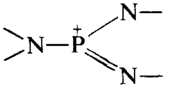


(28)

The crystal structure[132,133] shows that the P—N and P=N bonds can be distinguished. The central phosphorus atom has planar threefold coordination, the P=N bonds are very short. This planarity favours strong p_π—p_π bonds and also contributes to the stability of the coordinatively unsaturated phosphorus atom. There is little or no contribution from dipolar forms **(29)**, **(30)**.



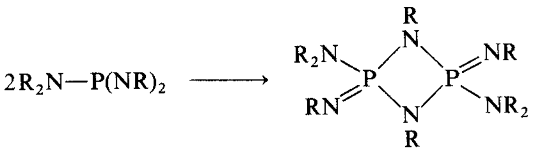
(29)



(30)

The longer P=N bonds in the phosphorus (III) compound compared to the phosphorus (V) compound is a general feature of P=X bonds.[134]

Dimerisation of **(28)** gives a 4-membered heterocyclic compound.[123]

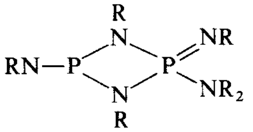


(120)

R = Me$_3$Si

The 2- and 3-coordinate phosphinimines undergo a 2 + 2 cycloaddition reaction.[123]

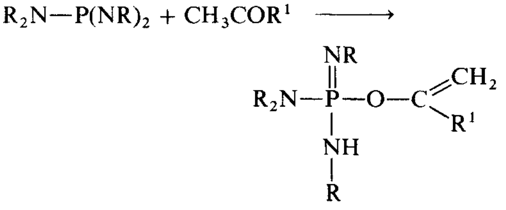
$$R_2N{-}P{=}NR + R_2N{-}P(NR)_2 \longrightarrow$$



(121)

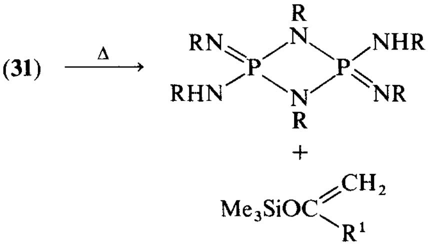
R=Me$_3$Si

Reaction of (Me$_3$Si)$_2$N—P(NSiMe$_3$)$_2$ with acetone or acetophenone[135] gives addition products, **(31)**, thermolysis of these gives corresponding diazadiphosphetidines and silylenol ethers but reaction with DMSO or PMSO gives addition products where the sulphur compound is reduced to a thioether.



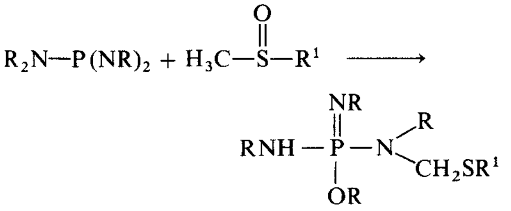
(122)

R^1 = CH$_3$, Ph **(31)**



(123)

R = Me$_3$Si



(124)

R^1 = CH$_3$, Ph

6 STRUCTURE AND PHYSICAL PROPERTIES

i) Structure

The X-ray crystal structures of the N-substituted phosphinimines Ph$_3$P=NSO$_2$ · C$_6$H$_4$ · CH$_3$(*p*),[136] Ph$_2$FP=NMe[137,138] and Ph$_3$P=NC$_6$H$_4$·Br(*p*)[139] have been published, as have the structures of the organometallic derivatives

(Me$_3$Si)$_2$N—P=NSiMe$_3$,[128]

(Me$_3$Si)$_2$N—P=N—tBu[129]

and

(Me$_3$Si)$_2$N—P(NSiMe$_3$)$_2$[132,133]

described above.

The structures of phosphinimines can be represented as a resonance hybrid of the double bond form (**32**) and the dipolar form (**33**).

(**32**) (**33**)

In $Ph_2FP{=}NMe$ the P=N bond length is 1.641 Å,[137,138] this compares with values from covalent radii[140] of 1.78 Å and 1.64 Å for single and double bonds respectively. The bond angles at phosphorus lie between 104.2° and 118.7°, which corresponds to approximate sp^3 hybridization. The P=N—C angle of 119.1° is consistent with sp^2 hybridization at nitrogen. The multiple phosphorus-nitrogen bond consists of one σ-bond and a π-bond formed from an unhydridized N(2*p*) orbital and a P(3*d*) orbital. The results from $Ph_3P{=}NC_6H_4 \cdot Br(p)$[136] are similar, the angles around phosphorus vary from 103.0° to 117.7° with a P=N—C angle of 124.2°, which is close to the expected trigonal value for sp^2 hybridization on nitrogen. The P=N bond is shorter than in $Ph_2FP{=}NMe$ at 1.567 Å. The values for the P=N bond lengths in phosphinimines indicate a large contribution from the double bond form (**32**) and little or no contribution from the dipolar form (**33**). (It is difficult to estimate a $R_3\overset{+}{P}—\overset{-}{N}$-bond distance but it is unlikely to be as short as 1.64 Å).[136] This is also supported by thermochemical data[141] which shows phosphinimines to have considerable resonance energy.

The structure of

$Ph_3P{=}NSO_2 \cdot C_6H_4 \cdot CH_3(p)$[136]

is consistent with a delocalised electronic structure in the P—N—S system, probably with a significant degree of *d*-orbital participation from sulphur and phosphorus.

ii) Infrared Spectra

The P=N stretching frequency in phosphinimines was shown to occur in the 1200–1300 cm^{-1} region.[142] Bock *et al.*[143] have studied the infrared spectra of some ^{15}N-substituted-phosphinimines, and as a result have extended the range to 1140–1375 cm^{-1}.

$Ph_3P{=}NC_6H_5$	ν(P=N) 1344 cm^{-1}
$Ph_3P{=}N \cdot SO_2 \cdot C_6H_4 \cdot CH_3(p)$	ν(P=N) 1147 cm^{-1}
$Cl_3P{=}N \cdot SO_2 \cdot C_6H_4 \cdot CH_3(p)$	ν(P=N) 1199 cm^{-1}

These values of ν(P=N) dropped 20 cm^{-1}, 23 cm^{-1}, and 16 cm^{-1} respectively on ^{15}N-substitution.

Bragin *et al.*[144] have recently undertaken a detailed investigation of the vibrational spectrum of N-methyltrimethylphosphinimine and its N-methyl-d_3 analogue. The results were consistent only with a C_s structure. The P=N stretching frequency of 1239 cm^{-1} was a broad, strong absorption which occurred at 1220 cm^{-1} in $Me_3P{=}NCD_3$. The low temperature ^1H n.m.r. spectrum of $Me_3P{=}NMe$ showed no change down to −100°C. If rotation about the P=N double bond was slow on the n.m.r. time scale, at low temperatures the methyl groups on phosphorus would become non-equivalent due to the non-linear P=N—C skeleton. The variable temperature spectrum can be explained by a low energy barrier to rotation about the P=N double bond, (see also Ref. 85). If −100°C is taken as the upper limit, ΔG^* for the rotation process is less than 33.5 kJ mol^{-1}.[145]

Roesky and Grimm[146] have shown that ν(P=N) increases with increasing electronegativity of the substituents on phosphorus. In agreement with this, Tarasevich and Egorov,[147] using ^{31}P-chemical shifts, have shown that in compounds of the type $R^1R^2R^3P{=}NR$, bond order increases with increase of the electronegativity of substituents on phosphorus and the bond order decreases with increasing electronegativity of the substituents on nitrogen.

iii) Dipole Moments

Zhmurova *et al.*[148] have measured the dipole moments of some triphenylphosphinimines and some (perhaloalkyl)P-substitutedphosphinimines.

