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Inorganic backbone phosphines

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Abstract

The synthesis, reactivity and structures of bidentate ligands P–E–P (E = main group atom or group of atoms) are reviewed.

Keywords: Phosphines; Bidentate ligands; Inorganic

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1. Introduction

It is without a doubt that tertiary mono- and diphosphines are the most extensively used ligands throughout inorganic and organometallic chemistry [1–4]. The most widely reported of the bidentate phosphorus ligands are $Ph_2PCH_2CH_2PPh_2$ [bis(diphenylphosphino)ethane, dppe] and $Ph_2PCH_2PPh_2$ [bis(diphenylphosphino)methane, dppm] both of which have become increasingly used because of their ready coordination to metal centres, through the lone pair of electrons on the two phosphorus atoms, and their variety of coordination modes (monodentate, chelating and bridging). Examples of diphosphines in which the carbon chain is longer than two [5–7] and those that have an aromatic link [8,9] between the two phosphorus atoms have also been reported.

The major application of metal complexes containing phosphine ligands is in homogeneous catalysis. Since Wilkinson's [10] original work on the catalytic activity of $Rh(PPh_3)_3Cl$ for hydrogenation reactions, phosphine complexes have been extensively developed and are now commonly in use in carbonylation, hydroformylation, isomerisation and other organic syntheses [11–14]. More recently, though, attention has been directed towards chiral complexes containing optically active backbones for asymmetric reactions [9,15].

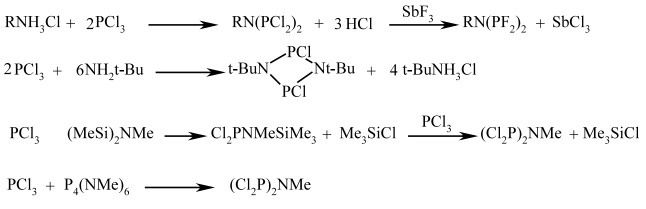
Compared to the vast body of data accumulated for diphosphines containing carbon backbones there has been very little coverage of diphosphine ligands with hetero atom or group backbones. Bis(diphenylphosphino)amine and bisphosphino hydrazine, for example, are isoelectronic with dppm and dppe, and demonstrate similar coordinative versatility, however, the different electronic properties of the carbon and nitrogen have significant effects on the reactivity. This is a similar case for other hetero atom backbones such as oxygen, sulfur, selenium and silicon.

This report intends to bring together much of the information on diphosphines with N, O, S and Se hetero atom or groups linking the two phosphorus atoms, reviewing their synthesis, reactivity and coordination chemistry. Starting with the simplest example where only one atom links the phosphorus, building up to larger and more complicated backbones. We have tried to be thorough but undoubtedly have omitted examples which could have been included—in this regard we apologise in advance to any author whose contribution has been neglected. It is becoming increasingly difficult to cope with the extensive literature and thus we hope this review provides at least an introduction into this diverse area.

2. One bridging atom

2.1. Bis(phosphino)amines

This is the first example of a diphosphine ligand in which the two phosphorus atoms are linked by a heteroatom or group. With the first synthesis being



Scheme 1. Synthesis of $(PX_2)_2NR$ ligands.

reported in the early sixties [16], subsequently a relatively large amount of work has been carried out in this area in comparison to other heteroatoms or larger hetero bridges. Bis(diphenylphosphino)amine is of particular importance as it is isoelectronic with bis(diphenylphosphino)methane (dppm), which is itself an increasingly used ligand [17].

2.1.1. Synthesis

The reaction of chlorodiphenylphosphine with a primary alkylamine leads to the production of compounds of the type $Ph_2P{-}NR{-}PPh_2$ (R = Me, Et, *n*-Pr) [18] (Eq. (1)). By similar methods, other derivatives can also be produced. The reaction of $HRNP(CF_3)_2$ with $(CF_3)_2PCl$ gives the compound $(CF_3)_2P{-}NR{-}P(CF_3)_2$ (R = H, Me) (Eq. (2)), in addition the tris(phosphino) amine $N[P(CF_3)_2]_3$ in which R is $P(CF_3)_2$, is produced by the reaction of $(CF_3)_2PCl$ with the sodium salt $NaN[P(CF_3)_2]_2$ [19] (Eq. (3)).

$$\mathrm{Clph_2p + RNH_2 \rightarrow Ph_2PN(R)PPh_2} \quad \mathrm{R = Me,\ Et,\ \mathit{n}\text{-}Pr} \tag{1}$$

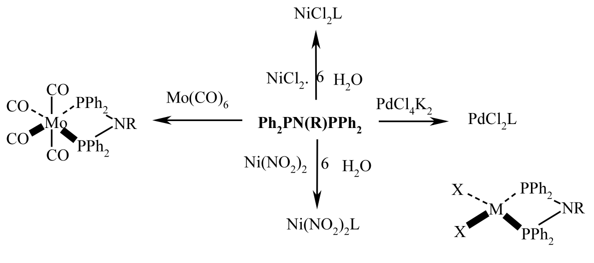
$$\mathrm{(CF_3)_2PCl + HRNP(CF_3)_2 \rightarrow (CF_3)_2PN(R)P(CF_3)_2} \quad \mathrm{R = H,\ Me} \tag{2}$$

$$\mathrm{NaN[P(CF_3)_2]_2 + (CF_3)_2PCl \rightarrow N[P(CH_3)_2]_3} \tag{3}$$

Ligands of the type $RN(PCl_2)_2$ can be synthesised by a variety of routes, the most common is the reaction of RNH_3Cl with two equivalents of PCl_3 (R = Me, Et) [22]. Analogous reactions using R = *i*-Pr, *t*-Bu give four membered heterocycles. Subsequent reaction of the chloro-ligand with antimony trifluoride yields the fluoro-derivative $RN(PF_2)_2$ [22]. Alternative routes to the ligand $(Cl_2P)_2NMe$ involve reactions with silanes and ring opening reactions [25] (Scheme 1).

2.1.2. General chemistry

Bis(diphenylphosphino)alkylamines behave as diphosphines in many of their reactions. Oxidation occurs with ozone or manganese dioxide to produce the corresponding dioxide, whilst reaction with sulfur yields the disulfides [18]. Separation of the two phosphorus atoms by the *N*-alkyl group does not always permit them to react independently and so only the 1:1 adduct is formed on reaction with alkyl iodide. For example, the reaction of methyl iodide with bis(diphenylphosphino)alkylamine gives the product $[(Ph_2PMe)N(Ph_2P)]^+I^-$, in which the phosphorus is a quaternary centre and so the product is a phosphonium salt [22]. The production of a 1:1 adduct supports theories of delocalisation in the trivalent P–N system due to pπ–dπ bonding.



Scheme 2. Coordination of $Ph_2PN(R)PPh = 2$.

The P–N bond is cleaved when the free ligand is reacted with gaseous HCl, producing the corresponding alkylamine hydrochloride and chlorodiphenylphosphine. Whilst dilute aqueous HCl hydrolyses the P–N bond to the alkylammonium ion and diphenylphosphinous acid, which then disproportionates and is oxidised to diphenylphosphinic acid. Concentrated aqueous HCl does not hydrolyse the bond, but forms the corresponding hydrochlorides [18].

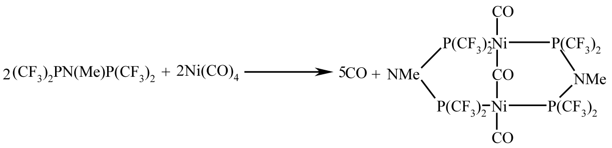
In comparison the bis(trifluoromethyl phosphino)amines are more resistant to cleavage and will not react with protic or Lewis acids such as HCl, BCl_3 or BF_3, neither do they react with vapour phase ammonia [19,22]. Similarly alkylamino bis(difluorophosphines) do not form adducts with BF_3, but do react with gaseous hydrogen chloride with cleavage of both P–N bonds to form chlorodifluorophosphine [22].

2.1.3. Coordination chemistry

Bis(diphenylphosphino)alkylamine acts as a bidentate, chelating ligand on coordination with Ni(II) and Pd(II), to form complexes of the type LMX_2 [18], where $L = (Ph_2P)_2NR$. Reaction of the ligand with nickel chloride hexahydrate, nickel nitrate hexahydrate or potassium tetrachloropalladate yields these complexes (Scheme 2).

This ligand also forms complexes with molybdenum, where again the ligand is in *cis* geometry, but in this case, the complex is octahedral, $MoL(CO)_4$ [20]. The molybdenum complex has been particular of interest due to shifts in CO frequencies which are used as a measure of π-bonding in the phosphine ligand. Changes in frequency are due to changes in the degree of π-bonding in the carbon monoxide and in-turn π-bonding in the other ligands as well. Payne and Walker [20] have shown no significant changes in stretching frequency due to the nitrogen bridge, this is because of a balance between the N–P π-bonding and the electronegativity of nitrogen.

Reaction of the ligand $(CF_3)_2PN(R)P(CF_3)_2$ (R = H, Me) with $Ni(CO)_4$ in equimolar quantities produces the complex $L_2Ni_2(CO)_3$ [21,23], where $L = \{(CF_3)_2P]_2NMe\}$ (Eq. (4)). IR spectra show the complex to contain both terminal and bridging carbon monoxide, on heating the complex in CO the original ligand is produced, proving the ligand remains intact during complexation [21]. The complex has been shown to have a bicyclic structure in the vapour phase [23] and it has been assumed the two hexatomic rings have a cyclohexane chair conformation. Under other conditions, the structure remains uncertain.



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2.1.4. NMR studies [24]

NMR studies of the ligand type PNP have been conducted on alkyl and aryl aminobis(difluorophosphines), $RN(PF_2)_2$ (R = Me, Et, Ph, *m*-ClC_6H_4). On analysis of the phosphorus and fluorine spectra it was found the phosphines were examples of the XX′AA′X″X‴ spin system (A = phosphorus, X = fluorine), showing the chemically equivalent fluorine and phosphorus are magnetically inequivalent. Constants for phosphorus–phosphorus, direct phosphorus–fluorine, remote phosphorus–fluorine and two remote fluorine–fluorine coupling constants have been measured.

In the fluorine spectrum the effect of proton coupling only slightly broadens the lines, except in the case R = Me, where each fluorine resonance is seen as a 1:3:3:1 quartet [J_{FH} (1.6 Hz)].

The ^{31}P spectra show much larger coupling to both the direct and distant fluorine in comparison to similar ligands (R_2NPF_2, $RNHPF_2$), which is an effect of the presence of four electronegative fluorine atoms per molecule. More interesting are the unusually high values of the geminal phosphorus–phosphorus coupling constants (370–446 Hz), which are larger than many directly bonded phosphorus–phosphorus, coupling constants and decrease in the order R = Me ~ Et > Ph ~ *m*-ClC_6H_4.

2.2. Chiral bidentate phosphines

There has been great coverage of the use of complexes containing bidentate phosphine ligands as homogeneous catalysts, in the late seventies attention turned to catalysts for asymmetric reactions, hence a need for chiral catalysts. Chiral, bidentate phosphine complexes can have the chiral centre on the backbone joining the two phosphorus nuclei or away from the backbone on the alkyl substituent of nitrogen.

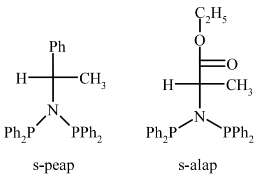
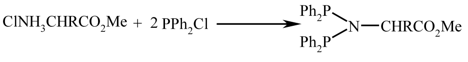


Fig. 1. Structures of *s*-peap and *s*-alap.

