ELSEVIER

Coordination Chemistry Reviews
176 (1998) 451–481

COORDINATION CHEMISTRY REVIEWS

Bidentate organophosphorus ligands formed via P–N bond formation: synthesis and coordination chemistry

Tuan Q. Ly*, J.D. Woollins

Department of Chemistry, Loughborough University, Leicestershire, Loughborough LE11 3TU, UK

Received 3 March 1998; accepted 11 May 1998

Contents

Abstract

This article outlines two related bidentate organophosphorus ligand systems prepared by phosphorus–nitrogen (P–N) bond formation — $R_2(E)PNHPR_2$, $RC(E)NHPR_2$ (E = O, S, or Se) and their derivatives. The focus is on the extensive coordination chemistry exhibited

---

* Corresponding author.

0010-8545/98/$ - see front matter © 1998 Elsevier Science S.A. All rights reserved.
PII S0010-8545(98)00147-7

by these systems to transition metals. A brief description of the syntheses of the ligands and metal complexes is given. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Coordination; Organophosphorus; Phosphorus–nitrogen; Tranisition metal

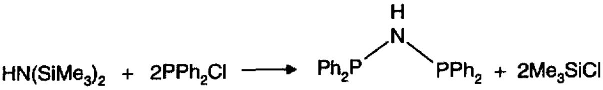
---

1. General introduction

Coordination chemistry contains numerous examples of bidentate ligands, which form ring closure through the donor atoms binding to the same metal. The most used ligands are those derived from that containing carbon, nitrogen, oxygen, phosphorus and sulphur atoms. Such chelates are widely used in catalysis, metal extraction, bioinorganic chemistry, tribology and many other fields. Heteroatom ligands containing a phosphorus–nitrogen bond have been known for over three decades. Phosphorus groups have been shown to form bonds with nitrogen groups with relative ease, and compounds containing phosphorous–nitrogen (P–N) bonds are chemically very stable. These facts make any investigation of ligands containing P–N bonds an interesting project.

2. Bis(diphenylphosphino)amine, $Ph_2PNHPPh_2$ (DPPA)

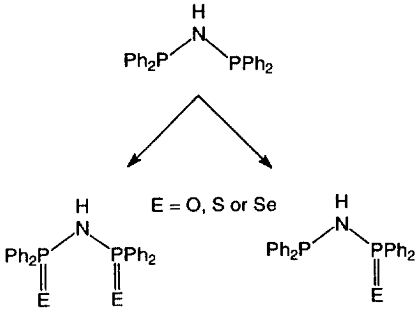
Bis(diphenylphosphino)amine has generated much interest since its discovery. Numerous examples of derivatives and metal complexes have been prepared [1,2]. The condensation of hexamethyldisilazane with chlorodiphenylphosphine gives DPPA in good yield (Eq. (1)) [3]. The P–N bonds are fused together, with the loss of trimethylsilyl chloride providing the thermodynamic driving force for the reaction.



$$HN(SiMe_3)_2 + 2PPh_2Cl \longrightarrow Ph_2P{-}\overset{H}{N}{-}PPh_2 + 2Me_3SiCl \qquad (1)$$

Both phosphorus(III) atoms can be sequentially oxidised by selected chalcogen elements (i.e. oxygen, sulphur or selenium) to make a range of possible ligands (Scheme 1).

Double oxidation of DPPA gives another set of ligands, $[Ph_2(E)NHP(E)Ph_2]$ (E = O, S or Se), that have shown an extensive coordination chemistry with numerous metals (see Section 4). Imidodiphosphinates, $[HN\{P(S)Ph_2\}_2]$, were first synthesised by Schmidpeter et al. [4]. Later, the seleno $[HN\{P(Se)Ph_2\}_2]$ analogue was prepared by oxidation of $Ph_2PNHPPh_2$ (DPPA) with potassium selenocyanate followed by acidic work up[5], or by direct reaction with grey selenium at reflux in toluene [6].



Scheme 1. Heteroatom ligands derived from DPPA.

3. Coordination chemistry of $Ph_2NHP(E)Ph_2$ (E = O, S or Se)

Recently, the monosubstituted compounds of DPPA with oxygen, sulphur and selenium have been prepared by direct oxidation of one of the two phosphorus(III) groups with hydrogen peroxide, elemental sulphur and grey selenium, respectively. Monochalcogenides of DPPA, $Ph_2NHP(E)Ph_2$ (E = O, S or Se), have been shown to coordinate with a number of metals affording five-membered ring metallacycles of the generic structure MPNPE (Fig. 1).

The coordination of these compounds can be described by two possible resonance structures, a neutral chelating ligand (**a**) or a chelating anion with the loss of

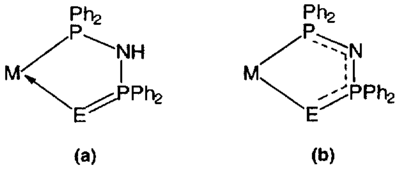
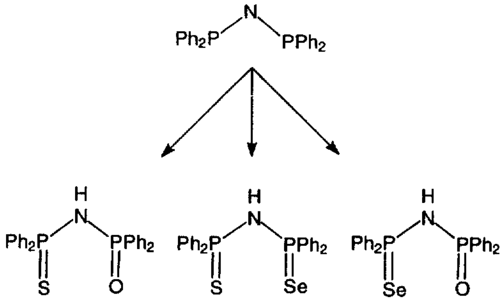


Fig. 1. Coordination pattern of monochalcogenides of DPPA.



Scheme 2. Unidentate complexes of $[Ph_2(O)PNHPPh_2]$ with Rh, Ir, Pd, Pt and Au [9–11].

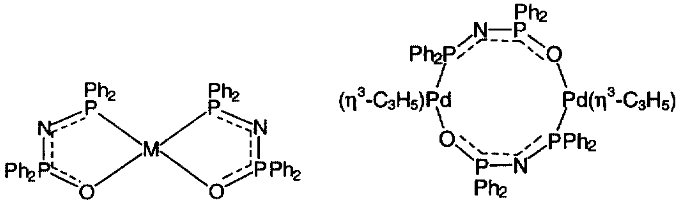


Fig. 2. The structures of *cis*-[M{$Ph_2P(O)NPPh_2$}$_2$] and [Pd(η^3-C_3H_5){$Ph_2PNP(O)Ph_2$}]$_2$ [12].

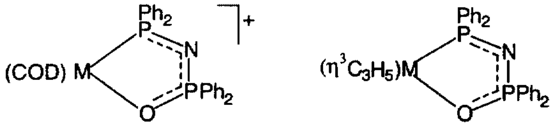


Fig. 3. The structures of [M(COD){$Ph_2P(O)NPPh_2$}]$^+$ and [M(η^3-C_3H_5){$Ph_2P(O)NPPh_2$}] (M = Pd or Pt) [12].

the imido proton in the neutral chelate ring (**b**). Rossi et al. [7] have reported rhenium complexes with the neutral $Ph_2P(O)NHPPh_2$ and the deprotonated $Ph_2P(O)NPPh_2]^-$ ligands from $[AsPh_4][ReOCl_4]$ and $Ph_2PNHPPh_2$. A cobalt(II) complex with both a chelating DPPA and a unidentate P-bound $Ph_2P(O)NPPh_2]^-$ ligand has been prepared [8]. The neutral $Ph_2P(O)NHPPh_2$ ligand containing a hard and a soft donor, mostly acts as a unidentate compound with coordination through the phosphorus(III) atom — several examples involving Rh^I, Ir^I, Pd^{II}, Pt^{II} and Au^I are illustrated in Scheme 2.

The ligands, when attached to a metal in a unidentate fashion, can subsequently be deprotonated by potassium tertbutoxide. Upon deprotonation the free oxygen atom may be coordinated to the same metal centre (M = Pd or Pt) or to a second metal, to form either P,O-chelate complexes or P,O-bridging complexes (Figs. 2 and 3).

Mono-oxidation of bis(diphenylphosphino)phenylamine with sulphur or selenium gives $Ph_2P(E)NphPPh_2$ (E = S or Se). These compounds act as bidentate chelate ligands towards metal forming complexes of the type $(CO)_4M(L)$ (M = Mo or W), CO(Cl)Rh(L) and $Cl_2M(L)$ (M = Pt or Pd), where [L = $Ph_2P(E)NPhPPh_2$ (E = S or Se)] (Scheme 3).

In [Pt{$Ph_2P(Se)NHPPh_2$)$_2$]Cl_2, the platinum centre has been shown to have a square-planar geometry from the coordination of two neutral $Ph_2P(Se)NBPPh_2$

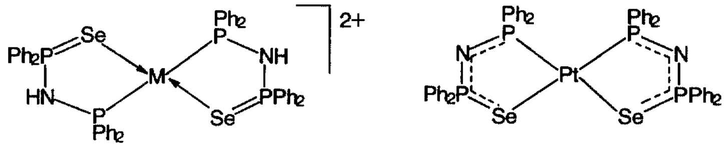
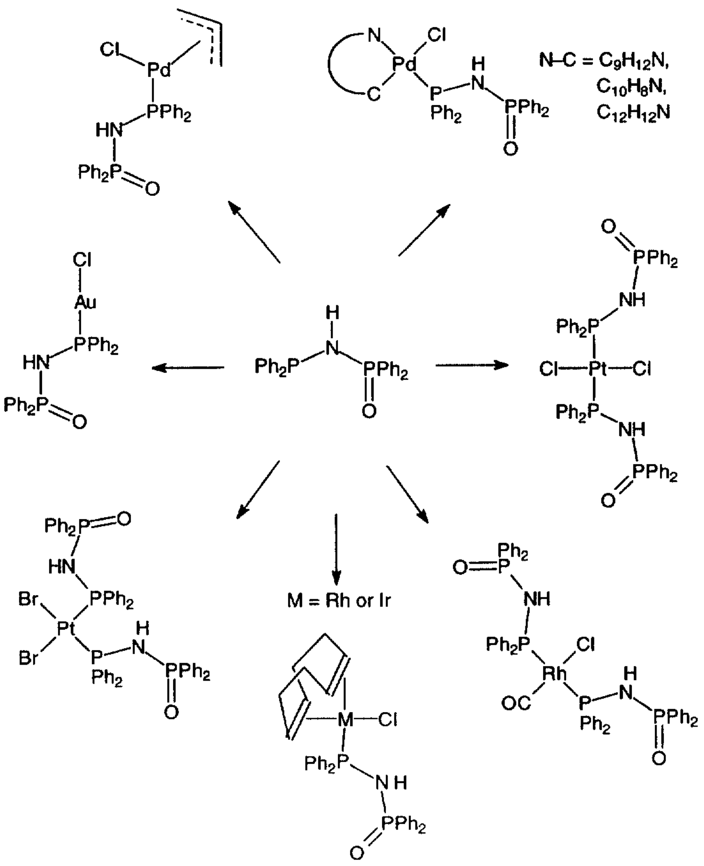


Fig. 4. The structures of [Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2 and [Pt{$Ph_2P(Se)NPPh_2$}$_2$] [14].



Scheme 3. Complexation of $Ph_2(E)PNPhPPh_2$ with Mo, W, Rh, Pd and Pt [13].