$Ph_3P{=}NH$	3.8D
$Ph_3P{=}NPh$	3.1D
$(Cl_3C)_2ClP{=}NH$	1.2D
$Cl_3P{=}NCCl_3$	2.6D

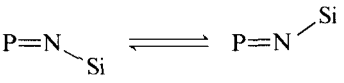
iv) Photoelectron Spectra

Photoelectron spectra have been recorded for a few trimethylphosphinimines[149] and compared to the corresponding P=C ylids;

$Me_3P{=}NH$, $Me_3P{=}NSiMe_3$,

$Me_3P{=}C(H)SiMe_2SiMe_2—N{=}PMe_3$.

The spectrum of $Me_3P{=}NH$ has two bands, the band at 8.2 eV is assigned to π-ionisation while that at 9.2 eV is assigned to the lone pair ionisation. $Me_3P{=}NSiMe_3$ has only one band, at 8.3 eV, arising from two degenerate π-type orbitals from a linear system or from



having a low force constant.

The π-electron structures of some N-substituted triphenylphosphinimies,

$Ph_3P{=}NR$ (R=Ph, (*o*), (*m*), (*p*) $(Me_2N) \cdot C_6H_4$, (*o*), (*m*), (*p*)$CH_3 \cdot C_6H_4$),

have been calculated using the Hückel molecular orbital method.[150]

v) Mössbauer Spectra

The Mössbauer spectra of $PhMe_2P{=}NSnPh_3$ and $Ph_3P{=}NSnPh_3$ have been reported,[151] the Sn isomer shifts are 1.35 mms^{-1} and 1.38 mms^{-1} respectively, the quadrupole splittings are zero.

vi) N.M.R. Spectra

Yolles and Woodland[152] have discussed the ^{31}P- and ^{19}F-n.m.r. spectra of fluorine-substituted N-arylphosphinimines and some N-(triarylsilyl)triarylphosphinimines, and have shown that the $R_3P{=}N$-group (R=aryl) is a good supplier of electron density by induction and by resonance. There is no evidence for a resonance structure between Si and N in the N-(triarylsilyl)triarylphosphinimines studied.

Gibson and Schmutzler[153] have studied the ^{19}F-n.m.r. spectra of some fluorine-substitutedphosphinimines which contain P=N and C=N bonds; $F_2RP{=}N{-}C(CF_3){-}N{=}C(CF_3)_2$, R=Me, Et, Ph.

^{13}C-n.m.r. studies on phosphinimines are surprisingly limited (see Table I), Schweizer *et al.*[154] have reported data for $Ph_3P{=}NPh$ and its phosphonium salt $[Ph_3P{-}NHPh]^+Br^-$, and Buchner and Wolfsberger[155] have reported data for the silylphosphinimines $R^1R^2_2P{=}NSiMe_3$. The ability of silicon to participate in π-bonding gives rise to the possibility of extensive delocalisation over the Si—N—P system in silylphosphinimines:

$$R^1_3P{=}NSiR_3 \longleftrightarrow R^1_3\overset{+}{P}{-}\bar{N}{-}SiR_3 \longleftrightarrow R_3{}^1\overset{+}{P}{-}N{=}\overset{-}{Si}R_3.$$

This is a possible explanation of the downfield shift of C_1 in the silylphosphinimines $Ph_3P{=}NSiMe_3$ and $PhMe_2P{=}NSiMe_3$ compared to C_1 on the P-phenyl groups in $Ph_3P{=}NPh$. The coupling constants $J(^{13}C{-}^{31}P)$ for the silylphosphinimines are slightly larger than the corresponding coupling constants in $Ph_3P{=}NPh$. It is thought that the effects of change in the $R^1_3P{=}N{-}Y$ bonding system are mainly reflected in $\delta(C_1)$ and $^1J(^{13}C{-}^{31}P)$ and only to a small extent in $\delta(C)$ and $J(^{13}C{-}^{31}P)$ for C_2, C_3 and C_4.[154]

On going from the phosphonium salt, $[Ph_3P{-}NHPh]^+Br^-$, to the phosphinimine, $Ph_3P{=}NPh$, the P-phenyl carbon atoms experience a downfield shift and a small reduction in coupling constants. The N-phenyl carbon atoms show similar chemical shifts in both the salt and the phosphinimine, apart from C_1, which experiences a considerable downfield shift. The downfield shift of the P-phenyl carbon atoms in the phosphinimine is caused by loss of the positive charge on the phosphorus atom, whilst the lowering of the coupling constants is due to a reduction in the *s* character of the orbitals forming the carbon to phosphorus bond on going from the salt (sp^3) to the phosphinimine (sp^3d).

^{31}P chemical shifts for silylphosphinimines containing only Me or Ph groups fall in the range +1.5 to +4.2 (relative to H_3PO_4) whereas in compounds containing a β-Me group the phosphorus atom experiences a large upfield shift, this is explained by a mechanism involving intramolecular coordination of the β-Me group to the phosphorus using *d*-orbitals.[155]

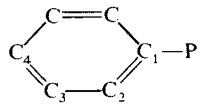
7 COORDINATION CHEMISTRY

Until recently the coordination chemistry of phosphinimines had received little attention, the first reported complexes were poorly characterised and considered relatively unimportant. However, the phosphinimine ligand and its derivatives are now known to be very versatile ligands, the phosphinimine group being able to act as a 1, 2 or 4 electron donor.

TABLE I

^{13}C-n.m.r. and ^{31}P-n.m.r. data for some phosphinimines

$\delta(C)^d$/ppm $J(^{13}C\text{-}^{31}P)$/Hz	P—C— (^1J)	P—C—CH$_3$ (^2J)	C_1 (^1J)	C_2 (^2J)	C_3 (^3J)	C_4 (^4J)	C_1' ($^1J'$)	C_2' ($^2J'$)	C_3' ($^3J'$)	C_4' ($^4J'$)	$(P)^e$/ppm	^2J(P—Si)/Hz
$Me_3P{=}NSiMe_3^a$	22.2 (+69.2)										+3.5	19.6
$Et_3P{=}NSiMe_3^a$	23.8 (+66.8)	8.0 (−4.7)									−14.1	22.4
$t\text{-}Bu_3P{=}NSiMe_3^a$	41.2 (54.0)	30.9 (+1.1)									−31.9	26.3
$PhMe_2P{=}NSiMe_3^a$	22.2 (+69.1)		138.5 (100.2)	130.6 (10.1)	129.1 (11.6)	131.3 (2.8)					+4.2	20.8
$Ph_3P{=}NSiMe_3^a$			136.4 (101.6)	132.6 (10.2)	128.7 (12.0)	131.3 (2.8)					+1.5	21.8
$Ph_3P{=}NPh^b$			131.2 (98.7)	132.4 (9.6)	128.4 (11.9)	131.5 (2.8)	151.0 (2.4)	123.4 (17.5)	128.5 (f)	117.3 (f)		
$[Ph_3P\text{-}NHPh]^+Br^{-c}$			119.8 (102.5)	133.5 (11.6)	130.0 (13.4)	135.2 (f)	137.8 (2.4)	123.5 (18.3)	129.2 (f)	121.8 (6.7)		



