Pergamon

Polyhedron Vol. 14, No. 23–24, pp. 3367–3388, 1995
Elsevier Science Ltd
Printed in Great Britain
0277–5387/95 $9.50+0.00

0277–5387(95)00103–4

POLYHEDRON REPORT NUMBER 56

BIS(DIPHENYLPHOSPHINO)AMINE AND RELATED CHEMISTRY

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1. INTRODUCTION

Throughout inorganic and organometallic chemistry few ligands have been as widely employed as tertiary mono- and diphosphines.[1–4] It is still perhaps true to say that the most commonly used diphosphine to date is bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$ (dppe), a molecule adept at forming five-membered chelate rings. Over the past two decades its homologue bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$ (dppm), has become an increasingly used ligand.[5–7] The versatility of dppm arises from its ready coordination to metal centres through the lone pair of electrons at one or both of the phosphorus atoms, while deprotonation of the methylene group by strong bases generates a tridentate ligand $[Ph_2PCHPPh_2]^-$ (Fig. 1). The oxidized compounds $Ph_2PCH_2P(E)Ph_2$ and $Ph_2P(E)CH_2P(E)Ph_2$ (E = chalcogen or imine), prepared either by oxidation of dppm[8,9] or from condensation of smaller fragments,[10–12] have been found to be excellent ligands. Here the P=E centres coordinate to metals via the lone pairs of E.

Compared with the vast body of data accumulated on diphosphines in which the phosphorus nuclei are linked by a carbon atom or chain, less has appeared on ligands where the backbone of the molecule comprises a heteroatom or group. In this respect diphosphinoamines and cyclodiphosphazanes, where the phosphorus nuclei are connected by one or two nitrogen atoms, respec-

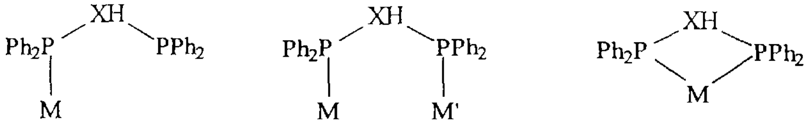

Fig. 1. Coordination modes of dppm and its anion (X = CH or C).

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tively, have received little coverage (Fig. 2).[7,13] Bis(diphenylphosphino)amine, $Ph_2PNHPPh_2$ (dppa), isoelectronic with dppm, demonstrates a similar coordinative versatility to the methylene compound, both in its neutral form and as the anion $[Ph_2PNPPh_2]^-$. Oxidation at the phosphorus atoms to generate new ligands and participation in cyclocondensations leading to heterocycle formation are two features which dppa has in common with dppm, although several differences in their reactivity are also apparent. These points will be discussed in turn, following a brief review of synthetic routes to dppa.

2. SYNTHETIC ASPECTS

The condensation of hexamethyldisilazane with chlorodiphenylphosphine leads to dppa in good yield [eq. (1)].[14]

$$2\,Ph_2PCl + NH(SiMe_3)_2 \longrightarrow Ph_2PNHPPh_2 + 2\,Me_3SiCl \qquad (1)$$

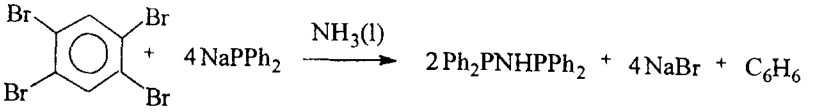
While conversion is clean in toluene,[15] variation of the conditions can lead to the salts $[(Ph_2P)_3NH]Cl$ or $[(Ph_2P)_4N]Cl$.[14] Addition of tertiary amines[16] or ammonia[17] is reported to increase the yield of dppa. The condensation of chlorophosphines with silylated amines,[18,19] a general route to diphosphinoamines, is limited by the availability of suitable silylamines. Treatment of primary amines with PCl_3[20] or Ph_2PCl[21] allows introduction of substituents at the nitrogen atom [eqs (2) and (3)].

$$2\,PCl_3 + RNH_2 \longrightarrow RN(PCl_2)_2 + 2\,HCl \qquad (2)$$

$$2\,Ph_2PCl + RNH_2 \longrightarrow RN(PPh_2)_2 + 2\,HCl \qquad (3)$$

R = alkyl or aryl

Unexpected formation of dppa has been noted in a few instances. The reaction between 1,2,4,5-tetrabromobenzene and sodium diphenylphosphide in liquid ammonia does not give the anticipated compound 1,2,4,5-$(Ph_2P)_4C_6H_2$,[22] whilst Lewis acid catalysed cyclization of *cis*-Ph_2PNH_2 groups in a molybdenum(0) complex has led to the formation of coordinated dppa [eqs (4) and (5)].[23]



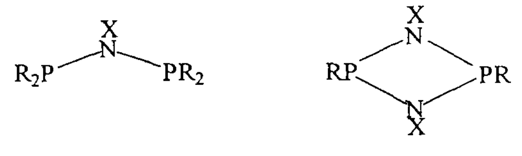
(4)

$$cis\text{-}[Mo(CO)_4(Ph_2PNH_2)_2] \xrightarrow{BF_3\cdot Et_2O} [Mo(CO)_4(dppa)] \qquad (5)$$

The latter reaction must be in part due to the instability of free Ph_2PNH_2, which decomposes to dppa below 100°C.[24] Similar cyclizations to *cis*-$[Mo(CO)_4(Ph_2PEPPh_2)]$, for E = O or S, have been observed.

3. GENERAL CHEMISTRY OF DPPA

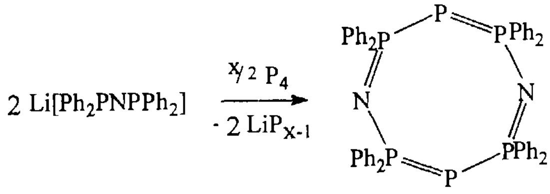
The presence of an acidic amine proton opens up several pathways parallel to dppm. Dppa is converted to its lithium salt $Li[Ph_2PNPPh_2]$ by n-butyllithium.[25] Although N-deuteration occurs upon treatment with CH_3OD,[25] the nitrogen atom is not appreciably more nucleophilic upon deprotonation. Whereas dppa reacts with methyl iodide to produce $[Ph_2P(Me)N(Me)PPh_2]I$ in 95% yield,[26] treatment of $[Ph_2PNPPh_2]^-$ with organic halides RX results exclusively in phosphorus



R = alkyl, aryl, halogen or alkoxy; X = alkyl, aryl or H

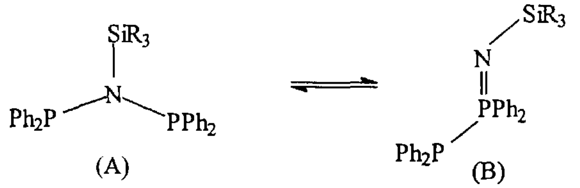
Fig. 2. Diphosphinoamines and cyclodiphosphazanes.

alkylation to give iminium salts $[Ph_2P(R)NP(R)Ph_2]X$.[27–29] $Li[Ph_2PNPPh_2]$ reacts with Ph_2PCl to give tris(diphenylphosphino)amine $(Ph_2P)_3N$ in just 8% isolated yield,[30] or with Me_2PCl to give only $Ph_2P—N{=}PPh_2—PMe_2$.[31] $Li[Ph_2PNPPh_2]$ reacts with white phosphorus in THF to generate an eight-membered heterocycle, again demonstrating the reluctance of the anion to form a third P—N bond [eq. (6)].[32]



(6)

Recently,[33] iodine oxidation of $[Ph_2PNPPh_2]^-$ and $[Ph_2PCHPPh_2]^-$ has been studied. The dppa system gives $Ph_2P—N{=}PPh_2—PPh_2{=}N—PPh_2$, whilst the dppm system yields $(Ph_2P)_2C{=}PPh_2—CH_2—PPh_2$. Cross coupling of the two anions with iodine gives $Ph_2P—N{=}PPh_2—PPh_2{=}CH—PPh_2$. N-silylation occurs in the reaction of $Li[Ph_2PNPPh_2]$ and R_3SiCl (R = alkyl or aryl), although this is dependent upon the substituents at the silicon atom [eq. (7)].[31]



Solely (A) for R_3= Me_3, Et_3, $MePh_2$
Equilibrium between (A) and (B) for R_3= $^i Pr_3$, $^i Pr_2Cl$, Me_2Cl
Solely (B) for R_3= Ph_3, Me_2Ph

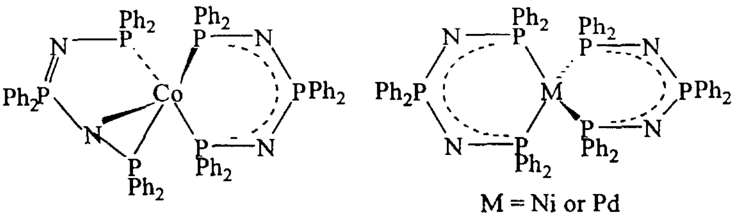
(7)

