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P–N–S/Se-containing metallacycles

J. Derek Woollins*

Department of Chemistry, Loughborough University, Loughborough, Leics. LE11 3TU, UK

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The synthesis of metal complexes containing main-group ligand backbones (*i.e.* no carbon atoms) is an interesting challenge. These types of complexes may provide a means of stabilising otherwise non-isolatable anions as in S–N,[1,2] Se–N[3] and P–S[4] chemistry where there have been many exciting developments in recent times. Examples of SN anions that are known in complexes include $[S_2N_2]^{2-}$, $[S_3N]^-$, $[S_2N_3]^{3-}$, $[S_3N_2]^{2-}$, $[S_3N_4]^{2-}$ and $[S_4N_3]^-$ (Fig. 1). Furthermore metal complexes may also be used to stabilise the otherwise very reactive S_2N_2 and more recently even Se_2N_2 has been stabilised in this fashion[5] (Fig. 2). These types of ligand systems are usually obtained by reactions from larger main-group clusters in ring-cleavage reactions, though occasionally they are formed from reactions in liquid ammonia using simple sulfur starting materials [equations (1)–(3)]. Apart from the ability of main-group metallacycles to stabilise reactive anions they may also be useful as precursors to metal-based polymers.[6,7]

$$NH_3(l) \xrightarrow[(2)\,[PtCl_2(PR_3)_2]]{(1)\,SOCl_2} cis\text{-}[Pt(NSO)_2(PR_3)_2] \quad (1)$$

$$NH_3(l) \xrightarrow[(2)\,[PtCl_2(PR_3)_2]]{(1)\,SO_2Cl_2} cis\text{-}[Pt\{(HN)_2SO\}_2(PR_3)_2] \quad (2)$$

$$NH_3(l) \xrightarrow[(2)\,[PtCl_2(PR_3)_2]]{(1)\,[S_4N_3]^-,\ SeCl_4} [Pt(SeSN_2)(PR_3)_2] \quad (3)$$

One group of metallacycles which has recently been studied extensively is those based on $[E\text{–}Pr_2N\text{–}PR_2E]^-$ ligands (E = O, S or Se). Apart from interest in the conformational properties of the rings these ligands have a number of potential applications. The R groups are readily manipulated thus enabling solubilisation and study in a range of solvents.

It is interesting to consider the relationship of these mixed P–N–E ligands to simple S–N and organic systems (Fig. 3). It is evident that the β-diketonate system offers the same number of electrons for co-ordination and will have an equivalent number of π electrons (in the anion) as that of the $[E\text{–}PR_2\text{–}N\text{–}PR_2\text{–}E]^-$ anion. However, the geometries at carbon in β-diketonate are restricted to sp^2 and so one can predict that these ligands should form planar rings. In the EPNPE systems the P atoms are sp^3 hybridised and make use of their d orbitals for multiple bonding. One can anticipate that the backbone of these E–P–N–P–E systems need not be planar.

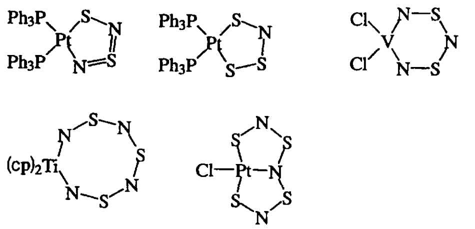

Fig. 1 Examples of complexes containing S–N anions; cp = η-C_5H_5

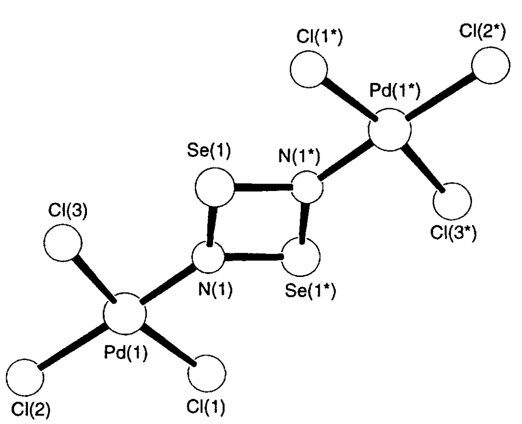

Fig. 2 Crystal structure of the $[Cl_3Pd(Se_2N_2)PdCl_3]^{2-}$ anion[5]

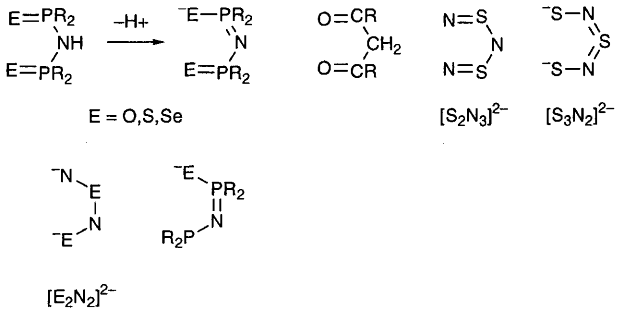

Fig. 3 Comparison of S–N and P–N–E ligands

$$2R_2PCl + NH(SiMe_3)_2 \longrightarrow R_2P\text{–}NH\text{–}PR_2 \quad (4)$$

$$R_2PNHPR_2 \xrightarrow{E=O,\,S,\,Se} R_2P(E)NHP(E)R_2 \quad (5)$$

Synthesis of Ligands

Symmetric species may be prepared by a simple condensation reaction to give the phosphorus(III) compound followed by oxidation[8] [equations (4) and (5)]. Similar coupling reactions may also be performed using, for example, heptamethyldisilazane to yield the $R'_2P(E)NRP(E)PR'_2$ systems (R = alkyl, R′ = Ph;[9,10] R = alkyl, R′ = EtO[11]).

The coupling reactions of phosphorus(V) systems do not work as efficiently for $R_2P(E)Cl$ but phosphoryl halides can be coupled[12–14] as shown in equation (6) (X = Cl or F; E, E′ =

$$2X_3P(E) + NMe(SiMe_3)_2 \longrightarrow X_2P(E)NMeP(E')X_2 \quad (6)$$

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* E-Mail:J.D.Woollins@lboro.ac.uk

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O, S but not all permutations). Interestingly, the $(Cl_2P)_2NR$ systems do not react directly with S_8 but the reaction can be catalysed by the addition[15] of a trace of $AlCl_3$ [equation (7)].

$$(Cl_2P)_2NR \xrightarrow{S_8,\ AlCl_3} Cl_2PNRP(S)Cl_2 \xrightarrow{S_8,\ AlCl_3} Cl_2P(S)NRP(S)Cl_2 \qquad (7)$$

Similar coupling can be accomplished with hydrazine derivatives[16] [equation (8)]. Attempts at the coupling reactions

$$Me_2NN(H)PF_2(S) + SPF_2Br + NEt_3 \longrightarrow F_2P(S)N(NMe_2)P(S)F_2 \qquad (8)$$

(6)–(8) are less successful when alkylphosphine halides are used; in these cases simple amine derivatives are formed[17] [equation (9)] (R = Me, Et or Pr^n; X = Cl or Br). Non-symmetric

$$R_2P(S)X + NH(SiMe_3)_2 \longrightarrow R_2P(S)NSiMe_3 + SiMe_3X \qquad (9)$$

systems may be synthesised[9,18] by condensation of appropriate preformed amines and chlorophosphorus systems, for example as in equation (10).

