New main group ligands for complexation with transition and inner transition elements

S S KRISHNAMURTHY

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Abstract. Symmetrical and unsymmetrical diphosphinoamines of the type $X_2PN(R)PX_2$ and $X_2PN(R)YY'$ offer vast scope for the synthesis of a variety of transition metal organometallic complexes. Diphosphinoamines can be converted into their dioxides which are also accessible from appropriate (chloro)phosphane oxide precursors. The diphosphazane dioxides form an interesting series of complexes with lanthanide and actinide elements. Structural and spectroscopic studies have been carried out on a wide range of transition metal complexes incorporating linear P–N–P ligands and judiciously functionalized cyclophosphazanes and cyclophosphazenes.

**Keywords.** P–N–P framework ligands; transition metal complexes; diphosphinoamines.

1. Introduction

Tertiary phosphanes play a key role as ancillary ligands in organometallic chemistry and stabilize a variety of complexes formed by transition metals in their low-oxidation states. The metal–phosphorus bond has both σ- and π-components. Traditionally the empty phosphorus $3d$-orbitals have been implicated in π-back donation from metal to phosphane ligands. Recent theoretical studies, however, indicate that the acceptor orbital on the phosphorus is primarily a P–X σ^* orbital and the $3d$-orbitals of phosphorus play only a minor role in influencing the π-acidity of the phosphane ligand (Reed and Schleyer 1990; Fantucci 1992; Pacchioni and Bagus 1992). Either model would predict an enhanced M–P π-bonding if the substituents attached to phosphorus become highly electronegative as in PF_3. Compared to monophosphanes, diphosphanes such as the diphosphanoalkanes $R_2P(CH_2)_nPR_2$ ($n = 1, 2$) display rich and varied transition metal chemistry. However, it is not easy to modify these ligand systems by varying the substituents attached to phosphorus and carbon. On the other hand, a more extensive range of ligands with the prospect of fine-tuning their π-acidity and steric bulk can be realized with the non-carbon bridged phosphorus–nitrogen ligand systems, $X_2P–(NR)_n–PX_2$ ($n = 1, 2$) (Balakrishna et al 1994; Katti et al 1995; Mague 1995). Continuing our interest in the transition metal chemistry of phosphorus–nitrogen ligands (Balakrishna et al 1994), we have turned our attention in recent years to the synthesis of unsymmetrically substituted and chiral diphosphazanes and their transition metal complexes as well as the transition metal chemistry of cyclic P–N compounds. We have also synthesized several linear diphosphazane dioxides and studied their complexes with f-block elements. A review of our recent results is presented in this paper.
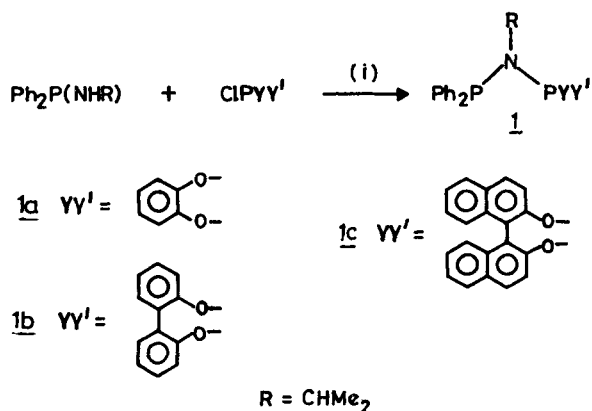
Scheme 1.   (i) Et_3N/toluene/0°C.
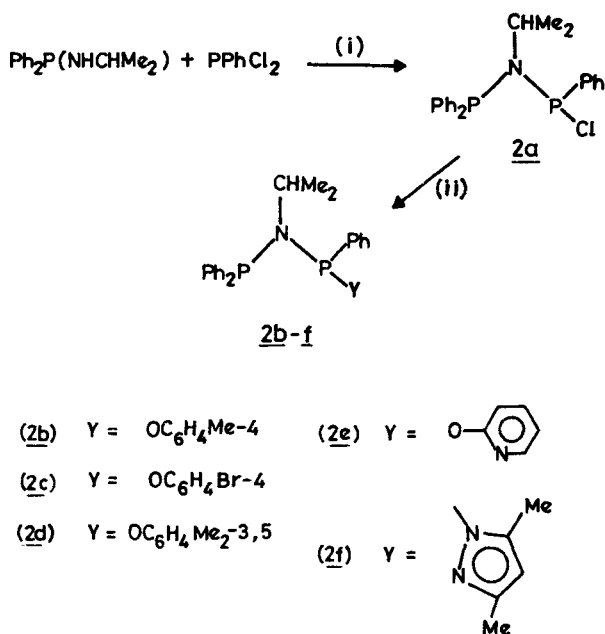
Scheme 2.   (i) Et_3N/toluene/25°C; (ii) YH/Et_3N/toluene/0°C.