[a] Reference 155, in C_6D_6 solution.
[b] Reference 145, in $CDCl_3$ solution.
[c] Reference 145, in d_6-DMSO solution.
[d] Chemical shifts relative to TMS.
[e] Chemical shifts relative to H_3PO_4.
[f] Coupling unresolved.

i) Complexes with Lewis Acids

One of the most interesting aspects of the chemistry of the organometallic phosphinimines is their reaction with a wide range of Lewis acids to form a variety of adducts and complexes.

Silylphosphinimines form 1:1 adducts with Group III metal halides[35] and metal alkyls.[34]

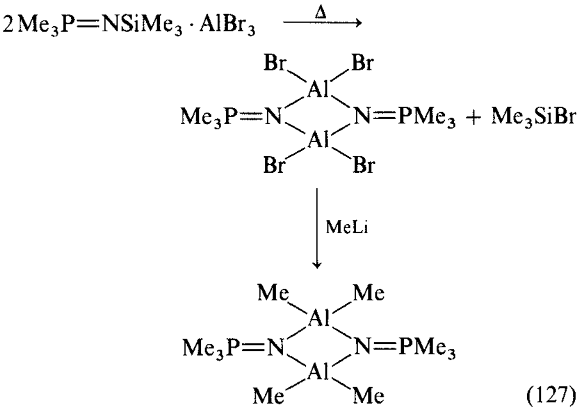
$$MX_3 + R_3P{=}NSiMe_3 \longrightarrow R_3P{=}NSiMe_3 \cdot MX_3 \quad (125)$$

M=Al, Ga, In; X=Cl, Br, I

$$R_3P{=}NSiMe_3 + MR^1_3 \longrightarrow R_3P{=}NSiMe_3 \cdot MR^1_3 \quad (126)$$

M=Al, Ga, In; R^1=Me, Et

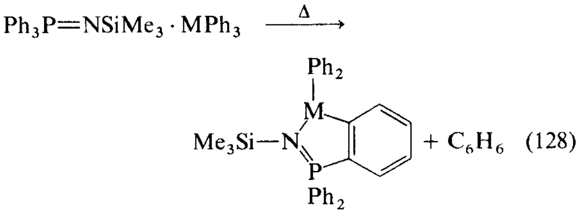
Thermolysis of $Me_3P{=}NSiMe_3 \cdot AlBr_3$[35] produced a dimer and elimination of Me_3SiBr, treatment of this dimer with methyl lithium gave the corresponding methyl substituted complex.



(127)

Thermolysis of the trimethylaluminium adduct regenerates the reactants.

The adducts formed from $Ph_3P{=}NSiMe_3$ and MPh_3(M=Al, Ga) undergo elimination of benzene on thermolysis.[156]



(128)

M = Al, Ga

Germanyl- and stannylphosphinimines are cleaved by metal alkyls much more readily than their silicon analogues, some of their adducts being unstable even at low temperature. Germanylphosphinimines form stable 1:1 adducts with some metal alkyls but the corresponding stannylphosphinimines, under identical conditions, undergo cleavage of the Sn—N bond.[157]

$$R_3P{=}NGeMe_3 + MMe_3 \longrightarrow R_3P{=}NGeMe_3 \cdot MMe_3 \quad (129)$$

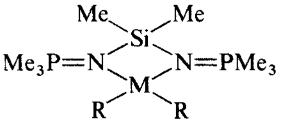
R=Me, Et; M=Al, Ga, In

$$R_3P{=}NSnMe_3 + MMe_3 \longrightarrow Me_4Sn + (R_3P{=}N \cdot MMe_2)_2 \quad (130)$$

The bis(phosphinimino)silane,

$(Me_3P{=}N)_2SiMe_2$,

reacts with zinc and cadmium alkyls,[158] but not mercury alkyls, to yield 1:1 crystalline complexes with the silane acting as a 1,3-bidentate ligand.

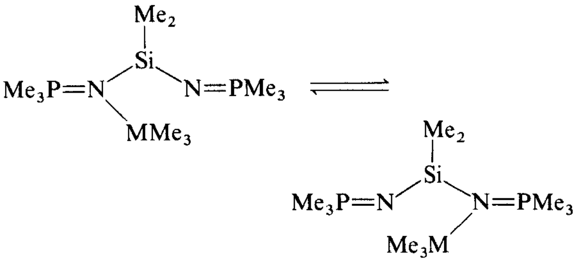


M = Zn, Cd; R = Me, Et

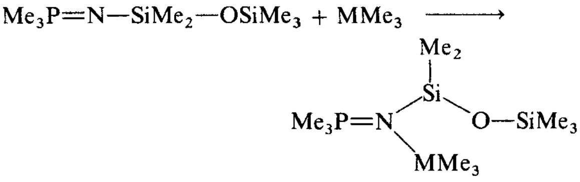
Reaction of $(Me_3P{=}N)_2SiMe_2$ with Group III trimethyl compounds gives 1:1 adducts[159] which were shown by n.m.r. to be non-rigid. The analogous compounds with

$Me_3P{=}N{-}SiMe_2{-}OSiMe_3$

give rigid, 1:1 adducts with coordination via the nitrogen atom.



(131)



(132)

M = Al, Ga, In

Triorganophosphinimines also react with a range of Lewis acids, including boron halides,[160] boranes[58] and Group III metal alkyls.[58,161]

$$Ph_3P{=}NH + BF_3 \longrightarrow Ph_3PNH \cdot BF_3 \quad (133)$$

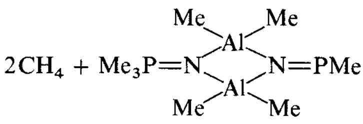
$$Ph_3P{=}NH + BPh_3 \longrightarrow Ph_3PNH \cdot BPh_3 \quad (134)$$

$$R_3P{=}NH + AlMe_3 \longrightarrow R_3PNH \cdot AlMe_3 \quad (135)$$

R = Me, Et

Such complexes are stable only at low temperature and decompose irreversibly above room temperature.

$$2Me_3P{=}NH \cdot AlMe_3 \longrightarrow$$

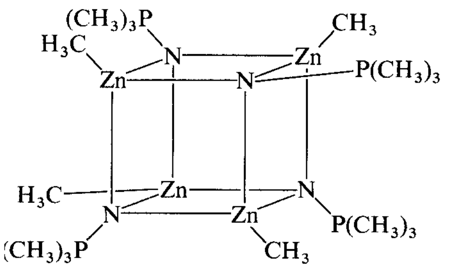


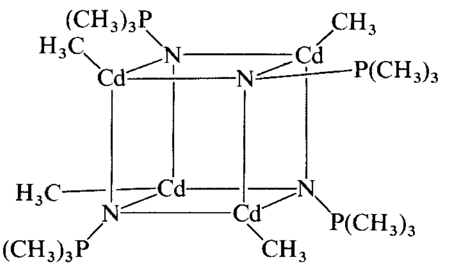
(136)