$$(RO)_2P(S)Cl + H_2N(S)PR'_2 \xrightarrow{Base} (RO)_2P(S)NHP(S)R'_2 \qquad (10)$$

In recent times a number of monoxidised systems as well as monoselenium systems have been prepared. Generally they have been obtained by adaptations of the routes in equations (4), (5) and (10). Thus, careful addition of peroxide to $Ph_2PNHPPh_2$ yields $Ph_2PNHP(O)Ph_2$ which may be treated with S_8 or Se to give $Ph_2P(E)NHP(O)Ph_2$ (E = S or Se). Alternatively, coupling of the O- and S-substituted chloride and amines as shown in equation (10) gives $R_2P(O)NHP(S)R'_2$. Related to the above systems are some organically substituted complexes which are outside the scope of this review. One illustrative reaction[19] is that of $(PhO)_2P(O)NCS$ with a secondary phosphine [equation (11)].

$$(PhO)_2P(O)NCS + PPh_2H \longrightarrow (PhO)_2P(O)NHC(S)PPh_2 \qquad (11)$$

Structure and Reactivity

(*a*) $R_2P(E)NHP(E)R_2$ Systems

The solid-state structures of $R_2P(E)NHP(E)R_2$ have been of considerable interest since these systems can exist in two different tautomeric forms [equation (12)]. Early IR and NMR

$$R_2P(E)NHP(E)R_2 \longleftrightarrow R_2\underset{\substack{|\\ EH}}{P}{=}N{-}P(E)R_2 \qquad (12)$$

studies[9] established that the NH form exists for R = Ph, E = S. Methylation proceeds at sulfur to give $[Ph_2P(SMe)NP(SMe)Ph_2]X$ (X = PF_6^-, BPh_4^- or $SbCl_6^-$). X-Ray studies[20] of $Ph_2P(E)NHP(E)Ph_2$ (E = S or O) established that whilst the sulfur compound is well represented by this formula, the oxygen compound exists in the solid state with protonation at the oxygen. The selenium compound has also been characterised crystallographically;[21] it is isomorphous with the sulfur compound. They pack to form N–H $\cdots$ E hydrogen-bonded dimer pairs (Fig. 4) with the two S/Se atoms being *anti* with respect to each other. As would be anticipated, the P–N bond lengths are substantially shorter in the oxygen compound compared to the S/Se cases (average 1.53 Å for E = O, *versus* 1.68 Å for E = S or Se) as a consequence of the different tautomeric forms observed. The oxygen compound packs into infinite zigzag chains along the *b* direction. Two further structure determinations[22] on $Ph_2P(S)NHP(S)Ph_2$ have been reported subsequent to the original work by Nöth.[20] The structure of $(PhO)_2P(S)NHP(S)(OPh)_2$ also consists of dimer pairs in the solid state.[23]

It is interesting to note the effect of the R group on the conformations in these systems. In the methyl case[24] the molecule adopts a similar *anti* conformation to that of the phenyl analogue, but packs into chains *via* N–H $\cdots$ S hydrogen bonds. The isopropyl compound[25] also adopts a chain-like structure in the solid state (Fig. 5) but the P=S groups are approximately *gauche* with respect to each other. Table 1 compares the most important structural parameters in $R_2P(E)NHP(E)R_2$ systems. It appears that the P–E distances for the hydrogen-bonded chalcogenide are always significantly enlarged with respect to the 'free' E atom. Differences in the hydrogen bonding in the R = Ph, Pr^i, Me cases as well as substituent effects influence the P=S bond lengths, but it would appear that the non-hydrogen-bonded P–S length is fairly insensitive to the R group suggesting that the longest P=S

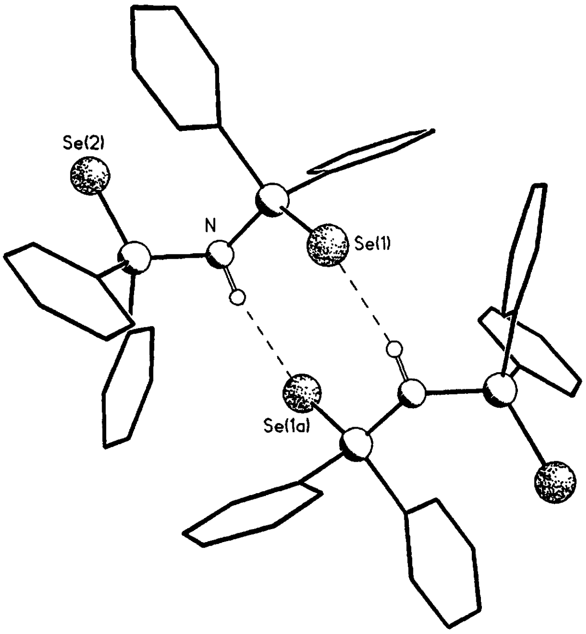

Fig. 4 Crystal structure of $Ph_2P(Se)NHP(Se)Ph_2$ (E = S or Se) showing the hydrogen-bonded dimer pairs[21]

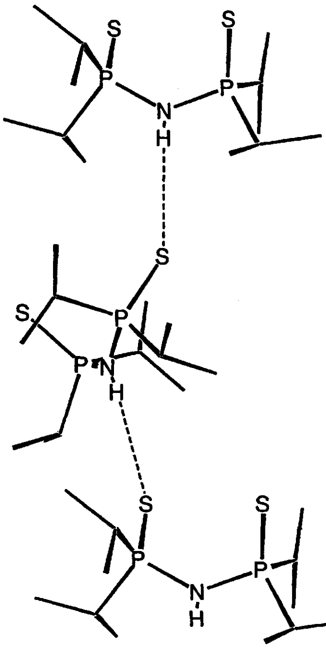

Fig. 5 Packing of the molecules in $Pr^i_2P(S)NHP(S)Pr^i_2$[25]

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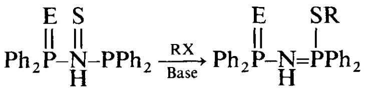
observed in these three compounds is involved in the strongest hydrogen-bond interaction. It may be possible by careful study to adjust the R groups and enable this type of hydrogen-bond to be understood in more detail.

Apart from X-ray studies, many of these systems have been investigated by NMR spectroscopy. In non-symmetric systems the coupling constants vary; ^2J(PNP) coupling constants vary considerably both as a function of R and E.[26–31] Selenium-containing systems give apparently complex spectra[21,32] as a consequence of the presence of superimposed AA′X and A type spectra. It is evident from vibrational studies that solid-state hydrogen-bonding patterns are not always mirrored in solution.[33,34]

Although the majority of the reactions reported for $\mathrm{R_2P(E)NHP(E)R_2}$ are complexation, there are a number of other interesting features. For example, alkylation according to equation (13) [E = O or S; R = alkyl, ester, amide or allyl



$$\mathrm{Ph_2\overset{E}{\overset{\|}{P}}-\underset{H}{N}-\overset{S}{\overset{\|}{P}}Ph_2 \xrightarrow[Base]{RX} Ph_2\overset{E}{\overset{\|}{P}}-\underset{H}{N}=\overset{SR}{\overset{|}{P}}Ph_2} \qquad (13)$$

(but not all permutations); X = halide] gives a range of compounds which are active fungicides. The most active species have[35] E = O, R = $\mathrm{CH_2Ph}$ and E = S, R = $\mathrm{CH_2Ph}$.