2.2.1. Synthesis

The reaction of chlorodiphenyl phosphine with a-aminoacidmethylesterhydrochloride produces the corresponding amino phosphine, *N*,*N*-bis(diphenylphosphino)-α-alkylaminoacidmethylester (Eq. (5)). Ligands synthesised have included R = H, Me (l), CH_2Ph (l), CH_2CH_2SMe (dl) [26].



$$ClNH_3CHRCO_2Me + 2\,PPh_2Cl \longrightarrow (Ph_2P)_2N{-}CHRCO_2Me$$

(5)

R=H, Me, CH_2Ph, i-Pr, CH_2CH_2SMe

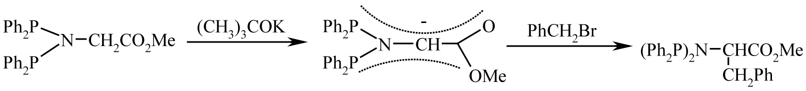
The same reaction can be used to produce $(PPh_2)_2NCHMePh$ (*s*-peap) and $(PPh_2)_2NCHMeCO_2Et$ (*s*-alap) [27] (Fig. 1), where the amine acts as a nucleophile attacking the phosphorus centre. The starting materials for these two reactions are $(-)_{589}$-*s*-a-phenylethylamine and $(-)_{589}$-*s*-alanine ethylester hydrochloride, respectively.

2.2.2. General chemistry

The P–N bond of the free ligand $(Ph_2P)_2NCH_2CO_2Me$ is readily cleaved by HCl, however on complexation the ligand is stabilised and the P–N bond is not cleaved by HCl [26]. Surprisingly alkylation of $(Ph_2P)_2NCH_2CO_2Me$ does not occur at the phosphorus, but rather at the carbon bonded to nitrogen, for example, in the reaction with $KOBu^t$ followed by benzyl bromide, the *N*-benzylated product is obtained [27] (Eq. (6)). The potassium butoxide removes one of the hydrogens, leaving a carbanion which is stabilised by the phosphorus and oxygen, the stabilised anion then reacts with the benzyl bromide.

2.2.3. Coordination chemistry

Planar complexes of palladium, platinum and rhodium can be synthesised by reaction of the complex with the diphenyl phosphino-α-aminoacid methylester [26] (Scheme 3). The amino acid ester ligand coordinates through both phosphorus atoms in a *cis* geometry. The platinum and palladium complexes have only one amino acid ester ligand coordinated, whilst two coordinate to



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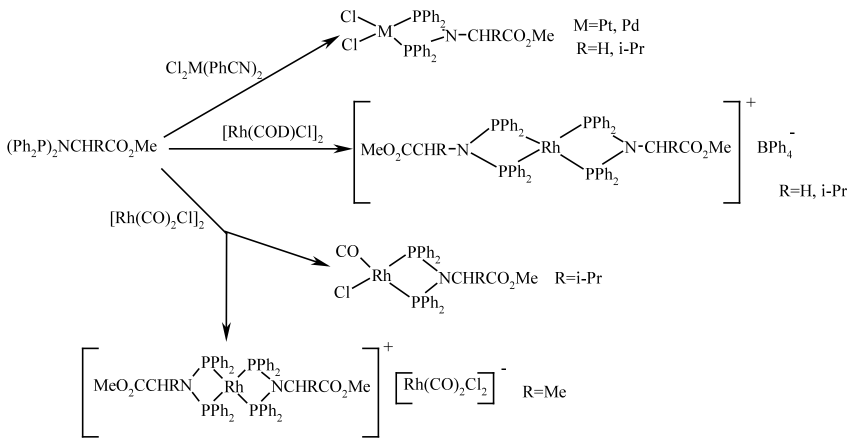
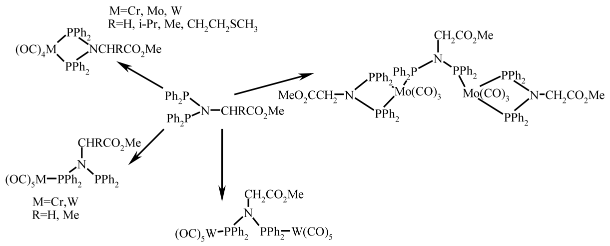
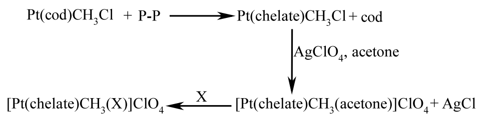


Scheme 3. Coordination of $(Ph_2P)_2NCHRCO_2Me$ to Rh, Pt, Pd.



Scheme 4. Coordination of $(Ph_2P)_2NCHRCO_2Me$ to Cr, Mo, W.



P-P=$(Ph_2P)_2NCC(CH_3)Ph$, $(Ph_2P)_2NCH(CH_3)CO_2Et$
X=YC_5H_4N (Y=Me, Et, CHO, CO_2CH_3, H, NMe_2), $AsPh_3$, $SbPh_3$, PPh_3, PEt_3, PPr_3

Scheme 5.

rhodium, however if $(PPh_2)_2NCH(i\text{-}Pr)CO_2Me$ is reacted with $[Rh(CO)_2Cl]_2$ a rhodium complex containing only one chelate ligand can be produced, $Rh(CO)Cl[(PPh_2)_2NCH(i\text{-}Pr)CO_2Me]$.

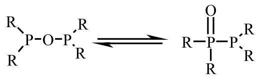
A variety of complexes of chromium, molybdenum, tungsten and manganese can be formed (Scheme 4). The complex produced depends on the relative amounts of the starting complex and the amino acid ester ligand, and the ligands on the starting complex. The coordination of the amino acid ester ligand varies from chelating in a regular octahedral geometry, to bridging or coordination via only one phosphorus.

In the case of *s*-alap and *s*-peap chelate complexes of the form $Pt(P{-}P)CH_3Cl$ and $[Pt(P{-}P)CH_3(X)]ClO_4$ can be formed [27]. Displacement of 1,5-cyclooctadiene (cod) in $Pt(cod)CH_3Cl$ by either *s*-alap or *s*-peap forms the halide complex, further reaction of this with $AgClO_4$ in acetone produces the acetone adduct $[Pt(P{-}P)CH_3acetone]^+$ with perchlorate as the non-coordinating anion. The acetone can then be displaced by X, which is a group V donor molecule that readily displaces acetone, to give the final complex $[Pt(P{-}P)CH_3X]ClO_4$. X can be a *para*-substituted pyridine or one of a number of phosphorus, arsenic or antimony ligands (Scheme 5).

There are some interesting features in the NMRs of these complexes, when compared to the analogues in which there is a carbon instead of nitrogen. The amine complexes show greater $Pt{-}CH_3$ coupling [27] due to the poorer donor ability of these phosphines. The poor donor ability is due to the electronegative nitrogen and delocalisation of the lone pair on phosphorus, causing greater *s*-character of the $Pt{-}CH_3$ bond and hence larger coupling.

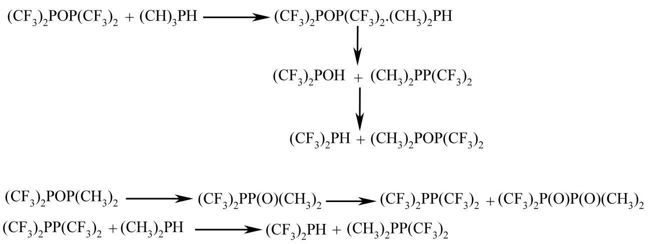
2.3. Diphosphoxanes

Diphosphoxanes are a series of ligands in which the backbone is P–O–P. These were initially difficult ligands to produce due to Arbuzov rearrangement and disproportionation making them unstable;



However, if R is electron withdrawing, such as a fluorocarbon group, the phosphorus is so weakly basic in the $(CF_3)_2P{-}O^-$ type molecule it is unable to bind to a $+P(CF_3)_2$ group as strongly as oxygen does, hence no rearrangement. Additionally the electron acceptor character of the $(CF_3)_2P$ group supports two way dative π-bonding between the oxygen lone pairs and the 3d orbitals on the phosphorus, where as in $(CF_3)_2P(O)P(CF_3)_2$ only one phosphorus would be involved.

Also interesting is the coordination of diphosphoxane ligands. The two tautomeric forms and the presence of both hard (P=O) and soft (P) donor sites leads to an increased number of coordination modes; monodentate, chelating or bridging via P or O.



Scheme 6. Formation of $(CF_3)_2POP(CH_3)_2$ and side reactions.

2.3.1. Synthesis

The diphosphoxane $(CF_3)_2POP(CF_3)_2$ is readily produced in high yields in the reaction $2(CF_3)_2PI + Ag_2CO_3 \rightarrow (CF_3)_2POP(CF_3)_2 + CO_2 + 2AgI$ [28]. Whilst the synthesis of μ-oxo-bisdifluorophosphine, F_2POPF_2, was found when Rudolph et al. [30] were making P_2F_4. The synthesis of P_2F_4 involves a coupling reaction between molar equivalents of Hg and PF_2I, however, if Cu_2O is used instead of Hg the product is F_3PO. By having two equivalents of PF_2I and one equivalent of Cu_2O the diphosphoxane F_2POPF_2 is produced.

Reaction of Ph_2PCl with $CH_2{=}CHCO_2H$ and $CH_2{=}CHCH_2CO_2H$ gives $Ph_2PO_2CCH{=}CH_2$ and $Ph_2PO_2CCH_2CH{=}CH_2$, respectively. Both of which undergo intermolecular reactions to produce $Ph_2PP(O)Ph_2$ [34]. This exists as the oxide rather than the diphosphoxane because of the phenyl groups are not electron withdrawing enough. As will be shown shortly the oxide can be coordinated to metals forming diphosphoxane ligands.

2.3.2. General chemistry

The diphosphoxane $[(CF_3)_2]_2O$ is inert towards Lewis acids (BF_3, SO_2), but instead acts as a Lewis acid itself forming the adduct $(CF_3)_2POP(CF_3)_2 \cdot (CH_3)_3N$ [28]. It is easily converted to $(CF_3)_2PCl$ and $(CF_3)_2POH$ with HCl, with the $(CF_3)_2POH$ not further rearranging further to $(CF_3)_2PHO$ because of the fluorocarbon group reducing the basicity of the phosphorus to such an extent the oxygen holds the hydrogen more firmly than the phosphorus would [29]. This ligand also undergoes chlorination to form the phosphinyl chloride $(CF_3)_2P(O)Cl$ and the analogous bromination reaction also occurs [29].

Replacement of the CF_3 group with one that does not accept electrons, such as alkyl groups, increases the basicity of the phosphorus and so Arbuzov type rearrangements can occur, the reaction of $(CF_3)_2POP(CF_3)_2$ with $HPMe_2$ is an example of this (Scheme 6). Griffiths and Burg [29] had aimed to produce $(CH_3)_2POP(CF_3)_2$ using this reaction, although the desired product had probably been made, it had quickly undergone rearrangement to form $(CH_3)_2P(O)–P(CF_3)_2$. Further reaction then occurs via P–P bond exchange to form $(CH_3)_2P(O)–P(O)(CH_3)_2$ and $(CF_3)_2P–P(CF_3)_2$, the fluoro compound then reacting with $HPMe_2$ to form $(CF_3)_2PH$ and $(CH_3)_2P–P(CF_3)_2$.

2.3.3. Coordination chemistry

The thermodynamic favoured form of tetraphenyldiphosphine oxide is $Ph_2PP(O)Ph_2$ and so the free ligand contains both hard (P=O) and soft (O) donor sites. The diphosphine oxide and its isomer, diphosphoxane, can act as monodentate, chelating and bridging ligands. Direct reaction of OP_2Ph_4 with $Mo(CO)_6$ in ethanol produces the monosubstituted complex $Mo(CO)_5(OP_2Ph_4)$ [31], in which the diphosphine oxide ligand is coordinated via the trivalent phosphorus with the P–P bond still intact and the oxygen atom is uncoordinated. The overall conformation around the P–P bond is staggered with the four phenyl rings adopting a gauche conformation (Fig. 2).