2.   Synthesis of heterofunctional and chiral diphosphazenes

Unsymmetrically substituted diphosphazanes of the type $X_2PN(R)PYY'$ ($\underline{1}$) are readily accessible by a condensation reaction between a chlorophosphane $ClPYY'$ and an (amino)diphenyl phosphane, $Ph_2P(NHR)$, as shown in scheme 1. Another approach for unsymmetrically substituted diphosphazanes is the nucleophilic substitution of chlorine from $Ph_2PN(Pr^i)PPhCl$ ($\underline{2a}$) readily prepared by the reaction of $Ph_2P(NHPr^i)$ with $PhPCl_2$. This methodology is illustrated in scheme 2. The use of $Ph_2P(NHR)$ ($R = S$-$CHMePh$) derived from S-α-methyl benzylamine in the above
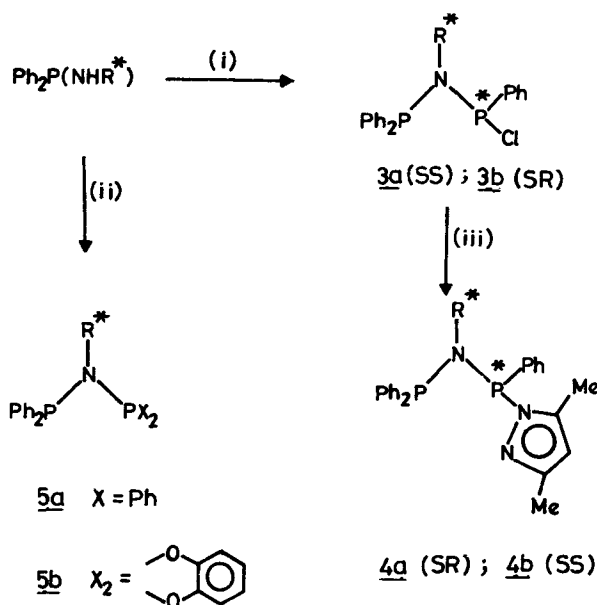
Scheme 3. (i) $PhPCl_2/Et_3N/toluene/0°C$; (ii) $X_2PCl/Et_3N/toluene/0°C$; (iii) 3,5-$HN_2C_3HMe_2/Et_3N/toluene/0°C$.

condensation reaction results in the formation of a pair of diastereomeric diphos-phazanes 3a and 3b. Treatment of 3a/3b with dimethyl pyrazole gives the heterofunc-tional chiral diphosphazane 4a/4b (scheme 3). The less abundant diastereomer 4a has been separated by fractional crystallization and its structure established by X-ray crystallography. It turns out to be the *SR*-diastereomer; consequently the more abundant diastereomer is assigned the *SS*-configuration. Some of these diphos-phazanes (e.g. 2e, 2f and 4a/b) contain a "hard" nitrogen donor site in addition to the two phosphorus centres and can function as potential tridentate ligands. Variable temperature ^{31}P NMR measurements on 1a, 2b and 2e show that at least two conformers are present in solution (Babu *et al* 1995a, b).