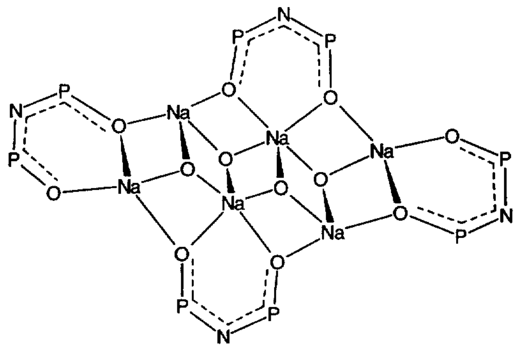


Fig. 5. The structure of $Na[(PhO)_2(O)PNP(O)(OPh)_2]$ with two bridging chelates at the front, and the back omitted for clarity [15].

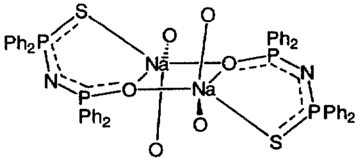


Fig. 6. The structure of $Na[Ph_2(O)PNP(S)Ph_2] \cdot 2THF$ with carbon atoms of THF omitted for clarity [16].

ligands arranged in the *trans*-bis configuration. However, the ligand has been shown to coordinate to a platinum in the *cis* configuration in its deprotonated form (Fig. 4). The bond lengths of the anionic chelates are shorter, with the exception of P–E which is longer than that in $[Pt\{Ph_2P(Se)NHPPh_2\}_2]Cl_2$. These differences support the notion of partial delocalisation within the chelate ring, as illustrated in Fig. 4.

4. Coordination chemistry of $HN\{P(E)R_2\}_2$ (E = O, S or Se)

Salts of the imidophosphinate, $[R_2P(E)NP(E')R_2\}_2]^-$, often display cross-coordination, resulting in interesting three-dimensional (3D) structures. In the 3D cluster core $[Na_6O_{12}]^+$, the complexation is accomplished by long Na ··· O=P interactions (2.23–2.50 Å) in a hexameric form (Fig. 5). The salt of the ligand with mixed donor atoms, $Na[Ph_2(O)PNP(S)Ph_2]$, displays a dimeric structure with two tetrahydro-

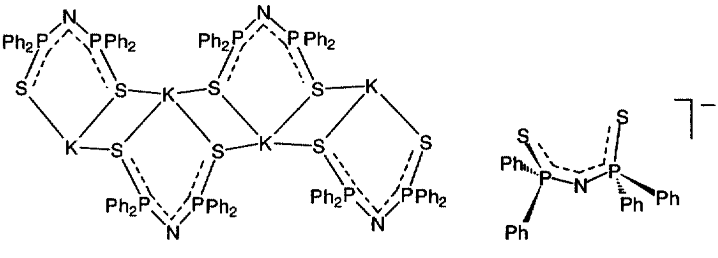


Fig. 7. The structures of $K[N\{P(S)Ph_2\}_2]$ [17] and $[K(18\text{-crown-}6)]^+$ $[N\{P(S)Ph_2\}_2]^-$ [18].

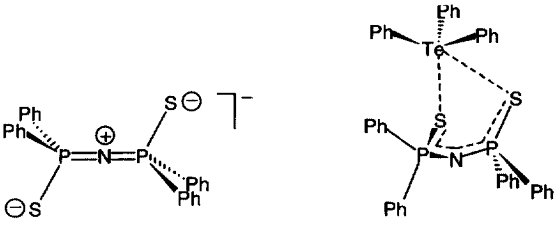
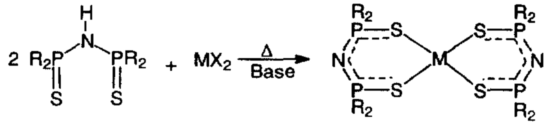


Fig. 8. The structures of $[N(PPh_3)_2]$ $[N\{P(S)Ph_2\}_2]$ [19] and $[TePh_3]^+$ $[N\{P(S)Ph_2\}_2]^-$ [20].


(2)

furan molecules completing the coordination sphere (Fig. 6). The P–O distance is similar to that in $[Ph_2(O)PNHP(S)Ph_2]$, but the P–S bond is lengthened [1.925(14)–1.979(4) Å], whilst the P–N bonds have contracted [1.577(9) and 1.606(9) from 1.694(4), and 1.668(5) Å].

Salts of the imidothiophosphinate, $[N\{P(S)Ph_2\}_2]^-$, with four cations, K^+, $[K(18\text{-crown-}6)]^+$, $[N(PPh_3)_2]^+$ and $[TePh_3]^+$, have revealed interesting structural configurations. In the potassium salt, the structural feature of the anion is much like a chelating ligand, with long-range interactions linking the potassium atoms in a zigzag fashion (Fig. 7). The $[K(18\text{-crown-}6)]^+$ (1,4,7,10,13,16-hexaoxacyclooctadecane) cation shows no interaction with the anion, and it has adopted a *syn* orientation (Fig. 7). The organic salt, $[N(PPh_3)_2]^+$, revealed an unusual linear P–N–P [180.0(1)°] in the anion, that is rationalised in terms of double bond character in the P–N bonds (Fig. 8). No cation–anion interactions were found. The molecular structure of $[TePh_3][N\{P(S)Ph_2\}_2]$ displays weak cation–anion Te···S secondary interactions [3.264 and 3.451 Å]. The P–S bonds are in the *syn* conformation with close similarity to that seen in the $[K(18\text{-crown-}6)]^+$ salt (Fig. 8). The $K[N\{P(Se)Ph_2\}_2]$ salt has an angular P–N–P bond and forms a ladder structure similar to that in $K[N\{P(S)Ph_2\}_2]$.

The coordination chemistry of $[R_2(E)PNP(E')R_2]^-$ has been widely investigated and reviewed [21,22]. Selected metal complexes with these ligands are discussed. The first substantial investigation into the coordination chemistry of $[HN\{P(S)Ph_2\}_2]$

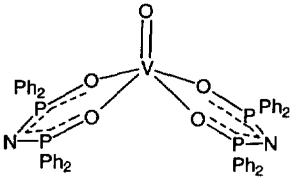


Fig. 9. The structure of $[V(O)\{(Ph_2(O)P)_2N\}_2]$ [24].

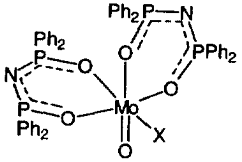


Fig. 10. The structure of $[MoX(O)\{(Ph_2(O)P)_2N\}_2]$ (X = Cl or O) [25].

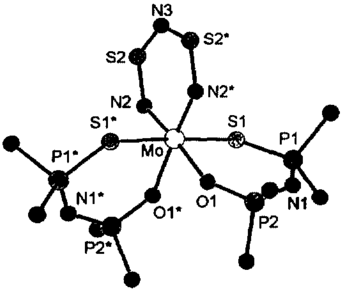


Fig. 11. Molecular structure of [Mo(N$_3$S$_2$){R$_2$(O)PNP(S)R$_2$}$_2$] (R = Ph or ^{i}Pr) [26].

was reported in 1978 [23]. The typical preparation of metal complexes required the reactions at reflux, of a ligand or its salt, with a metal dihalide (Eq. (2)).

No complexes of the imidodiphosphinates with the metals from group 2, 3 or 4 have been reported.

4.1. Group 5: V, Nb and Ta

In [V(O){{Ph$_2$(O)P)$_2$N}$_2$], the metal is in the centre of a square-based pyramid with the rings nearly planar (Fig. 9). No complexes with niobium or tantalum have been structurally characterised.

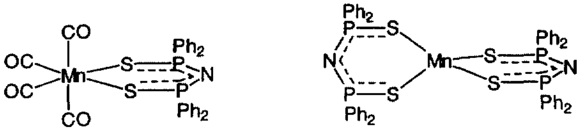


Fig. 12. The structures of [Mn(CO)$_4${(Ph$_2$(S)P)$_2$N}] [27] and [Mn{(Ph$_2$(S)P)$_2$N}$_2$] [28].

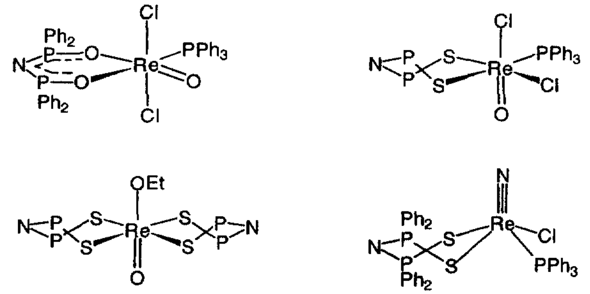


Fig. 13. The structures of [Re(O)Cl$_2${(Ph$_2$(O)P)$_2$N}(PPh$_3$)], [Re(O)Cl$_2${(Ph$_2$(S)P)$_2$N} (PPh$_3$)], [ReO(OEt){(Ph$_2$(S)P)$_2$N}$_2$] [29] and [Re(N)Cl{(Ph$_2$(S)P)$_2$N}(PPh$_3$)] [30].

4.2. Group 6: Cr, Mo and W

The coordination geometry of the dioxygen complexes of molybdenum, $[MoCl(O)\{(Ph_2(O)P)_2N\}_2]$ and $[MoO_2\{(Ph_2(O)P)_2N\}_2]$, are both octahedral and have *cis* conformation (Fig. 10).

In $[MO(N_3S_2)\{R_2(O)PNP(S)R_2\}_2]$, molybdenum(V) is at the centre of an octahedral coordination complex (Fig. 11). The oxygen donors lie *trans* to nitrogen in both compounds.

4.3. Group 7: Mn, Tc and Re

The manganese(I) complex with one chelate ligand is arranged octahedrally, whilst the manganese(II) compound contains two chelate ligands in a tetrahedron geometry (Fig. 12).

Rhenium has been subjected to coordination of the ligands with oxygen, sulphur and selenium donor groups. The molecular structures of four metal complexes are shown in Fig. 13. The upper two compounds are octahedrally coordinated with the oxo in the *cis* or *trans* (with respect to oxygen and sulphur)

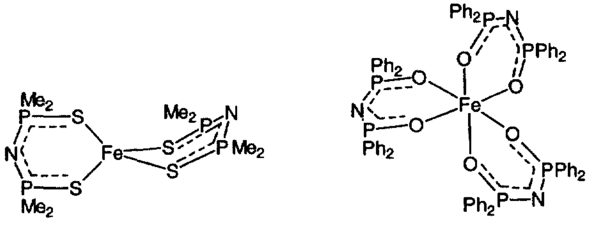


Fig. 14. The structures of $[Fe\{(Me_2(S)P)_2N\}_2]$ [31] and $[Fe\{(Ph_2(O)P)_2N\}_3]$ [32].

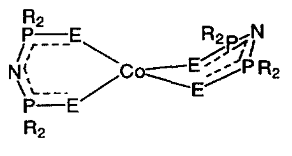


Fig. 15. The structures of $[Co\{(Me_2(S)P)_2N\}_2]$ and $[Co\{(Ph_2(Se)P)_2N\}_2]$ [33].