In $\mathrm{Ph_2P(S)NHP(S)Ph_2}$ one or both sulfur atoms may be displaced quite readily[36] [equations (14) and (15)]. The

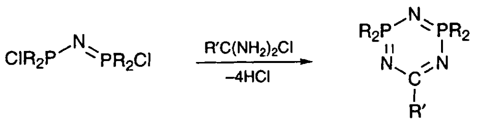
$$\mathrm{Ph_2P(S)NHP(S)Ph_2 \xrightarrow{Cl_2} [ClPh_2P{=}N{-}PPh_2Cl]Cl} \qquad (14)$$

$$\mathrm{Ph_2P(S)NHP(S)Ph_2 + PCl_5 \longrightarrow Ph_2P(S){-}N{=}PPh_2Cl + PSCl_3 + HCl} \qquad (15)$$

monochloro compound undergoes reaction with water to give the mixed O,S system, equation (16). The halide-substituted

$$\mathrm{Ph_2P(S)N{=}PPh_2Cl + H_2O \longrightarrow Ph_2P(S)NHP(O)Ph_2} \qquad (16)$$

systems are also good sources of cyclic molecules. Thus thermolysis of $\mathrm{Cl_2P(S)NRPCl_2}$ gives[15] $\mathrm{[ClP(S)NR]_2}$. Alternatively, condensation reactions are possible[37] [equation (17)].



(17)

Deprotonation reactions proceed with a wide range of bases to give $\mathrm{[R_2P(E)NP(E)R_2]^-}$ which undergoes complexation with many metals. With water $\mathrm{K[Ph_2P(Se)NP(Se)Ph_2]}$ gives the oxygen-bridged $\mathrm{Ph_2P(Se)N{=}PPh_2{-}O{-}PPh_2{=}NP(Se)Ph_2}$, illustrated in Fig. 6. Coupling reactions like this might well lead to a new class of macrocycles.

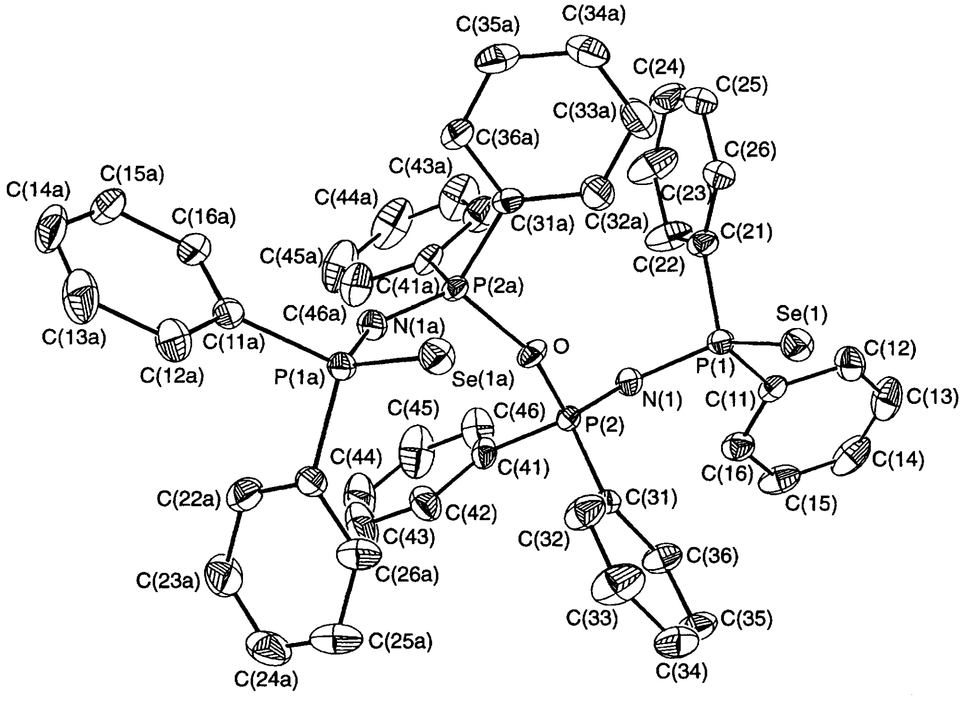


Fig. 6 Crystal structure of $\mathrm{Ph_2P(Se)N{=}PPh_2OPPh_2{=}NP(Se)Ph_2}$[38]

Table 1 Comparison of important bond lengths (Å) and angles (°) in $\mathrm{R_2P(E)NHP(E)R_2}$. To enable meaningful comparisons the hydrogen-bonded E atom is denoted as E(A) throughout

	R = Ph, E = S[20]	R = OPh, E = S[23]	R = Ph, E = Se[21]	R = Me, E = S[24]	R = Pr^i, E = S[25]
P(A)–E(A)	1.950(1)	1.911(1)	2.101(1)	1.962(2)	1.949(1)
P(A)–E(B)	1.936(1)	1.894(1)	2.085(1)	1.939(2)	1.941(1)
P(A)–N(A)	1.671(2)	1.653(2)	1.678(4)	1.675(3)	1.684(2)
P(B)–N(B)	1.684(2)	1.662(1)	1.686(3)	1.679(3)	1.682(3)
P–N–P	132.6(1)	130.4(1)	132.3(2)	133.2(2)	131.6(1)
E–P···PE relationship	*anti*	*anti*	*anti*	*anti*	*gauche*

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There have been three studies on salts of $[Ph_2P(S)NP(S)Ph_2]^-$. In all cases the P=S bond is lengthened and the P–N bond is shortened upon deprotonation. The potassium salt[39] displays a number of long-range interactions to give a 'supramolecular structure' (Fig. 7) whilst the K(18-crown-6)$^+$ salt[40] (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) and the $[N(PPh_3)_2]^+$ salts[41] do not have any cation–anion interactions. In the two different potassium salts the anion has a bent geometry with a similar P–N–P angle to that of the neutral starting material, but in the $[N(PPh_3)_2]^+$ salt the anion has a linear P–N–P arrangement. The P–N bond lengths in the linear anion are slightly shorter than in the bent anion (by *ca.* 0.04 Å) which can be interpreted on the basis of different contributions from alternative canonical forms in the anion (Fig. 8). Thus the linear anion could be described as displaying more π delocalisation than the bent anion (sp^3-hybridised N atom). The $K[Ph_2P(Se)NP(Se)Ph_2]$ salt[38] has a bent P–N–P angle and forms a ladder structure which is similar to that of its sulfur analogue. Further synthetic and theoretical studies into the conformational properties of these (and longer) chains will doubtless prove to be worthwhile. When[42] $(PhO)_2P(O)NHP(O)(OPh)_2$ is deprotonated in dry benzene, using sodium hydride, a hexameric salt $\{Na[(PhO)_2P(O)NP(O)(OPh)_2]\}_6$, is formed (Fig. 9). The compound has a lipophilic 'skin' made up of phenyl rings which encloses the $[Na_6O_{12}]^{6+}$ core and is stable to moisture.

The co-ordination chemistry of $[R_2P(E)NP(E)R_2]^-$ anions has been studied by a number of groups and early work[34,43–45] has been reviewed previously.[46] Here I shall concentrate on compounds which have been characterised crystallographically. The complexes display quite a range of ring geometries and are able to support some unusual co-ordination geometries at the various metal centres.