Analogous reactions of $Cr(CO)_6$ and $W(CO)_6$ in ethanol give different products. Instead, the hexacarbonyl complexes of chromium and tungsten react with OP_2Ph_4 in diglyme solvent to give *cis*-$(CO)_4M(Ph_2POPPh_2)$ which is a disubtituted complex. The monosubstituted $(CO)_5M(PPh_2P(O)Ph_2)$ complexes of chromium and tungsten are prepared from the appropriate $(CO)_5M(CH_3CN)$ complex rather than the hexacarbonyl.

The disubstituted molybdenum complex is made by prolonged heating of $(CO)_5Mo(OP_2Ph_4)$ which loses carbon monoxide (as does the monosubstituted chromium and tungsten complexes), and also by reaction of *cis*-$(CO)_4Mo(PPh_2O)_2H^-$ with chlorophosphine and acyl chlorides [31]. In the disubstituted complexes the ligand functions as a diphosphoxane chelate, and can be shown to be this by IR where there is an absence of terminal P=O stretch in the 1100–1200 cm^{-1} region but strong absorption in the range 750–785 cm^{-1} corresponding to P–O–P. The crystal structure shows a planar four-membered M–P–O–P ring, which together with the four carbonyls forms a distorted octahedral coordination geometry around the metal centre [32]. The thermal conversion of $(CO)_5M(Ph_2PP(O)Ph_2)$ to *cis*-$(CO)_4M(Ph_2POPPh_2)$ goes via an intermediate complex in which there is a monodentate diphosphoxane ligand (Eq. (7)):

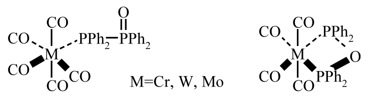


Fig. 2. Monosubstituted and disubstituted complexes with P_2OPh_4 ligand.

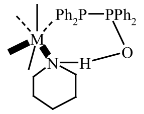
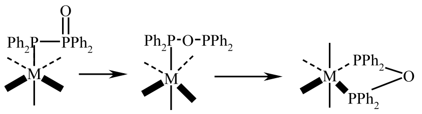
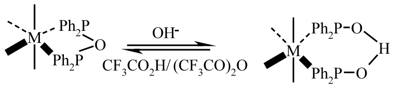


Fig. 3. Piperidine containing complex [31].


(7)

The four-membered chelate ring can be hydrolysed in aqueous THF under basic conditions, forming a six-membered ring containing the ligand P–O–H$^-$–O–P (Eq. (8)). The ring opening to form the *cis*-(CO)$_4$M[(PPh$_2$O)$_2$H]$^-$ anion is readily reversed by treatment with trifluoroacetic acid in trifluoroacetic anhydride [32].



(8)

As the monosubstituted complexes, (CO)$_5$M(Ph$_2$P-P(O)Ph$_2$), of chromium and tungsten are prepared from (CO)$_5$M(CH$_3$CN) it might be expected that are similar reaction could be used in the formation of the disubstituted complexes. In this case the reaction of *cis*-(CO)$_4$M(NHC$_5$H$_{10}$)$_2$ (M = Mo, Cr, W) with excess OP$_2$Ph$_4$ in methylenechloride would be the loss of the two piperidine groups and replacement by the diphosphoxane. In practice [31] this does not happen, only one piperidine is displaced to produce complexes of the type *cis*-(CO)$_4$M(OP$_2$Ph$_4$)(NHC$_5$H$_{10}$) (Fig. 3). The ^{31}P-NMR shows the predicted AB pattern and phosphorus–phosphorus coupling values associated with a P–P bond. Additionally the downfield shift of the δ(PO) values together with significant shifts for P–O and N–H in the IR suggest intramolecular H-bonding. Indeed, the structure of the complex has the piperidine and the diphosphine oxide coordinating *cis* with a H-bond between the diphosphine oxide oxygen and the amino hydrogen.

Interestingly, work by Wong et al. [33] has shown that Mo complexes with diphosphoxane ligands can also exist with coordination number seven. Seven coordinate complexes are rare and have no uniquely favoured stereochemistry. In these examples, the complexes are produced by direct reaction of elemental halogens with Mo(CO)$_3$(R$_2$POPR$_2$) to give Mo(II) complexes of the type Mo(CO)$_3$X$_2$(R$_2$POPR$_2$) (R = Ph, *p*-tolyl X = I, Br). The solid-state geometry about the metal is best described as a pentagonal bipyramid with the equatorial plane comprising one carbonyl, both halogens and the chelating diphosphine, and the apical positions occupied by the remaining two carbonyls. The ^{31}P-NMR shows, however, that the complex where X = I and R = Ph exists as two species in solution in equilibrium A:B, where the ratio is temperature dependant. The major species A is the pentagonal bipyramid as in the solid state, whilst the minor species B is likely to be a capped trigonal prism.

Reaction of RhCl(PPh$_3$)$_2$ with two equivalents of Ph$_2$PO$_2$CCH=CH$_2$ over several days produces the complex RhCl(PPh$_3$)(Ph$_2$POPPh$_2$). The rhodium is coordinated to three phosphorus and a chloride in a severly distorted square-planar arrangement [34]. The four-membered ring is also planar with the two chelating phosphorus brought very close together. Further reaction of this complex with just less than one equivalent of TlPF$_6$ produces [Rh(PPh$_3$)$_2$-(Ph$_{22}$POPPh$_{22}$)][PF$_6$]. The mechanism for the reaction is not via the intramolecular conversion of Ph$_2$PO$_{22}$-CCH=CH$_2$ to Ph$_2$PP(O)Ph$_2$ followed by coordination to Rh, but by some other mechanism, as reactions of Ph$_2$PP(O)Ph$_2$ with RhCl(PPh$_3$)$_3$ do not give the desired product.

Reaction of two equivalents of Ph$_2$PO$_2$CCH=CH$_2$ with one equivalent of [RhCl(C$_8$H$_{14}$)$_2$]$_2$ produces RhCl(Ph$_2$PO$_{22}$CCH=CH$_2$)$_2$ and [RhCl(Ph$_2$PO$_2$CCH=CH$_2$)]$_2$(Ph$_2$POPPh$_2$) as the major products. The former is a five coordinate complex with two bidentate Ph$_2$PO$_2$CCH=CH$_2$ ligands, whilst the later contains a tetraphenyldiphosphoxane bridge and two bidentate ligands.

2.4. Thiobisphosphines and bisphosphinoselenides

In Section 2.2, the difficulties of synthesising diphosphoxanes was discussed with reference to Arbuzov isomerisations. The same problem is applicable here to a certain extent, where the oxygen has been replaced by sulfur or selenium. Again the presence of electron withdrawing groups (e.g. CF$_3$) attached to the phosphorus is often needed to prevent rearrangement to phosphine sulfides. In general though, the thiophosphines have appreciably greater resistance to rearrangement. For example, neither CH$_3$SP(CF$_3$)$_2$ nor *t*-C$_4$H$_9$SP(CF$_3$)$_2$ can be converted to the corresponding phosphine sulfides, but the oxygen analogues are easily converted [35].

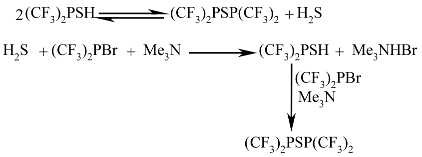
2.4.1. Synthesis

Synthesis of the thiophosphine (CF$_3$)$_2$P–S–P(CF$_3$)$_2$ is achieved by reaction of bistrifluoromethyliodophosphine with silver sulfide [36] (Eq. (9)).

$$3(CF_3)_2PI + Ag_2S \rightarrow (CF_3)_2PSP(CF_3)_2 + 2AgI \qquad (9)$$

Alternatively the thiophosphine can be produced by the condensation reaction of the thiophosphinous acid HSP(CF$_3$)$_2$ [35] (Eq. (10)). This reaction is not observed for (CF$_3$)$_2$POH because the O$_{2p}$–P$_{3d}$ π-bond is much stronger in comparison to the S$_{3p}$–P$_{3d}$ π-bond. A similar condensation reaction to produce the bisphosphine monosulfide involves hydrogen sulfide reacting with (CF$_3$)$_2$PBr in the presence of trimethylamine to give the thiophosphinous acid HSP(CF$_3$)$_2$. Subsequent condensation reaction of HSP(CF$_3$)$_2$ with (CF$_3$)$_2$PBr produces di(bistrifluoromethylphosphino)sulfide, [(CF$_3$)$_2$P]$_2$S [36] (Eq. (11)).

$$2(CF_3)_2PSH \rightleftharpoons (CF_3)_2PSP(CF_3)_2 + H_2S \qquad (10)$$



(11)

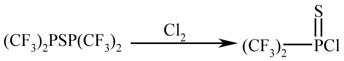
Bis(difluorophosphino)sulfide is prepared in the exchange reaction of PBr_2 with $S(SnBu_3)_2$ and similarly $Se(PF_2)_2$ is produced when $PBrF_2$ is reacted with $Se(SiH_3)_2$ [40]

2.4.2. General chemistry

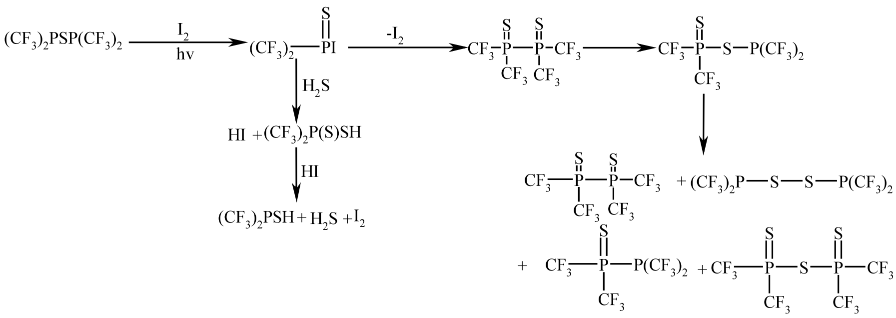
The thiophosphine $(CF_3)_2PSP(CF_3)_2$ is inert to mercury up to 150 °C, which causes loss of sulfur in the analogous thiobiarsine compound. The P–S–P chain is more stable than the As–S–As chain due to deeper energy levels in the phosphorus compound [35]. However, PSP bond cleavage does occur in the presence of hydrogen bromide [36] and hydrogen chloride [35]. HBr reacts to form the bistrifluoromethylthiophosphinous acid and bistrifluorobromophosphine, with the reaction not going to completion. Similarly the same reaction with HCl is not quantitative cleavage, with the production of less than one $HSP(CF_3)_2$ and more than one $(CF_3)_2PCl$. This is brought about by a secondary effect in which $HSP(CF_3)_2$ condenses to form $[(CF_3)_2P]_2S$ and H_2S, the $[(CF_3)_2P]_2S$ being available for further cleavage. This is equivalent to direct cleavage of $HSP(CF_3)_2$ by HCl, leading to larger amounts of $(CF_3)_2PCl$ than predicted.

The dithiophosphinic acid, thiophosphinic acid chloride and the thiophosphinic acid iodide derivatives of $[(CF_3)_2P]_2S$ have also been reported [37]. Dithiophosphinic acid, $(CF_3)_2PS_2H$, is formed in a two stage process in which the bisphosphine sulfide is heated with excess sulfur to produce $(CF_3)_2PS_3P(CF_3)_{22}$, which then reacts with hydrogen sulfide to give the thiophosphinic acid (Eq. (12)). Reaction of the bisphosphine sulfide with excess chlorine gives the acid chloride $(CF_3)_2P(S)Cl$ (Eq. (13)). The reaction to produce the acid iodide in comparison is not so straight forward, with a number of side reactions occurring (Eq. (14). Photochemical cleavage of $[(CF_3)_2P]_{22}S$ by iodine produces $(CF_3)_2P(S)I$, the thiophosphinic acid iodide. This then looses iodine, a process that can be speeded up by shaking the mixture with mercury, eventually reproducing the bisphosphine sulfide. A proposed mechanism for this reaction involves the initial production of a diphosphine disulfide, which then under goes an anti-Arbuzov rearrangement. The resulting P(S)–S–P compound exchanges groups forming a diphosphine monosulfide, P(S)–P, which then undergoes an anti-Arbozov rearrangement also to give $[(CF_3)_2P]_2S$. Alternatively another side reaction involves the thiophosphinic acid iodide reacting with hydrogen sulfide to give $(CF_3)_2PS_2H$ and then further reaction forming $(CF_3)_2PSH$ and $[(CF_3)_2P]_2S$.

$$(CF_3)_2PSP(CF_3)_2 \xrightarrow{S_8} (CF_3)_2PS\text{-}S\text{-}SP(CF_3)_2 \xrightarrow{H_2S} (CF_3)_2PSSH \qquad (12)$$



$$(CF_3)_2PSP(CF_3)_2 \xrightarrow{Cl_2} (CF_3)_2\overset{S}{\overset{\|}{P}}Cl \qquad (13)$$



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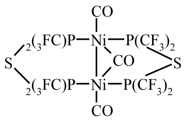


Fig. 4. Structure of the nickel complex $Ni_2[(CF_3)_2PSP(CF_3)_2](CO)_3$.