4. COORDINATION CHEMISTRY OF $Ph_2PNHPPh_2$ AND $[Ph_2PNPPh_2]^-$

Despite the inherent strain associated with the formation of four-membered metallacycles, both dppa and $[Ph_2PNPPh_2]^-$ form stable chelates. Square-planar cations $[M(dppa)_2]^{n+}$ are known for Rh^I, Ir^I ($n = 1$) and Pt^{II} ($n = 2$),[34,35] whilst neutral complexes $[M(Ph_2PNPPh_2)_2]$ are obtained from the reaction between $Li[Ph_2PNPPh_2]$ with $PdCl_2$ or $K_2[PtCl_4]$ in the presence of PMe_3.[36] With $NiCl_2/PMe_3$ the chloro-bridged dimer $[Ni_2(Ph_2PNPPh_2)_2(\mu\text{-}Cl)_2]$ is produced. Under prolonged reflux, however, the reaction of $Li[Ph_2PNPPh_2]$ with anhydrous metal chlorides MCl_2, M = Co, Ni or Pd, leads to novel products [eq. (8)].[37,38]

$$3\,MCl_2 + 6\,Li[Ph_2PNPPh_2] \xrightarrow{\text{toluene}} [M(Ph_2PNPPh_2NPPh_2)_2] + 6\,LiCl + 2\,M + 2\,N(PPh_2)_3 \qquad (8)$$

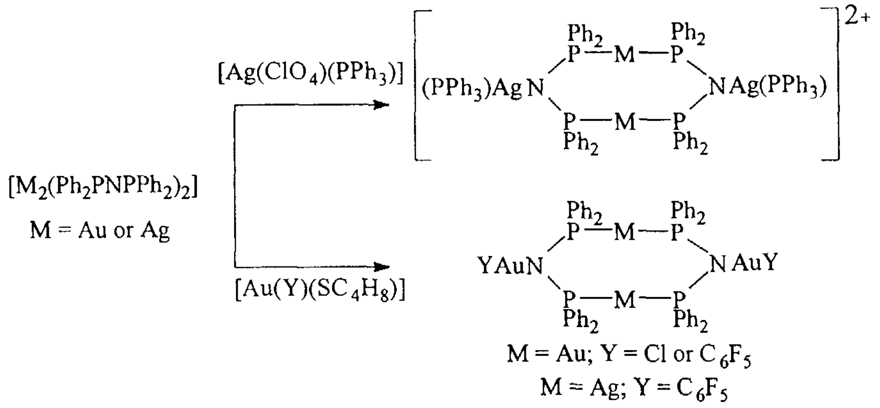
Crystallographic analysis reveals that for nickel and palladium the $[Ph_2PNPPh_2NPPh_2]^-$ ligands chelate through the terminal phosphorus atoms with distorted square-planar geometry at the metal, producing six-membered metallacycles (Fig. 3). In $[Co(Ph_2PNPPh_2NPPh_2)_2]$ one of the anions functions as a tridentate P,N chelating ligand, giving a penta-coordinate cobalt atom. A redox



M = Ni or Pd

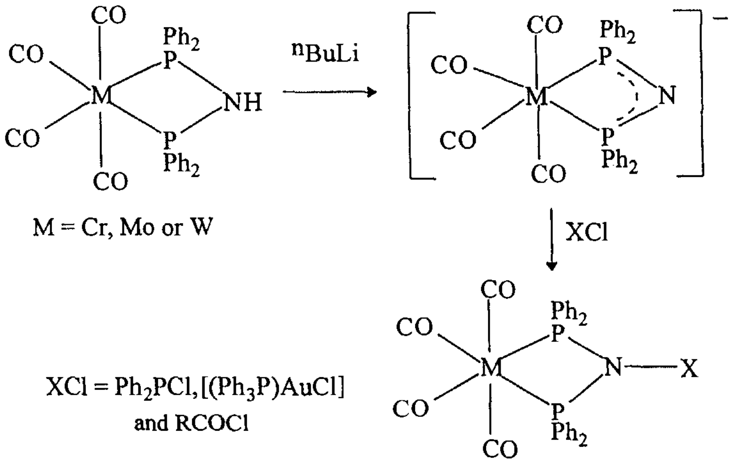
Fig. 3. $[M(Ph_2PNPPh_2NPPh_2)_2]$, M = Co, Ni or Pd.

mechanism in which $[Ph_2PNPPh_2]^-$ is oxidized to the nitrene [N—PPh_2], with concomitant reduction of $M^{(II)}$ to M^0, is proposed to account for the products isolated. However, no reasons as to why this pathway predominates over the formation of simple chelates $[M(Ph_2PNPPh_2)_2]$ have been given. Reaction of dppa with *cis*-$PtCl_2(PR_3)_2$ gives [PtCl(PR_3)dppa]Cl, which have been characterized by NMR and, in a number of cases by X-ray crystallography.[39] Treatment of $[AuCl(PPh_3)]$ with $Li[Ph_2PNPPh_2]$ gives the insoluble dimer $[Au_2(\mu\text{-}Ph_2PNPPh_2)_2]$, characterized by ^{197}Au Mossbauer spectroscopy.[40] The diprotonated compound $[Au_2(\mu\text{-dppa})_2]^{2+}$ also exists.[41] Both dppa and dppm undergo deprotonation on reaction with $[AuCl(CH_2PPh_3)]$ and $[Au(acac)(PPh_3)]$ to give $[Au_2(\mu\text{-}Ph_2PXPPh_2)_2]$, (X = CH or N).[42–45] Dppm, however, does not react with $[Ag(CH_2PPh_3)_2]ClO_4$, whereas dppa gives $[Ag_2(\mu\text{-}Ph_2PNPPh_2)_2]$, which can also be obtained from $AgBF_4$ and $Li[Ph_2PNPPh_2]$.[46] The gold(I) complexes $[Au_2(\mu\text{-}Ph_2PXPPh_2)_2]$, X = CH or N, possess sufficient electron density at X for further metallation at this site [eq. (9)].[42,43]



(9)

Group VI metal carbonyl complexes *cis*-$[M(CO)_4(dppa)]$, M = Cr, Mo or W, are deprotonated by n-butyllithium and react with Ph_2PCl, PhCOCl or $[AuCl(PPh_3)]$ at the nitrogen atom.[31,47] This resembles the behaviour of the coordinated anion in $[M(CO)_4(Ph_2PCHPPh_2)]^-$, M = Cr, Mo or W, for whom reaction with electrophiles leads to bond formation at the methanide carbon atom [eq. (10)].[48,49]



(10)

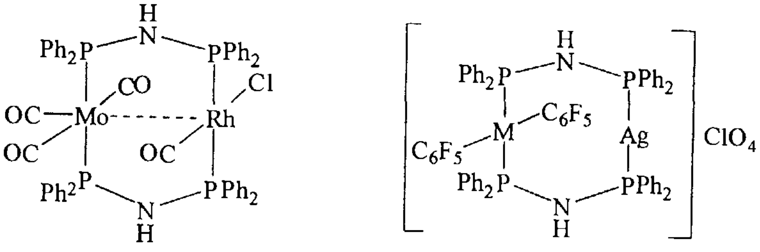
As depicted in Fig. 1, a shared feature of both dppm and $[Ph_2PCHPPh_2]^-$ is the formation of bimetallics.[50–54] In general bimetallic species are of interest as the close proximity of two metal atoms may greatly modify their reactivity, particularly so for mixed-metal systems. As demonstrated by the existence of the dimeric Au^I and Ag^I complexes described above, dppa readily forms bimetallic compounds which are isostructural with their dppm analogues [eqs (11)–(13)].[41,55–61]

$$[PdCl_2(NCPh)_2] + 1/2[Pd_2(dba)_3] + 2\,dppa \rightarrow [Pd_2Cl_2(\mu\text{-dppa})_2] \quad (11)$$

$$[Rh(\mu\text{-Cl})(CO)_2]_2 + 2\,dppa \rightarrow [Rh_2Cl_2(\mu\text{-CO})_2(\mu\text{-dppa})_2] \quad (12)$$

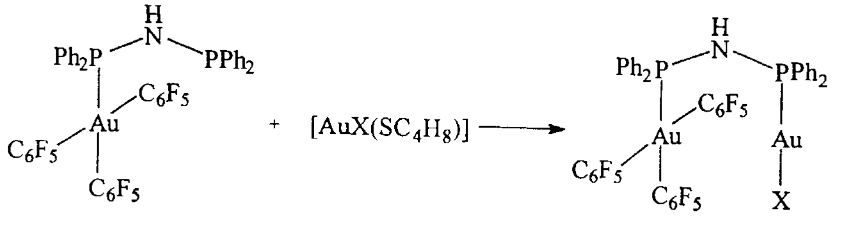
$$2\,[\mathrm{Re(CO)_5FBF_3}] + \mathrm{dppa} \rightarrow [\mathrm{Re_2(CO)_{10}}(\mu\text{-dppa})][\mathrm{BF_4}]_2 \qquad (13)$$

Heterobimetallics and mixed oxidation-state species can be derived from complexes containing a monodentate dppa ligand [eqs (14) and (15)],[41,62,63] their dppm analogues are available by similar routes.[63,64]



M = Pd or Pt

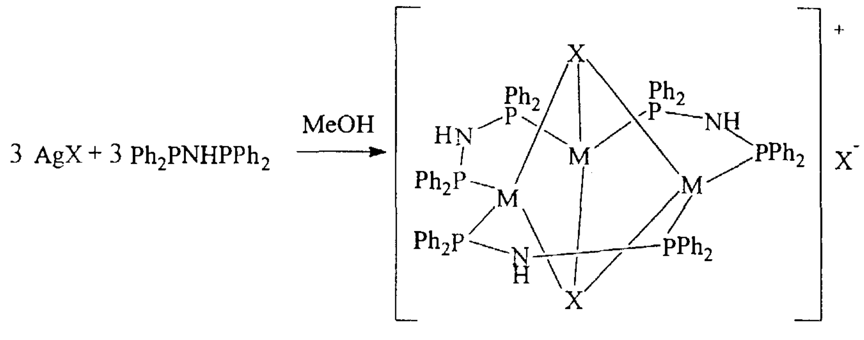
(14)



X = Cl or C_6F_5

(15)

The reaction of dppa with silver halides leads to trinuclear species, the only example of a cluster complex stabilized by this ligand [eq. (16)].[65]



X = Cl, Br or I

(16)

The dppm analogues were prepared by the same method for spectroscopic comparisons. The cations have a trigonal bipyramidal geometry, each diphosphine bridging two silver atoms in the equatorial plane with the halide ligands occupying capping positions. In view of the capacity of dppm to stabilize cluster units[5,7] it seems eminently reasonable that dppa will demonstrate the same capability.