Homoleptic tin(II) systems for $Ph_2P(E)NP(E)Ph_2$ (E = O or Se) provide some interesting comparisons. Thus, the oxygen compound[47] is ψ-trigonal bipyramidal (*TBPY*) (*i.e.* with a tin lone pair at one of the equatorial sites) in the solid state and fluxional in solution. In the selenium case the complex has been crystallised in both distorted *TBPY* and square-planar geometries[48] (Fig. 10); interestingly the two different forms also exhibit differences in the ring conformations with the *TBPY* complex containing a six-membered boat MEPNPE ring but with the prow and stern of the boat being the N and M atoms rather than the more commonly observed boat (see examples later). The square-planar tin(II) complex contains a pseudo-chair conformation for the SnSePNPSe ring. Several tin(IV) compounds have been described. Thus, $Sn[Ph_2P(O)NP(O)Ph_2]_2X_2$ (X = Cl, Br or I) display *cis* octahedral geometries[47] whilst reaction of SnR_2Cl_2 with $K[Ph_2P(E)NP(E)Ph_2]$ gives the *trans*-$SnR_2[Ph_2P(E)NP(E)Ph_2]_2$ systems (R = Me, E = S,[49] R = Bu^n, E = O,[50] R = Bu^n, E = Se[51]). Interestingly, whilst the analogous halide–β-diketonate compounds are air/moisture sensitive, all of the tin(IV) imidophosphinate complexes are quite stable in air. One fascinating structure is that of $\{SnMe_3[Ph_2P(S)NP(S)Ph_2]\cdot C_6H_6\}_x$. In the solid state[52] the trigonal-bipyramidal tin centres are linked *via* bridging $[Ph_2P(S)NP(S)Ph_2]^-$ ligands to give a covalently bonded polymer chain with the cavity along the *b* axis acting as a host for the benzene solvate (Fig. 11).

The compound $Pb[Ph_2P(S)NP(S)Ph_2]_2$ exists[53] in the solid state with an unusual unsymmetrical co-ordination of the chelating ligands [Pb–S 2.695(4) and 2.943(4) Å] and some P–N and P–S bond alternation although still with the familiar distorted-boat conformation of the six-membered rings. The long Pb–S bonds can be considered as axial whilst the short Pb–S distances are equatorial, though there are additional long-range interactions with phenyl rings of the ligand which would allow the lead(II) geometry to be described as octahedral. In the $Pb[Ph_2P(S)NP(O)Ph_2]\cdot C_6H_6$ complex[54] the distorted ψ-*TBPY* systems are linked to weak dimers *via* Pb···S interactions.

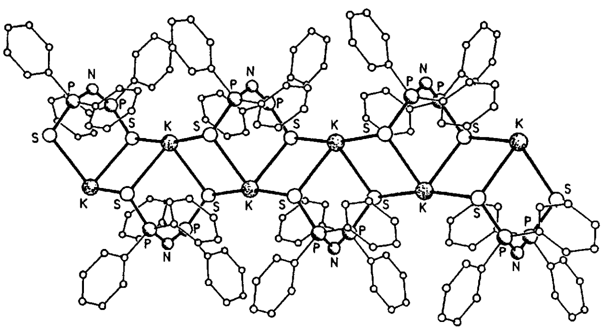

Fig. 7 Crystal structure of $K[Ph_2P(S)NP(S)Ph_2]$ illustrating the infinite-chain structure in the solid state[39]

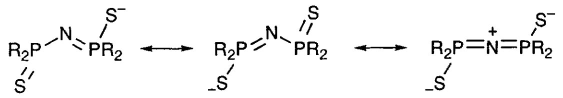

Fig. 8 Canonical forms in $[R_2P(S)NP(S)R_2]^-$

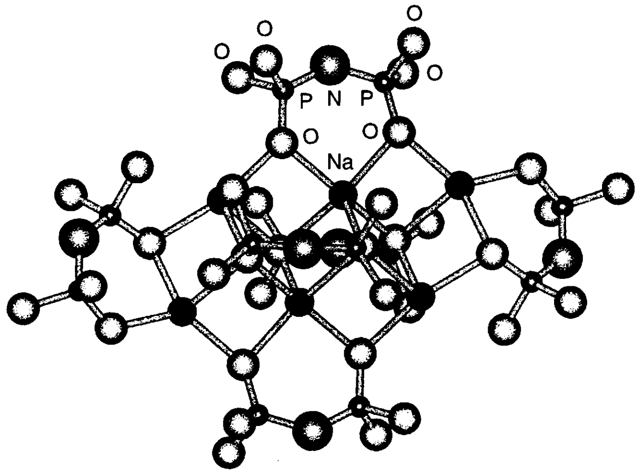

Fig. 9 Hexameric structure of $\{Na[(PhO)_2P(O)NP(O)(OPh)_2]\}_6$ in the solid state[42]

Other p-block complexes of imidophosphinates include[55] $Bi[Ph_2P(S)NP(S)Ph_2]_3$ as well as $SbPh_2Cl_2[Ph_2P(O)NP(E)Ph_2]$ (E = O or S).[56] Selenium and tellurium complexes may also be synthesised [equations (18) and (19)] (tu = thiourea).

$$[NH_4][Ph_2P(S)NP(S)Ph_2] + Se[(EtO)_2PS_2]_2 \longrightarrow Se[Ph_2P(S)NP(S)Ph_2]_2 \qquad (18)$$

$$[NH_4][Ph_2P(S)NP(S)Ph_2] + Te(tu)_4Cl_2\cdot 2H_2O \longrightarrow Te[Ph_2P(S)NP(S)Ph_2]_2 \qquad (19)$$

In the tellurium case[57] the square-planar complex is fairly symmetrically co-ordinated with the six-membered rings adopting a pseudo-chair conformation in one of the crystallographically independent molecules and a pseudo-boat conformation in the other. This degree of conformational freedom is a common feature in these MEPNPE rings (see below). The selenium complex[58] is also approximately planar, though the S–Se bonds are not equivalent: two 'normal' and two long (the normal and long bonds are arranged *trans* to each other). Within the six-membered rings there is also a degree of bond alternation which is illustrated schematically in Fig. 12. A localised scheme closer to single co-ordination through only one S group clearly has a large effect on the structure. This may be a consequence of the ability of the ligand to 'close down' to