2.4.3. Coordination chemistry

The reaction of $[(CF_3)_2P]_2S$ with $Ni(CO)_4$ produces the complex $Ni_2[(CF_3)_2PSP(CF_3)_2](CO)_3$ [21] (Fig. 4). IR shows that the thio-derivative, like the amine

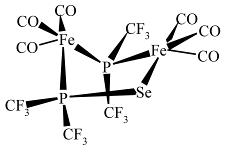


Fig. 5. Structure of the iron–selenium complex $Fe_2(CO)_6P_2(CF_3)_4Se$.

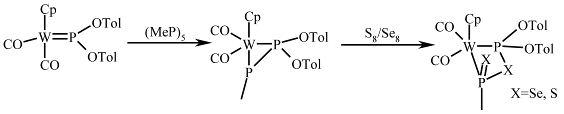
analogue, has both terminal and bridging carbonyls (2088, 2075, 1894 cm^{-1}). X-ray crystallography [38] has shown the structure of the complex to be the same as the amine, the two $[(CF_3)_2P]_2S$ and one carbonyl bridging the nickels and then one other carbonyl per metal. However, the thio-nickel complex also has a Ni–Ni bond (2.577 Å) and there is an unusual five-membered Ni_2P_2S ring present.

Reaction of the bisposphine sulfides and selenides, $[(CF_3)_2P]_2E$ (E = S, Se), with iron carbonyls produces a variety of complexes, often with unexpected structures [39]. Reaction of the sulfide and the selenide with $Fe(CO)_2(NO)_2$ produces complexes of the type $Fe(CO)(NO)_{22}[(CF_3)_2PEP(CF_3)_2]$. The ^{19}F-NMR of both complexes has two peaks of equal intensity, one close to that of the corresponding free ligand showing the complexes have unidentate bisphosphine ligands that are coordinated via a phosphorus. It is a similar case for the complex $Fe(CO)_4[(CF_3)_2PSP(CF_3)_2]$, which is produced from the complex $Fe_2(CO)_9$. Again, this complex has a unidentate bis-phosphine ligand.

Interestingly the reaction of the selenide with $Fe_2(CO)_9$ produces a binuclear complex $Fe_2(CO)_6P_2(CF_3)_4Se$ (Fig. 5). The complex contains a five-membered Fe_2P_2Se ring and six terminal carbonyls. The ligand $[(CF_3)_2P]_2Se$ is cleaved in the complexation process.

Similarly there is P–E bond cleavage when the bisphosphine ligands react with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. In this example it been proposed that initial attack is at or by the Fe–Fe bond, followed by P–E bond cleavage. This produces equal amounts of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ and $(\pi\text{-}C_5H_5)Fe(CO)_2[P(E)(CF_3)_2]$.

Cyclized phosphinidene (metallo) phosphoranes, $Cp(CO)_2W[P(Me)–P(OTol)_2]$, are obtained from the reaction of $Cp(CO)_2W=P(OTol)_2$ and $(MeP)_5$ [41]. Treatment of the phosphorane with elemental sulfur or selenium produces a four-membered metallocycle $Cp(CO)_2W[P(OTol)_2XP(X)Me]$ (X = Se, S), that has a PXP ligand (Eq. (15). The reaction proceeds via oxidation of the phosphinidene-phosphorus followed by insertion of the sulfur or selenium in to the P–P bond.



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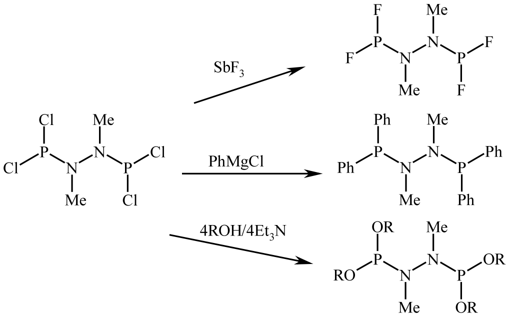


R=Ph, O-$C_6H_4(CH_2CHCH_2)$, Me, Et, CH_2CF_3, CH_2CHCH_2, $(CH_2)_7CH_3$, $CH(CH_3)_2$, C_6H_4Br-p

Scheme 7. Formation of diphosphine hydrazine derivatives.

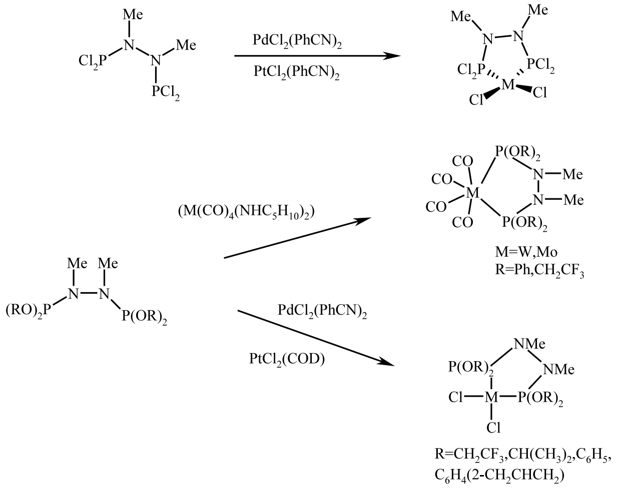
3. Two bridging atoms

3.1. *Bisphosphinohydrazines*

There are many references to the chemistry of PNP type ligands, however, there are few reports on the next homologue in the series, the bisphosphinohydrazines, where the two phosphorus atoms are linked by a dinitrogen bridge. The development of these ligands in transition metal chemistry is of particular significance because they are the nitrogen equivalent of bisphosphinoethane, $R_2P(CH_2)_2PR_2$, which has already demonstrated useful applications in catalysis.

3.1.1. *Synthesis*

The limited use of hydrazine bridged phosphine ligands was initially due to a lack of rational synthetic routes. Gilje et al. [43] and Noth et al. had pioneered the synthesis with the reaction of the cage compound $P(NCH_3NCH_3)_3P$ with PCl_3 (Eq. (16)), giving the unstable product $Cl_2PN(CH_3)N(CH_3)PCl_2$ which decomposed to give $ClP(N(CH_3)N(CH_3))_2PCl$ then further to an uncharacterised solid. Secondly by the hydazino-



Scheme 8. Coordination of diphosphine hydrazine ligands.

lysis of PCl_3 with $HN(CH_3)N(CH_3)H$ at −196 °C (Eq. (17)).

$$\text{Xs } PCl_3 + P(NCH_3NCH_3)_3P \rightarrow Cl_2PNCH_3NCH_3PCl_2 \quad (16)$$

$$\text{Xs } PCl_3 + HNCH_3NCH_3H \rightarrow Cl_2PNCH_3NCH_3PCl_2 \quad (17)$$

These methods were limited due to low yields and instability of the products, and the practicality of the experimental conditions.

Katti and Reddy [45] developed a 1-step synthesis involving the addition of PCl_3 to dimethylhydrazine·dihydrochloride (Eq. (18)), which gave high yield (92%) and high purity, even at large scale.

$$2PCl_3 + HNCH_3NCH_3H \cdot 2HCl \rightarrow Cl_2PNCH_3NCH_3PCl_2 \quad (18)$$

Bis(dichlorophosphino)hydrazine is a useful starting point for the synthesis of derivatives with other substituents on the phosphorus (Scheme 7). Conversion to the fluoro derivative[43] is by reaction with SbF_3, whilst the reaction with PhMgCl gives the phenyl derivative [46] $Ph_2PNCH_3NCH_3PPh_2$. There has also been interest in synthesising the phosphoryl derivative, where the chlorine is replaced by an OR group. This method was developed by Reddy [45], in a reaction of the dichlorohydrazino derivative with the respective alcohol, in the presence of triethylamine, and has been extended to include a large range of R groups [44].

3.1.2. General chemistry

Gilje and Havlicek [43] have shown the chemistry of bis(dichlorophosphino)hydrazine to be irreproducible on reaction with B_2H_6 and BH_3, giving an uncharacterised yellow solid that decomposed on warming releasing BH_3. The reaction of the fluoro- derivative with B_2H_6 was dependent on molar ratio; a 1:1 ratio gave the monoborane adduct whilst excess B_2H_6 gave the bis borane adduct. A monoadduct is formed with BF_3.

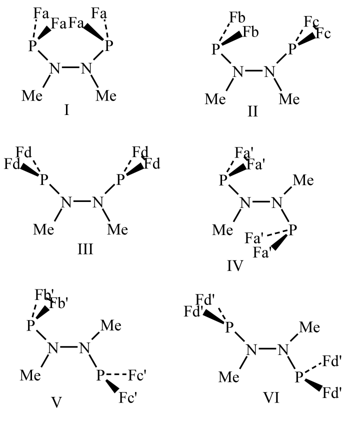


Fig. 6. The six conformers for the P–N–N–P frame work.

3.1.3. Coordination chemistry

Complexes were formed with Pt(II), Pd(II), W(0) and Mo(0) (Scheme 8). The complexes are all monomeric with the Pt and Pd in a typical square planar environment [44,45], whilst the W and Mo are in a distorted octahedral geometry [46]. All complexes have the ligand bound *cis* to the metal centre in a five-membered, planar metallocycle.

A few interesting features have been reported about the complexes. Firstly, there is considerable upfield ^{31}P chemical shift on going from the palladium (151.9 ppm) to the platinum (121.4 ppm) complex, assumed to be a result of the stronger M–P bonding interaction interaction in the platinum complex [44]. Secondly, the P–N bond distances (1.64–1.67 Å) for both the platinum and palladium complexes are shorter than the generally accepted P–N single bond lengths (1.75–1.8 Å) [45], suggesting multiple bond character. This shortening may be a consequence of the localization of electronic charge along M–P–N. Finally, the P–N distance of the palladium complex is shorter than in the tungsten complex [46], which is again a consequence of the localization of the electronic charge across the Pd–P–N segment of the planar ring. The tungsten complex has a non-planar ring and poor overlap of the π-orbitals giving a longer bond.

3.1.4. NMR studies

NMR studies have shown that for $F_2PN(CH_3)N(CH_3)PF_2$ [42] there is a temperature dependence of the ^{19}F-NMR, suggesting large torsional barriers about the P–N and N–N bonds. At −145 °C there is a complicated set of peaks, coalescence at −100 °C and +25°, then a well resolved doublet at +160 °C.If the P–N–N–P framework is planar and there is *cis*/*trans* geometry about the N–N bond six structures can be drawn, showing eight distinct fluorine environments (Fig. 6).

The twelve peaks on the spectra at −145 °C have been assigned as four doublets of equal intensity for conformers I–III and two doublets of twice the intensity for conformers IV–VI. The broadening, coalescence and reappearance as a single doublet between −145 and −40 °C of the peaks assigned to conformers I–III shows P–N rotation is observed at a lower temperature than N–N rotation. The coalescence due to N–N rotation appears at +25 °C. The torsional barrier of P–N can be attributed to the pπ–dπ bonding, whilst the barrier for the N–N rotation has been attributed to either lone pair repulsions or more probably pπ–pπ overlap.