Trimethylphosphinimine reacts with Group II metal alkyls to give tetrameric complexes which have a cubane structure.[161,162]

$$4Me_3P{=}NH + 4Me_2M \longrightarrow 4CH_4 + [MeMNPMe_3]_4 \quad (137)$$

M=Zn, Cd





ii) Complexes with Metal Halides

Triarylphosphinimines can act as 2 electron donors by coordination to a metal centre via the lone pair on nitrogen. N-Phenyltriphenylphosphinimine has been reported to form complexes with cadmium and mercury iodides[163] which were poorly characterised.

$$Ph_3P{=}NPh + MI_2 \longrightarrow (Ph_3P{=}NPh) \cdot MI_2 \quad (138)$$

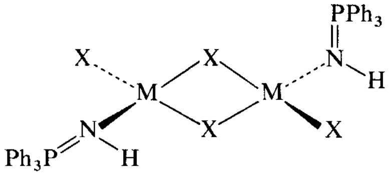
Triphenylphosphinimine forms air sensitive complexes with $CoCl_2$, $CuCl_2$ and NiI_2[164] (again, poorly characterised);

$(Ph_3P{=}NH)_2CoCl_2$, $(Ph_3P{=}NH)_2CuCl_2$

and

$(Ph_3P{=}NH)_4NiI_4 \cdot CH_3CN$.

Reaction of $Ph_3P{=}NSiMe_3$ with anhydrous dihalides of zinc, cadmium and mercury in ethanol results in cleavage of the Si—N bond of the phosphinimine to yield complexes of triphenylphosphinimine.[165] The products are air sensitive, soluble in $CHCl_3$ and all show $\nu(P{=}N)$ in the range 1106–1118 cm^{-1}. Complexes of the zinc dihalides and cadmium chloride were dimers $[MX_2L]_2$ with a *trans* tetrahedral dimeric structure with bridging halogens and terminal phosphinimine ligands. (The formation of only 1:1 complexes of the zinc dihalides is similar to their reaction with bulky tertiary phosphines whereas less bulky phosphine ligands yield 2:1 complexes ZnX_2L_2).

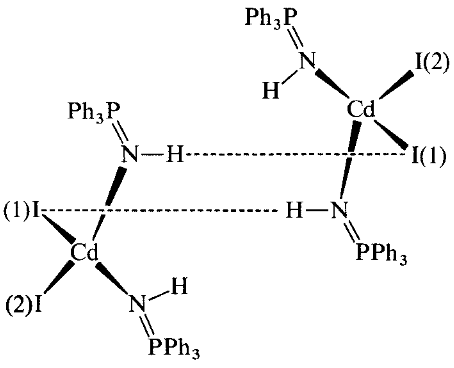


(34)

M = Zn; X = Cl, Br, I

M = Cd; X = Cl

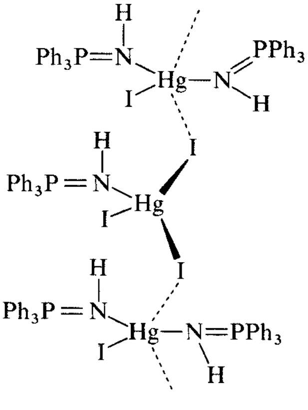
The structure of the CdI_2 complex has been shown to be a dimer $[CdI_2(Ph_3P{=}NH)_2 \cdot CHCl_3]_2$,[166] **(35)**.



(35)

The molecule contains two $CdI_2(Ph_3P{=}NH)_2$ units with nitrogen and iodine coordinated to cadmium in an approximately tetrahedral arrangement. The two Cd—N distances are equivalent but the two Cd—I distances are not equal. The iodine with the longer Cd—I bond (I(1)) forms a hydrogen bond with the N—H group of one of the phosphinimine ligands of the other unit of the molecule, giving an 8-membered ring. The P=N bond distance averages 1.57 Å.

The corresponding complexes of $HgCl_2$ and $HgBr_2$, $[HgX_2L \cdot CHCl_3]_2$ have a *trans* dimeric structure as in the zinc complexes. The complexes of HgI_2 and $CdBr_2$, however, have the stoichiometry $M_2X_4(Ph_3P{=}NH)_3$[165] and are considered to have a structure consisting of alternate 4- and 5-coordinate mercury (or cadmium) with bridging halide atoms (**36**), similar to that described for $Hg_2Cl_4(Me_2EtP)_3$.[167]



(**36**)

Recently tetrahedral complexes of metal dihalides with the bis-phosphinimine,

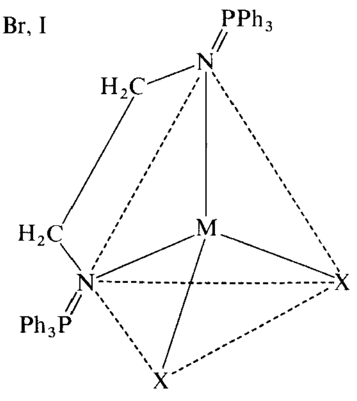
$Ph_3P{=}NCH_2CH_2N{=}PPh_3$,

have been described.[168]

$$Ph_3P{=}NCH_2CH_2N{=}PPh_3 + MX_2 \longrightarrow MX_2 \cdot (Ph_3P{=}NCH_2CH_2N{=}PPh_3) \tag{139}$$

M = Co, Ni; X = Cl, Br, I

M = Cd, Hg; X = Cl



iii) *Reactions with Metal Carbonyl Compounds*

The reactions of phosphinimines with metal carbonyl compounds is another area of phosphinimine chemistry that has received relatively little attention until recently, such reactions have now been shown to produce several interesting and unique complexes.

Triphenylphosphinimine reacts with vanadium hexacarbonyl[169] to form an ionic complex with a tetracoordinate V(II) cation.

$$4Ph_3P{=}NH + 3V(CO)_6 \longrightarrow [V(Ph_3P{=}NH)_4]^{2+}2[V(CO)_6]^- + 6CO \tag{140}$$

Malisch[170] has reacted the strongly acidic Group VI tricarbonyl halides

$[HM(CO)_3(\eta^5\text{-}C_5H_5)]$

with weakly basic phosphorus ylids and trimethylphosphinimine to yield anionic carbonyl metalates.

$$Me_3P{=}NH + [HM(CO)_3(\eta^5{-}C_5H_5)] \longrightarrow [Me_3PNH_2]^+[M(CO)_3(\eta^5{-}C_5H_5)]^- \tag{141}$$

M = Cr, Mo, W

In 1966 Bock and tom Dieck[171] described the preparation of some Group VI metal carbonyl complexes of the isoelectronic species $Ph_3P{=}NH$, $Ph_3P{=}O$ and $Ph_3P{=}CHCH_3$.