Unusual products have been isolated from the treatment of $[\mathrm{AsPh_4}][\mathrm{ReOCl_4}]$ with dppa, which are dependent upon the conditions employed.[66] In wet chloroform, the rhenium(III) complex $[\mathrm{ReCl_3(H_2O)}\{\mathrm{Ph_2PNHP(O)Ph_2}\}]$ can be isolated, whilst the neutral rhenium(IV) species $2[\mathrm{ReCl_4}\{\mathrm{Ph_2PNHP(O)Ph_2}\}]\cdot\mathrm{Cl^-}\cdot[\mathrm{AsPh_4}]^+$ is generated in the anhydrous solvent. This latter compound undergoes deprotonation with an excess of dppa in anhydrous chloroform to give $[\mathrm{AsPh_4}][\mathrm{Re\,Cl_4}\{\mathrm{Ph_2PNP(O)Ph_2}\}]$. Crystallographic analysis of these complexes indicate that one phosphorus atom of dppa coordinates to the rhenium centre while the other becomes bound to the oxygen atom; hence, the ligand may be regarded as having formed the diphosphine monoxide. Deprotonation of the nitrogen atom of the $\mathrm{Ph_2PNHP(O)Ph_2}$ ligand results in an increase in the P—O distance and a shortening of the P—N bond lengths, indicating π-electron delocalization within the PNPO fragment. Phosphorus–oxygen bond formation also occurs in the reaction between $[\mathrm{ReOCl_3(PPh_3)_2}]$

and dppm, leading to $[ReCl_4\{Ph_2PCH_2P(O)Ph_2\}]$.[67] Attack on coordinated oxygen seems limited to the Re^V-oxo unit, no P—N bond formation is observed upon treatment of Re^V-imido or -nitrido complexes with either dppa or dppm [eqs (17) and (18)].[67,68]

$$[Re(NMe)Cl_3(PPh_3)_2]+(Ph_2P)_2XH \longrightarrow [Re(NMe)Cl_3(Ph_2PXHPPh_2)] \qquad (17)$$

$$[ReNCl_2(PPh_3)_2]+2(Ph_2P)_2XH \longrightarrow [ReNCl(Ph_2PXHPPh_2)_2]Cl$$
$$X = CH \text{ or } N \qquad (18)$$

It will be of interest to see whether attack on coordinated oxygen occurs for other high-valent metal-oxo species. In a similar vein, the reaction between dppa and $[Cr(CO)_4(CH_2SOMe_2)_2]$ leads to $[Me_3SO][Cr(CO)_4(CH_2PPh_2NPPh_2)]$, which contains an ylid with the atomic sequence CPNP,[69] while the reaction of $Ph_2PNRPPh_2$, (R = Me or Ph) with $[Cr(CO)_5(CH_2SOMe_2)]$ gives $[Cr(CO)_4(CH_2PPh_2NRPPh_2)]$.

5. HETEROCYCLE FORMATION

One line of research which merits further investigations is the generation of heterocycles from dppa (Fig. 4). The reaction of $Li[Ph_2PNPPh_2]$ with P_4 also falls within this category. The Et_3N-catalysed cyclocondensation of dppa with aminoimines leads to six-membered rings isoelectronic with cyclophosphazenes, with CCl_4 present as a source of chloride ions in these reactions.[70–72] Dppa reacts with (2-chloromethyl),3-chloroprop-1-ene to give a 2-azadiphospha-1,3-benzene after deprotonation of the intermediate cation by $Et_3P{=}CHMe$.[73] With gallium and aluminium trialkyls, dppa is deprotonated and becomes unsymmetrically coordinated in a six-membered ring [eq. (19)].[74]

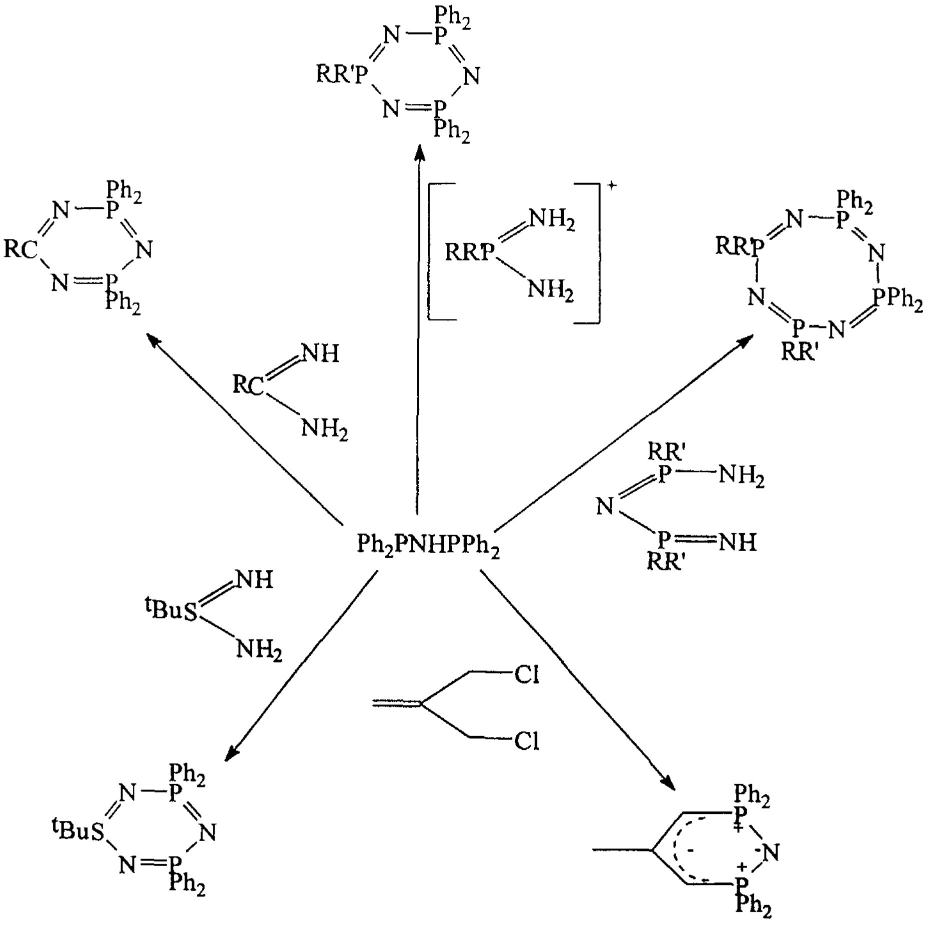
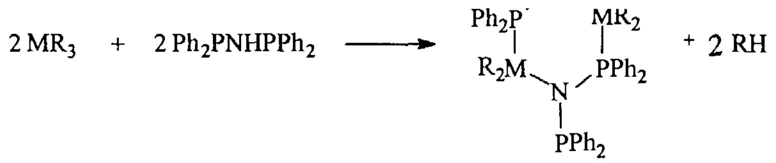


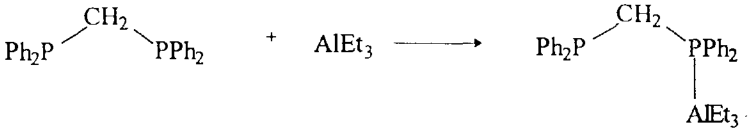
Fig. 4. Heterocycles derived from dppa



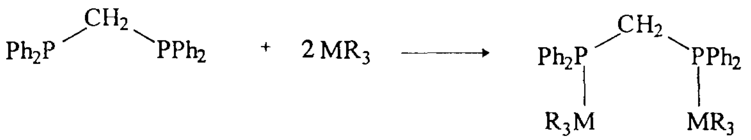
(19)

M = Al or Ga; R = Me or Et.

With the gallium compounds a symmetrical P,P coordinated isomer $[R_2Ga(\mu\text{-}Ph_2PNPPh_2)]_2$, containing an eight-membered ring is believed to be part of an equilibrium in solution. The crystal structure of the Me_2Al compound indicates that the ring exists in a twist conformation, with a trigonal planar configuration at the nitrogen atoms and exocyclic P—N lengths *ca* 0.05 Å longer than those within the ring. Simple adducts are the only products isolated from the corresponding reactions between dppm and metal trialkyls [eqs (20) and (21)].[75]



(20)



(21)

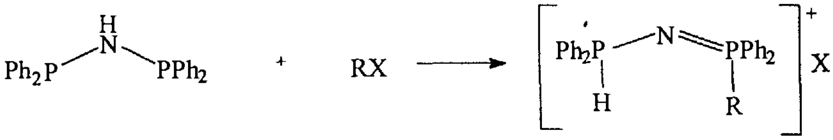
M = Al, $R_3 = Me_3$

M = Ga, $R_3 = Me_3$, Et_3 and Me_2Cl

This is quite unexpected considering the facile deprotonation on the methylene group of dppm by strong bases.