3. Transition metal chemistry of unsymmetrical and chiral diphosphazanes

Unsymmetrical diphosphazanes form chelate complexes of the type $[Mo(CO)_4L]$ (L = 1a, 1b, 2b–2f) and $[PdCl_2L]$ (L = 1b, 1c, 2b–2d, 2f). The ^{31}P NMR chemical shifts of the Mo(O) complexes occur downfield to those of the free ligands. Typically, the PPh_2 phosphorus resonance lies in the region 40·6 to 46·9δ whereas the extent of downfield shift for the other phosphorus nucleus (PYY') decreases with increasing electronegativity of Y and Y' (Babu and Krishnamurthy 1994). On the other hand, the ^{31}P chemical shifts for the Pd(II) complexes generally move upfield and the extent of shielding decreases in the order $O_2P-N > OCP-N > NCP-N > CCP-N$. The PPh_2 phosphorus is shielded to a lesser extent (3·6–12·8δ) for the complexes of 2b, 2c, 2d and 2f and is even slightly deshielded (15·7 and 15·9 ppm) for the complexes of 1b and 1c for which the highest shielding ($\delta_{complex} - \delta_{ligand} = -83·7$ and $-80·8$) is observed for the PO_2 phosphorus. The two-bond P–P coupling constants are the highest for the Mo(O)