$$M(CO)_6 + 2Ph_3P{=}NH \longrightarrow [(Ph_3P{=}NH)_2M(CO)_4] + 2CO \tag{142}$$

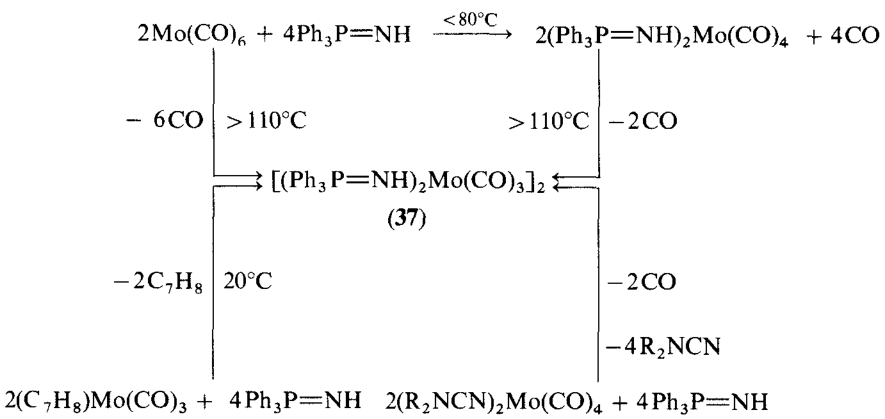
M = Mo, W

Treatment of the molybdenum complex under reflux in a high boiling solvent resulted in evolution of carbon monoxide and formation of a new complex which was extremely thermally stable. This complex was given the formula

$[(Ph_3P{=}NH)_2Mo(CO)_3]_2$ (**37**)

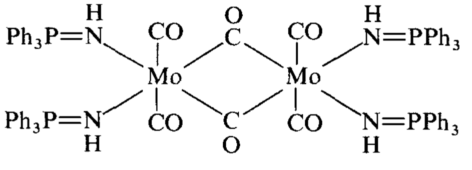
and was available from a number of other reactions, (Scheme IV).

The complex (**37**) showed two carbonyl stretching bands at 1894 cm^{-1} and 1770 cm^{-1} and on the basis that the latter was due to a bridging carbonyl group Bock and tom Dieck suggested structure (**38**). The infrared spectrum showed a very low $\nu(P{=}N)$ of 930 cm^{-1}, 220 cm^{-1} below that in *cis*$(Ph_3P{=}NH)_2MO(CO)_4$. Assuming that there is no metal-metal bond and that $Ph_3P{=}NH$ is



Scheme IV

acting as a 2-electron donor, complex (**38**) is 4-electrons short of satisfying the 18-electron rule.



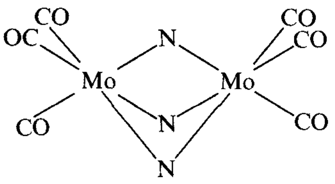
(**38**)

A more detailed investigation[172] showed that although ^{31}P-n.m.r. and ^{1}H-n.m.r. spectra were consistent with structure (**38**), ^{13}C-n.m.r. spectra were not, indicating that all carbonyl groups were equivalent down to $-90°$C. The ^{13}C-chemical shifts of the carbonyl carbons was unusually low at 218.4 ppm (relative to TMS).

The X-ray structure of (**38**)[172] showed this to be

$[Mo_2(CO)_6(\mu\text{-}Ph_3P{=}NH)_3]$, (**39**).

The two molybdenum atoms are octahedrally coordinated, sharing a face of 3 bridging atoms. Each CO is *trans* to a purely σ-donor, resulting in extensive back bonding and a high electron density on the carbon atoms. This explains the low $\nu(C{=}O)$ and the low ^{13}C-chemical shifts.

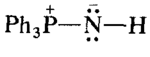


N = $Ph_3P{=}NH$

(**39**)

The nitrogen has sp^3 hybridization and the ligand is in the dipolar form (**39A**) and not the double bonded form which predominates in

cis$(Ph_3P{=}NH)_2Mo(CO)_4$.



$Ph_3\overset{+}{P}—\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}—H$

(**39A**)

The 18-electron rule is satisfied with the phosphinimine ligand acting as a 4-electron donor via the 2 lone pairs on nitrogen. The P=N bond is essentially a single bond which accounts for the low $\nu(P{=}N)$ of 930 cm^{-1}.

Recently Dilworth *et al.*[173] have described a phosphinimine complex from the reaction of $TiCl_4$ and $Ph_3P{=}NSiMe_3$, $[TiCl_4(Ph_3P{=}NSiMe_3)]$. This also has a very low $\nu(P—N)$ of 975 cm^{-1} which suggests to us that the phosphinimine ligand is acting as a 4-electron donor as described above.

Reaction of $[Rh(CO)_2Cl]_2$ and $Ph_3P{=}NH$ results in cleavage of the chlorine bridge and formation of

cis$[Rh(CO)_2Cl(Ph_3P{=}NH)]$.[165]

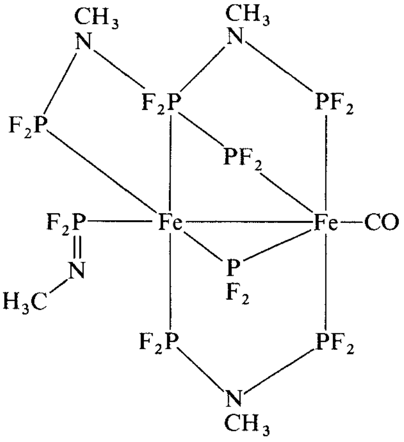
The phosphinimine can be displaced by Ph_3P and Ph_3As.

Treatment of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in ether under UV irradiation gave

$[CH_3N(PF_2)_2]_4Fe_2(CO)$,[174] (**40**).

The Fe—Fe distance is 2.725 Å, indicating a metal-metal bond, this is bridged by $3CH_3N(PF_2)_2$ ligands and one PF_2 group. The terminal $CH_3N{=}PF_2$ group acts as a one electron donor.

Alternatively the $FePF_2NCH_3$ unit may be regarded as a substituted phosphinimine, this is confirmed by the P—N distance of 1.59 Å while other P—N bond distances in the complex lie between 1.647 and 1.676 Å.



(40)

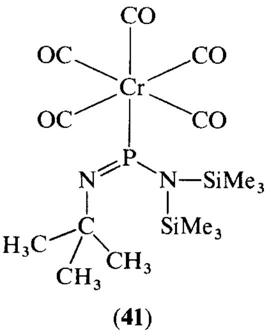
The 2-coordinate P(III) phosphinimine

$(Me_3Si)_2N—P{=}N—t\text{-}Bu$, **(24A)**,

reacts with $Cr(CO)_6$, displacing one CO ligand and complexing via the phosphorus atom to give

$Cr(CO)_5P(N—t\text{-}Bu)N(SiMe_3)_2$,[175] **(41)**.

The phosphorus atom has trigonal planar coordination, for steric reasons the ligand adopts a *cis* configuration with a N—P—N angle of 119.6°. The P—N single and double bonds are distinguishable.