6. PROTOTROPISM

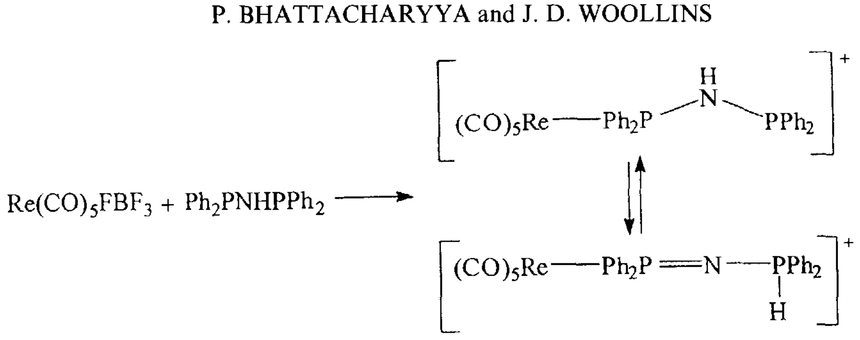
Phosphorus monoalkylation of dppa by $[Ph_3C][PF_6]$ or $MeSO_3CF_3$ leads to proton migration, prototropism within the cation, detectable by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy [eq. (22)].[76]



(22)

R = CPh_3 or Me

Prototropism is also observed upon alkylation of $Ph_2PNHP(Bu^t)_2$ by the same reagents, but not with $Ph_2PN(Me)PPh_2$ or dppm. To explain this selectivity it was suggested that formation of the phosphonium centre sufficiently reduced the basicity of the nitrogen atom below that of the remaining P^{III} atom to induce the proton to shift to the more basic site within the molecule. It was reasoned that the methylene protons of dppm were insufficiently acidic for prototropism to occur, whilst the methyl group of $Ph_2PN(Me)PPh_2$ would be oblivious to changes in basicity. Phosphorus-31 and ^1H NMR spectroscopy indicates that prototropism occurs in solution for $[Re(CO)_5(dppa)]^+$ [eq. (23)].[61]



(23)

In this instance η^1-coordination to the rhenium atom has a similar effect to alkylation. No evidence of a tautomeric equilibrium exists for any other complex containing monodentate dppa, so it is pertinent to ask why it has been observed in this case.

7. OXIDIZED DERIVATIVES OF $Ph_2PNHPPh_2$

Oxidation of both phosphorus(III) centres within dppa generates new ligands whose coordination chemistry resembles that of the corresponding molecules $Ph_2P(E)CH_2P(E)Ph_2$ [eqs (24)–(26)].[15,77]

$$Ph_2PNHPPh_2 \xrightarrow{H_2O_2} \underset{\mathbf{1}}{Ph_2P(O)NHP(O)Ph_2} \tag{24}$$

$$Ph_2PNHPPh_2 \xrightarrow{2E} Ph_2P(E)NHP(E)Ph_2$$

$$E = S(\mathbf{2})\ \text{or}\ Se(\mathbf{3}) \tag{25}$$

$$Ph_2PNHPPh_2 \xrightarrow[\text{(ii) } NH_3]{\text{(i) } Br_2} \underset{\mathbf{4}}{[Ph_2P({=}NH_2)NP({=}NH_2)]Br} \tag{26}$$

No ditelluride $Ph_2P(Te)NHP(Te)Ph_2$ is known. Compounds of this type are also accessible by condensation routes [eqs (27)–(29)].[78–81]

$$Ph_2P(S)NH_2 + Ph_2P(S)Cl \longrightarrow Ph_2P(S)NHP(S)Ph_2 \tag{27}$$

$$(RO)_2P(S)Cl + R'_2P(S)NH_2 \longrightarrow (RO)_2P(S)NHP(S)R'_2 \tag{28}$$

$$R = Me, Pr^i;\ R' = OMe, OPr^i\ \text{or}\ Ph$$

$$Me_2P(S)Br + Me_2P(S)NH_2 \longrightarrow Me_2P(S)NHP(S)Me_2 \tag{29}$$

Single crystal X-ray diffraction studies indicate that **2** and **3** are isostructural, with the P=E bonds oriented in *anti* positions and hydrogen-bonding interactions between P=E and NH groups of adjacent molecules responsible for dimer formation in the solid state [Figs 5(a) and (b)].[77,82] Several compounds based upon a P—NH—P backbone possess a similar structure.[83] In contrast, **1** exists in the solid state as the tautomer shown with a linear P—N—P arrangement, *syn*-P=O groups and a symmetrical intramolecular hydrogen bond [Fig. 5(c)].[84] Selected crystallographic data for these molecules are presented in Table 1.

For **1**–**3** the P—N bond lengths are significantly shorter than the sum of the covalent radii for phosphorus and nitrogen (1.80 Å), suggesting multiple bond character. Significant structural changes occur upon deprotonation. The potassium salt $K[(SPPh_2)_2N]$ has a *syn*-conformation of the SPNPS chain, with the sulphur atoms coordinating the cation.[85] Shortening of the P—N bonds and increases in the P—S lengths and N—P—S angles compared with the neutral molecule reflects increased electron delocalization within the anion. In the phosphazene cation $[Ph_2P(NH_2)—N—P(NH_2)Ph_2]Cl$, the terminal P—N bonds (1.66 and 1.64 Å) are distinctly longer than the internal lengths (1.57 and 1.58 Å) with a central PNP bond angle of 136°.[86]

The reaction of **1**–**3** with metal ions almost invariably leads to deprotonation of the NH group and E,E′ chelation of the anion to give complexes containing $[(EPPh_2)_2N]^-$ ligands, termed imidodiphosphinates. The alkali metal salts of the compounds have often been used instead of the neutral molecules. The anions can be considered to be inorganic analogues of β-diketonates $[R_2C(O)$

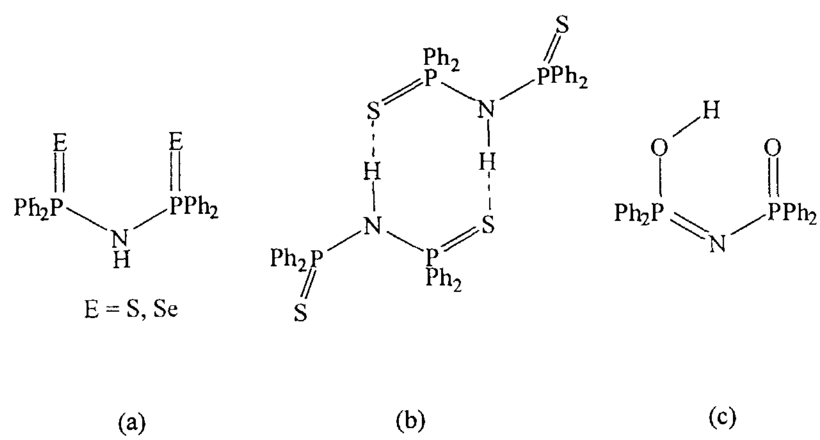


Fig. 5. (a) Molecular structure of $Ph_2P(E)NHP(E)Ph_2$, E = S, Se; (b) solid-state dimer formation in $Ph_2P(S)NHP(S)Ph_2$; (c) molecular structure of $Ph_2P(O)NHP(O)Ph_2$.

Table 1. Selected crystallographic data for dppa and its chalcogenides

		Lengths (Å)		Angles (°)	
	P—E	P—N	N—H	NPE	PNP
$(Ph_2P)_2NH$[83]	—	1.692(2)	0.977(4)	—	118.9(2)
1[84]	1.519(2)	1.535(1)	—	116.69(8)	180.0
2[84]	1.950(1)	1.671(2)	0.807(20)	114.73(7)	132.62(11)
	1.936(1)	1.684(2)		115.53(7)	
3[77]	2.101(1)	1.686(3)	0.94	116.1(1)	132.3(2)
	2.085(1)	1.678(4)		114.5(1)	
$K[(SPPh_2)_2N]$[85]	1.978(1)	1.592(2)	—	120.7(1)	128.6(2)

$CHC(O)R_2]^-$ (R = alkyl or aryl), widely used in coordination chemistry.[87,88] The dioxo- and dithioimidodiphosphinates, complexes of which are known for most of the transition metals and several main group elements,[7,89–92] have been more extensively studied than their selenium analogue. Crystallographic analysis of complexes containing imidodiphosphinate ligands indicates that the rings are free to take up quite varied conformations, but planarity is not observed. An increase in electron delocalization within the EPNPE chain upon deprotonation seems responsible for the acidity of the amine proton in $(EPPh_2)_2NH$ (Fig. 6).