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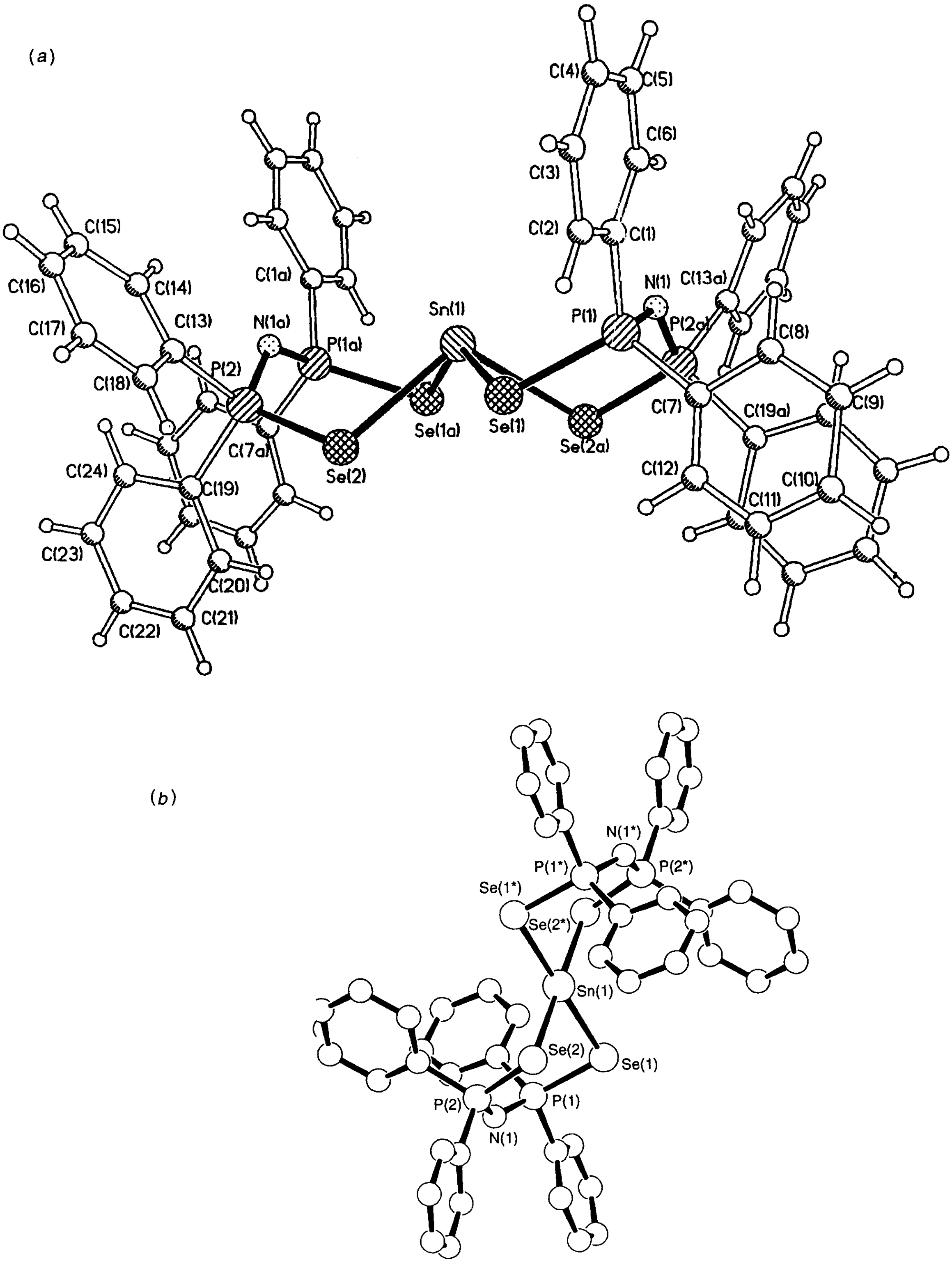

Fig. 10 Different geometries observed in the solid state for $Sn[Ph_2P(Se)NP(Se)Ph_2]_2$[48]

the required angle, though there does not appear to be any ring strain in other systems. A weakly co-ordinated compound $[TePh_3]^+[Ph_2P(S)NP(S)Ph_2]^-$ has recently been reported (Te••• S 3.26, 3.45 Å).[59]

Transition-metal complexes have been studied over several years and I shall only comment on relatively recent work. Simple metathesis reactions proceed smoothly for a number of systems, thus reaction of $[Mn(CO)_5Br]$ with $K[Ph_2P(S)NP(S)Ph_2]$ gives $[Mn(CO)_4\{Ph_2P(S)NP(S)PPh_2\}]$ in good yield.[60] The conformational freedom of the MSPNPS ring is well illustrated by this complex. The two crystallographically independent molecules display pseudo-boat and -chair conformations of their six-membered rings with the latter having a very much reduced S–Mn–S bond angle compared to the former [89.2(1) *versus* 100.5(1)°]; both of the S–Mn–S angles are significantly less than that in[61] $[Mn\{Ph_2P(S)NP(S)Ph_2\}_2]$ which is 109.5(22)°.

The tris iron(III) complex $[Fe\{Ph_2P(O)NP(O)Ph_2\}_3]$ may be obtained *via* simple metathesis or by a reaction which is analogous to that observed in β-diketonate chemistry [equation

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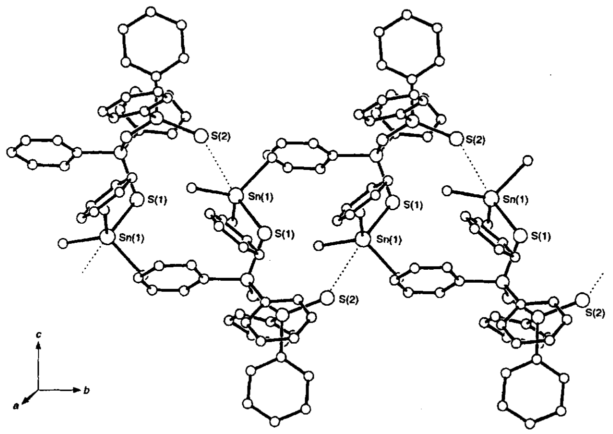

Fig. 11 Polymer character in $\{SnMe_3[Ph_2P(S)NP(S)Ph_2]\cdot C_6H_6\}_x$[52]

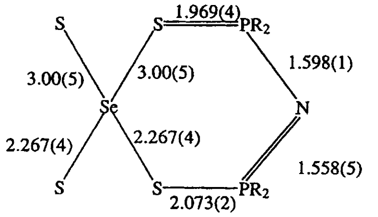

Fig. 12 Bond alternation in $Se[Ph_2P(S)NP(S)Ph_2]_2$; the distances (Å) are averages for the two rings[58]

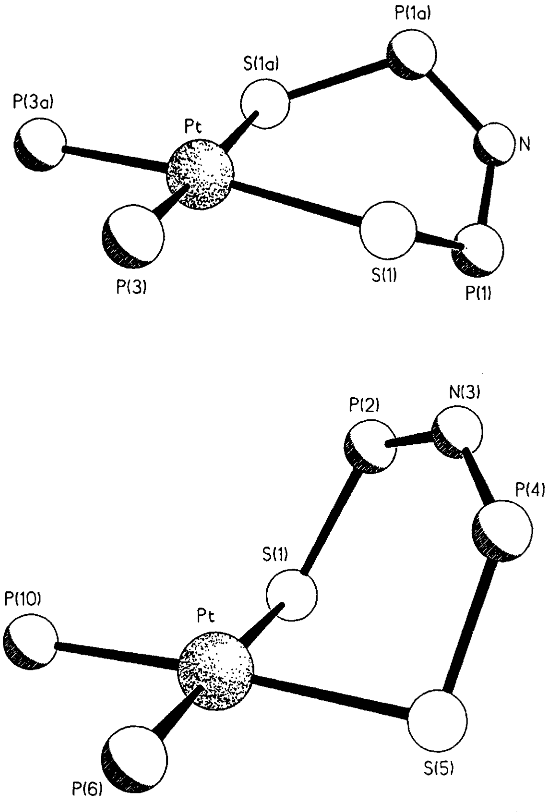

Fig. 13 Core geometries[64] in $[Pt\{Ph_2P(S)NP(S)Ph_2\}(PEt_3)]^+$ (upper) and $[Pt\{(PhO)_2P(S)NP(S)(OPh)_2\}(PMe_3)_2]^+$ (lower)