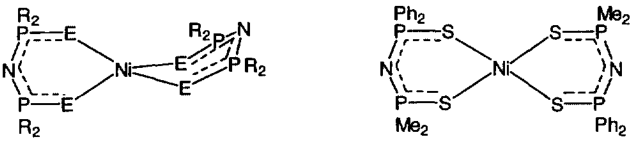


Fig. 16. The structures of $[Ni\{(Ph_2(S)P)_2N\}_2]$ [6,34,35], $[Ni\{(Me_2(S)P)_2N\}_2]$ [36,37], $[Ni\{(^iPr_2(S)P)_2N\}_2]$ [38] and $[Ni\{Ph_2(S)PNP(S)Me_2\}_2]$ [39].

conformation, depending on the donor groups on the chelate ligands. In $[ReO(OEt)\{(Ph_2(S)P)_2N\}_2]$, the rhenium atom is octahedrally coordinated with the two chelate ligands lying *trans* to each other. The rhenium complex, $[Re(N)Cl\{(Ph_2(S)P)_2N\}(PPh_3)]$, displays a square pyramid with the Re–N bond considered to be a triple bond [1.630(1) Å]. The structure of the compound with selenium donor groups has yet to be determined.

4.4. Group 8: Fe, Ru and Os

The iron(II) complex with sulphur donor groups consists of two chelate ligands in a tetrahedral configuration. However, iron(III) complexes with oxygen donor groups displays an octahedral Tris-chelate geometry (Fig. 14).

4.5. Group 9: Co, Rh and Ir

The cobalt(II) complexes shown in Fig. 15 are both tetrahedral with sulphur and selenium donor groups.

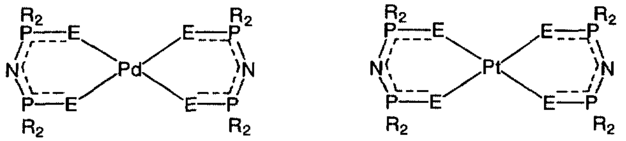


Fig. 17. The structures of $[Pd\{(PhO)_2(S)PNP(S)(OPh)_2\}_2]$ [41], $[M\{(^{i}Pr_2(S)P)_2N\}_2]$ (M = Pd or Pt} (D. Cupertino, R. Keyte, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, unpublished work) and $[Pd\{Ph_2(O)PNP(Se)Ph_2\}_2]$ (R = Ph or ^{i}Pr) [40].

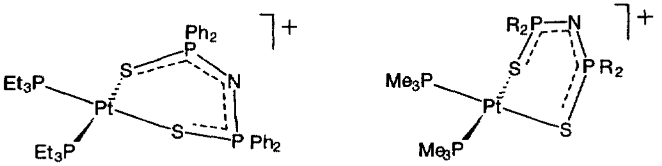


Fig. 18. The structures of $[Pt\{N\{P(S)Ph_2\}_2\}(PEt_3)_2]^+$ and $[Pt\{(PhO)_2(S)PNP(S)(OPh)_2\}(PMe_3)_2]^+$ [43].

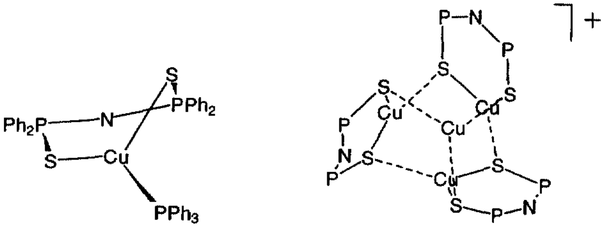


Fig. 19. The structures of $[Cu(PPh_3)\{(Ph_2(S)P)_2N\}]$ [44] and $[Cu_4\{(Ph_2(S)P)_2N\}_3]^+$ $[CuCl_2]^-$ (with phenyls omitted for clarity) [45].

4.6. Group 10: Ni, Pd and Pt

The nickel(II) complexes adopt tetrahedral geometry with symmetrical ligands. In $[Ni\{(Ph_2(S)P)_2N\}_2]$, $[Ni\{(Me_2(S)P)_2N\}_2]$ and $[Ni\{(^iPr_2(S)P)_2N\}_2]$, the compounds display the tetrahedral configuration whilst the mixed R system $[Ni\{Ph_2(S)PNP(S)Me_2\}_2]$ is square planar (Fig. 16).

The palladium and platinum complexes $[M\{(Ph_2(E)P)_2N\}_2]$ (E = S or Se) are all square planar, with the chelate rings in the pseudo-boat conformation (Fig. 17). The pseudo-boat conformation is also found in the chelate ring with mixed donor atoms coordinated to platinum $[Pt(C_8H_{12}OMe)\{Ph_2(O)PNP(S)Ph_2\}_2]$ [40]. The boat conformation of the chelate ring in $[Pt\{Ph_2(S)PNP(S)Ph_2\}(PEt_3)_2]^+$ is rearranged to a chair conformation by putting an oxygen atom between the phenyl and the phosphorus groups, $[Pt\{(PhO)_2(S)PNP(S)(OPh)_2\}_2(PMe_3)_2]^+$ (Fig. 18).

4.7. Group 11: Cu, Ag and Au

The copper(I) complex, $[Cu(PPh_3)\{(Ph_2(S)P)_2N\}]$, displays a monocyclic structure with three atoms bound to the copper atom (Fig. 19). In $[Cu_4\{(Ph_2(S)P)_2N\}_3]^+$ $[CuCl_2]^-$, the third coordination of the copper atom is completed by bonding to another sulphur donor atom, in such a way that a small cluster of four copper atoms with three chelate ligands is formed (Fig. 19).

The reaction of $[HN(P(S)Ph_2)_2]$ with $[AuCl_2(THT)]$ gives $[AuCl_2\{(Ph_2(S)P)_2N\}]$, with the loss of a proton. The gold atom is tetracoordinated in a square-planar configuration (Fig. 20). The Reaction of $[HN\{P(S)Ph_2\}_2]$ with $[AuR_2Cl]$ gives $[AuR_2\{(Ph_2(S)P)_2N\}]$ [47].

4.8. Group 12: Zn, Cd and Hg

Zinc(II) and cadmium(II) complexes with $[HN\{P(S)^iPr_2\}_2]$ are isostructural in the tetrahedral configuration (Fig. 21). The geometry of the chelate rings is puckered with a pseudo-boat conformation.

4.9. Group 13: B, Al, Ga, In and Tl

The thallium(III) complex, $[TlPh_2\{(Ph_2(S)P)_2N\}]$, is prepared by reacting

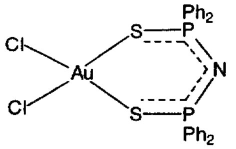


Fig. 20. The structure of $[AuCl_2\{(Ph_2(S)P)_2N\}]$ [46].

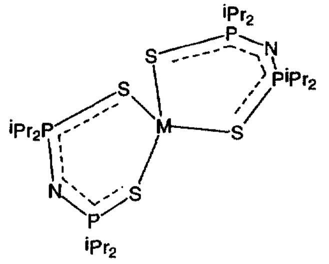


Fig. 21. The structure of $[\mathrm{M}\{(^i\mathrm{Pr}_2(\mathrm{S})\mathrm{P})_2\mathrm{N}\}_2]$ (M = Zn or Cd) [38].

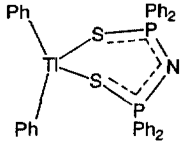


Fig. 22. The structure of $[\mathrm{TlPh}_2\{(\mathrm{Ph}_2(\mathrm{S})\mathrm{P})_2\mathrm{N}\}]$ [48].

diphenylthallium(III) bromide with $\mathrm{K[N\{P(S)Ph_2\}_2]}$. The metal has a tetrahedral coordination (Fig. 22).

4.10. Group 14: C, Si, Ge, Sn and Pb

This group is well represented, and is dominated by tin compounds that display coordination with oxygen, sulphur and selenium donor groups. The tin complexes with oxo ligands are illustrated in Fig. 23. When the ligand $[\mathrm{HN\{P(O)Ph_2\}_2}]$ is reacted with tin(II) acetate, the resulting structure is a distorted trigonal bipyramid. The geometry at the tin atom suggests the presence of a lone pair of electrons at the vacant equatorial site (Fig. 23). In $[\mathrm{SnI_2(Ph_2(O)P)_2N)\}_2}]$, the coordination at

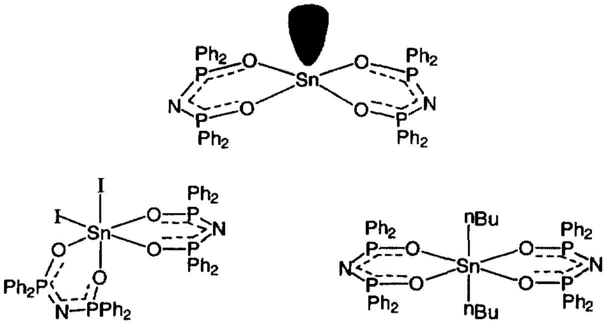


Fig. 23. The structures of $[\mathrm{Sn(Ph_2(O)P)_2N\}_2}]$, $[\mathrm{SnI_2\{(Ph_2(O)P)_2N\}_2}]$ [49] and $[\mathrm{Sn(^nBu)_2\{(Ph_2(O)P)_2N\}_2}]$ [50].

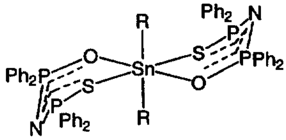


Fig. 24. The structure of $[SnR_2\{Ph_2P(S)NP(O)Ph_2\}_2]$ (R = Me or Ph) [51].

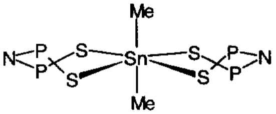


Fig. 25. The structure of $[SnMe_2\{(Ph_2(S)P)_2N\}_2]$ [52].

the tin atom is octahedral with the iodine atoms in the *cis* position. However, it is interesting to note with the substitution of the iodine atoms for ^{n}butyl groups, $[Sn(^nBu)_2\{(Ph_2(O)P)_2N\}_2]$, the two chelate ligands formed in the *trans* position to each other.

When one oxygen is replaced by a sulphur the planarity of the ME_2P_2N ring (E = O or S) is lost and a boat conformation is observed (Fig. 24). It is interesting to note the isomer in which the sulphur and oxygen are *trans* to one another is preferred. This may be explained by the fact that the Sn–S and P–S bonds are generally 0.5 Å longer than Sn–O and P–O bonds, and the Sn–O–P angle is almost 30° greater than the Sn–S–P angle. The *trans* geometry probably reduces steric hindrance and any ring strain.

The dimethyltin complex with the thio chelate ligand, $[SnMe_2\{(Ph_2(S)P)_2N\}_2]$, has the tin atom in an octahedral configuration (Fig. 25). The chelate ligands approximate to a square planar geometry in a boat conformation.