The preference for linear coordination of Au^I centres ensures that a bridging geometry of the $[(SPPh_2)_2N]^-$ ligand is adopted in $[Au_2\{\mu\text{-}(SPPh_2)_2N\}_2]$.[43,45,93] Both bidentate bridges and chelate rings exist in $[Cu_4\{(SPPh_2)_2N\}_3][CuCl_2]$, obtained from $CuCl_2 \cdot 2H_2O$ and $Na[(SPPh_2)_2N]$.[94] The tetramethyl ligand $(SPMe_2)_2NH$[95–97] and the related imidodiphosphonates $[EP(OR')_2]_2NH$, (R′ = alkyl or aryl; E = O or S)[98–100] have a similar chemistry to their tetraphenyl analogues, with E,E′

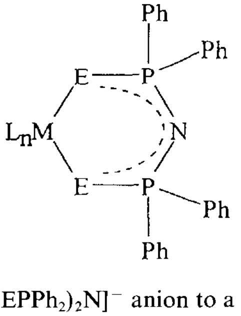
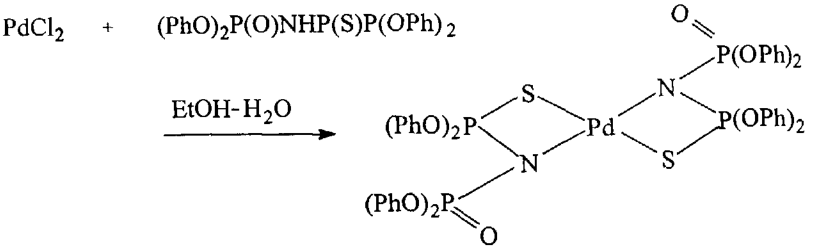


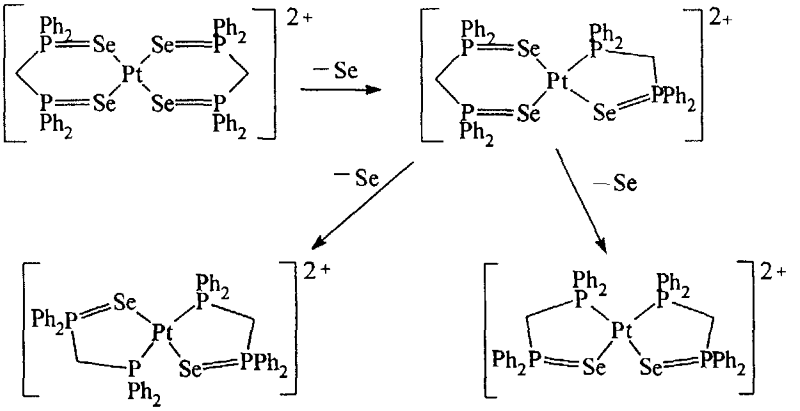
Fig. 6. Coordination of the $[(EPPh_2)_2N]^-$ anion to a metal centre (E = O, S or Se).

chelation the favoured mode of coordination. Uniquely, $(PhO)_2P(O)NHP(S)(OPh)_2(LH)$ functions as a S,N chelate in the complex $[PdL_2]$, with the phosphoryl groups pendant [eq. (30)].[101]



(30)

A handful of rhenium(V)-imido and -nitrido complexes containing $[(SePPh_2)_2N]^-$ ligands exist.[68] The Re^V-oxo compound $[ReOCl\{(SePPh_2)_2N\}_2]$, generated by the reaction of either $[ReOCl_3(PPh_3)_2]$ or $[AsPh_4][ReOCl_4]$ with $K[(SePPh_2)_2N]$, is unstable in $CHCl_3$, losing one selenium atom per ligand to give $[ReOCl\{Ph_2PNP(Se)Ph_2\}_2]$.[102] Recrystallization from CH_2Cl_2–ethanol gave the ethoxo derivative $[Re(O)(OEt)\{Ph_2PNP(Se)Ph_2\}_2]$, the crystal structure of which revealed two approximately planar five-membered metallacycles with the selenium atoms *trans* to each other. The instability of $[Re(O)Cl\{SePPh_2)_2N\}_2]$ is attributed to the "hard" nature of the $[Re{=}O]^{3+}$ core favouring donors of a similar character. Selenium extrusion from a Pt—Se—P bond has been observed in one case for the $(SePPh_2)_2CH_2$ ligand [eq. (31)].[103]



(31)

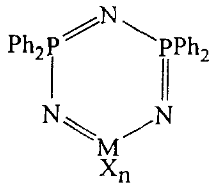
Imidodiphosphonates $(PhO)_2P(X)NHP(Y)(OPh)_2$ (X, Y = O or S; X = O, Y = S) show potential as metal extractants.[98–100] Benzene solutions of these ligands extract ions such as Ag, Sc, Hg, Yb, Hf, Au or Pd from acidic aqueous media by behaving as weak acids in the aqueous phase, giving metal complexes soluble in the organic phase. The observed cation selectivity was found to be dependent upon the chalcogens X and Y. The relatively straightforward syntheses of such molecules may permit "tailoring" of these ligands to obtain metal selectivity, by variation of the substituents at the P^V centres.

The coordination chemistry of $[Ph_2P(NH_2)—N—P(NH_2)Ph_2]X$ (**4**) (X = Cl or Br) is similar in many respects to that of **1**–**3**. Reaction of **4** with metals in high oxidation states proceeds with loss of four protons to give cyclometallaphosphazenes containing the $[Ph_2P(N)NP(N)Ph_2]^{3-}$ anion, coordinated through the terminal nitrogen atoms (Fig. 7), a field pioneered by Herbert Roesky and co-workers.[104–106]

Cyclometallaphosphazenes are prone to exchange and rearrangement reactions in which the coordinated nitrogen atoms are replaced by oxygen, particularly when treated with sterically demanding alcohols [eq. (32), 1.33].[107,108]

$$[MoCl_3\{Ph_2P(N)NP(N)Ph_2\}] \xrightarrow{Ph_3SiOH} [Mo(O)_2Cl_2\{(OPPh_2)_2NH\}] \qquad (32)$$

$$[VCl_2\{Ph_2P(N)NP(N)Ph_2\}] \xrightarrow{Bu^tOH} [VO\{(OPPh_2)_2N\}_2] \qquad (33)$$



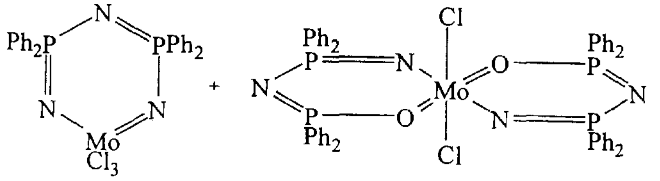
M = Mo(VI), Nb(V), W(VI), V(V) or Re(VII);

X = halogen

Fig. 7. Coordination of the $[(NPPh_2)_2N]^{3-}$ anion to a metal centre.

The reaction of $MoOCl_4$ with **4** leads to a mixture of products, which are separable by fractional crystallization [eq. (34)].[107]

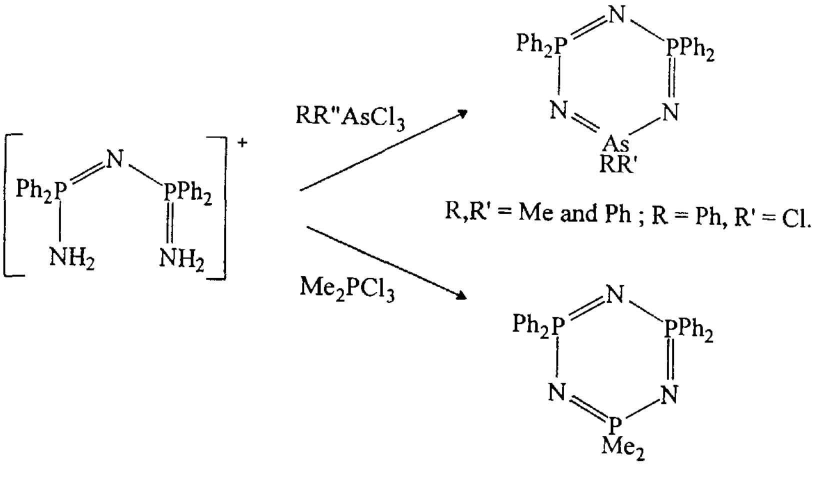
$$2\,MoOCl_4 + 2\,[Ph_2P(NH_2)NP(NH_2)Ph_2]Cl \xrightarrow{CHCl_3}$$



(34)

The crystal structure of the N,O bonded product indicates that the rings are coplanar; it is also notable that the ^{31}P NMR spectrum contains only singlets, where a more complicated pattern would be expected.

Cyclophosphazenes resembling those obtained from cyclocondensation of dppa are generated by the reaction of **4** with P^V and As^V chlorides [eq. (35), 1.36].[109,110]



R,R' = Me and Ph ; R = Ph, R' = Cl.

(35)

(36)

8. COMPARATIVE BEHAVIOUR OF $(EPPh_2)_2XH$, X = CH OR N

The acidity of the amine proton in $(EPPh_2)_2NH$ creates a major difference between the chemistry of these molecules and their methylene analogues $(EPPh_2)_2CH_2$ (E = chalcogen). Whereas E,E′ chelation is widely observed for $(EPPh_2)_2CH_2$,[94,111–115] further coordination modes exist for the anion $[(EPPh_2)_2CH]^-$, for which sufficient electron density resides at the bridging carbon atom to allow further metallation at this site (Fig. 8).