(20)]. The reaction is believed to proceed[62] *via* metal-assisted oxidation of the $Ph_2PNHPPh_2$ followed by oxidation of Fe^0 to Fe^{III} with elimination of $\frac{3}{2}H_2$. Interestingly in the tris chelate the rings appear to be only slightly distorted from planar.

$$[Fe_2(CO)_9] + 6Ph_2PNHPPh_2 \longrightarrow [Fe\{Ph_2P(O)NP(O)Ph_2\}_3] \quad (20)$$

Steric and electronic effects have been investigated for complexes of Ni^{II} and Co^{II}. Thus $[Co\{Me_2P(S)NP(S)Me_2\}_2]$ and $[Co\{Ph_2P(Se)NP(Se)Ph_2\}_2]$ are tetrahedral[24] as are $[Ni\{Ph_2P(S)NP(S)Ph_2\}_2]$[21] and $[Co\{Ph_2P(Se)NP(Se)Ph_2\}_2]$,[38] but reducing the steric demands at one phosphorus centre gives $[Ni\{Ph_2P(S)NP(S)Me_2\}_2]$ which is square planar.[63]

Platinum and palladium complexes $[M\{Ph_2P(E)NP(E)Ph_2\}_2]$ (E = S or Se) may be obtained by reaction of $[MCl_2(cod)]$ (cod = cycloocto-1,5-diene) with $Na[Ph_2P(E)NP(E)Ph_2]$ in organic solvents or directly from the neutral starting material with MCl_2 in acetone–water. They are all square planar with pseudo-boat conformation six-membered rings.[21] The crystal structure of $[Pd\{(PhO)_2P(S)NP(S)(OPh)_2\}_2]$ is similar.[23] Synthesis of $[Pt\{R_2P(S)NP(S)R_2\}(PR'_3)_2]^+$ reveals[64] that changing R from Ph to OPh has a marked effect on the ring geometry with the phenyl system having a boat and the OPh system a chair conformation (Fig. 13). The P–S bond lengths in the chair conformation system are substantially shorter than those in the boat [average 1.989(4) *versus* 2.021(4) Å], but this may well be a consequence of the difference in electron-withdrawing powers of Ph and OPh. An opportunity to examine this effect further is provided by $[M\{Pr^i_2P(S)NP(S)Pr^i_2\}_2]$ (M = Pd or Pt).[65] Interestingly, in the palladium case a pseudo-boat conformation is observed, whereas in the platinum case a pseudo-chair geometry is seen (Fig. 14). Table 2 compares bond lengths and angles in these two molecules with those of $[PdCl\{Pr^i_2P(S)NP(S)Pr^i_2\}\{Pr^i_2P(S)NHP(S)Pr^i_2\}]$ which contains one non-deprotonated ligand and with tetrahedral $[Zn\{Pr^i_2P(S)NP(S)Pr^i_2\}_2]$.[25]

A number of complexes of the type $[M\{Ph_2P(E)NP(E)Ph_2\}(PR_3)_2]X$ (M = Pd or Pt; E = S or Se; R = alkyl or aryl; X = Cl or PF_6 but not all combinations) have been obtained[66,67] by reaction of $K[Ph_2P(E)NP(E)Ph_2]$ with the appropriate $[MCl_2(PR_3)_2]$. Similarly, reaction of $K[Ph_2P(Se)NP(Se)Ph_2]$ with $[\{RhCl(cod)\}_2]$ gives $[Rh\{Ph_2P(Se)NP(Se)Ph_2\}(cod)]$.[66] Although one would anticipate that these complexes would be quite stable, during recrystallisation[67] $[Pt\{Ph_2P(S)NP(S)PPh_2\}(PPh_3)_2]Cl$ eliminates phosphine according to equation (21). Similarly, during the work-up of $[Pd\{Ph_2P(Se)NP(Se)Ph_2\}(PMe_2Ph)_2]Cl$ small traces of $[Pd\{Ph_2P(Se)NP(Se)Ph_2\}\{Ph_2P(Se)NPPh_2\}]$ which contains both six-membered MSePNPSe and five-membered MSePNP rings (Fig. 15) are obtained.[66]

$$[Pt\{Ph_2P(S)NP(S)Ph_2\}(PPh_3)_2]Cl \longrightarrow [PtCl\{Ph_2P(S)NP(S)Ph_2\}(PPh_3)] + PPh_3 \quad (21)$$

Interestingly, during reactions [*e.g.* equations (22) and (23)] or during the syntheses of a range of $Ph_2PNHPPh_2$ and $Ph_2P(E)NHP(E)Ph_2$ (E = O or S) complexes of rhenium, Rossi *et al.*[68,69] noted the formation of mixed-donor MEPNP rings although in this case it was by the oxidation of $Ph_2PNHPPh_2$ to give MOPNP rings, rather than an elimination of selenium. This work by Rossi *et al.*[70] is the first example of co-ordinated $[Ph_2PNP(O)Ph_2]^-$ and has led to a more detailed investigation of this ligand (see below).

$$[ReNCl_2(PPh_3)_2] + Ph_2P(E)NHP(E)Ph_2 \xrightarrow{E\,=\,S,\,Se} [ReNCl\{Ph_2P(S)NP(S)Ph_2\}(PPh_3)] + [ReN\{Ph_2P(E)NP(E)Ph_2\}_2] \quad (22)$$

$$[ReOCl_n(PPh_3)_2] + xPh_2P(S)NHP(S)Ph_2 \longrightarrow [ReOCl_{n-x}\{Ph_2P(S)NP(S)Ph_2\}_x(PPh_3)] \quad (23)$$
$$n = 3, 2; x = 1, 2$$

Simple homoleptic copper(II) complexes of $[R_2P(S)NP(S)R_2]^-$ (R = Me or Ph) have been investigated as models for copper enzymes.[43,71,72] However, they tend to

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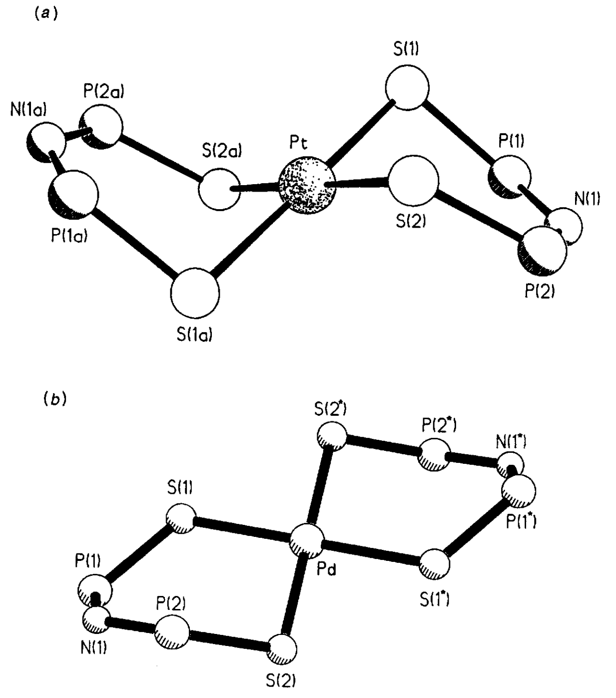

Fig. 14 Comparative core geometries of $[\mathrm{M\{Pr^i_2P(S)NP(S)Pr^i_2\}_2}]$ [M = Pt (*a*) or Pd (*b*)]^{65}

Table 2 Comparative bond lengths for $[\mathrm{ML_2}]$ [M = Zn, Pd or Pt; L = $\mathrm{Pr^i_2P(S)NP(S)Pr^i_2}$] and $[\mathrm{PdL(HL)}]\mathrm{Cl}^{25,65}$