4. Three bridging atoms

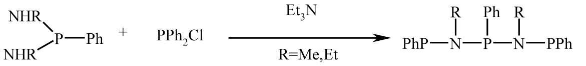
The synthesis and general chemistry of compounds of diphosphines containing three bridging atoms between the two phosphorus groups have been far more widely reported than those containing two bridging atoms. Examples are fairly varied including PNENP where E = P, S, Si and POEOP where E = Si, H.

4.1. Bis(phosphinoamino)phosphines

Bis(phosphino-*N*-alkylamino)-phosphines, the next example in the aminophosphine series, based on the P^{III}–N–P–N–P^{III} backbone and can be neutral [47–50] or anionic [51–53] depending on the method of synthesis. They present an interesting ligand due to the central phosphorus being in a different chemical environment to the two terminal phosphorus atoms.

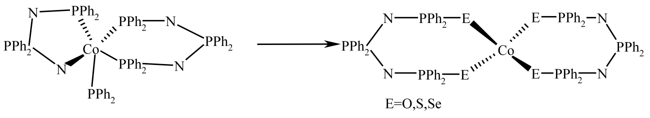
4.1.1. Synthesis

Bis-(diphenylphosphino-*N*-alkylamino)-phenylphosphine where alkyl = methyl, ethyl [47–49] (Eq. (19)) have both been prepared by the reaction of chlorodiphenylphosphine with the corresponding di(alkylamino)phenyl phosphine in the presence of triethylamine:



(19)

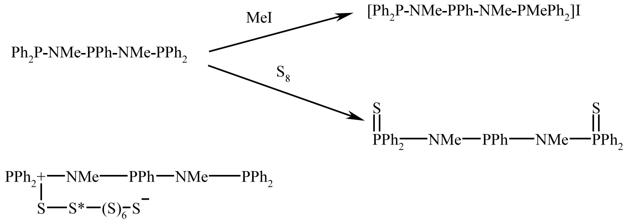
The phosphazene anion, $[Ph_2P–N–PPh_2–N–PPh_2]^-$ (Eq. (19)), is synthesised by the treatment of MCl_2 (M = Ni, Pd, Co) with $LiN(PPh_2)_2$ in a molar ratio 1:2 [51,52]. This produced a spirocyclic metallophosphazene containing three rings of differing size. The anionic ligand acts as a bidentate phosphorus ligand and a tridentate phosphorus and nitrogen chelating ligand. The reaction is thought to proceed via the oxidation of $N(PPh_2)_2^-$.



(20)

4.1.2. General chemistry

The reactivity of $Ph_2P–NMe–PPh–NMe–PPh_2$ differs at the two phosphorus environments. The terminal phosphorus atoms have been shown to be more reactive as demonstrated by the quaternarisation reaction with methyliodide [47,49] and the addition of sulfur [48] in which the reaction takes place preferentially at the terminal phosphorus. Keat [48] suggested the reason behind this behaviour is: (a) nucleophilicity of P_T is relatively more than P_C due to the presence of the two nitrogens; and (b) P_C is more stearically hindered. The central phosphorus is only sulfurated on prolonged heating (17 h) with excess sulfur. In the sulfuration reaction only the disulfide was isolated for both one and two molar equivalent of sulfur (Scheme 9). The reaction could proceed via the following intermediate [48] where the unsulfurated terminal phosphorus is in a favourable position for nucleophilic attack at S(*).



Scheme 9. Sulfuration of the terminal phosphorus.

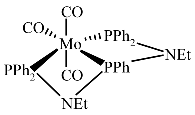


Fig. 7. Structure of the Mo complex showing the tridentate ligand.

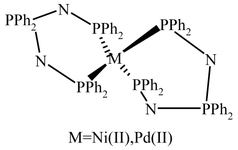
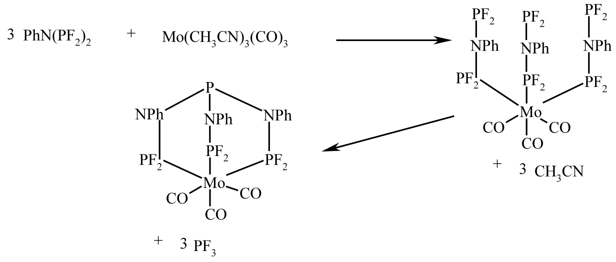


Fig. 8. Spirocyclic cobaltophosphazene [51].

4.1.3. Coordination chemistry

Lai et al. [49] have shown that bis(diphenylphosphino-*N*-ethylamino)phenyl phosphine acts as a tridentate ligand when reacted with molybdenum hexacarbonyl to give $MoL(CO)_3$, L = $Ph_2P–N(Et)–PPh–N(Et)–PPh_2$ (Fig. 7). X-ray crystallography and ^1H-NMR show that the ligand L only functions as a phosphine ligand in a geometry that deviates considerably from a regular octahedron. The three coordinating phosphorus atoms produce two nearly planar four-membered chelate rings. The Mo–P distance is on average 2.476 Å, the Mo–C distance is 1.95 Å, which are both shorter than the predicted single bond length (2.71 and 2.30 Å, respectively). The distance is considered evidence for dπ–dπ Mo–P backbonding in the presence of stronger dπ–pπ Mo–C backbonding. Whilst the observed P–N distance (1.70 Å) is not considerably different than the predicted value (1.80 Å) indicating the



Scheme 10. Formation of the tris-phosphine.

absence of pπ–dπ N–P backbonding. Bis(diphenylphosphino-*N*-ethylamino)-phenylphosphine also forms complexes with Co(II) and Ni(II) [47].

The spirocyclic cobaltophosphazene (Eq. (20)), as synthesised by Ellerman et al. [51] can be described as either an N1-capped CoP_4 tetrahedron or a distorted tetragonal pyramid with an apical phosphorus and a N–P–P–P base. The P–N bonds all take on some double bond character as the values all lie between P–N single bond (1.77 Å) and P–N double bond (1.56 Å). In comparison the complexation with Ni(II) and Pd(II) [52] has the metal centre occupying a mid position between tetrahedral and square planar with only the terminal phosphorus coordinating to form two six-membered rings (Fig. 8). As with Co(II) the P–N bonds (~ 1.60 Å) all have some double bond character.

4.1.4. NMR studies [50]

NMR studies of ligands of the type $[Ph_2P{-}NR{-}PPh{-}NR'PPh_2]$ are limited to a small part of a study on conformational effects on P–N–P coupling. In this report Keat studied the $^{31}P\{^1H\}$-NMR of bis-(diphenylphosphino-*N*-alkylamino)-phenylphosphine where R = Me, Et, and concluded that there was no evidence for restricted rotation about the P–N bond as there was no temperature dependence of the spectra. The magnitude of the coupling *J*(PNP) decreases (280–25.1 Hz) on changing Me to Et and there is significant coupling between the terminal phosphorus groups.

4.2. Tris[phenyl(difluorophosphino)amino]phosphine

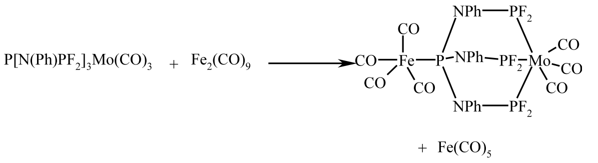
The phosphine family in which the back-bone is PNPNP can be extended to include the example where R on the central phosphorus atom is replaced with $NR'PR_2$. This example is tris[phenyl(difluorophosphino)amino]phosphine and has three phosphorus atoms that can potentially coordinate to the metal producing cage structures [54].

4.2.1. Synthesis

The tris-phosphine ligand is formed on the metal and is not isolable as a separate species. The mechanism of formation (Scheme 10) is thought to involve the simple ligand substitution of *N*,*N*-bis(difluorophosphino)aniline with *fac*-$(CH_3CN)_3Mo(CO)_3$ giving the intermediate *fac*-$[C_6H_5N(PF_2)_2]_3Mo(CO)_3$. The close proximity of the three uncomplexed phosphorus groups and the tendency to form six-membered rings induces the elimination of PF_3 to yield the product $P[N(Ph)PF_2]_3Mo(CO)_3$ [54].

4.2.2. Coordination chemistry

The molybdenum complex is octahedral with the three coordinating phosphorus atoms in a *fac* geometry. The tridentate ligand with the molybdenum forms a cage structure of three interlocking six-membered rings, similar to bicyclo[2.2.2]octane, with the central phosphorus and the Mo forming the bridge heads. X-ray crystal data shows the Mo–P bond lengths (2.343 Å) to be the shortest observed for trivalent phosphorus bound to Mo, whilst the Mo–C bonds (2.050 Å) are the longest observed for carbonyl similarly bound, providing evidence for the strong π-acceptor character of PF_2 groups. A further interesting feature of this complex is the uncoordinated trivalent phosphorus. This phosphorus is able to coordinate to transition metals and so forming heterobimetallic complexes. The reaction of $P[N(Ph)PF_2]_3$ with $Fe_2(CO)_9$ produced an iron-molybdenum complex, $(OC)_4FeP[N(Ph)PF_2]_3Mo(CO)_3$ [55] (Eq. (21)).



(21)

4.3. PNENP (E = S, Si)

The chemistry of PNENP (E = S, Si) ligands is very similar to that when E=P, except the presence of the Si–N bond makes the complexes more susceptible to hydrolysis. The coordination chemistry of the two ligands has shown some interesting differences with the silicon complex often produces non-planar metallocycles [56] due to the structure of the ligand and only one example of a planar silicon containing ring has been reported so far [57]. The sulfur containing ligand is commonly bridging [59,60].

4.3.1. Synthesis

The synthesis of *N*,*N*′-bis(diphenylphosphino)azasiltrane is achieved by the substitution reaction of the azasilatrane with chlorodiphenylphosphine [56]. The reaction is thought to proceed by via the monosubstituted intermediate $EtOSi(NHCH_2CH_2)_2(NPPh_2CH_2CH_2)N$. The synthesis can also be achieved by the reaction of the azasilatrane with butyl lithium and chlorodiphenylphosphine. Substitution of all three nitrogen groups was not observed, even with a large excess of chlorodiphenylphosphine, this attributed to steric overcrowding in the hypothetical trisubstituted compound.

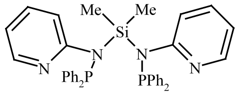
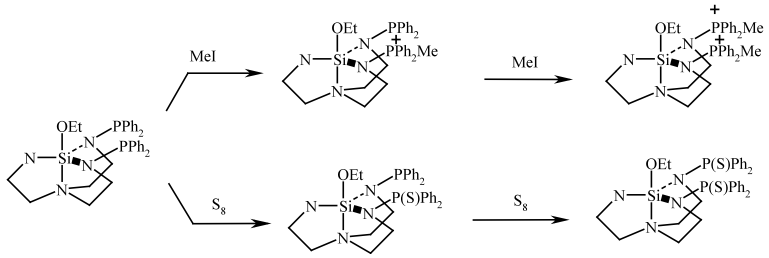


Fig. 9. Structure of the planar silicon ligand.



Scheme 11. Reactions of P–N–Si–N–P ligands.

Deprotonation of the phosphinoamine Ph_2PNH–2-pyridine with *n*-butyl lithium or LDA, followed by reaction with dichlorodimethylsilane yields the diphosphine ligand $(Ph_2PN(2\text{-pyridine}))_2SiMe_2$ [57] (Fig. 9). The pyridine groups adopt a staggered conformation and the P–N bonds are single.