The selenium analogue exists in two forms: a distorted square (tetragonal) pyramid with the MSe_2P_2N ring adopting the boat conformation (red crystals); and a square planar complex with the MSe_2P_2N ring adopting the chair conformation (yellow crystals, Fig. 26). The two isomers were recrystallised from the same yellow chloroform/hexane solution of $Sn[N\{P(Se)Ph_2\}_2]_2$, suggesting that the difference in energy between the two conformers is very little,

The lead(II) complex, $[Pb\{(Ph_2(S)P)_2N\}_2]$, has two chelate ligands bound to the

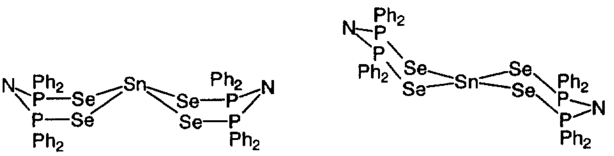


Fig. 26. The structures of boat-$[Sn\{(Ph_2(Se)P)_2N\}_2]$ (red crystals) and chair-$[Sn\{(Ph_2(Se)P)_2N\}_2]$ (yellow crystals) [53].

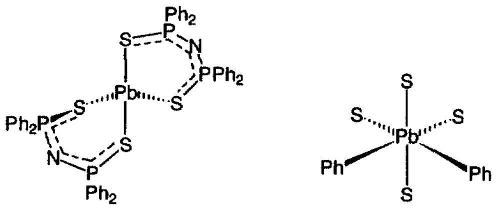


Fig. 27. The structure of [Pb$\{(Ph_2(S)P)_2N\}_2$] [54].

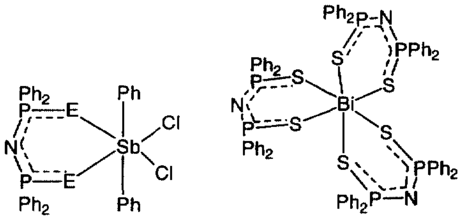


Fig. 28. The structures of [$SbPh_2Cl_2\{(Ph_2(O)P)_2N\}$], [$SbPh_2Cl_2(Ph_2(S)PNP(O)Ph_2\}$] [55](E = 0 or S) and [$Bi\{(Ph_2(S)P)_2N\}_3$] [56].

lead atom. Close inspection of the structure revealed a pseudo octahedral coordination geometry with the interaction of two phenyl groups, from the ligands, completing the coordination sphere (Fig. 27).

4.11. Group 15: N, P, As, Sb and Bi

In diphenylantimony(V) compound, [$SbPh_2Cl_2\{(Ph_2(O)P)_2N\}$], the antimony atom is octahedrally coordinated with a monocyclic chelate ring. The oxo-thio analogue, [$SbPh_2Cl_2\{Ph_2(S)PNP(O)Ph_2\}$], displays similar features with normal bond lengths (Fig. 28). The bismuth(III) complex, [$Bi\{(Ph_2(S)P)_2N\}3$], has three chelate ligands organised octahedrally around the bismuth atom (Fig. 28).

4.12. Group 15: O, S, Se, Te and Po

The square planar complexes of [$HN\{P(S)Ph_2\}_2$] with selenium and tellurium

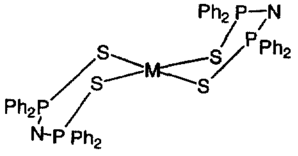
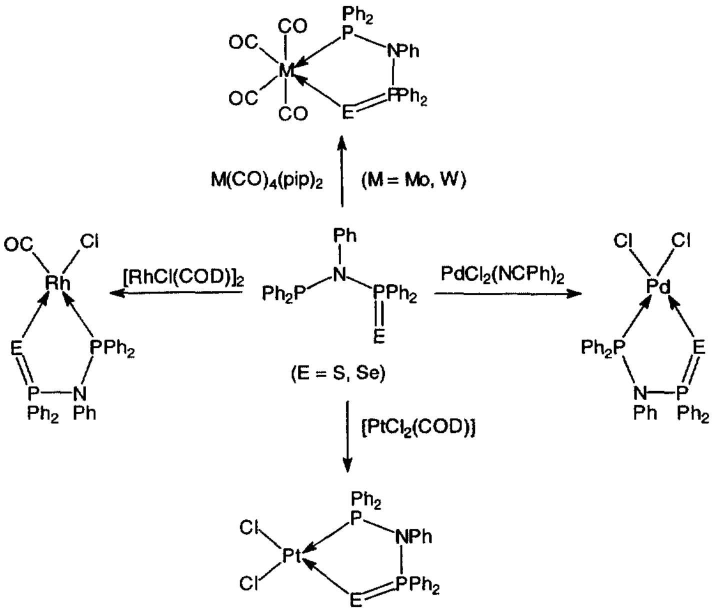


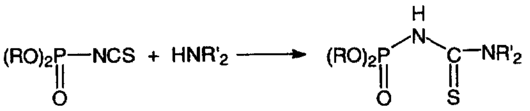
Fig. 29. The structures of [$Se\{(Ph_2(S)P)_2N\}_2$] [57] and [$Te\{(Ph_2(S)P)_2N\}_2$] [58].



Scheme 4. Heteroatom ligands from selective oxidation of DPPA.

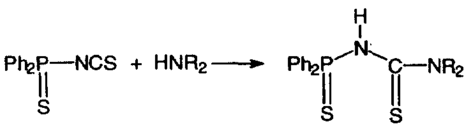
have been reported (Fig. 29). The SeS_2P_2N ring is a slightly distorted chair as opposed to the TeS_2P_2N ring, which is a near perfect chair conformation.

The range of ligands derived from DPPA is numerous, and in some cases there are as many as four different atom types in the chelate skeletal (e.g. $[Ph_2(Se)PNHP(O)Ph_2]$, $[Ph_2(Se)PNHP(S)Ph_2]$ and $[Ph_2(S)PNHP(O)Ph_2]$ shown in Scheme 4). Compared with the extensive research on DPPA and its derivatives, less research has been carried out on phosphorus(III) systems such as diphenylphos-



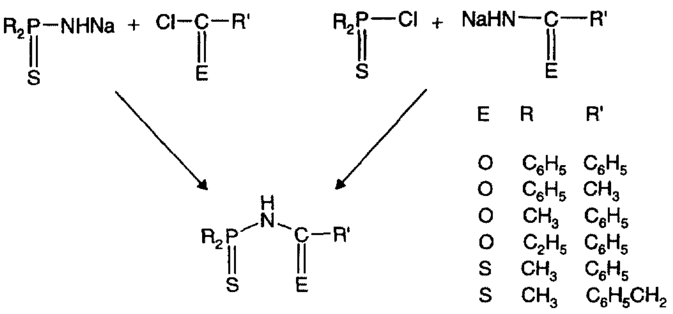
$$(RO)_2\underset{\underset{O}{\|}}{P}\text{—}NCS + HNR'_2 \longrightarrow (RO)_2\underset{\underset{O}{\|}}{P}\text{—}\overset{H}{N}\text{—}\underset{\underset{S}{\|}}{C}\text{—}NR'_2 \qquad (3)$$

$$Ph_2P(S)Cl + NH_4SCN \longrightarrow Ph_2P(S)NCS + NH_4Cl$$



$$Ph_2\underset{\underset{S}{\|}}{P}\text{—}NCS + HNR_2 \longrightarrow Ph_2\underset{\underset{S}{\|}}{P}\text{—}\overset{H}{N}\text{—}\underset{\underset{S}{\|}}{C}\text{—}NR_2$$

$R_2 = H_2$, $(Me)_2$, (H, Me), $(Et)_2$, (H, Ph), (H, naphthyl), (H, tolyl) (4)



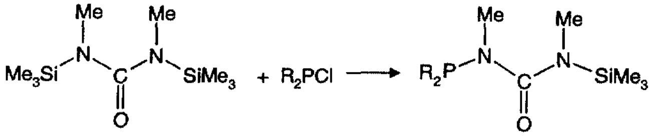
E	R	R'
O	C_6H_5	C_6H_5
O	C_6H_5	CH_3
O	CH_3	C_6H_5
O	C_2H_5	C_6H_5
S	CH_3	C_6H_5
S	CH_3	$C_6H_5CH_2$

Scheme 5. Synthesis of $Ph_2P(S)NHC(E)R'$.

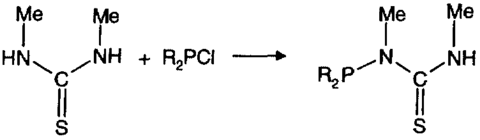
phino thioureas, $Ph_2PNHC(S)R$ (DPPTs). The DPPTs systems can be oxidised to form diphenylthiophosphinyl thioureas $Ph_2P(S)NHC(S)R$ (DPTPTs) and related compounds.

5. Diphenylphosphinyl ureas and thioureas

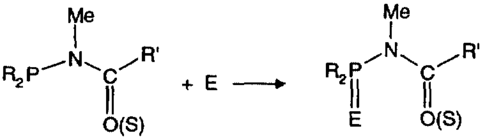
Diphenylphosphinyl thioureas, $Ph_2P(O)NHC(S)R$, have been prepared from the reaction of phosphoroisothiocyanatidates with amines (Eq. (3)) [59–61]. The reac-



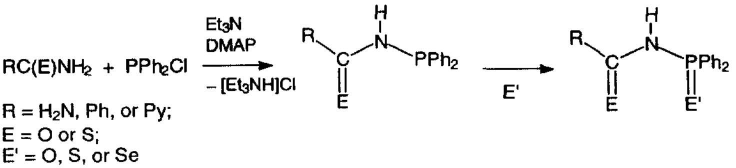
$R_2 = (^t\text{Bu, Ph})$ (5)



$R_2 = Me_2, {}^i\text{Pr}_2, Ph_2, (^t\text{Bu, Ph})$, and (Me, Ph) (6)



E = S or Se (7)



(8)

tion proceeds by nucleophilic amine-attack upon the carbon atom of the isothiocyanate, followed by the loss of a proton to the nitrogen of the isothiocyanate at room temperature. The choice of oxygen and sulphur donor atoms in the ligands can be changed by manipulating the starting material — see Eq. (4).

The synthesis of the ligands with sulphur donors, such as diphenylthiophosphinyl thioureas (DPTPT), in quantitative yields, was reported by the addition of amines to the isothiocyanate group (Eq. (3))[62–67].

The compounds can also be prepared by clipping the metallated acid amides together with acid chlorides or chlorophosphine [68] (Scheme 5). The reactions proceed via P–N bond formation the two reagents — the driving force in these reactions is the formation of sodium chloride.

Another route for synthesising these compounds was investigated by Schmutzler et al. [69], who used the condensation of silylated ureas and thioureas with chlorophosphines, followed by direct oxidation with sulphur or selenium (Eqs. (5)–(7)).

One advantage of this synthetic method is that the phosphorus group can be selectively oxidised by oxygen, sulphur or selenium, in a similar fashion to the chemistry of DPPA (e.g. Scheme 4).

Woollins et al. [70] later prepared this ligand system at a faster rate, with the introduction of a catalyst, 4-dimethylaminopyridine. The resulting phosphorus(III) intermediate can then be oxidised selectively with the desired chalcogenides (oxygen, sulphur or selenium; Eq. (8)).