Treatment of metal complexes containing strongly basic ligands with $(EPPh_2)_2CH_2$ gives rise to the E,E′ coordinated monoanion,[43,44,116] whilst double deprotonation of the methylene group occurs during the reaction of $(SPPh_2)_2CH_2$ with $[Pt(\mu\text{-}Cl)(MeOcod)]_2$, finally leading to

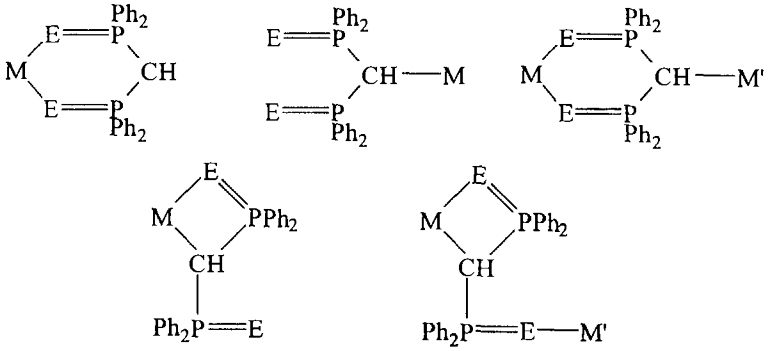
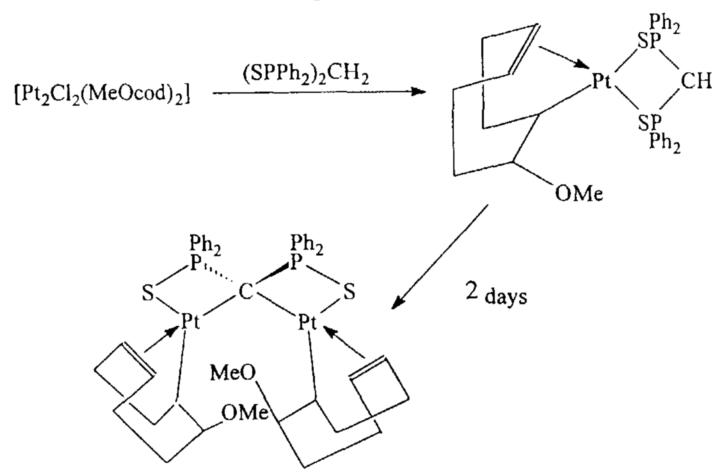


Fig. 8. Coordination modes of the $[(EPPh_2)_2CH]^-$ anion (E = O, S or Se).

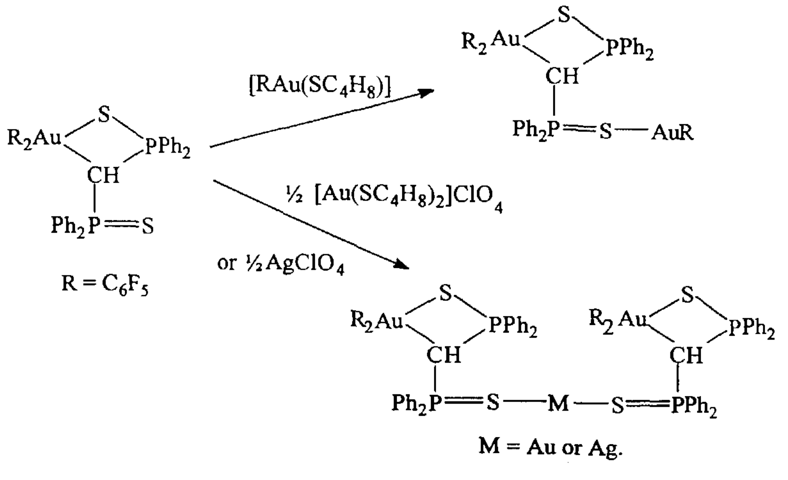
$[Pt_2\{Ph_2P(S)CP(S)Ph_2\}(MeOcod)_2]$ [eq. (37)].[117] X-ray analysis reveals the dianion bridges between both platinum atoms in addition to acting as a C,S chelate to each metal.



(37)

Treatment of $[Au(acac)(PPh_3)]$ with $(SPPh_2)_2CH_2$ leads to $[Au(PPh_3)\{CH(PPh_2S)_2\}]$ and $[(Ph_3P)Au\{Ph_2P(S)CP(S)Ph_2\}Au(PPh_3)]$, in which coordination to the Au^I atoms is solely through the methanide carbon of the anion.[45] Similarly, $[(OPPh_2)_2CH]^-$ functions as a C-donor to Pd^{II} and Pt^{II} centres.[118,119]

Where the methanide carbon and one E atom are bound to the same metal centre to generate a C,E chelate, fluxional behaviour involving exchange between the free and coordinated P=E groups is often detected by ^{31}P NMR spectroscopy.[119,120] The pendant P=E group can coordinate to another metal centre, generating polymetallic complexes [eq. (38)].[94,121] Thus, the coordinative repertoire of $[(EPPh_2)_2CH]^-$ is more varied than the simple E,E′ coordination of the nitrogen-bridged anions $[(EPPh_2)_2N]^-$.



(38)

9. NEUTRAL LIGANDS

Although deprotonation may appear integral to the reactivity of **1**–**3**, adducts containing the undissociated molecules do exist. Adding chloroform solutions of **2** to $ZnCl_2$ or $CuBr_2$ in boiling ether gives $[ZnCl_2\{(SPPh_2)_2NH\}]$ and $[CuBr_2\{(SPPh_2)_2NH\}]$, respectively, whilst the reaction with $K_2[PdBr_4]$ in acidified acetone leads to $[PdBr_2\{(SPPh_2)_2NH\}]$.[122] The sensitivity of these adducts is such that boiling in methanol is sufficient for dissociation of the amine proton from these complexes. The reaction of metal dihalides MX_2 (M = Pd or Pt; X = Cl, Br or SCN) with **2** yielded only one complex containing the undissociated ligand, with $PdBr_2$. With the other salts used, dissociation of the NH proton could not be suppressed even where relatively large amounts of acid had been added. Adduct formation is not limited to **2**. Neutral moisture-sensitive Ti^{IV} and V^{IV} adducts have been obtained with $(SPMe_2)_2NH$,[123] while protonation of the nitrogen atom in $[SnX_2\{(OPPh_2)_2N\}_2]$ (X = halide) by $HClO_4$ gives the corresponding cation without disruption of the complexes.[124]

10. MONO-OXIDIZED DERIVATIVES OF DIPHOSPHINOAMINES

The mono-oxidized molecules $Ph_2PCH_2P(E)Ph_2$ (E = chalcogen or imine) and their anions possess a rich coordination chemistry. P,E chelation,[113,125–127] bidentate bridging[128,129] and monodentate[130] coordination of these ligands to metal centres have been reported. In addition metallation at the methanide carbon atom of the coordinated anion has been achieved (Fig. 9).[131] In contrast, the coordinative potential of mono-oxidized diphosphinoamines has not been fully realized. Synthesis, as with the dioxidized molecules, can be accomplished by direct oxidation[132,133] or condensation[134] [eqs (39)–(41)].

$$Ph_2PN(Ph)PPh_2 + E \longrightarrow Ph_2PN(Ph)P(E)Ph_2 \tag{39}$$

$$(RO)_2PN(R')P(OR)_2 + E \longrightarrow (RO)_2PN(R')P(E)(OR)_2 \tag{40}$$

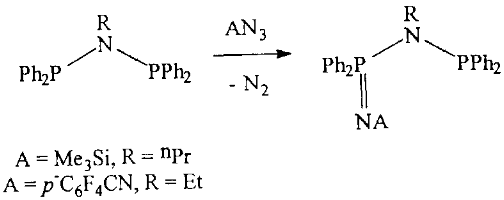
$$(R, R' = \text{alkyl or aryl}) \qquad E = S \text{ or } Se$$

$$Ph_2PN(Me)SiMe_3 + XCl \longrightarrow Ph_2PN(Me)X$$

$$X = PCl_2, PPh_2, P(O)Cl_2 \text{ or } P(S)Ph_2 \tag{41}$$

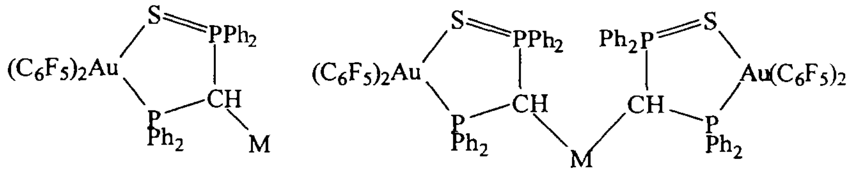
The pentaphenyl molecules of eq. (39) form simple five-membered chelates with Mo^0, W^0, Rh^I, Pt^{II} and Pd^{II} centres, in which the P^{III} and chalcogen atoms are coordinated to the metal.[132] The X-ray crystal structure of $[PtCl_2\{Ph_2PN(Ph)P(S)Ph_2\}] \cdot H_2O$ reveals a trigonal-planar nitrogen atom with N—P^{III} and N—P^V lengths of 1.737 and 1.674 Å, respectively.

Diphosphinoamines undergo limited monoxidation by azides [eq. (42)].[135] From the limited structural details published to date, it is apparent that the P^{III}—N—P^V angle is close to 120°, whilst the bond lengths are in the order P^{III}—N(bridge) > P^V—N(bridge) > P^V=N(terminal).



A = Me_3Si, R = ^nPr
A = p-C_6F_4CN, R = Et
A = $P(O)(OPh)_2$, R = Me or Et

(42)



M = Au(I) or Ag(I) M = Au(I), Ag(I) or Au(III)

Fig. 9. C-metallation of coordinated $[Ph_2PCHP(S)Ph_2]^-$.

Little has appeared on the mono-oxidized derivatives of dppa. Coordinated $Ph_2PNHP(O)Ph_2$ and $[Ph_2PNP(E)Ph_2]^-$, E = O or Se, have of course been derived unexpectedly as mentioned earlier,[67,102] indicating that the acidity of the amine proton is intermediate between that of dppa and the fully oxidized molecules. In the presence of $AlCl_3$, dppa is oxidized by elemental sulphur to $Ph_2PNHP(S)Ph_2$.[136] In this instance the compound was further alkylated at the P^{III} centre by organic halides RX (RX = alkyl or aryl) under basic conditions to generate thiophosphinoamides $Ph_2P(S)N{=}P(R)Ph_2$, which possessed fungicidal activity against *Pseudoperonospora cubensis*.