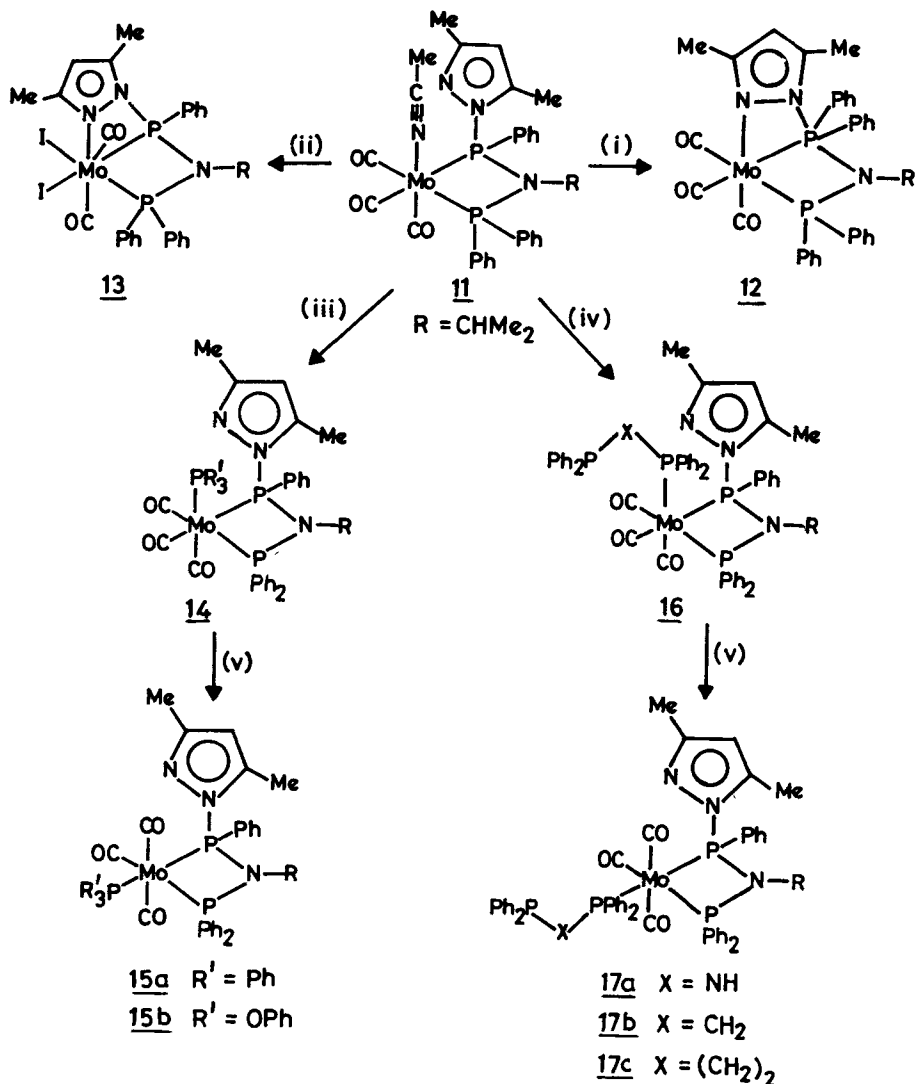6a Y = Ph , Y' = OC$_6$H$_4$Me-4

6b Y = Ph, Y' = OC$_6$H$_3$Me$_2$-3,5

R = CHMe$_2$

8

7a Y = Ph , Y' = OC$_6$H$_4$Me-4

7b Y = Ph, Y' = OC$_6$H$_3$Me$_2$-3,5

9   +   10
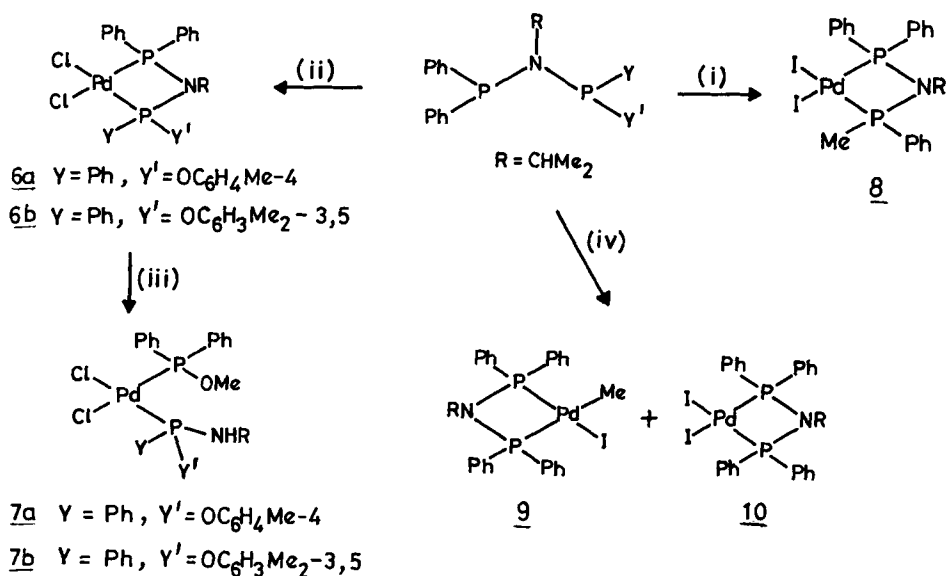
Scheme 4. (i) [Pd$_2$(dba)$_3$]·CHCl$_3$ + MeI/toluene/− 70°C (Y = Ph, Y' = OC$_6$-H$_4$Me-4 or 3,5-dimethyl pyrazolyl); (ii) PdCl$_2$(COD)/CH$_2$Cl$_2$; (iii) MeOH/25°C/24 h; (iv) Pd$_2$(dba)$_3$·CHCl$_3$ + MeI/toluene/− 70°C (Y = Y' = Ph).

and Pd(II) complexes of 1b (33 and 31 Hz respectively) while they are in the range 15·8–19·0 Hz for the Mo(O) complexes of 2b–2d and 17–18 Hz for the Pd(II) complexes of the same ligands. Electronic factors seem to play a dominant role in determining the ^{31}P chemical shifts although the presence of a four-membered ring is a major factor as evident from the considerable downfield shift of the ^{31}P resonances for the complexes (7a, 7b) resulting from the cleavage of the four-membered ring (see below).