6. Structure of $RC(E)NHP(E')Ph_2$ (E and E′ = O or S)

DPTPT, closely related to $Ph_2(E)PNHP(S)Ph_2$ (E = O or S), can exist in three possible tautomeric forms (Scheme 6). Infrared and NMR spectroscopy suggest the compound is in the imido form. X-ray studies of $R_2(E)PNHC(E)R'$ (E = O or S) established that this system is predominantly in the imido form and is well represented by many examples. Selected bond lengths and angles of the compounds to follow are listed in Table 1.

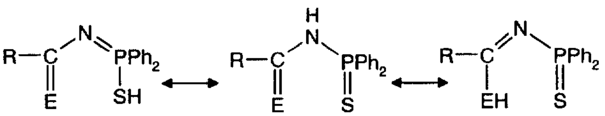
Single crystal X-ray diffraction studies of [PhC(O)NHP(O)Ph(OMe)], indicate the oxygen atoms are arranged in the *anti* orientation (Fig. 30). The phosphoryl and imido groups are *syn* coplanar, whilst the carbonyl and imido are *anti* coplanar.

The phosphoryl oxygen and the imido hydrogen are involved in an inter-

Table 1

Selected bond lengths (Å) and angles (°) of RC(E)NHP(E′)R′

Compound	PO(S)	PN	NC	CO(S)	PNC	Ref.
[PhC(O)NHP(O)Ph(OMe)]	1.469(5)	1.673(6)	1.393(8)	1.216(8)	122.0(4)	[71]
[Ph(Me)NC(O)NHP(O)(OPh)$_2$]	1.462(4)	1.646(5)	1.406(8)	1.213(7)	125.6(4)	[72]
[MeC(O)NHP(O)(OMe)(SMe)]	1.463(3)	1.641(4)	1.365(5)	1.219(4)	123.9(3)	[73]
[PhC(S)NHP(O)(O^{i}Pr)$_2$]	1.457(1)	1.672(1)	1.360(2)	1.646(1)	127.9(9)	[74]
[Ph$_2$PC(S)NHP(O)(OPh)$_2$]	1.460(1)	1.658(2)	1.372(2)	1.637(2)	130.5(1)	[75]
[PhHNC(S)NHP(O)(NH^{i}Pr){(N(C$_2$H$_4$Cl)$_2$}]	1.493(4)	1.694(4)	1.376(6)	1.670(6)	129.5(4)	[76]
[PhC(O)NHP(S)Ph$_2$]	1.941(6)	1.720(1)	1.360(2)	1.220(2)	120(1)	[70]
[Ph(Mc)NC(S)NHP(S)(OPh)$_2$]	1.895(2)	1.671(3)	1.378(6)	1.664(3)	127.5(2)	[72]
[PhC(S)NHP(S)(O^{i}Pr)$_2$]	1.912(1)	1.686(3)	1.354(5)	1.635(4)	—	[85]
[(PhO)$_2$P(O)NHC(O)NHC(O)N(^{n}Pr)$_2$]	1.445(2)	1.646(3)	1.370(4)	1.211(4)	128.1(2)	[86]
[Ph$_2$(S)PNHC(O)NBP(S)Ph$_2$]	1.931(1)	1.702(2)	1.367(3)	1.219(3)	121.8(2)	[87]
	1.942(1)	1.686(2)	1.379(3)	—	134.6(2)	



Scheme 6. Tautomeric structures of diphenylthiophosphinyl urea and thiourea (E = O or S).

molecular hydrogen bond to an adjacent molecule in a dimer formation. In [Ph(Me)NC(O)NHP(O)(OPh)$_2$], the molecules display isostructural arrangement to the above compound with a similar hydrogen-bonding interaction (Fig. 30). Interestingly, a similar compound, [MeC(O)NHP(O)(SMe)OMe], was found to have the two oxygen atoms arranged in the *syn* orientation (Fig. 30). There are intermolecular P=O ··· H–N hydrogen bonds in the crystal structure of this compound, but instead of seeing a dimer, a chain like arrangement was found.

This system containing mixed donor atoms e.g. [PhC(S)NHP(O)(O^{i}Pr)$_2$], has the phosphoryl oxygen atom in the *anti* orientation relative to the thiocarbonyl group. The molecules are arranged as dimers (back-to-back) formed by intermolecular P=O ··· H–N hydrogen bonds between two adjacent molecules (Fig. 31). However, the structure of [PhHNC(S)NHP(O)(NH^{i}Pr) {(N(C$_2$H$_4$Cl)$_2$}] demonstrates a very different configuration — the molecules are arranged in the *anti* orientation with the phosphoryl and imido groups are *anti* coplanar, whilst the thiocarbonyl and imido are *syn* coplanar. The intramolecular hydrogen bond between the phosphoryl oxygen and the amino hydrogen forms a ring closure to give a pseudo six-membered ring (Fig. 31).

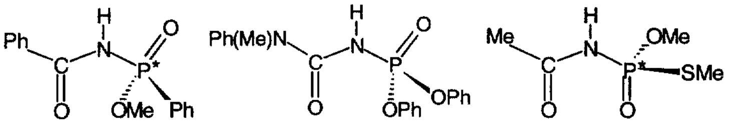


Fig. 30. The structures of [PhC(O)NHP(O)Ph(OMe)] (chiral) [71], [Ph(Me)NC(O)NHP(O)(OPh)$_2$] [72] and [MeC(O)NHP(O)(SMe)OMe] (chiral) [73].

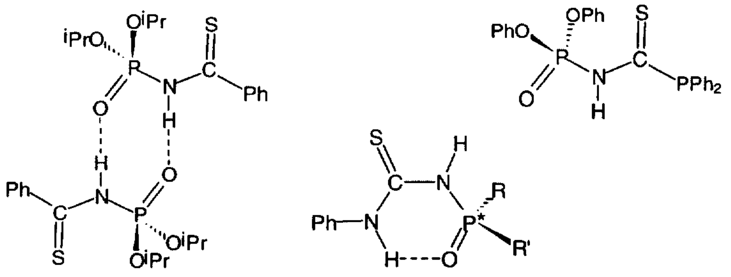


Fig. 31. The structures of [PhC(S)NHP(O)(O^{i}Pr)$_2$] [74], [Ph$_2$PC(S)NHP(O)(OPh)$_2$] [75] and [PhHNC(S)NHP(O)(NH^{i}Pr) {(N(C$_2$H$_4$Cl)$_2$}] (R=NH^{i}Pr,R'=N(C$_2$H$_4$Cl)$_2$) [76].

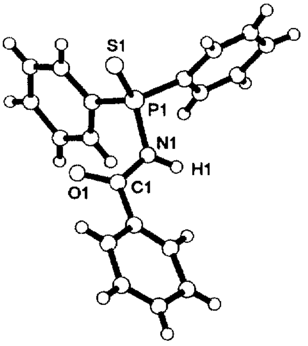


Fig. 32. Molecular structure of [PhC(O)NHP(S)Ph_2] [70].

In [PhC(O)NHP(S)Ph_2], the X-ray structure shows the compound is in the keto form (Fig. 32). However, the chalcogen groups lie in the *syn* orientation whilst the compounds above have them in the *anti* orientation.

The structure of the disulphide analogue, [Ph(Me)NC(S)NHP(S)$(OPh)_2$], shows the compound is in the keto form, with the proton bonded to the nitrogen and not to either sulphur atoms (Fig. 33). It is best described as Z, Z′ with absolute values of torsion angles [ω_1(S1–C1–N1–P1)] = 5.1° and [ω_2(C1–N1–P1–S2)] = 55.0°. In [PhC(S)NHP(S)$(O^iPr)_2$], a similar *syn* orientation was found (Fig. 33). The P–S bond length in [Ph(Me)NC(S)NHP(S)$(OPh)_2$] (1.895(2) Å) is amongst the shortest for a P=S bond — comparable lengths are found in [β-P_4S_7] (1.890 Å) [77], [$(^iPrO)_2P$(S)SS(S)P$(O^iPr)_2$] (1.890 Å)[78], [$(MeO)_2P$(S)SS(S)P$(OMe)_2$] (1.898 and 1.903 Å) [79], [$(PhO)_2P$(S)SS(S)P$(OPh)_2$] (1.898 and 1.900 Å) [80,81], $(PhS)_3P$=S] (1.899 Å) [82], [1,3,5-$^tBu_3C_6H_2P(=S)_2$] (1.890, 1.891 Å) [83] and [1-Me,3,5-$^tBu_2C_6H_2P(=S)_2$] (1.894, 1.900 Å) [84]. The C–S bond length in thiourea compounds is generally longer than that in benzamide compounds (Table 1). This is probably due to some distribution of the π-bond in the C=S bond to the adjacent nitrogen atoms, which would account for the contraction of the C–N bonds — in particular the C–N(R,R′) bond as oppose to the C–NH bond.

In [$(PhO)_2P$(O)NHC(O)NHC(O)$N(^nPr)_2$], the phosphinyl group, attached to a biuret backbone, exists in the *anti* orientation relative to the central carbonyl group (Fig. 34). Strong inter and intramolecular hydrogen bonding between the amine protons and the carbonyl groups are responsible for the *anti*, *anti* orientation. The end carbonyl group is positioned *syn* coplanar to the second imido group, and a ring closure influenced by an intramolecular hydrogen bond is formed.

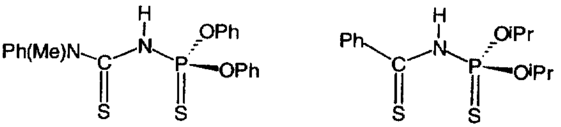


Fig. 33. The structures of [Ph(Me)NC(S)NHP(S)$(OPh)_2$] [72] and [PhC(S)NHP(S)$(O^iPr)_2$] [85].

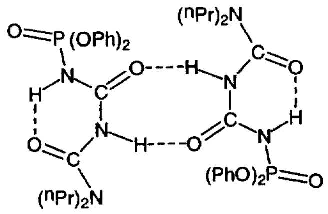


Fig. 34. The structure of $[(PhO)_2P(O)NHC(O)NHC(O)N(^nPr)_2]$ [86].

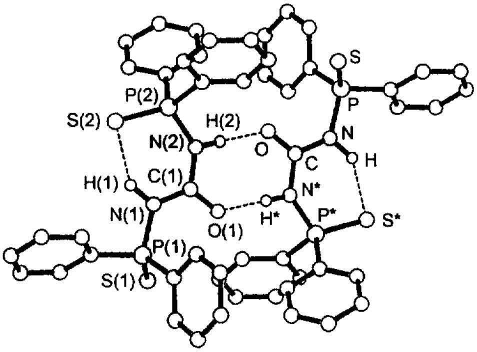


Fig. 35. The structure of $[Ph_2(S)PNHC(O)NHP(S)Ph_2]$ [87].

The solid state structure of $[Ph_2(S)PNHC(O)NHP(S)Ph_2]$ has one P=S group lying in a *syn* orientation relative to the central C=O, whilst the other P=S group is in the *anti* orientation (Fig. 35). The *syn* coplanarity between one P=S group and an imido group is influenced by an intramolecular hydrogen bond formed by those two groups. Further, the molecules are inverted, which can be described as dimer pairs resulting from intermolecular hydrogen bond interactions between the central carbonyl group and the *syn* coplanar imido to the adjacent molecule.