11. NMR STUDIES

The NMR spectral parameters of diphosphinoamines have been widely investigated. Low-temperature ^{31}P NMR and multiple resonance experiments suggest that for the free molecules, the magnitude and sign of $^2J(^{31}P{-}^{31}P)$ is related to the proportions of the conformers of Fig. 10.[137] Here the symmetries relate to the PNP skeleton, not to the X and R groups. The nitrogen atom is trigonal planar, with its lone pair orthogonal to those on the phosphorus atoms. Steric interactions prevent conformers of C'_{2v} symmetry from participating to any significant extent in conformational equilibria. The C_s conformer is associated with low (negative) values of $^2J(^{31}P{-}^{31}P)$, whereas the C_{2v} conformer gives rise to large positive values. For symmetrical molecules $R_2PN(X)PR_2$ (R = H or alkyl; X = Ph, Cl, F or NMe_2), values of $^2J(^{31}P{-}^{31}P)$ lie between −23.9 Hz for $Ph_2PN(Pr^i)PPh_2$ and +731.9 Hz for $F_2PN(Bu^t)PF_2$.[137] $^1H\text{-}\{^{31}P\}$ NMR experiments indicate that bulky substituents at the phosphorus atoms increase the magnitude of $^2J(^{31}P{-}^{31}P)$, whereas the opposite effect is observed upon increasing the size of the nitrogen substituents.[138,139] Presumably this is a result of the predominance of one conformation over the other due to steric interactions between the X and R groups. X-ray diffraction studies reveal that the molecular conformation favoured in solution at low temperatures is close to that found in the solid state. Thus, $Ph_2PN(Pr^i)PPh_2$, *erythro*-$(Pr^i)N[PhP(Pr^iNH)][PhP(EtNH)]$, *meso*-$(Pr^i)N[PhP(Pr^iNH)]_2$ and *meso*-$(Pr^i)N[PhP(PhNH)]_2$, for whom $|^2J(^{31}P{-}^{31}P)|$ lies in the range 15.9–23.9 Hz, all possess a C_s conformation in the solid state.[137,140]

Oxidation of diphosphinoamines leads to a reduction in the range of magnitudes observed for $^2J(^{31}P{-}^{31}P)$. Typical magnitudes for $P^{III}{-}P^V$ couplings are from 78 Hz for (Me)(Ph)PN(Me)P(S)(Me)(Ph)[19] to 126 Hz for $Cl_2PN(Ph)P(S)Cl_2$,[142] whilst $P^V{-}P^V$ couplings of between 11 and 43 Hz[141–143] in magnitude have been reported.

Evidently, $^2J(^{31}P{-}^{31}P)$ is sensitive to the electronegativity of the substituents, the effect of steric bulk on conformational preferences for the oxidized molecules an additional factor. Coordination to a metal centre also affects this coupling. Chelation in particular locks the molecule into a C_{2v} type conformation whilst providing an additional pathway for coupling of the phosphorus nuclei, through the metal atom. Another effect generally accompanying chelation is a coordination shift to low frequency in the ^{31}P NMR. This is not universal, a point clearly demonstrated by the Group VI metal carbonyls $[M(CO)_4(dppa)]$, M = Cr, Mo or W, for whom shifts to high frequency of 54.1, 27.5 and 3.6 ppm, respectively, are noted, cf. $(Ph_2P)_2NH$ $\delta(P)$ 42.1 ppm.[144] Analogous low-frequency

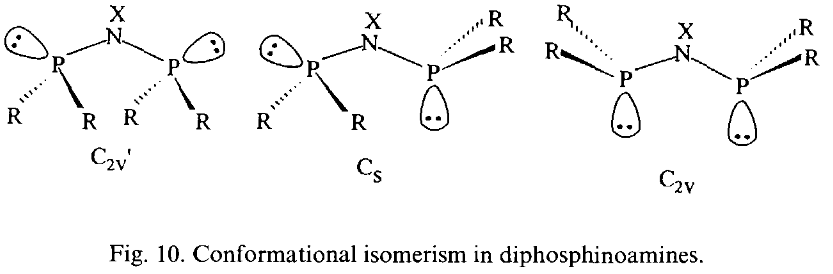


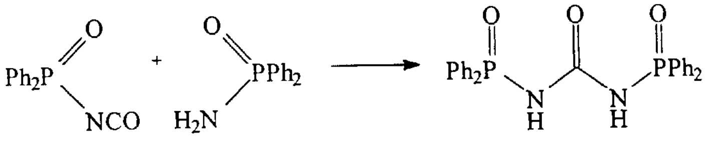
Fig. 10. Conformational isomerism in diphosphinoamines.

shifts for dppm upon the formation of four-membered metallacycles is attributed to distortions around the phosphorus atoms.[145]

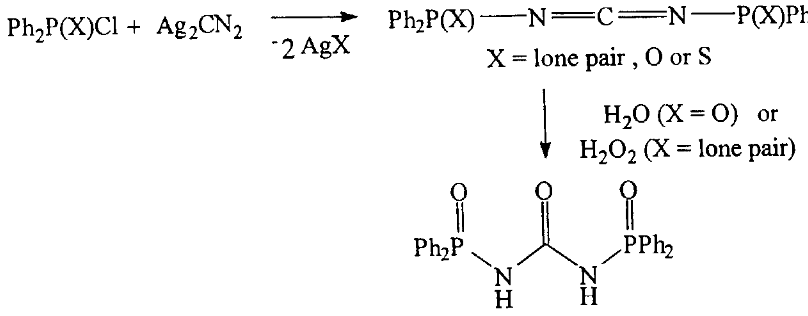
12. OTHER P—N LIGANDS

The principal route to diphosphinoamines, outlined in Section 2, is the condensation of chlorophosphines with primary amines, or their trimethylsilyl derivatives. By a similar methodology, phosphorus-substituted derivatives of urea and thiourea can be prepared. Extending the analogies to diphosphinoamines a little further, oxidation of the P^{III} centres produces new series molecules which are expected to have their own rich coordination chemistry, in much the same way that the reactivity of dppa is modified upon formation of its chalcogenides. The following brief overview of phosphorus-containing derivatives of urea and thiourea will concentrate on the chemistry of acyclic mono- and diphosphine derivatives. Cyclic molecules such as diazaphosphetidinones and -thiones (A), spiro compounds (B), triazaphosphinanediones (C), diazaphosphorinanones (D) (Fig. 11) and compounds containing P—P bonds will not be considered here.

The earliest reports of diphosphines based upon a urea skeleton date back to the mid 1960s, derived by condensation of isocyanates with a phosphinic amide[146] or via phosphorus-substituted carbodiimides[147] [Eqs (43) and (44)].



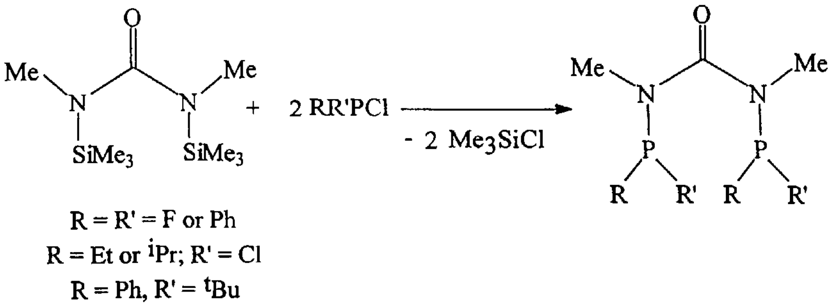
(43)



(44)

The carbodiimide $Ph_2P—N=C=N—PPh_2$, stable only as its silver halide complex, undergoes oxidation by sulphur in CS_2 to produce $Ph_2P(S)—N=C=N—P(S)Ph_2$; surprisingly hydrolysis, which would presumably lead to $Ph_2P(S)—NHC(O)NH—P(S)Ph_2$ was not attempted.

Following these early efforts this field became dormant until the 1980s, when silylated compounds became the precursor of choice for the preparation of diphosphines. Organophosphine-substituted derivatives of urea are readily accessible from N,N′-bis(trimethylsilyl)-N,N′-bis(dimethyl)urea [eq. (45)].[148–150]



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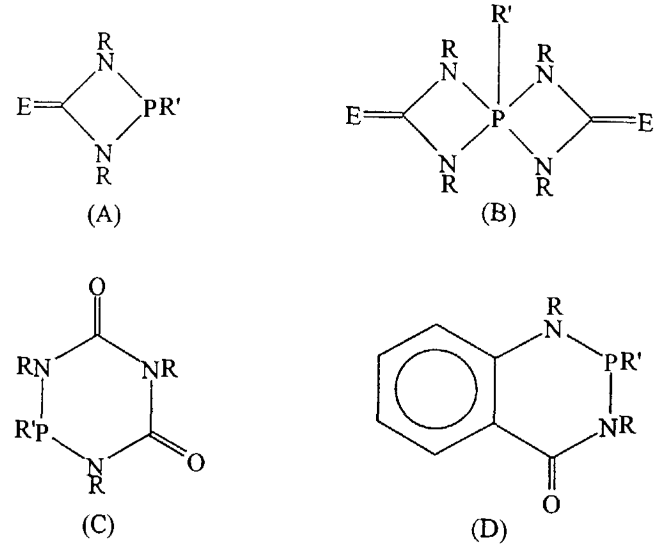
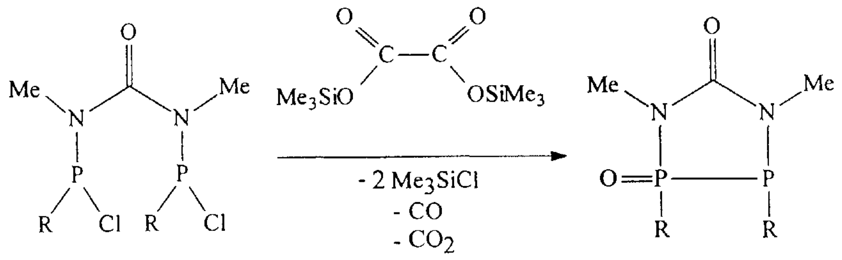


R, R' = alkyl or aryl; E = O or S

Fig. 11. Cyclic derivatives of urea and thiourea.