(41)

iv) Platinum and Palladium Complexes

The first platinum and palladium complexes of phosphinimines have recently been reported. Reaction of dichlorobis(benzonitrile)-palladium(II) and N-arylphosphinimines[176] gave quantitative yields of:

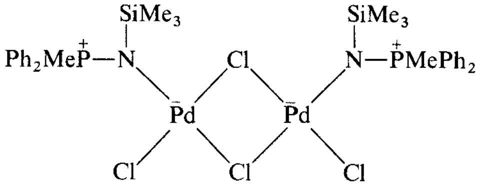
$[(Ph_3P{=}NC_6H_4\cdot X(p))PdCl_2]_2$,

$X = NO_2$, COOEt, Cl, H, CH_3.

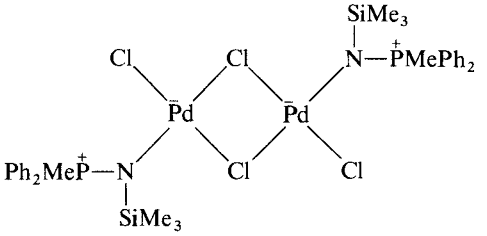
On recrystallisation from CH_3CN/CH_3COOEt the chloride bridge was broken to give the monomeric species

trans$[(Ph_3P{=}NC_6H_4\cdot X(p))PdCl_2(CH_3CN)]$.

The reaction of dichlorobis(benzonitrile)palladium (II) with $Ph_2MeP{=}NSiMe_3$ gave a stable dimeric complex $[(Ph_2MeP{=}NSiMe_3)PdCl_2]_2$ which was shown, by ^1H-n.m.r., to be a mixture of *cis* and *trans* isomers (1:2). The large decrease in $\nu(P{=}N)$ from 1307 cm^{-1} in the free ligand to 1070 cm^{-1} in the complex was attributed to the exclusive contribution of the zwitterionic structure.



cis



trans

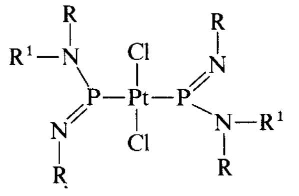
The Si—N bond in these complexes was found to be stable to hydrolysis.

Zeise's salt undergoes reaction with the 2-coordinate P(III) phosphinimine

$(Me_3Si)(t\text{-}Bu)N—P{=}N—t\text{-}Bu$

to give a complex where the ligand is coordinated via the phosphorus atom, a P—Pt σ bond is proposed.[177]

$$\mathrm{K[PtCl_3(C_2H_4)] + 2RR^1N{-}P{=}NR \xrightarrow[-C_2H_4]{-KCl}}$$

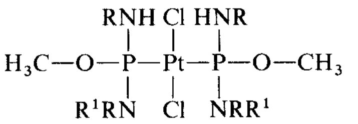


(42)

R = *t*-Bu; $R^1 = Me_3Si$ (143)

This is supported by reaction of the complex **(42)** with methanol, which does not cleave the P=N bonds.

(42) + MeOH ⟶

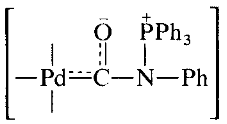


$$\mathrm{H_3C{-}O{-}\overset{RNH}{\underset{R^1RN}{P}}{-}\overset{Cl}{\underset{Cl}{Pt}}{-}\overset{HNR}{\underset{NRR^1}{P}}{-}O{-}CH_3} \quad (144)$$

v) *Wittig-type Reactions*

Treatment of $PdCl_2$ with N-phenyltriphenylphosphinimine under an atmosphere of carbon monoxide leads to products from a Wittig-type reaction.[178]

$$\mathrm{2Ph_3P{=}NPh + PdCl_2 + CO \longrightarrow}$$



$$\left[-\underset{|}{\overset{|}{\mathrm{Pd}}}\cdots\overset{\bar{\mathrm{O}}}{\overset{\Vert}{\mathrm{C}}}-\overset{\overset{+}{\mathrm{P}}\mathrm{Ph_3}}{\overset{|}{\mathrm{N}}}-\mathrm{Ph}\right]$$

$$\longrightarrow \mathrm{[(Ph_3P{=}NPh)PdCl_2(CNPh)] + Ph_3P{=}O} \quad (145)$$

(43)

The isocyanide ligand of **(43)** can be replaced with carbon monoxide.

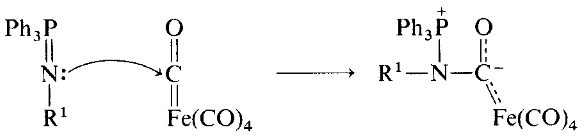
$$\mathrm{[(Ph_3P{=}NPh)PdCl_2(CNPh)] + CO \longrightarrow [(Ph_3P{=}NPh)PdCl_2(CO)]} \quad (146)$$

The reaction of iron pentacarbonyl with N-aryltriphenylphosphinimines[179] led to a novel deoxygenation of a carbonyl group without cleavage of the iron-carbon bond.

$$\mathrm{Ph_3P{=}NR^1 + Fe(CO)_5 \longrightarrow Fe(CO)_4(C{\equiv}N{-}R^1) + Ph_3P{=}O + Fe(CO)_3(C{\equiv}N{-}R^1)_2} \quad (147)$$

$R^1 = (o), (m), (p)CH_3 \cdot C_6H_4$

The mechanism is thought to involve attack of the phosphinimine nitrogen on a metal carbonyl carbon giving a dipolar intermediate **(44)**.



(44)

$$\longrightarrow \mathrm{Fe(CO)_4(C{\equiv}N{-}R^1) + Ph_3P{=}O} \quad (148)$$

Chatt and Dilworth[180] have shown that $Ph_3P{=}NPh$ and $Ph_3P{=}NCOPh$ react with the Re=O bond of $[ReCl_3(O)(PPh_3)_2]$ in a manner analogous to that of a C=O bond to give an organo-nitrene complex.

$$\mathrm{[ReCl_3(O)(PPh_3)_2] + Ph_3P{=}NPh \longrightarrow [ReCl_3(NPh)(PPh_3)_2] + Ph_3P{=}O} \quad (149)$$

$$\mathrm{[ReCl_3(O)(PPh_3)_2] + Ph_3P{=}NCOPh \longrightarrow [ReCl_3(NCOPh)(PPh_3)_2] + Ph_3P{=}O} \quad (150)$$

N-Aroylphosphinimines, $Ph_3P{=}NCO \cdot C_6H_4R$

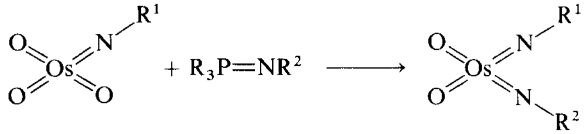
(R=H, (*p*)MeO, (*p*)Cl),

react with $[OsCl_3(O)(PPh_3)_2]$ to give not the corresponding aroylnitrene complexes but the aryl-nitrene complexes

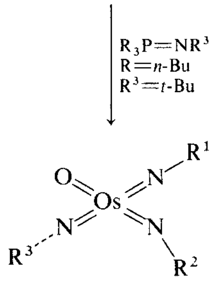
$[OsCl_3(NC_6H_4 \cdot R)(PPh_3)_2]$.