The Pd(II) complexes (6a, 6b) undergo a facile P–N bond cleavage in methanol to yield the complexes [PdCl$_2${η^1–Ph$_2$P(OMe)} {η^1–PhP(NHPr^i)Y'}] Y' = OC$_6$H$_4$Br–4 or OC$_6$H$_3$Me$_2$–3,5) (7a, 7b) (scheme 4). Reaction of 2b or 2d with Pd$_2$(dba)$_3$·CHCl$_3$ (dba = dibenzeylidene acetone) in the presence of methyl iodide gives cis-[PdI$_2$(η^2–Ph$_2$PN(Pr^i)PPhMe) (8) as the major product formed as a result of the cleavage of the P–N (pyrazolyl) or P–O bond and the formation of a P–C (Me) bond accompanied by the oxidation of the metal from zero to the divalent state. Under the same reaction conditions, the symmetrical diphosphazane ligand, Ph$_2$PN(Pr^i)PPh$_2$(L) gives the alkyl palladium complex [PdI$_2$Me(η^2–L) (9) and the diiodo complex PdI$_2$(η^2–L) (10) (scheme 4). These complexes have been characterized by their ^{1}H and ^{31}P NMR spectra. The structures of 7b and 8 have been confirmed by X-ray crystallography (Babu 1995).

The unsymmetrical diphosphazane 2f shows ambient coordination behaviour towards metal carbonyl moieties. Treatment of 2f with Mo(CO)$_3$(MeCN)$_3$ in acetonitrile gives the tricarbonyl complex 11 containing a labile acetonitrile attached to the metal. Pyrolysis of 11 in heptane gives 12 in which the diphosphazane displays a tridentate mode of coordination (scheme 5). Oxidative addition of iodine to 11 gives the molybdenum(II) complex 13 which also features a tridentate coordination of the diphosphazane ligand 2f as revealed by X-ray crystallography. The geometry around the metal in 13 is capped trigonal prismatic.

13   (ii) ←   **11**
R = CHMe₂   (i) →   **12**

(iii) ↓   (iv) ↘

14   **16**

↓ (v)   ↓ (v)

15a R' = Ph
15b R' = OPh

17a X = NH
17b X = CH₂
17c X = (CH₂)₂

Scheme 5. (i) Heptane/90°C/1 h; (ii) I₂/benzene; (iii) PR'₃/benzene/25°C; (iv) Ph₂PXPPh₂ (X = Nh, CH₂ or (CH₂)₂/toluene/25°C; (v) isomerization.

The labile acetonitrile ligand in 11 can be readily replaced by a monophosphane (PPh₃) or a diphosphane such as Ph₂P(CH₂)ₙPPh₂ ($n = 1$ or 2) or (Ph₂P)₂NH to give initially the *facial* complexes 14 or 16 which undergo isomerization to yield the corresponding meridional derivatives 15 or 17. The *fac*-complexes 14 and 16 could not be isolated but were identified only by ³¹P NMR spectroscopy. The mer-complexes 15 and 17 can be isolated by column chromatography. The uncoordinated phosphorus centre in 17 should in principle be capable of binding to other transition metals to form polymetallic complexes. However, only 17c containing a two-carbon spacer unit between the two phosphorus centres forms a trinuclear complex [PtCl₂(η¹–17c)₂] whereas neither 17a nor 17b forms such a complex. This result is in contrast to the ready formation of a heterobimetallic complex with a bridging Ph₂P(CH₂)PPh₂(dppm) ligand

in the reaction of *fac-* or *mer-*Mo(CO)$_3$(η^2-dppm) (η^1-dppm) with PtCl$_2$(COD) (COD = 1,5-cyclooctadiene). These results bring out the differences in reactivity of diphosphazanes and that of diphosphanoalkanes towards transition metal derivatives (Babu *et al* 1993, 1995c).