Free ligand of the type $R_2PNSNPR_2$ is only known for R = *t*-Bu and is synthesised in the reaction of K_2SN_2 with R_2PX (X = Cl, Br) [58]. Other derivatives, R = Et, Cy, Ph could not be isolated [60]. Ligands of this type are more commonly produced by direct synthesis of the complex, three methods are available:

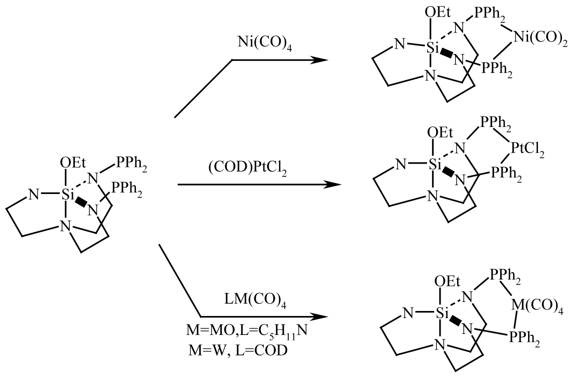
1) Treatment of complexes of the type $L_nM(Ph_2PNSO)$ with a base produce binuclear complexes $L_nMP(Ph_2)NSN(Ph_2)PML_n$. An example of which is the reaction of $(CO)_5Mo(Ph_2PCl)$ with KNSO or K_2SN_2 to produce $((CO)_5MoP(Ph)_2N)_2S$ [60].
2) A similar method uses complexes of the type $ML_n(Ph_2PCl)_x$ (x = 1,2) with K_2SN_2 to produce both mononuclear and binuclear complexes [59,60]:

$$2\mathrm{MLn(Ph_2PCL)} + \mathrm{K_2SN_2} \times \xrightarrow[\mathrm{MLn=Cr(CO)_5,\ Mo(CO)_5,\ MnCp(CO)_2}]{} \mathrm{LnMP(Ph)_2} \times \mathrm{NSN(Ph)_2PMLn}$$

$$cis\text{-}\mathrm{M(CO)_4(Ph_2Cl)_2} + \mathrm{K_2SN_2} \xrightarrow[\mathrm{M=Cr,\ Mo}]{} cis\text{-}\mathrm{M(CO)_4} \times \mathrm{(P(Ph_2)NSN(Ph)_2P)} + 2\mathrm{KCl}$$

3) Direct reaction of the free ligand *t*-$Bu_2PNSNPt$–Bu_2 with metal carbonyls containing easily displaced ligands is also possible[60]:

$$\mathrm{M(CO)_5(THF)}\quad (\mathrm{M=Cr,\ Mo,\ W})$$
$$\mathrm{CpMn(CO)_2(THF)}$$
$$\mathrm{Os_3(CO)_{11}(CH_3CN)}$$



Scheme 12. Coordination of *N*,*N*′-bis(diphenylphosphino)azasilatrane.

4.3.2. General chemistry

The chemical reactivity of *N*,*N*′-bis(diphenylphosphino)azasilatrane is typical of a tertiary phosphine, undergoing the same quaternarization and oxidation as PNPNP (Scheme 11). Treatment of the bis(phosphino)azasilatrane with excess methyl iodide gives the bisphosphonium salt. The monoalkylated species is also detected as an intermediate. Oxidation of the free ligand with two equivalents of S_8 gives the corresponding bisphosphine sulfide, which also goes via the monosulfide intermediate.

The structure produced after oxidation was confirmed as a tricyclic skeleton, with the silicon atom in a distorted trigonal bypyramid and significantly displaced above the plane of the nitrogen [56].

$Ph_2PN(py)SiN(py)PPh_2$ reacts with selenium to produce the diselenide and with electrophiles with cleavage of the Si–N bond e.g. with chlorodiphenylphosphine it yields $Ph_2PN(pyr\text{-}2)PPh_2$ [57].

4.3.3. Coordination chemistry

Phosphine complexes are easily formed (Scheme 12) from the reaction of the bisphosphine azasilatrane with complexes of the type $L_nML'_m$ (m = 2,3 L′ = olefins, amine, CO) in which the ligand L′ is displaced [56]. The complexes formed are all air and moisture stable in the solid state, but have increased sensitivity to hydrolysis in solution. IR, NMR and mass spec show the complexes to be homonuclear, with the diphosphine as a bidentate chelating ligand. X-ray crystallography shows the pla-

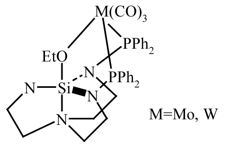


Fig. 10. Structure of the diphosphine azasilatrane complex of tungsten.

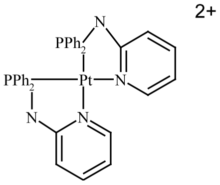


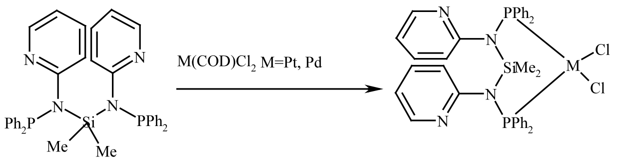
Fig. 11. Structure of the complex after hydrolysis.

tinum atom to be in a slightly distorted square planar geometry, with the six-membered chelate ring almost planar.

In the synthesis of the complex containing tungsten a second component is also identifiable, it contains only three carbonyls [56]. This complex has extra coordination by the oxygen in the EtO group. Complexes of this type can be produced by reaction of the azasiltrane ligand with $Mo(CO)_3(\eta^3$-cyclohepatriene) or by photolysis of THF solutions of the corresponding tetracarbonyls (Fig. 10).

The coordination of the silyl ether leaves the three carbonyls in a *fac*-geometry. The tridentate ligand is facilitated by the chelate effect and the electron releasing capability of the azasilatranyl group, which enhances the nucleophilicty of the oxygen atom compared to alkyl substituted silyl ethers. The metal–oxygen interaction is extremely labile, with substitution of the EtO in the tridentate ligand occurring readily with CO in the reverse of the photolytic reaction. In contrast, the corresponding $Ni(CO)_2$ is stable to loss of CO under thermal and photolytic conditions.

Reaction of the ligand $(Ph_2PN(2\text{-py}))_2SiMe_2$ with $M(COD)Cl_2$ (M = Pt, Pd) gives the dichloro complex in which the two phosphorus atoms coordinate to the metal centre forming a six membered ring [57] (Eq. (22)).



(22)

The metal complex is susceptible to hydrolysis by atmospheric moisture with cleavage of the Si–N bond, producing a complex in which there is phosphorus and nitrogen coordination (Fig. 11). The metal centre is in a square planar geometry with chloride ions outside the coordination sphere. The hydrolysis is thought to be aided by the favourable formation of two chelating ligands.

The platinum dimethyl complex is formed by reaction of the ligand with $Pt(COD)Me_2$. The platinum is again in a square planar geometry and the Pt–P–N–Si–N–P ring adopts a puckered boat conformation. The dimethyl complex is significantly less susceptible to hydrolysis, but reacts with *cis*-$Pt(Ph_2PCl)_2Cl_2$ to yield a bridged complex, *cis*-$[Me_2Pt\{\mu\text{-}Ph_2PN(2\text{-pyr})$\hscaleto 125$PPh_2\}_2PtCl_2]$, containing an eight membered PtPNPPtPNP ring.

The structure of the mononuclear complexes [60] containing the ligand $Ph_2PNSNPPh_2$ are all discrete molecular units with the metal atom in an approximate octahedral geometry. The PNSNP ligand coordinates via the phosphorus atoms only to form a six membered, planar ring with the metal. The two S=N bonds are both *cis*. Whilst the homodinuclear complexes [59,60] have the sulfur diimide ligand in a *cis*, *trans* conformation, bridging the two octahedral metal centres (Fig. 12).

4.3.4. NMR studies

The ^{31}P-NMR studies of the dinuclear complexes containing $Ph_2PNSNPPh_2$ report a temperature dependence between −90 and +20 °C [59,60]. For the molybdenum complex two equally intense singlets are present at −90 °C which broaden on raising the temperature and collapse at −60 °C, then reappear as a single sharp singlet at +20 °C. The temperature dependence is due to rapid *cis*, *trans* to *trans*, *cis* interconversion, via the *cis*, *cis* intermediate. The interconversion barrier for molybdenum is 9.4 kcal mol^{-1} [59], whilst the barrier for chromium and manganese are larger (10.1 and 13.4 kcal mol^{-1} [60] respectively). The higher barrier for the manganese complex has been attributed to the relatively stronger $N(p\pi)–P(d\pi)$ bonding in this complex, brought about by the +1 charge on the manganese making the $CpMn(CO)_2$ substituent a weaker π-donor to the phosphorus and consequently the $N(p\pi)–P(d\pi)$ is stronger.

4.4. Phosphite and phosphinite ligands [61]

4.4.1. Synthesis

The free ligand $R_2PO\cdots H\cdots OPR_2$ is unknown and so all reported examples have involved the direct synthesis of the complex. The method primarily employed is the

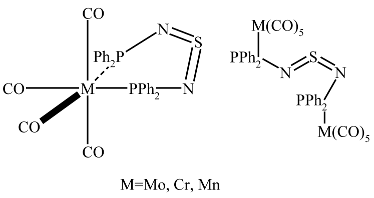
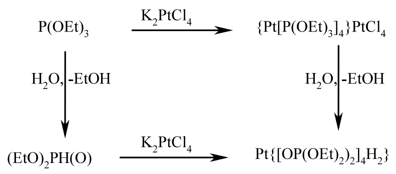
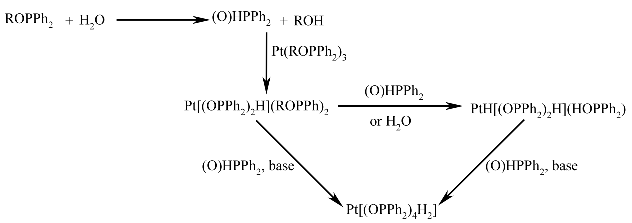


Fig. 12. Di-imide complex.



Scheme 13. Formation of phosphite and phosphinite ligands.



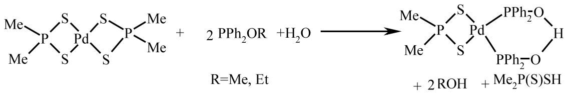
Scheme 14. Formation of the diphenyl phosphinite.

hydrolysis of the phosphite or alkyl/aryl phosphinite, demonstrating the adventitious effects traces of water in organic solvents can have.

The earliest examples of these complexes are the dialkylphosphito Pt(II) compounds produced in 1944 by Grindberg and Troitskaya. This reaction (Scheme 13) involves treating K_2PtCl_4 with $P(OEt)_3$ in aqueous solution to yield $\{Pt[P(OEt)_3]_4\}PtCl_4$ and then $Pt\{[O\text{-}P(OEt)_2]_4H_2\}$ after hydrolysis.

Troitskaya et al. subsequently reported the preparation of the methyl, propyl and butyl platinum derivatives and the Pd(II) complexes of ethyl and isopropyl phosphates, whilst Kong and Roundhill showed the method could be applied to diphenyl phosphite and phosphinite. The diphenyl phosphinite can also be produced by a slightly modified procedure involving the Pt(0) complex $Pt(ROPPh_2)_3$ ($R = Me$, n-Bu) (Scheme 14). In this method the alkyl diphenyl phosphinite is hydrolysed to diphenylphosphinous acid, which then undergoes oxidative addition to the Pt(0) complex to give a Pt(II) hydride intermediate, before conversion to the final product.

There are many further examples of the hydrolysis mechanism with a variety of reaction conditions. These include the prolonged exposure of $Pd(S_2PMe_2)_2$ to a solution of excess methyl or ethyl diphenylphosphinite, leading to the formation of the complex $Pd[(OPPh_2)_2H]\text{-}(S_2PMe_2)$ (Eq. (23)). Whilst the analogous reaction with ruthenium (Eq. (24)) requires more vigorous conditions, pyrolysis for 12 h to produce the complex $(MeOPPh_2)_2(HOPPh_2)RuCl_3 \cdot Ru[(OPPh_2)_2H]$.