Reaction of oxo-osmium(VIII) compounds with phosphinimines gives rise to nitrene complexes[181] in a Wittig type reaction.

$$\mathrm{OsO_4 + R_3P{=}NR^1 \longrightarrow}$$



R = Ph, *n*-Bu; R^1 = *t*-Bu R^2 = *t*-Bu, adamantyl



These complexes proved to be useful for the vicinal diamination of olefins.

vi) Complexes of the Phosphinimidate Ligand

In 1973 Griffith and Pawson[182] noted the unusual behaviour of some osmium nitride complexes with triphenylphosphine. [n-Bu_4N][$OsNX_4$] reacted with excess triphenylarsine or triphenylstibine to give

$[OsNX_3(AsPh_3)_2]$ (X=Cl, Br)

or

$[OsNX_3(SbPh_3)_2]$ (X=Cl).

Treatment with triphenylphosphine, however, yielded a paramagnetic species of empirical formula

$[OsNCl_3(PPh_3)_3]\cdot Me_2CO$ (**45**),

which reacted with chlorine to give

$[OsNCl_3(PPh_3)_2]$.

A protonated form of (**45**),

$[OsNHCl_4(PPh_3)_2]\cdot Me_2CO$

was isolated, this could be deprotonated to

$[OsNCl_3(PPh_3)_2]$

with excess Et_3N in the presence of triphenylphosphine.

These complexes were formulated as Os(IV) derivatives of triphenylphosphinimine. i.e.

$[Os(N{=}PPh_3)Cl_3(PPh_3)_2]\cdot Me_2CO$

and

$[Os(HNPPh_3)Cl_4(PPh_3)]\cdot Me_2CO$

respectively. It was proposed that the formation of these complexes proceeded by nucleophilic attack of the phosphine on the coordinated nitrogen atom which behaves as an electrophilic nitrene.

This work was soon extended to include new complexes of osmium and ruthenium[183,184]

$[M(N{=}PR_3)Cl_3(PR_3)_2]$ (M=Os, Ru;

PR_3= $PPhEt_2$, PPh_2Et, PPh_2Me, PEt_3).

The osmium complexes were shown to have magnetic moments of 1.9 BM and the ruthenium complexes 2.9 BM, values typical for M(IV) species. All complexes exhibited strong, broad bands in the 1050–1200 cm^{-1} region, attributed to the $\nu(P{=}N)$ stretching mode of $(R_3P{=}N{-})^-$.

An X-ray crystal structure determination of

$[Ru(N{=}PPhEt_2)Cl_3(PPhEt_2)_2]$[185]

confirmed the suggestion that the complexes contained a phosphinimidate ligand. The ruthenium atom has a slightly distorted octahedral coordination with the phosphinimidate ligand coordinated in an almost linear fashion and a Ru—N—P angle of 175.0°. The P=N distance of 1.57 Å is typical of phosphorus-nitrogen double bonds in phosphinimines. The mean Ru—Cl (*trans* to Cl) distance of 2.388 Å compared to the Ru—Cl (*trans* to N) distance of 2.398 Å suggests that the $(PhEt_2P{=}N)^-$ ligand exerts little, if any, *trans* influence.

A series of novel complexes also containing the $(R_3P{=}N)^-$ ligand has been isolated by Scott and Wedd[186,187]. Reaction of $[MoCl_4(R_2R^1P)_2]$ with p-toluene sulphonylazide results in oxidation of the phosphine ligands by nitrogen and oxygen from the azide.

$$2[MoCl_4(R_2R^1P)_2] + 2(p)CH_3\cdot C_6H_4\cdot SO_2N_3 \longrightarrow$$
$$2[MoCl_4(N{=}PR_2R^1)(R_2R^1P{=}O)]$$
$$+ (p)CH_3\cdot C_6H_4\cdot S\cdot SO_2\cdot C_6H_4\cdot CH_3(p) + 2N_2 \quad (152)$$

R=Ph; R^1 = Et, n-Pr, Ph

R=Me; R^1 = Ph

R=Et; R^1 = Et

The complexes

$[MoCl_4(N{=}PPh_2n\text{-}Pr)(Ph_2n\text{-}PrP{=}O)]$

and

$[MoCl_4(N{=}PPhMe_2)(PhMe_2P{=}O)]$

have also been isolated together with other products, from reaction of $MoCl_5(NO)$ with Ph_2n-PrP or $PhMe_2P$.[188] Formation of the phosphinimidate ligand may arise from nucleophilic attack of phosphine on the coordinated nitrogen oxide, thus weakening the N—O bond and facilitating removal of oxygen by another phosphine molecule.

Reaction of $Ph_3P{=}NSiMe_3$ with

$[Ti(\eta^5\text{-}C_5H_4R)Cl_3]$ (R=H, Me)

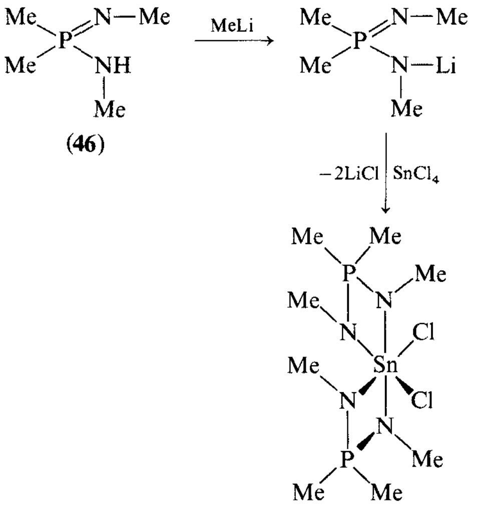
also gives a complex containing a phosphinimidate ligand,

$[Ti(\eta^5\text{-}C_5H_4R)Cl_2(N{=}PPh_3)]$[173]

which has $\nu(P{=}N)$ at 1150 cm^{-1}.

vii) Other complexes

A new type of phosphinimino ligand has been synthesised by Scherer and Schabl[189] **(46)**, who have begun to investigate its chelating abilities.

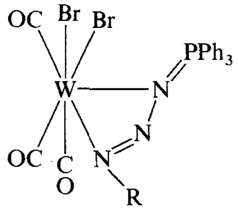


(153)

Treatment of $[WBr_2(CO)_3(PPh_3)_2]$ with $(p)CH_3 \cdot C_6H_4 \cdot N_3$ gives a complex where all three nitrogen atoms are retained **(47)**[190], this is the first complex of a phosphazide, the compound shows no bands in the infrared spectrum due to an azide group.

$$[WBr_2(CO)_3(PPh_3)_2] + 2RN_3 \longrightarrow \underset{(47)}{[WBr_2(CO)_3(RN_3PPh_3)]} + RNPPh_3 + N_2 \quad (154)$$

$R{=}(p)CH_3 \cdot C_6H_4$



(47)

8 BIS(TRIPHENYLPHOSPHINE)IMINIUM SALTS, $[(PPh_3)N(PPh_3)]^+$

The isolation of labile complex anions of air sensitive species is often facilitated by combination with bulky organic cations since these render the products soluble in organic solvents, enhance their stability and make crystallisation easier. The bis(triphenylphosphine)iminium cation,

$[(Ph_3P)N(PPh_3)]^+$,

has a remarkable ability to perform such a function which has been demonstrated on numerous occasions.[191–205]

Recently $[(Ph_3P)N(PPh_3)]^+$ salts of small inorganic ions have been described.[206]

The name of the $[(PPh_3)N(PPh_3)]^+$ cation has been the subject of some discussion but bis(triphenylphosphine)iminium cation seems the most popular and Martinsen and Songsted[206] have suggested the abbreviation $[PNP]^+$.