4. Transition metal complexes of λ^3-cyclophosphazanes

We have also investigated the transition metal organometallic chemistry of tri-fluoroethoxy- or aryloxy-substituted λ^3-cyclodi- and λ^3-cyclotriphosphazanes. Reactions of λ^3-cyclodiphosphazanes with group-VI metal-carbonyl species often give a mixture of products owing to *cis–trans* isomerization of the ligands when free as well as when coordinated to the metal. Some reactions are summarized in scheme 6. Mono-and dimetallic complexes containing monocoordinated or bridging cyclophosphazane in its *cis* or *trans* isomeric form have been isolated. Di- and trimetallic complexes bearing two bridging *cis*-cyclodiphosphazanes can be prepared by using mononuclear complexes as building blocks. The chelating mode of binding is not observed.

The P$_2$N$_2$ ring in *trans*-cyclodiphosphazanes is planar whereas it is puckered in *cis*-cyclodiphosphazanes. The puckering is more pronounced in the dinuclear complex (<u>24</u>) than in the heterobimetallic complex (<u>22</u>) or the monocoordinated complex (<u>21</u>) (Reddy *et al* 1992, 1994, 1995).

In contrast to the behaviour of λ^3-cyclodiphosphazanes, λ^3-cyclotriphosphazanes form chelate complexes in addition to functioning as bridging ligands. The reaction of Mo(CO)$_4$(NBD) with either *trans*-[EtNP(OR)]$_3$ (R = C$_6$H$_3$Me$_2$-2,6) or *cis*-[EtNP(OR)]$_3$ (R = C$_6$H$_4$Br–4) give chelate complexes [Mo(CO)$_4$(L)] (<u>26a, b</u>). However, the *cis*-isomer of [EtNP(OR)]$_3$ (R = CH$_2$CF$_3$) under the same conditions gives a dinuclear complex <u>27</u> in which two Mo(CO)$_4$ moieties are bridged by two cyclotriphosphazane rings (figure 1). The conformation of the six-membered P–N ring and the orientation of the substituents change markedly upon coordination as revealed by the structures of the ligands and the complexes. The nitrogen atom connecting the two phosphorus centres chelated to the metal in <u>26b</u> deviates considerably from planar geometry whereas the other nitrogen atoms (and also the nitrogen atoms in <u>27</u>) display planar geometry. The implications of the results for understanding the nature of the P–N bond are discussed elsewhere (Murugavel *et al* 1993, 1994). We have also synthesized a bicyclic phosphazane monoxide and its molybdenum carbonyl complex (<u>28</u>). The twist-boat conformation of the two six-membered rings in the bicyclic ligand changes to a chair conformation in the complex; concomitantly the pseudoaxial orientation of the aryloxy groups changes to equatorial disposition (N Thirupathy, unpublished results).