Interestingly, the X-ray structure of the phosphorus(III) analogue, $[Ph_2PNHC(S)$

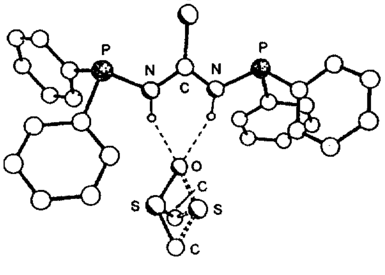


Fig. 36. Molecular structure of $[Ph_2PNHC(S)NHPPh_2]\cdot Me_2SO$ [87].

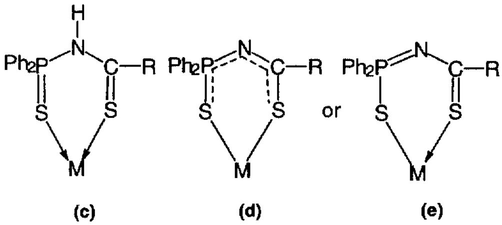


Fig. 37. Coordination patterns of diphenylthiophosphinyl thioureas.

NHP-Ph$_2$], has the PNC(S)NP section planar. Intermolecular hydrogen bonding to dimethyl sulphoxide may be a contributing factor for the *syn*, *syn* orientation (Fig. 36).

7. Coordination chemistry of diphenylthiophosphinyl ureas and thioureas

These ligands can form cyclic structures with a metal, either as the neutral ligand or in the deprotonated form (Fig. 37). The coordination of the deprotonated ligands can take two possible patterns — delocalised or localised bonding [pattern (d) and (e) in Fig. 37, respectively]. When the interatomic distances are between single and double bonds then the delocalised pattern is used. Selected bond lengths and angles of the compounds to follow are listed in Table 2.

The potassium salt of this system with mixed chalcogen donor atoms, K[PhC(O)NP(S)Ph$_2$], displays a dimeric structure (Fig. 38). Close analysis of the coordination of potassium revealed that both atoms are octahedrally bound; three oxygen, two sulphur and a π interaction from a phenyl group.

The manner of dimerisation is accomplished by an *anti* arrangement, with cross coordination from oxygen and sulphur atoms. Each potassium atom is bound in a distorted octahedral sphere by three oxygen, two sulphur and a π-bond from a nearby phenyl group.

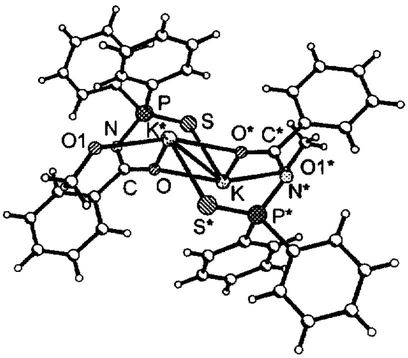


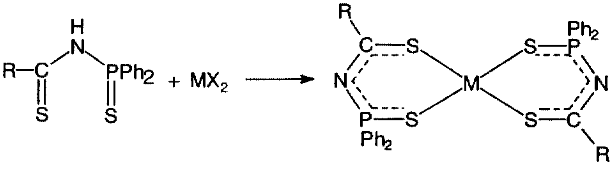
Fig. 38. Molecular structure of K[PhC(O)NP(S)Ph$_2$]$_2$ · 2CH$_3$OH [70].

Table 2

Selected bond lengths (Å) and angles (°) of $M\{RC(E)NP(E')R'_2\}_x$ (M = K, Ni, Pt, Cu, Hg, Pb, or Sm; E and E′ = O or S)

Compound	MO(S)	MO(S)	PO(S)	PN	NC	CO(S)	PNC	Ref.
$K[PhC(O)NP(S)Ph_2]_2 \cdot 2CH_3OH$	2.667(3)	3.244(2)	1.951(2)	1.617(4)	1.333(6)	1.243(5)	119.5(3)	[70]
$[Ni\{(^nPr)_2NC(S)NP(S)(Oph)_2\}_2]$	2.226(1)	2.205(1)	1.978(1)	1.574(3)	1.321(4)	1.745(4)	127.5(3)	[87]
$[Ni\{MeHNC(S)NP(S)Ph_2\}_2]$	2.216(3)	2.214(4)	2.016(5)	1.610(9)	1.294(14)	1.760(9)	125.6(6)	[88]
$[Pt\{H_2NC(S)NP(S)Ph_2\}$	2.33(1)	2.312(9)	1.97(1)	1.68(3)	1.37(4)	1.78(3)	130(2)	[70]
$\{H_2NC(S)NHP(S)Ph_2\}]^+ Cl^-$	2.31(1)	2.315(9)	1.98(1)	1.59(3)	1.34(4)	1.73(4)	129(3)	—
$[Pt\{H_2NC(S)NP(S)Ph_2\}_2]$	2.321(4)	2.313(4)	1.986(7)	1.62(1)	1.34(2)	1.71(2)	128(1)	[70]
$[Cu(PhO)_2P(S)NC(S)N(Et)_2]_3$	2.249(2)	2.220(2)	1.965(2)	1.581(5)	1.309(6)	1.785(5)	135.9(4)	[89]
	2.263(2)	2.230(2)	1.958(2)	1.571(5)	1.313(7)	1.776(6)	131.1(4)	—
	2.275(2)	2.224(2)	1.957(2)	1.596(5)	1.312(7)	1.768(5)	129.5(4)	—
$[Hg\{PhC(S)NP(S)(O^iPr)_2\}_2]$	2.553(3)	2.470(3)	1.980(4)	1.610(9)	1.286(13)	1.733(11)	133.1(8)	[90]
	2.548(3)	2.474(4)	1.981(4)	1.618(9)	1.290(13)	1.726(2)	131.8(8)	—
$[Pb\{PhC(S)NP(O)(O^iPr)_2\}_2]$	2.703(2)	2.488(5)	1.492(50	1.634(6)	1.268(1)	1.740(8)	125.0(6)	[74]
	2.703(2)	2.417(5)	1.470(6)	1.630(7)	1.294(1)	1.741(8)	127.7(6)	—
$[Sm(EtO)_2P(O)NHC(O)NHC(O)Ph]_3$	2.394(4)	2.532(4)	1.455(4)	1.663(5)	1.366(8)	1.211(6)	127.5(4)	[91]
	2.398(5)	2.543(4)	1.465(4)	1.655(6)	1.365(10)	1.205(7)	125.9(5)	—
	2.398(5)	2.528(4)	1.459(5)	1.655(6)	1.343(10)	1.223(8)	127.3(5)	—

DPTPT demonstrates a similar coordinative versatility to its carbon free analogue. The first substantial investigation into the coordination chemistry of diphenylthiophosphinyl thioureas was reported by Ojima et al. [62,63]. The compounds behave as bidentate ligands and have been shown to form a number of metals complexes. Typical coordination chemistry of these ligands is with direct reaction to MX_2 (M = Co, Ni, Cu or Pd; X = Cl) at room temperature (Eq. (9)). Interestingly, these reactions proceed at room temperature, compared with $[Ph_2(S)PNHP(S)Ph_2]$ which requires heating at reflux.



(9)

The nickel(II) and palladium(II) complexes containing this ligand system are square planar, while the complex containing cobalt is tetrahedral. Ojima et al. proposed that some diphenylphosphinothioylthioureato metal(II) complexes have a chelate structure containing five different atoms — C, N, P, 2S and M(II) — in their six-membered ring metallacycles. The structure of the nickel(II) complex was later established by Iwamoto et al. from X-ray studies (Fig. 39). The nickel atom is bound to sulphur donors of the ligands in a square planar *trans* configuration. The expansion of the P–S and the C–S bonds are observed [2.016(9) and 1.760(9) Å]. The P–N and the N–C bonds are contracted [1.610(9) and 1.294(14) Å]. These changes in the chelating ligands are similar to those observed with the imidophosphinate ligands. The structure of a similar nickel complex, $[Ni\{(PhO)_2P(S)NC(S)N(^nPr)_2\}_2]$ [87], also displays a square planar geometry. The P–S and the C–S are shorter [1.978(1) and 1.745(4) Å]; the P–N and the N–C bonds are observed at 1.574(3) and 1.321(4) Å.

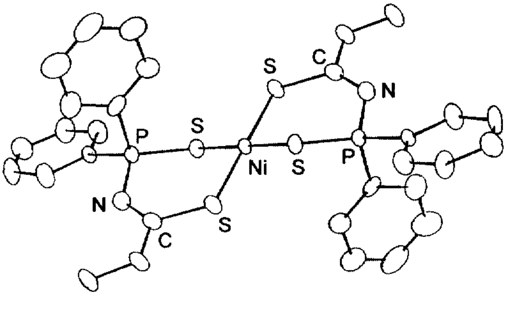


Fig. 39. Molecular structure of $[Ni\{MeHNC(S)NP(S)Ph_2\}_2]$ [88].

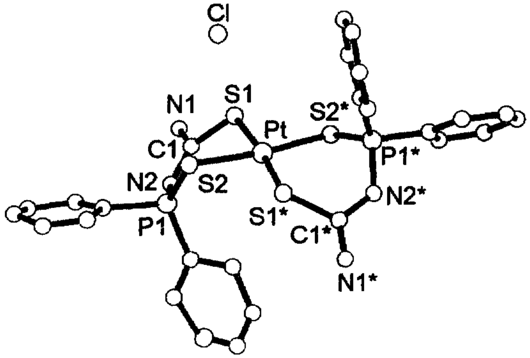


Fig. 40. Molecular structure of $[Pt\{H_2NC(S)NP(S)Ph_2\}(H_2NC(S)NHP(S)Ph_2\}]^+Cl^-$ [70].

The platinum complex, $[Pt\{H_2NC(S)NP(S)Ph_2\}$ $(H_2NC(S)NHP(S)Ph_2\}]^+$ Cl^-, was prepared by the reacting $[PtCl_2(COD)]$ with $2[H_2NC(S)NHP(S)Ph_2]$. Its X-ray structure revealed the chelates are arranged in the *trans* orientation around platinum (Fig. 40). One chelate is deprotonated and displays a contraction of the chelate backbone [SPNCS] with respect to its protonated counterpart.

The neutral platinum complex containing this ligand system is achieved reacting $[PtCl_2(COD)]$ with two equivalents of $K[H_2NC(S)NP(S)Ph_2]$ to give

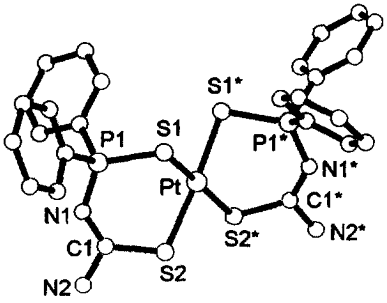


Fig. 41. Molecular structure of $[Pt\{H_2NC(S)NP(S)Ph_2\}_2]\cdot(Et_2O)$ [70].