				$[\mathrm{PdL(HL)}]^+$	
	$[\mathrm{ZnL_2}]$	$[\mathrm{PtL_2}]$	$[\mathrm{PdL_2}]$	Ring 1^a	Ring 2^b
M–S(1)	2.345(1)	2.338(3)	2.341(1)	2.359(3)	2.329(3)
M–S(2)		2.334(2)	2.347(1)	2.353(4)	2.314(3)
S(1)–P(1)	2.032(1)	2.034(3)	2.030(2)	2.008(5)	2.045(4)
P(1)–N(1)	1.581(2)	1.586(4)	1.597(4)	1.65(1)	1.587(10)
N(1)–P(2)	1.581(2)	1.575(4)	1.588(4)	1.64(1)	1.590(10)
P(2)–S(2)	2.032(1)	2.038(2)	2.023(2)	1.976(5)	2.040(5)
S(1)–M–S(2)	112.4(1)	90.9(1)	100.7(1)	99.2(1)	100.5(1)
M–S(1)–P(1)	107.1(1)	99.6(1)	114.0(1)	103.4(2)	110.6(1)
S(1)–P(1)–N(1)	118.3(1)	116.5(1)	119.1(2)	111.6(4)	114.0(4)
P(1)–N(1)–P(2)	140.5(3)	135.0(2)	130.2(2)	128.7(6)	128.2(7)
N(1)–P(2)–S(2)	118.5(1)	118.3(1)	117.1(1)	115.8(4)	117.1(4)
P(2)–S(2)–M	107.1(1)	104.1(1)	108.6(1)	115.5(2)	110.5(2)

^{a} Ring 1 is protonated. ^{b} Ring 2 is sequentially numbered, *i.e.* S(3) corresponds to S(1) in Ring 1.

reduce the metal to Cu$^{\mathrm{I}}$ and a number of cluster compounds have been proposed. Trinuclear $[\mathrm{Cu_3\{Ph_2P(S)NP(S)Ph_2\}_4}]$ and $[\mathrm{Cu^I_3\{Ph_2P(S)NP(S)Ph_2\}_3}]$ are thought to exist,^{42,73,74} whilst the structure of the cation in $[\mathrm{Cu_4\{Ph_2P(S)NP(S)Ph_2\}_3}][\mathrm{CuCl_2}]\cdot\mathrm{CCl_4}$ has been established by X-ray crystallography^{73,75} as consisting of an adamantane-like $\mathrm{Cu_4S_6}$ core (Fig. 16).

Reaction of $[\mathrm{Cu(NO_3)(PPh_3)_2}]$ with $\mathrm{K[Ph_2P(S)NP(S)Ph_2]}^{76}$ or the selenium^{38} analogue gives simple three-co-ordinate $[\mathrm{Cu\{Ph_2P(E)NP(E)Ph_2\}(PPh_3)}]$ complexes. The MEPNPE rings are non-planar, but cannot be readily classified as chair- or boat-like in these copper complexes. Reaction of $\mathrm{Ph_2P(S)NHP(S)Ph_2}$ with [AuCl(tht)] (tht = tetrahydrothiophene) or $[\mathrm{AuR_2Cl}]$ gives bimetallic $[\{\mathrm{Au[Ph_2P(S)NP(S)Ph_2]}\}_2]$ and chelate $[\mathrm{AuR_2\{Ph_2P(S)NP(S)Ph_2\}}]$ complexes.^{77}

It is clear that the S–P–N–P–S backbone has a high degree of freedom. The bond lengths do not vary significantly within the $\mathrm{MS_2P_2N}$ rings when the ligand is deprotonated. Some of the internal ring angles have to change to accommodate different 'bites', *i.e.* tetrahedral zinc (cadmium or nickel)^{25} complexes have an enlarged S–M–S angle which does affect the other ring angles, but there do not appear to be any direct relationships. Perhaps the most noticeable change is that the 'chair-like' rings result in S–M–S angles close to 90° whilst the 'boat-like' rings give enlarged angles at the metal. This effect seems to be general. Table 2 also enables a comparison of geometries for protonated *versus* deprotonated rings; as expected, the deprotonated ring has longer P–S and shorter P–N bonds.

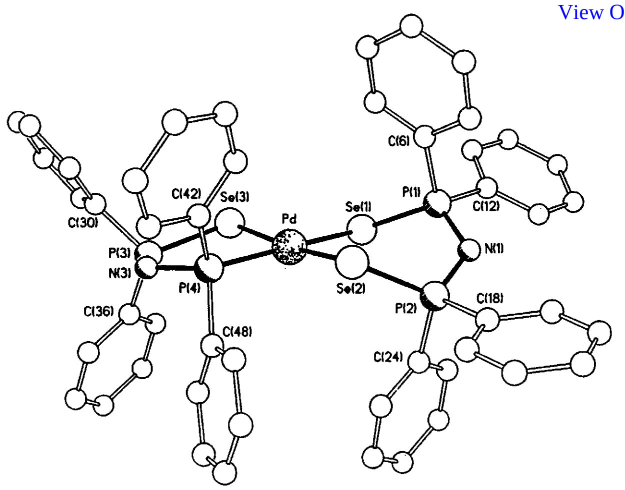

Fig. 15 Crystal structure of $[\mathrm{Pd\{Ph_2P(Se)NP(Se)Ph_2\}\{Ph_2P(Se)NPPh_2\}}]^{66}$

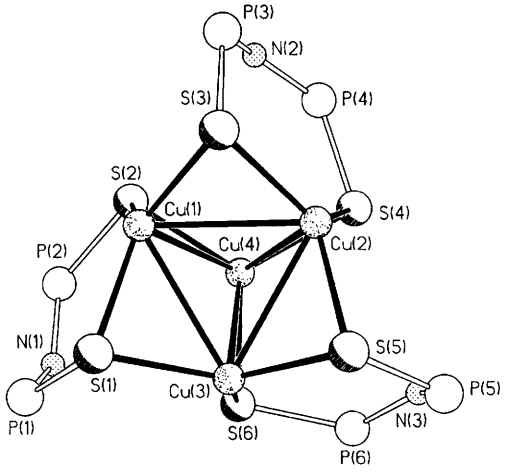

Fig. 16 Crystal structure of the core in $[\mathrm{Cu_4\{Ph_2P(S)NP(S)Ph_2\}_3}][\mathrm{CuCl_2}]\cdot\mathrm{CCl_4}^{73,75}$

(*b*) $\mathrm{Ph_2P(E)NHPPh_2}$ Systems

In section (*a*) it was mentioned that a rhenium complex of $[\mathrm{Ph_2PNP(O)Ph_2}]^-$ was synthesised by Rossi *et al.*^{70} in 1994. They treated $\mathrm{Ph_2PNHPPh_2}$ with $\mathrm{ReOCl_4}$ and obtained $[\mathrm{AsPh_4}][\mathrm{ReCl_4\{Ph_2P(O)NPPh_2\}}]$ with the oxygen thus deriving from the ReO group. Recently, there have also been reports on the formation of the oxidised ligand after complexation. Thus $[\mathrm{AuMe_2(Ph_2PNHPPh_2)}]\mathrm{Cl}$ is oxidised by air to give^{78} $[\mathrm{AuMe_2Cl\{Ph_2P(O)NPPh_2\}}]$ which has been characterised crystallographically and the ligand is monodentate *via* P. Reaction of $[\mathrm{Co_2(CO)_6}(\mu\text{-}\eta^2\!:\!\eta^2\text{-}\mathrm{HOCH_2C{\equiv}CCH_2OH}\text{-}C,C')]$ with $\mathrm{Ph_2PNHPPh_2}$ gives $[\mathrm{Co^I(CO)_2\{Ph_2P(O)NPPh_2\}(Ph_2PNHPPh_2)}]$ although in this case the exact source of the oxygen has not been identified.^{79}