(23)

$$[(MeOPPh_2)RuCl_3Ru(MeOPPh_2)_3]Cl \rightarrow (MeOPPh_2)_2 \times (HOPPh_2)RuCl_3Ru[(OPPh_2)_2H] \qquad (24)$$

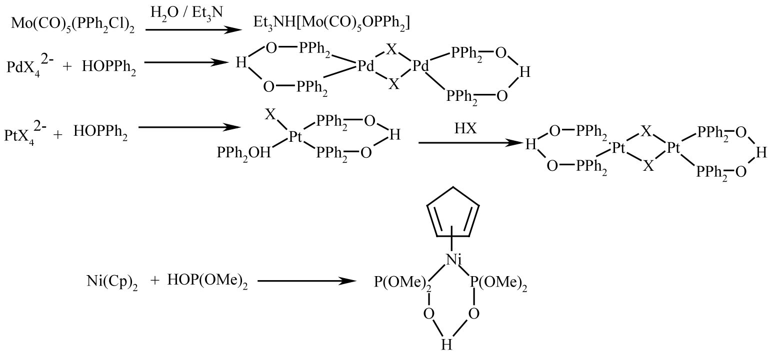
Complexes containing Ph_2PCCCF_3 ligands can form $\{PdCl[(OPPh_2)_2H]_2$ when $PdCl_2(Ph_2PCCCF_3)_2$ is left standing in aqueous ethanol. The proposed mechanism involves the nucleophilic attack of water on the alkynyl carbon bonded to the phosphorus resulting in the formation of diphenylphosphinous acid. This is an example of one of two mechanisms that have been put forward for the hydrolysis reaction, activation of the alkyl group to nucleophilic attack by coordination of the phosphorus to a metal centre. The second mechanism involves the dissociation of the phosphite ester followed by hydrolysis away from the metal centre. There has been no conclusive evidence so far as to which mechanism operates or if both do for the same reaction. Evidence has included the reaction,

$$[PtCl4]^{2-} + P(OR)_3 \underset{-Cl}{\rightarrow} \{Pt[P(OR)_3]_4\}PtCl_4$$
$$\times \overset{H_2O/OH^-}{\underset{-Cl}{\rightarrow}} Pt\{[OP(OR)_2]_4H_2\}$$

where it is suggested that nucleophilic displacement with water or hydroxide ions as the nucleophile occurs after initial activation to produce the diplatinum intermediate. However, in the case where R is phenyl it is not likely the nucleophilic attack would take place at a phenyl carbon and this mechanism would not be operative in this case.

Further examples have included a molybdenum complex, a nickel complex and platinum and palladium dimers (Scheme 15).

It has been frequently observed that complexes obtained using diphenylphosphinous acid or dialkylphosphites as ligands contain both a diphenylphosphinous acid and a diphenylphosphinito (or a dialkylphosphite and a dialkylphosphito). Further studies showed that

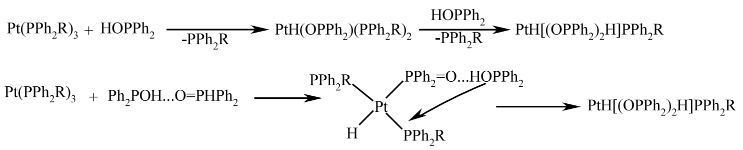


Scheme 15. Complexes containing phenyl–phosphinite ligands.

after coordination of the phosphorus atom to the metal the acid proton is hydrogen bonded between the oxygens producing two equivalent phosphorus groups. An example of this mechanism is the oxidative addition of diphenylphosphinous acid to $Pt(PPh_2R)_3$ (R = Me, Ph) producing the Pt(II) hydride $PtH[(OPPh_2)_2H]PPh_3R$.

$$Pt(PPh_2R)_3 + HOPPh_2 \xrightarrow[-PPh_2R]{} PtH(OPPh_2)(PPh_2R)_2 \times \overset{HOPPh_2}{\underset{-PPh_2R}{\rightarrow}} PtH[(OPPh_2)_2H]PPh_2R \qquad (25)$$

There have been two mechanisms proposed for this reaction, the first (Eq. (25)) involves the oxidative addition of one diphenylphosphinous acid with loss of a diphenylalkyl phosphine, followed by substitution of a second diphenylalkyl phosphine by a second diphenylphosphinous acid and hydrogen bonding between the two oxygens. The second mechanism (Eq. (26)) has the diphenylphosphinous acid existing as a hydrogen bonded dimer in solution, so when one is oxidatively added to the platinum the second is already attached, the chelate effect then ensures rapid substitution of the phosphine. Similar results were also observed for the oxidative addition of dimethyl phosphite to complexes of Rh(I) and Ir(I). When $[IrCl(cyclooctene)_2]_2$ is treated with two equivalents of triphenylphosphine and two equivalents of dimethylphosphite the corresponding hydride is formed, $IrHCl\{[OP(OMe)_2]_2H\}(PPh_2)_2$.



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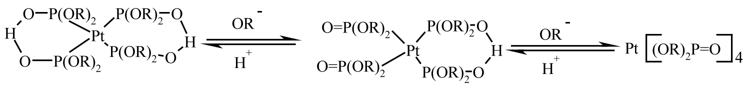
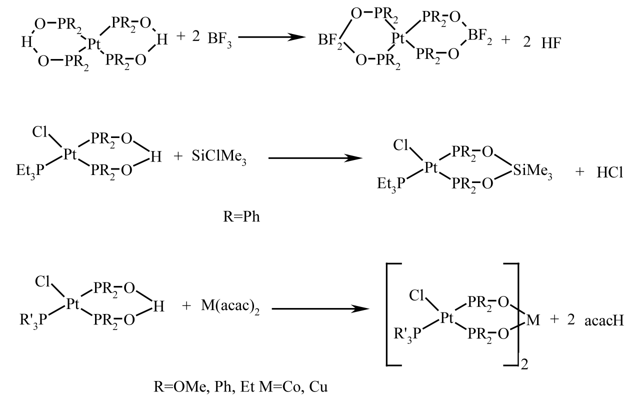


(27)

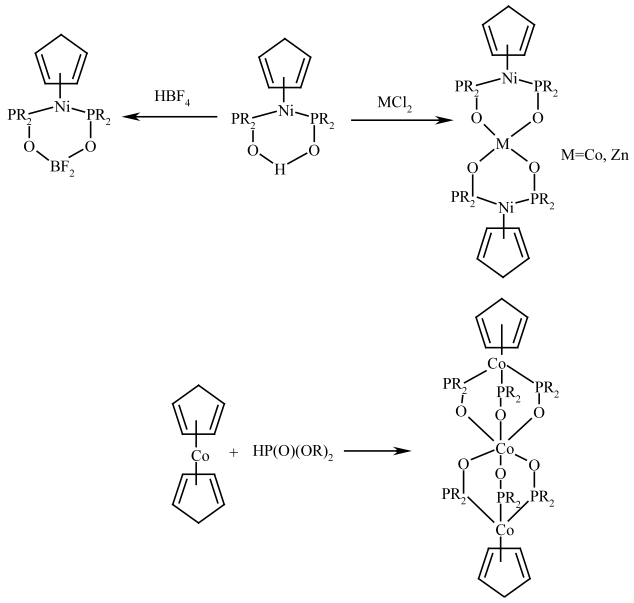
4.4.2. *General chemistry*

The hydrogen bonded between the oxygens in the given complexes is acidic and so is easily removed by bases or substituted by transition metal ions or lewis acids. This reactivity has made the complexes useful reagents for producing a variety of derivatives, including mixed metal oligomers, complexes containing boron and silicon and complexes with $R_2P{=}O$ ligands.

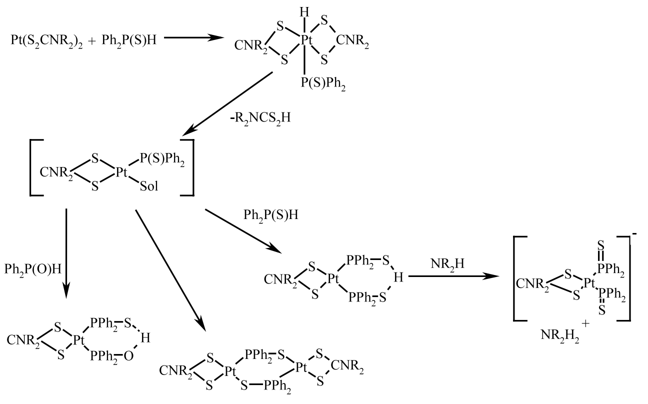
For complexes of the type $Pt\{[OP(OR)_2]_4H_2\}$ the two acidic protons can be removed sequentially by a base (Eq. (27)). The acidic hydrogen can also be substituted



Scheme 16. Reactions of phosphinite complexes.



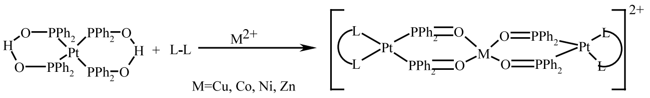
Scheme 17. Formation of mixed metal complexes.



Scheme 18. Synthesis of the thio-analogues.

by reaction with borontrifluoride, chlorotrimethylsilane and transition metal acetylacetonates (Scheme 16).

$M[PtCl(PR'_3)(R_2PO)_2]_2$ are examples of mixed metal complexes, similar complexes of this kind can be synthesised (Eq. (28)) by reaction of $Pt[OP(OMe)_2]_2$L–L (L–L = 1,2-bis(diphenylphosphino)ethane (dppe), *o*-pehnylenebis(dimethylarsine) (diars)) with the appropriate metal cation to give the cationic mixed metal oligomer.



(28)

A more specific example of mixed metal complexes is the 'triple sandwich' complexes of cobalt and nickel (Scheme 17). Both are prepared from $M(\eta^5\text{-Cp})_2$ and $HP(O)(OR)_2$ (R = Me, Et, Ph). In the case of nickel, a monomeric complex is formed first, which then undergoes substitution of with either boron trifluoride or a second metal, whilst for cobalt only the complex $(\eta^5\text{-Cp})_2Co_3[OP(OR)_2]_6$ is isolated.

The *trans* effect of ligands plays an important role in the complexes as many involve coordination to Pt(II). By comparing values of ν(Pt–Cl) in diphenyl phosphito and ν(Pt–H) in $PtH[(OPPh_2)_2H][n\text{-}BuOPPh_2]$ complexes it is clear the bidentate ligand is high in the trans influence series. Similar measurements of the Hg–P bond distance being larger in $Hg[OP(OEt)_2]_2$ than in $HgCl[OP(OEt)_2]$ have confirmed this position.

4.4.3. Structures

NMR studies and X-ray crystalographic studies have shown a symmetrical arrangement of the phosphorus ligands in a variety of the complexes. The ^{31}P-NMR of $Pt\{[OP(OR)_2]_4H_2\}$ (R = Me, Et, Ph) has a single resonance for the equivalent phosphorus nuclei. This shows the symmetric nature of the hydrogen bonded between the two oxygens, although it has been suggested the proton rapidly exchanges between the oxygens. This symmetric nature has been confirmed by the X-ray structures of $\{Pd(SCN)[(OPPh_2)_2H]\}_2$, $P[(OPPh_2)_2H](S_2PMe_2)$ and $(MeOPPh_2)_2(HOPPh_2)RuCl_3Ru[(OPPh_2)_2H](HOPPh_2)$, as they all have short, but equal, P–O (~1.54 Å) and O–O (~2.414 Å) distances, suggesting the symmetric hydrogen bond.