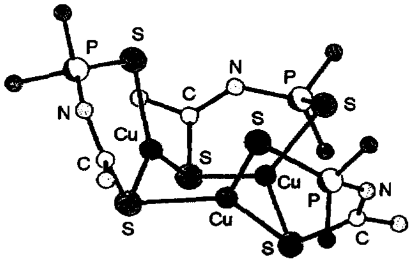


Fig. 42. Molecular structure of $[Cu(PhO)_2P(S)NC(S)N(Et)_2]_3$ (Et and Ph omitted for clarity) [89].

[Pt{$H_2NC(S)NP(S)Ph_2$}$_2$]. However, the X-ray structure of this complex shows the chelates are arranged in the *cis* orientation (Fig. 41).

The metal complex, [$Cu(PhO)_2P(S)NC(S)N(Et)_2$]$_3$, was formed by a reduction of copper(II) to copper(I) with [$(Et)_2NC(S)NHP(S)(OPh)_2$] in the presence of ethanol (Eq. (10)). It contains a ligand coordinated to a copper atom, with further coordination to an adjacent copper atom from the thiocarbonyl sulphur (Fig. 42). There are three metal complexes localised by second-order coordination, where the central part of the collective complexes displays Cu_3S_3 in a chair conformation. The Cu–S (phosphoryl) bond is longer than the Cu–S (thiocarbonyl) bond, but it is comparable with Cu–S from the adjacent thiocarbonyl group [(average) 2.626, 2.225 and 2.260 Å, respectively].

$$Cu_2^+ + 2HL \rightleftharpoons CuL_2 + 2H^+$$

$$6CuL_2 + 3CH_3OH \rightleftharpoons 2(CuL)_3 + 3CH_3CHO + 6HL \qquad (10)$$

The mercury complexes, [Hg{$RC(X)NP(Y)(OR')_2$}$_2$], are prepared from direct reaction of the ligand $RC(X)NP(Y)(OR')_2$ with mercury(II) oxide in an organic solvent at reflux (Eq. (11)). No reaction was observed when the ligand does not contain at least a sulphur donor atom. In the unit cell of the complex with *N*-(diisopropoxyphosphinothioyl)thiobenzamide, the mercury atom is in a tetrahedral coordination as a result of 4S atoms from two symmetrically independent ligands (Fig. 43). All four Hg–S bonds in the complex have a covalent character, in which the Hg–S bonds from the thiocarbonyl group are shorter than the Hg–S

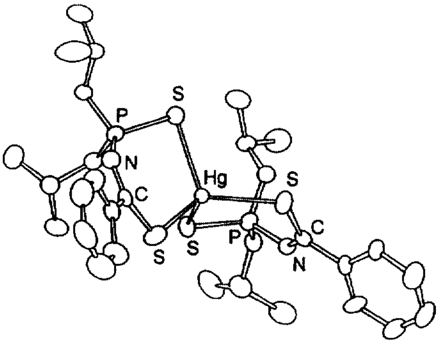
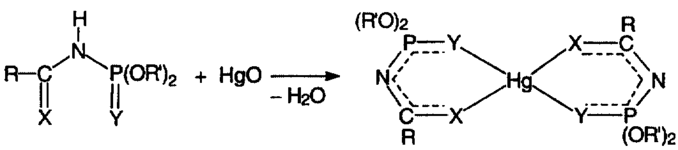


Fig. 43. Molecular structure of [Hg{$PhC(S)NP(S)(O^iPr)_2$}$_2$] [90].



(11)

bonds from the phosphoryl group [lengths 2.470–2.553 Å]. The C–S and the P–S bonds are longer than the C=S bond [1.635(4) Å] and the P=S [1.912(1) Å] in the free ligand. All the bond lengths in one chelate ring are closely matched in the other.

R=Ph, R=^{i}Pr, X=Y=S;
R=Me, R′=^{i}Pr, X=Y=S;
R=Ph, R′=Et, X=S, Y=O;
R=Ph, R′=^{i}Pr, X=S, Y=O;
R=Ph, R′=^{i}Pr, X=O, Y=S.

The lead(II) complexes of *N*-diisopropoxyphosphorylthiobenzamide and *N*-diisopropoxythiophosphorylthiobenzamide, [Pb{PhC(S)NP(O)(O^{i}Pr)$_2$}$_2$] and [Pb(PhC(S)NP(S)(O^{i}Pr)$_2$}$_2$], are prepared by direct reaction of the ligands with lead oxides in CCl_4, or by reacting lead nitrate with the sodium salt of the ligands in methanol. The coordination pattern in [Pb{PhC(S)NP(O)(O^{i}Pr)$_2$}$_2$] has a distorted tetrahedral structure with bonding from oxygen and sulphur of the two chelating ligands (Fig. 44). This metalla-heterocycle is a rare example of a compound containing six different atoms in a six-membered ring.

The Samarium Complex, [Sm(EtO)$_2$P(O)NHC(O)NHC(O)Ph]$_3$(ClO$_4$)$_3$ · 3H$_2$O, was found to be a nine-coordinate compound with oxygen donors (Fig. 45). The samarium atom is bonded to three phosphoryl oxygen atoms, three carbonyl oxygen atoms, and three oxygen atoms from water molecules. The [(EtO)$_2$P(O)NHC(O)NH–C(O)Ph] ligand behaves as a bidentate compound in this complex, where the phosphoryl group is induced to coordination as oppose to the possibility of coordination by both carbonyl groups. The chelate rings are close to planarity in this complex. All the Sm–O(P) bonds are shorter than that in Sm–O(C), indicating that the phosphoryl oxygen atom has a stronger coordinative function than that of the carbonyl oxygen.

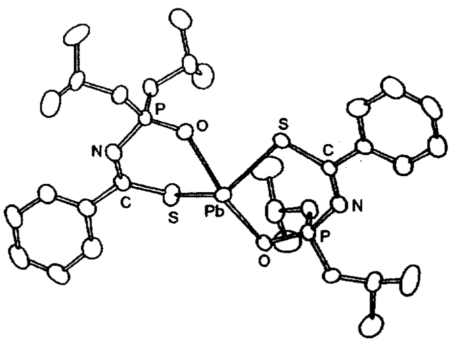


Fig. 44. Molecular structure of [Pb{PhC(S)NP(O)(O^{i}Pr)2}2] [72].

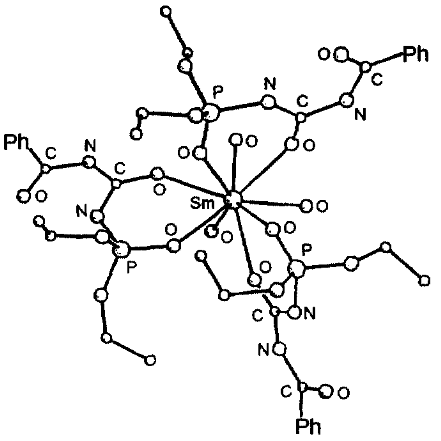


Fig. 45. Molecular structure of the cation in $[Sm(EtO)_2P(O)NHC(O)NHC(O)Ph]_3(ClO_4)_3 \cdot 3H_2O$ [91].

8. Summary

In comparision, with the well-established coordination chemistry of imidodiphosphinates, the chemistry of phosphinated ureas and thioureas is largely unexplored to date. The ligands can readily be prepared by:

- direct addition of amines to phosphorus isocyanate/isothiocyanate;
- clipping the metallated acid amides together with acid chlorides or chlorophosphines; and
- base-catalysed condensation, or use of silylated derivatives.

The above synthetic methods might well find a more general application in the synthesis of organophosphorus bidentate ligands. Further studies with this synthetic method to prepare other ligand systems should prove productive. Both systems are excellent chelating agents and are extensively studied for their extraction potential toward metals [92–106].

References

[1] M. Witt, H.W. Roesky, Chem. Rev. 94 (1994) 1163.
[2] P. Bhattacharyya, J.D. Woollins, Polyhedron 14 (1995) 3367.
[3] H. Noeth, L. Meinel, Z. Anorg. Allg. Chem. 349 (1967) 225.
[4] A. Schmidpeter, H. Groeger, Z. Anorg. Allg. Chem. 345 (1966) 106.
[5] F.T. Wang, J. Najdzionek, K.L. Leneker, H. Wasserman, D.M. Braitsch, Synth. React. Inorg. Met. Org. Chem. 8 (1978) 119.
[6] P. Bhattacharyya, J. Novosad, J. Phillips, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1995) 1607.
[7] R. Rossi, L. Marvelli, A. Marchi, L. Magon, V. Bertolasi, V. Ferretti, J. Chem. Soc., Dalton Trans. (1994) 339.
[8] D. Pohl, E. Ellermann, F.A. Knoch, M.J. Moll, J. Organomet. Chem. 495 (1995) C6.