5. Transition metal chemistry of λ^5-cyclotriphosphazenes

λ^5-cyclophosphazenes can coordinate to transition metals in a number of ways. Although coordination of a ring nitrogen atom of eight-membered cyclotetraphosphazene and higher membered rings is well established by the pioneering work of Paddock and coworkers (Gallicano and Paddock 1982) and later by Allcock and coworkers (Allcock *et al* 1987), the transition metal chemistry of the more rigid six-membered cyclotriphosphazene ring system is less well-developed. The versatile coordination chemistry of pyrazolyl derivatives prompted us to investigate the group-VI metal–carbonyl complexes of cyclotriphosphazenes. Reactions of *gem-*N$_3$P$_3$Ph$_4$(C$_3$HN$_2$Me$_2$)$_2$ or *gem-*N$_3$P$_3$
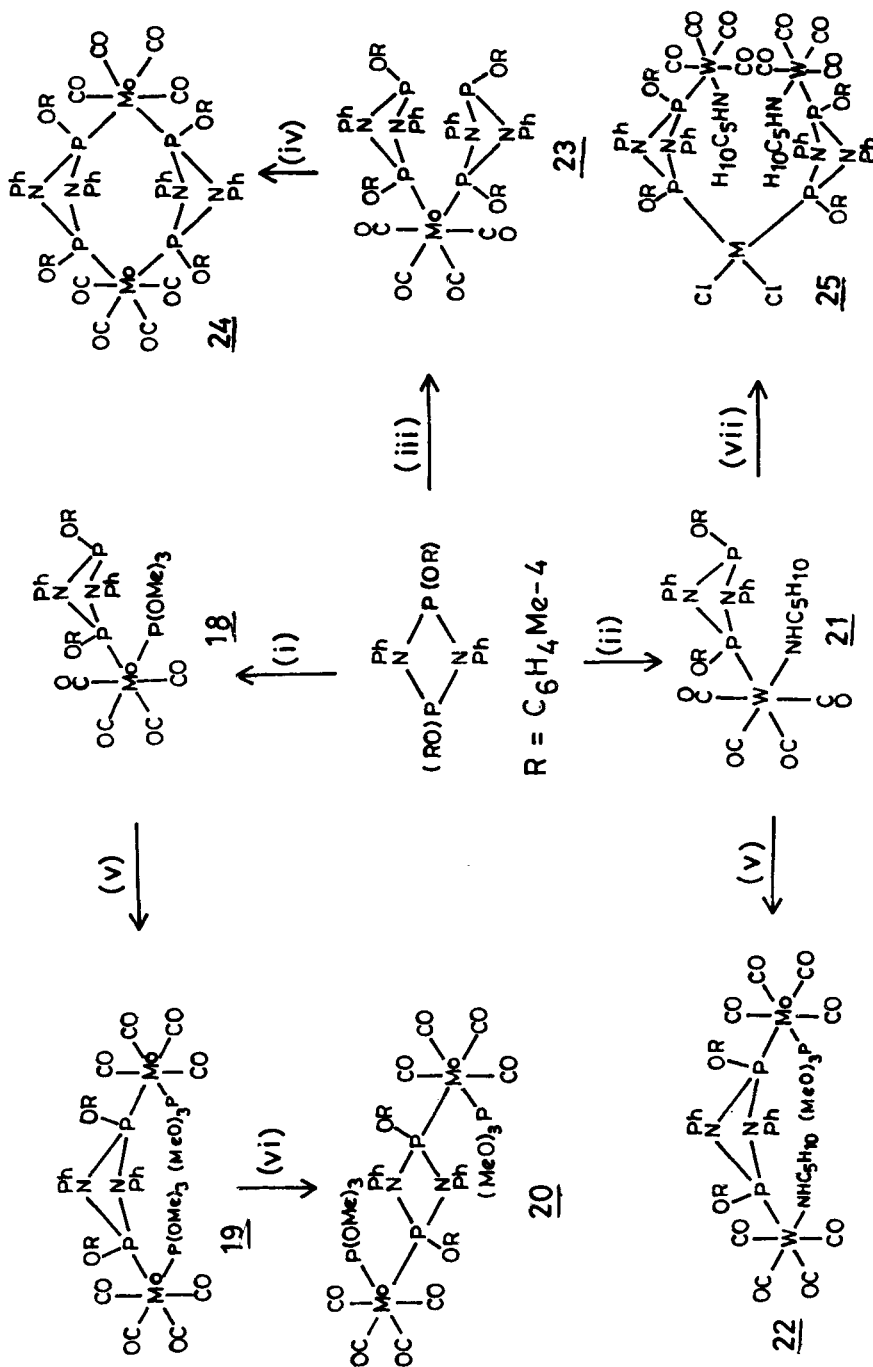
Scheme 6. (i) $Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})/CH_2Cl_2/25°C$; (ii) $W(CO)_4(NHC_5H_{10})_2/CH_2Cl_2$; (iii) $Mo(CO)_4(NHC_5H_{10})_2/CH_2Cl_2$; (iv) $Mo(CO)_4(nbd)/CH_2Cl_2$; (v) $Mo(CO)_4P(OMe)_3(NHC_5H_{10})/CHCl_3/45°C$; (vi) isomerization; (vii) $MCl_2(COD)$ (m = Pd or Pt).
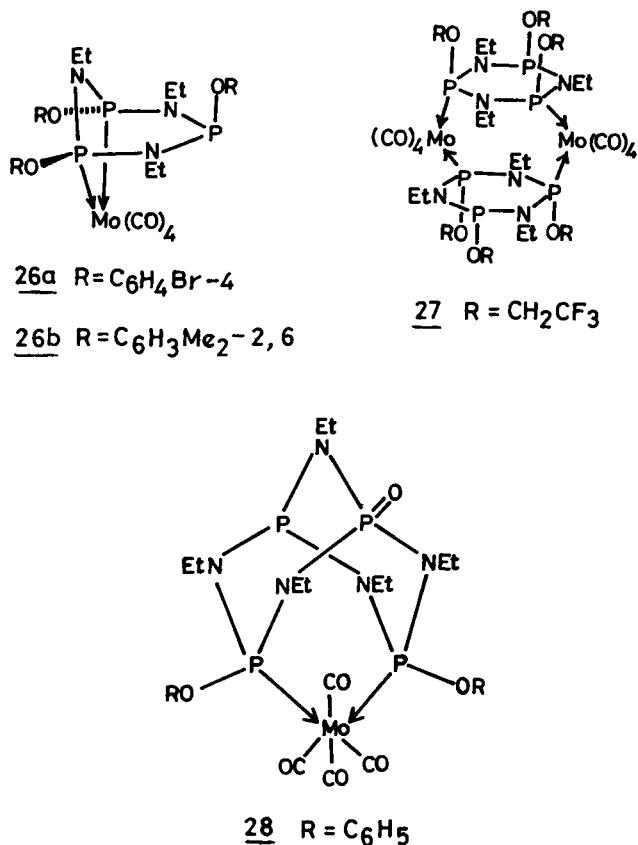
26a R = C₆H₄Br-4