Rational routes to monoxidised systems have been investigated. With heavier Group 16 elements it is quite feasible to prepare^{80} $\mathrm{Ph_2P(E)NHPPh_2}$ [equation (24)]. Reaction of

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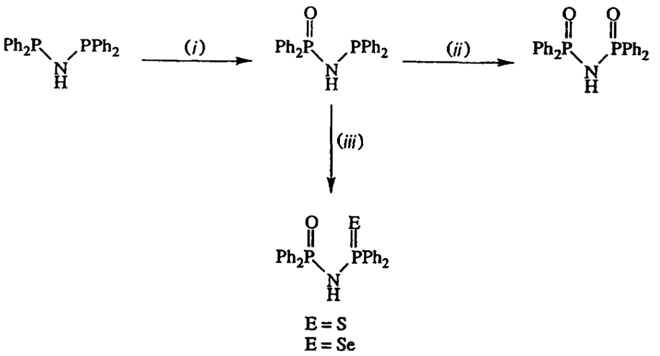
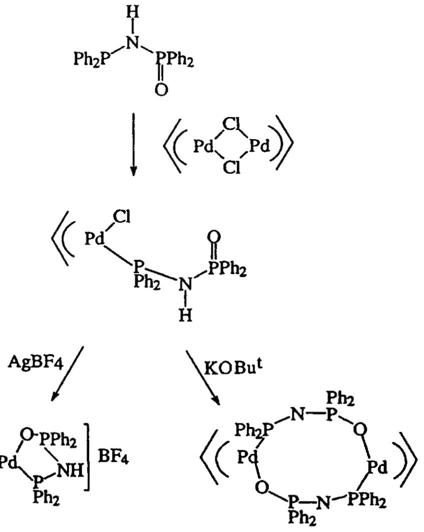


Scheme 1 Stepwise synthesis of $Ph_2P(O)NHP(E)Ph_2$ systems



Scheme 2 Complex formation of $Ph_2P(O)NHPPh_2$

$$Ph_2PNHPPh_2 + E \xrightarrow{E\,=\,S\text{ or }Se} Ph_2P(E)NHPPh_2 \quad (24)$$

$Ph_2P(E)NHPPh_2$ with $[MCl_2(cod)]$ (M = Pd or Pt) gives *cis*/*trans*-$[M\{Ph_2P(E)NHPPh_2\}]Cl_2$ and $[M\{Ph_2P(E)NPPh_2\}]$, in which the *cis* and *trans* isomers may be separated by crystallisation in most cases. The crystal structures reveal slightly puckered five-membered MEPNP rings.

Careful oxidation of Ph_2PNHPh_2 with peroxide gives $Ph_2P(O)NHPPh_2$[81] which exists in the solid state as hydrogen-bonded dimer pairs and may be further oxidised (Scheme 1). As might be expected, $Ph_2P(O)NHPPh_2$ behaves as a simple monodentate ligand through its phosphorus(III) centre and several examples involving Pd^{II}, Pt^{II}, Ir^{I}, Ir^{III} and Au^{I} have been established. If a suitable vacant site is made available, then P, O chelation of the neutral ligand can be induced[81,82] (Scheme 2). Subsequently the ligand may be deprotonated. Alternatively (Scheme 2), it is possible to form new ten-membered heterocycles by deprotonation of a P-bonded $Ph_2P(O)NHPPh_2$ system. The structure[83] of $[(C_3H_5)Pd\{Ph_2P(O)NPPh_2\}_2Pd(C_3H_5)]$ (Fig. 17) consists of a 'chair-like' metallacycle.

The ready availability of $Ph_2P(E)NHP(E')Ph_2$ will doubtless result in studies on mixed-donor complexes. It has already been found that $[Pd\{Ph_2P(O)NP(Se)Ph_2\}_2]$ illustrates many of the aspects mentioned earlier. It is readily formed, stable and exists in the solid state with different ring geometries for the two MOPNPSe six-membered rings (Fig. 18). As was the case in earlier examples, the chair-like ring has a Se–Pd–O angle which is much closer to ideal than in the boat-like ring [92.6(1)° *versus* 99.8(1)°]. Solution NMR studies show the two rings to be equivalent down to −70 °C.

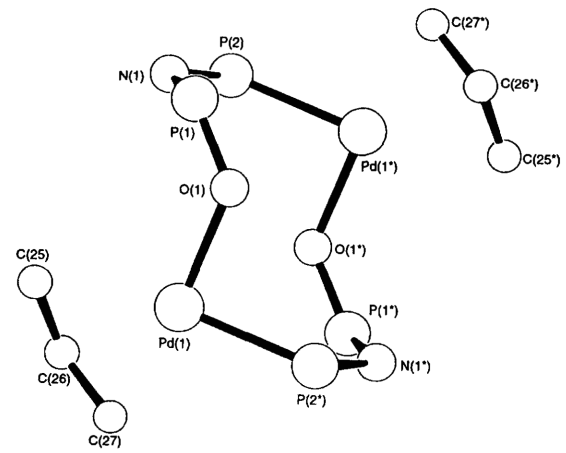


Fig. 17 The core of the crystal structure of $[(C_3H_5)Pd\{Ph_2P(O)NPPh_2\}_2Pd(C_3H_5)]$[83]

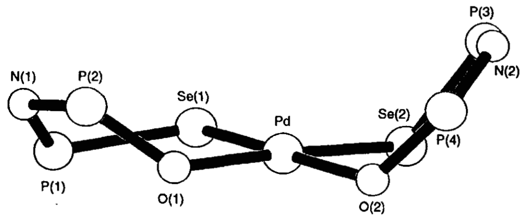


Fig. 18 The core of the crystal structure of $[Pd\{Ph_2P(O)NP(Se)Ph_2\}_2]$[84]

Conclusion

The $R_2P(E)NHP(E)R_2$ system is readily formed and variations in R and E can be accomplished although surprisingly little work in this regard has appeared to date. Furthermore, monoxidised species $R_2P(E)NHPR_2$ can also be formed quite easily. A wide range of complexes have been prepared and perhaps the most striking feature is the variation in ligand geometry which can be accommodated without any apparent difficulty. It is clear that although these inorganic chelates are analogous to acac (acetylacetonate) they are capable of displaying distinct and unique geometries and the extra steric demands of a PR_2 group relative to a CR group will influence their co-ordination chemistry. Further studies into the factors that influence the choice of ring geometry should prove interesting. One can anticipate that $R_2P(E)NHP(E)R_2$- and $R_2P(E)NHPR_2$-derived ligands will be capable of selective co-ordination which is not possible for acac. The P–N bond-forming reactions that are used for the synthesis of the ligands described here might well find more general application in the synthesis of bidentate (and macrocyclic) phosphorus-containing ligands. The formation of bi- and multi-metallic systems supported by these ligands is another exciting possibility.

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