4.4.4. Other examples

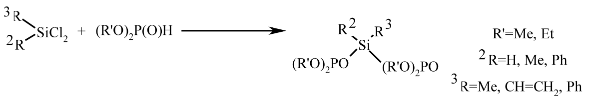
Ebsworth et al. [62] have reported the synthesis and structure of the thio-analogues. The reaction of $Pt(S_2CNR_2)_2$ with diphenylphosphane sulfide ($Ph_2P(S)H$) yielded a variety of products (Scheme 18) depending on the relative amounts of sulfide and water in the reaction mixture. If the reaction of $Pt(S_2CNR_2)_2$ is refluxed with excess $Ph_2P(S)H$ the major product is the anion $Pt(S_2CNR_2)(Ph_2PS)_2$, which is isolated as the dialkylammonium salt. The suggested reaction path goes via the thio-analogue $Pt(S_2CNR_2)[(Ph_2PS)_2H]$. The X-ray crystal structure of the final product, where R = Et, showed the platinum to be in a square planar geometry and the counter ion $NEt_2H_2^+$ to be lying close by. If the reaction is carried out in wet solvents the major product is the mixed chalcogenide complex $Pt(S_2CNR_2)[PPh_2S)(PPh_2O)H]$. They also reported their preliminary studies have shown the fluoro-derivative of the thio-analogue can also be produced, this is done by reacting $Pt(S_2CNR_2)_{22}$ with $PF_2(S)H$. The thio-analogue reacts similarly to the oxygen complexes, with lewis acids and transition metals.

4.5. Silylated di- and tri-phosphites

Silylated phosphates are based on the backbone P–O–Si–O–P. There has been relatively little investigation in to the chemistries of the silylated di- and tri-phosphites in comparison to the analogous phosphates. However, the work reported so far has shown them to be easy to synthesise with a variety of substituents and readily able to coordinate to tansition metals.

4.5.1. Synthesis

The synthesis of silylated diphosphites (Eq. (29)) $[(R'O)_2]_2SiR^2R^3$, involves the dropwise addition of dialkyldichloro silane ($Cl_2SiR^2R^3$) to the secondary phosphite $(R'O)_2P(O)H$ [63–65]. Synthesis of the triphosphites (Eq. (30)), $[(R'O)_2]_3SiR_2$, is the same, using the trichloro silane instead.



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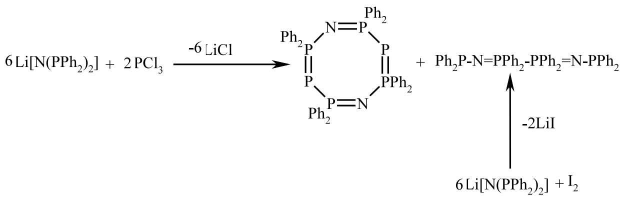
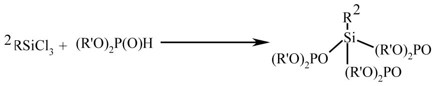


Scheme 19. Synthesis of the phosphazene ligand.

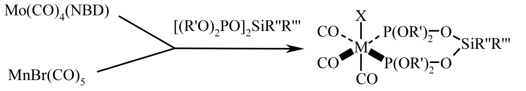


(30)

The silylated phosphites hydrolyse upon exposure to moist air [64,65]. The relative degree of sensitivity towards hydrolysis is dependent on the size of the substituents on the silicon. When R^2 or R^3 is small, like hydrogen or a methyl group, hydrolysis is much faster. This result is consistent with the S_N2–Si hydrolysis mechanism in which water attacks the silicon to produce a five coordinate intermediate whose stability depends on the size of the substituents on the silicon.

4.5.2. Coordination chemistry

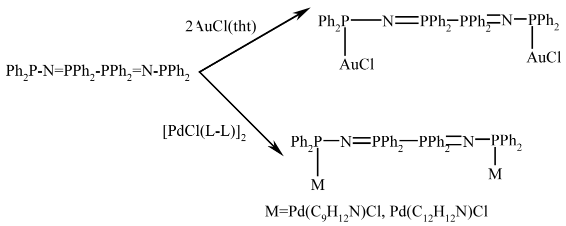
Examples of diphosphite complexation [63,64] involve the coordination to manganese or molybdenum (Eq. (31)). The complexes are formed by the reaction of the silylated phosphite with $MnBr(CO)_5$ or $Mo(CO)_4(NBD)$ (NBD = norbornadiene) and are of the form $MX(CO)_3[P(OR)_2O]_2SiR^2R^3$ (M = Mn X = Br, M = Mo X = CO).



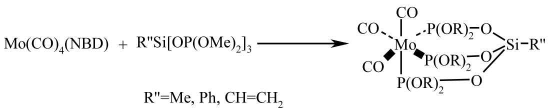
(31)

All complexes form a slightly distorted octahedral monomer with the carbon monoxide ligands in a facial arrangement. The chelate ring differs significantly from the chair conformation, the P–O–Si–O–P all lie in a plane whilst the manganese sticks up out of the plane [64]. The greater trans influence of the phosphorus over the bromine results in longer Mn–CO bonds trans to phosphorus than the Mn–Co bonds trans to bromine (183.3 pm compared to 180.2 pm).

When the silylated triphosphite containing $R' = R^2 =$ Me was reacted with $Mo(CO)_4(NBD)$ the complex $Mo(CO)_4\{P,P\text{-}[P(OMe)_2O]_2SiMe[OP(OMe)_2]\}$ was produced [65] (Eq. (32)). It contains two phosphorus groups coordinated to the metal and one pendulant phosphorus group. On heating this complex went on to produce several uncharacterised products, believed to be polynuclear phosphite-bridged species and the tridentate complex $Mo(CO)_3\{P,P,P\text{-}[P(OMe)_2O]_3SiMe\}$ in which all three phosphorus atoms are coordinated to the molybdenum. The tridentate complex has also been synthesised by reacting $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ with $[(MeO)_2PO]_3SiR^2$ (R = Me, Ph, CH = CH_2). The tridentate complexes all have a distorted octahedral geometry with similar bond distances to the diphosphite complexes. The six membered chelate ring is not as flexible as in the diphosphites and is constrained to the boat conformation. The carbonyls are again in a *fac* geometry.



Scheme 20. Formation of bridging complexes.



(32)

5. Larger bis-phosphine ligands

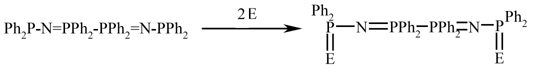
5.1. P–N–P–P–N–P

5.1.1. Synthesis

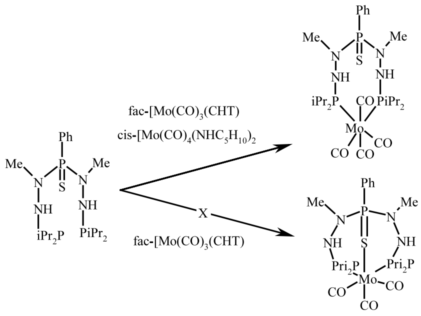
The reaction of $Li[N(PPh_2)_2]$ with tricloro phosphine or 1,2-dibromo ethane in a 3:1 ratio gave two products, the desired $Ph_2P{-}N{=}PPh_2{-}PPh_2{=}N{-}PPh_2$ and a heterocycle according to Scheme 19 [66]. The linear phosphine represents an oxidation product of $Li[N(PPh_2)_2]$. When iodine is used instead of PCl_3 only the linear phosphine is isolated.

5.1.2. General chemistry

Oxidation of the phosphazene (Eq. (33)) with sulfur or selenium goes without cleavage of the P–P bond, and the terminal P(III) are oxidised to P=S and P=Se [67]. X-ray crystal data shows the Se–P–N–P–P–N–P–Se backbone is planar and the Se groups are anti with respect to each other. The P=Se distance (2.120 Å) is typical of a double bond, whilst the length of the P–N bonds show a substantial degree of localised bonding along the chain. The analogous reaction using hydrogen peroxide or Bu^tOOH as the oxidising agent does not give $Ph_2P(O){-}N{=}PPh_2{-}PPh_2{=}N{-}P(O)Ph_2$ but instead $[Ph_2P(O)]_2NH$ [67].



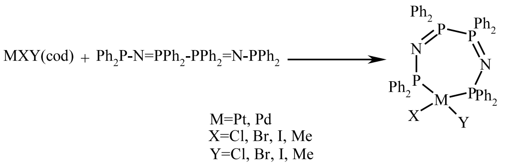
(33)



Scheme 21. Coordination of the two trivalent phosphorus atoms.

5.1.3. Coordination chemistry

Both the phosphazene chain and the oxidised derivative can coordinate to transition metals. The phosphazene ligand reacts with complexes of the type MXY(cod) (M = Pt, Pd X,Y = Cl, Br, I, Me) to give a square planar chelate complex [67,68] (Eq. (34)).

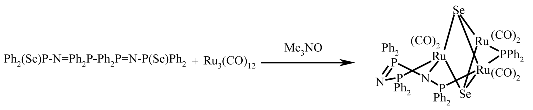


(34)

In the reaction with [Pd(μ-Cl)(L–L)]$_2$ (HL–L = *N*,*N*-dimethylbenzylamine or *N*,*N*-dimethyl-1-naphthylamine) or AuCl(tht) the phosphazene forms a bridging ligand [67,68] (Scheme 20). The AuCl groups are anti with respect to each other in a similar structure to the selenium derivative of the phosphazene.

Reaction of the phosphazene with M(PPh$_3$)$_4$ (M = Pd, Pt) via an oxidative addition reaction produces M(Ph$_2$PNPPh$_2$–P,P′)$_2$. The same reaction is not observed when the selenium and sulfur derivatives of the phosphazene are used, leaving only unreacted ligand. The P–P bond is not readily cleaved by M(PPh$_3$)$_4$ when the terminal phosphorus are oxidised, whilst in the unoxidised form it is readily cleaned [68].

The selenium-oxidised derivative reacts with Ru$_3$(CO)$_{12}$ and an oxidative-decarboxylation reagent Me$_3$NO to give the Ru$_3$(CO)$_6$(μ-Se)$_2$(μ-PPh$_2$)[Ph$_2$PNP-(Ph$_2$)NPPh$_2$] cluster [67] (Eq. (35)). In which there is an unsymmetric Ru$_3$ core, with the largest Ru–Ru distance associated with the PPh$_2$ bridging ligand. The two selenium atoms sit equidistant above and below the Ru$_3$ plane. The [Ph$_2$PNP(Ph$_2$)NPPh$_2$]$^-$ ligand is coordinated to ruthenium at each terminal phosphorus and by one nitrogen atom, this produces two fused Ru$_2$NP and RuN$_2$P$_2$ rings. There are then two six- and one five-coordinate ruthenium centres.

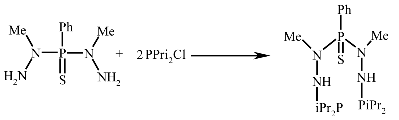


(35)

5.2. P–N–N–P–N–N–P backbone

5.2.1. Synthesis

The nucleophilic substitution reaction of the phosphorus hydrazide PhP(S)[N(Me)NH$_2$]$_2$ with (*i*-Pr)$_2$PCl yields the phosphorus hydrazido bridged diphosphine PhP(S)[N(Me)NHP(*i*-Pr)$_2$]$_2$ [69] (Eq. (36)).



(36)

5.2.2. Coordination chemistry

The two trivalent phosphorus groups enables the ligand to act as a π-acid donor and therefore coordinate to transition metals. The ligand reacts with *cis*-Mo(CO)$_4$(NHC$_5$H$_{10}$)$_2$ to produce a monomeric octahedral complex with the Mo(0). The PNNPNNP ligand chelates in a *cis* geometry producing an eight membered ring, the sulfur does not interact with the metal (Scheme 21). The lack of interaction between the sulfur and the metal is due to electronic effects rather than steric as the N–P–N angle (101.8°) is wide enough for the interaction.

The diphosphine can also form complexes with electron rich late transition metals. The complex PhP(S)[N(Me)NHP(*i*-Pr)$_2$]$_2$MCl$_2$ (M = Pt, Pd) is produced in the reaction of the ligand with PtCl$_2$(COD) or PdCl$_2$(PhCN)$_2$. This is again a neutral monomeric complex, but with the metal in a square planar geometry and the ligand coordinating *cis*. For both the octahedral and the square-planar complexes the –N(Me)- groups are in a trigonal-pyramidal geometry rather than trigonal-planar. The eight-membered metallocycles are non-planar, they have a twisted-chair conformation in the Mo(0) complex and a crown conformation in the Pt(II) complex.

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