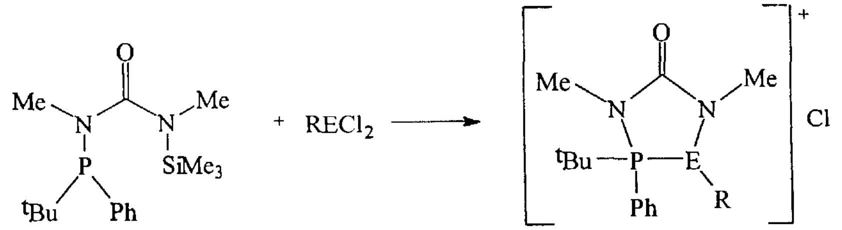
Dehalogenation of P-chloro substituted compounds with the bis(trimethylsilyl) ester of oxalic acid leads to mixed-valence heterocycles containing a P—P bond [eq. (46)].[148,149]



(46)

R = Me, Et, ^{i}Pr or Ph

Similar heterocycles can be constructed in a stepwise fashion [eq. (47)].[151]

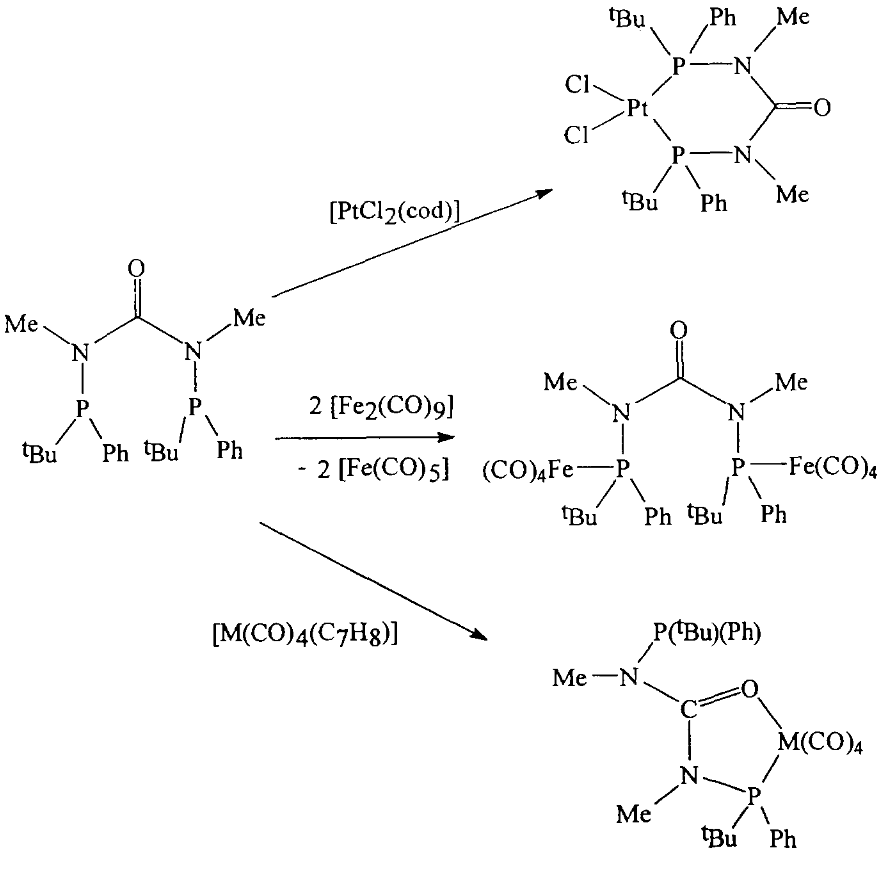


(47)

E = P or As; R = alkyl or aryl

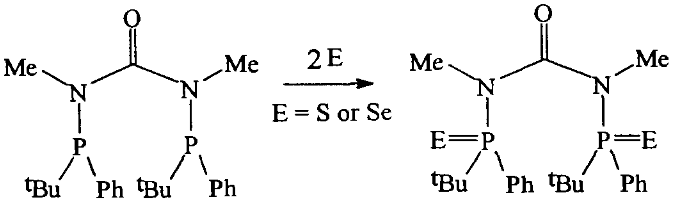
Reports of metal complexes containing linear diazaphosphapentanone ligands are few and far between. Simple P,P′ chelation of the difluorophosphine-substituted urea [(PF$_2$)NR]$_2$CO (R = H or alkyl) to Ni^0, Mo^0, Rh^I and Ir^I centres leads to six-membered chelate rings.[152,153] In contrast, [(Bu^t)(Ph)NMe]$_2$CO is more versatile [eqs (48–50)].[150] The difference in behaviour between the two presumably arises from the different basicity of the phosphorus centres in each molecule, and upon the flexibility of the skeleton. Oxidation of [(Bu^t)(Ph)NMe]$_2$CO by elemental sulphur or selenium leads to the corresponding disulphide and diselenide [eq. (51)].[150]

The chemistry of diphosphine-substituted thioureas is largely unexplored to date, owing to the difficulties associated with the formation of these molecules. Neither base-catalysed condensation or use of trimethylsilyl derivatives are completely satisfactory [eqs (52)–(56)].[154–156] Tautomerization of the thiourea is proposed to account for the different molecules obtained in eqs (54) and (55). Presumably steric effects associated with the phosphorus substituents are enough to dictate the stereoselectivity of these reactions. The formation of tetraphenyldiphosphine monosulphide [eq. (56)] is attributed to carbodiimide elimination from the C=N isomer [eq. (57)].[157]



M = Cr, Mo or W

(48)
(49)
(50)



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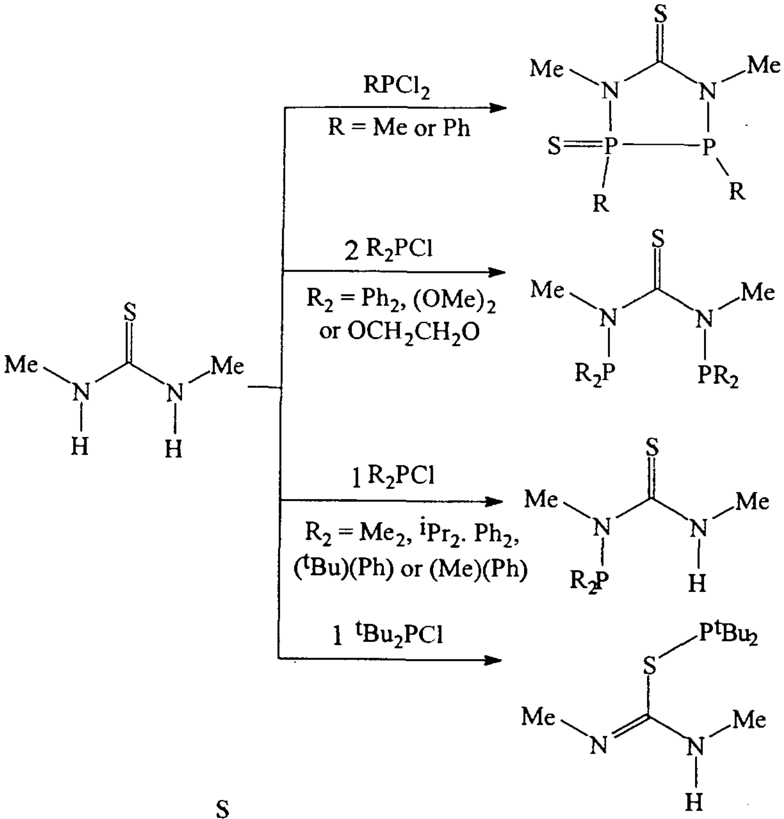

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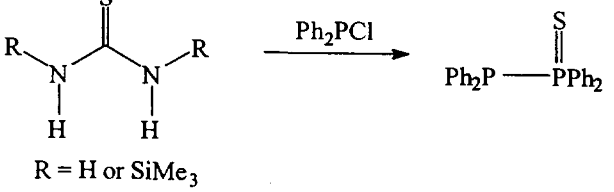

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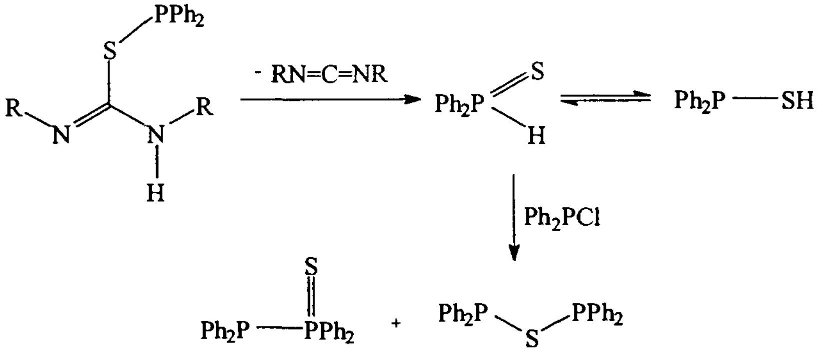

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