[9] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton. Trans. (1996) 1283.
[10] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, J.D. Woollins, Inorg. Chem. 35 (1996) 3675.
[11] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 4567.
[12] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, Polyhedron 15 (1996) 1579.
[13] M.S. Balakrishna, R. Klein, S. Uhlenbrock, A.A. Pinkerton, R.G. Cavell, Inorg. Chem. 32 (1993) 5676.
[14] P. Bhattacharyya, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1995) 3189.
[15] H. Bock, H. Schödel, Z. Havlas, E. Herrmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 1355.
[16] J. Yang, J.E. Drake, S. Hernández-Ortega, R. Rösler, C. Silvestru, Polyhedron 16 (1997) 4061.
[17] A.M.Z. Slawin, J. Ward, D.J. Williams, J.D. Woollins, J. Chem. Soc., Chem. Commun. (1994) 421.
[18] R. Cea-Olivares, H. Nöth, Z. Naturforsch. 42(b) (1987) 1507.
[19] I. Haiduc, R. Cea-Olivares, S. Hernández-Ortega, C. Silvestru, Polyhedron 14 (1995) 2041.
[20] A. Silvestru, I. Haiduc, R.A. Toscano, H.J. Breunig, Polyhedron 14 (1995) 2047.
[21] J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 2893.
[22] I. Haiduc, Coord. Chem. Rev. 158 (1997) 325.
[23] G.P. McQuillan, I.A. Oxton, Inorg. Chim. Acta 29 (1978) 69.
[24] M. Rietzel, H.W. Roesky, Y.V. Katti, M. Noltemeyer, M.C.R. Symons, A. Abu-Raqabah, J. Chem. Soc., Dalton Trans. (1991) 1285.
[25] M. Rietzel, H.W. Roesky, K.V. Katti, H.-G. Schmidt, R. Herbst-Irmer, M. Noltemeyer, M.C.R. Symons, A. Abu-Raqabah, J. Chem. Soc., Dalton Trans. (1990) 2387.
[26] T.Q. Ly, A.M.Z. Slawin, J.D. Woollins (in press).
[27] N. Zúñiga-Villarreal, C. Silvestru, M.R. Lezama, S. Hernández-Ortega, C.A. Toledano, J. Organomet. Chem. 496 (1995) 169.
[28] O. Simnan, H.B. Gray, Inorg. Chem. 13 (1974) 1185.
[29] R. Rossi, A. Marchi, L. Magon, U. Casellato, S. Tamburini, R. Graziani, J. Chem. Soc., Dalton Trans. (1991) 263.
[30] R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato, R. Graziani, J. Chem. Soc., Dalton Trans. (1993) 723.
[31] M.R. Churchill, J. Wormald, Inorg. Chem. 10 (1971) 1778.
[32] C.S. Browning, D.H. Farrar, D.C. Frankel, Inorg. Chim. Acta 241 (1996) 111.
[33] C. Silvestru, R. Rösler, I. Haiduc, R. Cea-Olivares, G. Espinosa-Pérez, Inorg. Chem. 34 (1995) 3352.
[34] S. Husebye, K. Maartmann-Moe, Acta Chem. Scand. A37 (1983) 439.
[35] R. Rösler, C. Silvestru, G. Espinosa-Pérez, I. Haiduc, R. Cea-Olivares, Inorg. Chim. Acta 241 (1996) 47.
[36] M.R. Churchill, J. Cooke, J. Wormald, K. Davison, E.S. Switkes, J. Am. Chem. Soc. 91 (1969) 6518.
[37] M.K. Churchill, J. Cooke, J.P. Fennessey, J. Wormald, Inorg. Chem. 10 (1971) 1031.
[38] D. Cupertino, R. Keyte, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, Inorg. Chem. 35 (1996) 2695.
[39] P.B. Hitchcock, J.F. Nixon, I. Silaghi-Dumitrescu, I. Haiduc, Inorg. Chim. Acta 96 (1985) 77.
[40] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 3659.
[41] M. Novomann, Z. Zák, E. Herrmann, O. Navrátil, Z. Anorg. Allg. Chem. 619 (1993) 11474.
[43] J. Phillips, A.M.Z. Slawin, A.J.P. White, D.J. Williams, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1995) 2467.
[44] I. Haiduc, R. Cea-Olivares, R.A. Toscano, C. Silvestru, Polyhedron 14 (1995) 1067.
[45] C.P. Huber, M.L. Post, O. Siiman, Acta Crystallogr. B34 (1978) 2629.
[46] A. Laguna, M. Laguna, M.N. Fraile, P. Jones, Inorg. Chim. Acta 150 (1988) 233.
[47] A. Laguna, M. Laguna, A. Rojo, M.N. Fraile, J. Organomet. Chem. 315 (1986) 269.
[48] J.S. Casas, A. Castiñeiras, I. Haiduc, A. Sánchez, J. Sordo, E.M. Vázquez-López, Polyhedron 14 (1995) 805.
[49] R.O. Day, R.R. Holmes, A. Schmidpeter, K. Stoll, L. Howe, Chem. Ber. 124 (1991) 2443.
[50] C. Silvestru, I. Haiduc, R. Cea-Olivares, A. Zimbron, Polyhedron 13 (1994) 3159.
[51] R. Rösler, J.E. Drake, C. Silvestru, J. Yang, I. Haiduc, J. Chem. Soc., Dalton Trans. (1996) 391.

[52] I. Haiduc, C. Silvestru, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Polyhedron 12 (1993) 69.

[53] R. Cea-Olivares, J. Novosad, J.D. Woollins, A.M.Z. Slawin, V. García-Montalvo, G. Espinosa-Pérez, P. García y García, J. Chem. Soc., Chem. Commun. (1996) 519.

[54] J.S. Casas, A. Castiñeiras, I. Haiduc, A. Sánchez, J. Sordo, E.M. Vázquez-López, Polyhedron 13 (1994) 2873.

[55] C. Silvestru, R. Rösler, I. Haiduc, R.A. Toscano, D.B. Sowerby, J. Organomet. Chem. 515 (1996) 131.

[56] D.J. Williams, C.O. Quicksall, K.M. Barkigia, Inorg. Chem. 21 (1982) 2097.

[57] S. Husebye, K. Maartmann-Moe, Acta Chem. Scand. A37 (1983) 219.

[58] S. Bjørnevig, S. Husebye, K. Maartmann-Moe, Acta Chem. Scand. A36 (1982) 195.

[59] J. Michalski, J. Wieczorkowski, Roczniki Chem. 29 (1955) 137.

[60] J. Michalski, J. Wieczorkowski, Roczniki Chem. 31 (1957) 585.

[61] D.T. Elmore, J.R. Ogle, J. Chem. Soc. (1959) 2286.

[62] A. Schmidpeter, H. Groeger, Chem. Ber. 100 (1967) 3052.

[63] I. Ojima, T. Iwamoto, T. Onishi, N. Inamoto, K. Tamaru, Chem. Commun. (1969) 1501.

[64] I. Ojima, T. Iwamoto, T. Onishi, N. Inarnoto, K. Tamaru, Bull. Chem. Soc. Jpn 44 (1971) 1150.

[65] I. Ojima, K.-Y. Akiba, N. Inamoto, Bull. Chem. Soc. Jpn 46 (1973) 2559.

[66] A. Spencer, J.M. Swan, H.B. Wright, Aust. J. Chem. 22 (1969) 2359.

[67] A. Ziegler, V.P. Botha, I. Haiduc, Inorg. Chim. Acta 15 (1975) 123.

[68] J. Bödeker, H. Zärtner, J. Prakt. Chem. 318 (1976) 149.

[69] R. Vogt, P.G. Jones, A. Kolbe, R. Schmutzler, Chem. Ber. 124 (1991) 2705.

[70] T.Q. Ly, A.M.Z. Slawin, J.D. Woollins (in press).

[71] E. Breuer, A. Schlossman, M. Safadi, D. Gibson, M. Chorev, H. Leader, J. Chem. Soc., Perkin Trans. 1 (1990) 3263.

[72] R. Richter, J. Sieler, H. Borrmann, A. Simon, N.T.T. Chau, E. Herrmann, Phosphorus, Sulfur Silicon 60 (1991) 107.

[73] V.N. Solovyov, I.V. Martynov, Phosphorus, Sulfur Silicon 57 (1991) 135.

[74] N.G. Zabirov, V.N. Solov'ev, F.M. Shamsevaleev, R.A. Cherkasov, A.N. Chekhlov, A.G. Tsifarkin, I.V. Martynov, J. Gen. Chem. USSR 61 (1991) 597.

[75] H. Wilhelm, E. Herrmann, Phosphorus, Sulfur Silicon 73 (1992) 81.

[76] R.-Y. Chen, H.-L. Wang, J. Zhou, R.-J. Wang, H.-G. Wang, Chinese J. Struct. Chem. (Regou Humue) 13 (1994) 307.

[77] D.T. Dixon, F.W.B. Einstein, B.R. Penfold, Acta Crystallogr. 18 (1965) 221.

[78] V.V. Tkachev, L.O. Atovmyan, S.A. Shchepinov, Zh. Strukt. Khim. 17 (1976) 945.

[79] M.J. Potrzebowski, J.H. Reibenspies, Z. Zhong, Heteroatom Chem. 2 (1991) 455.

[80] A.C. Gallacher, A.A. Pinkerton, Acta Crystallogr. C49 (1993) 701.

[81] P. Knopik, L. Luczak, M.J. Potrzebowski, J. Michalski, J. Blaswzyk, M.W. Wieczorek, J. Chem. Soc., Dalton Trans. (1993) 2749.

[82] R.K. Shibao, N.L. Keder, H. Eckert, Acta Crystallogr. C48 (1992) 1525.

[83] R. Appel, F. Knock, H. Kunze, Angew. Chem. Int. Ed. Engl. 22 (1983) 1004.

[84] H. Beckmann, G. Grossmann, G. Ohms, J. Sieler, Heteroatom Chem. 5 (1994) 73.

[85] V.N. Solov'ev, A.N. Cheklov, N.G. Zabirov, R.A. Cherkasov, I.V. Martynov, Zh. Strukt. Khim. 31 (1990) 103.

[86] E. Herrmann, N.T.T. Chau, G. Ohms, P.G. Jones, Z. Anorg. Allg. Chem. 594 (1991) 146.

[87] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, D.J. Williams, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 3647.

[88] Z. Zák, T. Glowiak, N.T.T. Chau, E. Herrmann, Z. Anorg. Allg. Chem. 586 (1990) 136.

[89] T. Iwamoto, F. Ebina, H. Nakazawa, C. Nakatsuka, Bull. Chem. Soc. Jpn 52 (1979) 1857.

[90] E. Herrmann, R. Richter, J. Sieler, N.T.T. Chau, Z. Anorg. Allg. Chem. 623 (1997) 403.

[91] N.G. Zabirov, V.N. Solov'ev, F.M. Shamsevaleev, R.A. Cherkasov, I.V. Martynov, J. Gen. Chem. USSR 61 (1991) 1608.

[92] W. Zhang, M. Tan, W. Liu, K. Yu, Polyhedron 11 (1992) 1581.

[93] O. Navrátil, E. Herrmann, N.T.T. Chau, C. Tea, J. Smola, Collect. Czech. Chem. Commun. 58 (1993) 798.

[94] E. Uhlemann, R. Schulz, A. Friedrich, Z. Chem. 27 (1987) 225.

[95] E. Herrmann, N.T.T. Chau, O. Navrátil, G. Ohms, L. Beyer, Phosphorus, Sulfur Silicon 51 (1990) 366.

[96] E. Herrmann, O. Navrátil, P. Sládek, Phosphorus, Sulfur Silicon 109 (1996) 201.

[97] Z.P. Vetrova, N.G. Zabirov, T.N. Shuvalova, L.S. Smerkovich, L.A. Ivanova, A.K. Gol'berg, N.T. Karabanov, J. Gen. Chem. USSR 63 (1993) 883.

[98] O. Navrátil, M. Fofana, J. Smola, Z. Chem. 24 (1984) 30.

[99] O. Navrátil, E. Herrmann, G. Grossmann, J. Teply, Collect. Czech. Chem. Commun. 55 (1990) 364.

[100] O. Navrátil, P. Sládek, A. Tokarova, E. Herrmann, M. Nouaman, Collect. Czech. Chem. Commun. 62 (1997) 620.

[101] O. Navrátil, P. Sládek, A. Tokarova, E. Herrmann, M. Nouaman, Collect. Czech. Chem. Commun. 62 (1997) 375.

[102] O. Navrátil, E. Herrmann, Collect. Czech. Chem. Commun. 57 (1992) 1655.

[103] E. Herrmann, M. Nouaman, Z. Zák, G. Grossmann, G. Ohms, Z. Anorg. Allg. Chem. 1994 (1879) 620.

[104] O. Navrátil, E. Herrmann, P. Slezák, Collect. Czech. Chem. Commun. 52 (1987) 1708.

[105] E. Herrmann, O. Navrátil, H. Nang, J. Smola, J. Friedrich, J. Prihoda, R. Dreyer, V.A. Chalkin, S. Kulpe, Collect. Czech. Chem. Commun. 49 (1984) 201.

[106] E. Herrmann, O. Navrátil, H. Nang, J. Smola, J. Friedrich, J. Prihoda, R. Dreyer, V.A. Chalkin, Z. Chem. 22 (1982) 346.