The rather lengthy preparation of $[PNP]^+Cl^-$, used in the metathesis of $[PNP]^+$ salts, first described by Appel and Hauss,[57] has been superseded by a more simple synthesis.[207]

$$2Ph_3PCl_2 + PPh_3 + NH_2OH \cdot HCl \longrightarrow [(Ph_3P)N(PPh_3)]^+Cl^- + Ph_3P{=}O + 4HCl \quad (155)$$

Structural determinations have shown the $[PNP]^+$ cation to have a bent geometry in most complexes[208–218] with a P—N—P angle in the range 135–142° and P—N bond distances in the region 1.566–1.586 Å. In $[PNP]^+[V(CO)_6]^-$[219] the $[PNP]^+$ cation has a linear structure with rather shorter P—N bond lengths (1.539 Å) than in the bent form.

The bis(triphenylphosphine)iminium cation has been the subject of an X-ray photoelectron spectroscopic study,[220] the authors concluded that the cation is best represented as structure **(48)** since the nitrogen atom carries a degree of negative charge and the two equivalent phosphorus atoms carry some positive charge.

$$[Ph_3P{-}\overset{+}{N}{-}PPh_3] \longrightarrow \underset{(48)}{[Ph_3\overset{+}{P}{-}\overset{-}{N}{-}\overset{+}{P}Ph_3]}$$

Under certain conditions $[Me_4P]Cl$ reacts with sodamide to form the double ylid

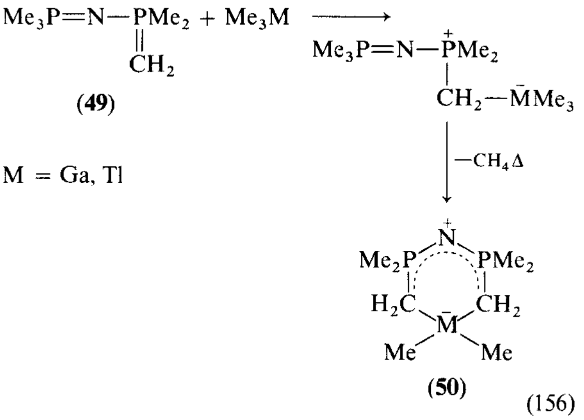
$(Me_3P{=}N)(CH_3)_2P{=}CH_2$,[221] **(49)**.

This conjugated double ylid undergoes rapid proton scrambling in solution and in the liquid. Treatment with $HX (X = Cl, Br, I)$ gives salts of the bis(trimethylphosphine)iminium cation,

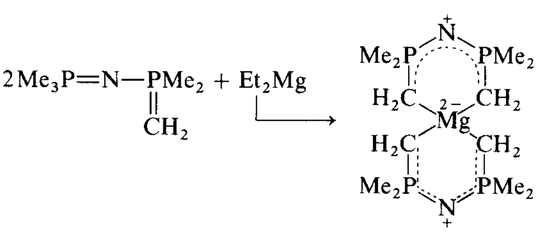
$[(Me_3P)N(PMe_3)]^+X^-$.

Reaction of **(49)** with Me_3Ga or Me_3Tl gives a 1:1 complex which upon thermolysis eliminates CH_4 and forms a cyclic complex **(50)**. Reaction of

(49) with Et_2Mg forms a 2:1 complex **(51)**; in complexes **(50)** and **(51)**, the central metal atom is participating in four strong M— σ-bonds.



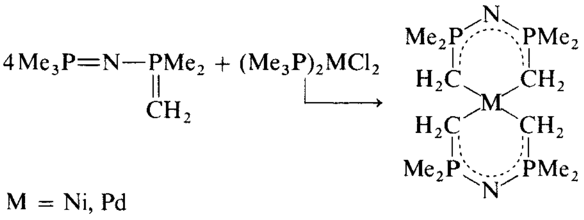
(156)



(51)

(157)

$(Me_3P{=}N)(CH_3)_2P{=}CH_2$ undergoes transylidation reactions with $(Me_3P)_2NiCl_2$, $(Me_3P)_2PdCl_2$, $[Me_2AuCl]_2$, $MR_2(M{=}Zn, Cd; R{=}Me, Et)$[222] and $[(1, 5\text{-}C_8H_{12})RhCl]_2$.[223]



$+ 2[(Me_3P)N(PMe_3)]^+Cl^-$

(158)

9 DIALKYLAMINOPHOSPHONIUM SALTS, $[R_2N—P—NR_2]^+$

Another interesting series of complexes recently discovered are those containing the dicoordinate phosphorus cation, $[R_2N—P—NR_2]^+$. Reaction of $(Me_2N)_2PCl$, or Me_2NPCl_2, with a series of Lewis acids gives salts containing the

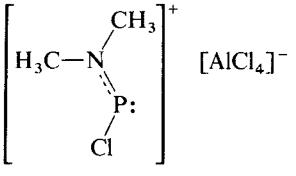
$[Me_2N—P—NMe_2]^+$

cation or the $[Me_2NPCl]^+$ cation.[224] In these cations the P atom is the most deshielded phosphorus yet recorded, at −325 ppm from H_3PO_4.

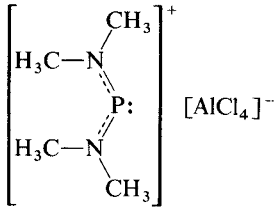
$$Me_2NPCl_2 + AlCl_3 \longrightarrow \underset{(52)}{[Me_2NPCl]^+}[AlCl_4]^- \qquad (159)$$

$$(Me_2N)_2PCl + AlCl_3 \longrightarrow \underset{(53)}{[Me_2N—P—NMe_2]^+}[AlCl_4]^- \qquad (160)$$

also with PF_6^-, $B_2F_7^-$, $GaCl_4^-$, $FeCl_4^-$.



(52)



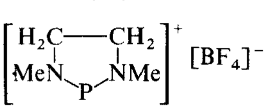
(53)

The crystal structure of

$[((i\text{-}Pr)_2N)_2P]^+[AlCl_4]^-$[225]

has shown the phosphorus atom to have approximately trigonal planar hybridization, with a N—P—N angle of 114.8°; reduction from 120° is presumably due to lone pair repulsions. The P—N bond length of 1.613 Å, which is shorter than in aminophosphines, is due to π-bonding between the phosphorus and nitrogen atoms. The phosphorus atom has a lone pair plus a formally vacant orbital and thus the cation can act as a Lewis acid.

The first report of a divalent phosphorus cation was in 1972,[226] the complex having a cyclic cation, **(54)**.



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