26b R = C₆H₃Me₂-2,6

27 R = CH₂CF₃

28 R = C₆H₅

Figure 1. Some complexes of λ^3-cyclotriphosphazanes and a bicyclic phosphazane monoxide.

$(MeNCH_2CH_2O)_2(C_3HN_2Me_2)_2$ with $M(CO)_6$ (M = Mo or W) afford tricarbonyl complexes (**29**) in which the cyclotriphosphazene functions as a novel tridentate NNN-donor ligand featuring coordination of a skeletal ring nitrogen atom to the metal (figure 2). The six-membered P_3N_3 ring undergoes substantial distortion from planarity. The M–N (phosphazene ring) distances in the complexes **29a** (M = Mo) and **29b** (M = W) are 2·394(2) and 2·310(7) Å indicating that the σ-donor ability of the phosphazene ring nitrogen atom can be varied by changing the substituents on the adjacent or remote phosphorus atoms (Chandrasekaran *et al* 1994a). We have also synthesized a cyclophosphazene derivative in which the two pyrazolyl substituents reside on different phosphorus centres in a *cis*-orientation to each other. In the palladium(II) chloride complex (**30**) of this non-geminal *bis*(pyrazolyl) cyclophosphazene, there is weak interaction between palladium and a phosphazene ring nitrogen atom as shown by the M....N distance (2·86 Å) which is less than the sum of the Van der Waals radii of palladium and nitrogen (Chandrasekaran *et al* 1993). Coordination of a phosphazene ring nitrogen atom has been observed in the Cu^{2+}, Co^{2+} and Ni^{2+} complexes of the pyrazolyl cyclotriphosphazenes, $N_3P_3Ph_2(C_3HN_2Me_2)_4$ and $N_3P_3(C_3HN_2Me_2)_6$ (Chandrasekhar and Thomas 1993; Thomas *et al* 1995).
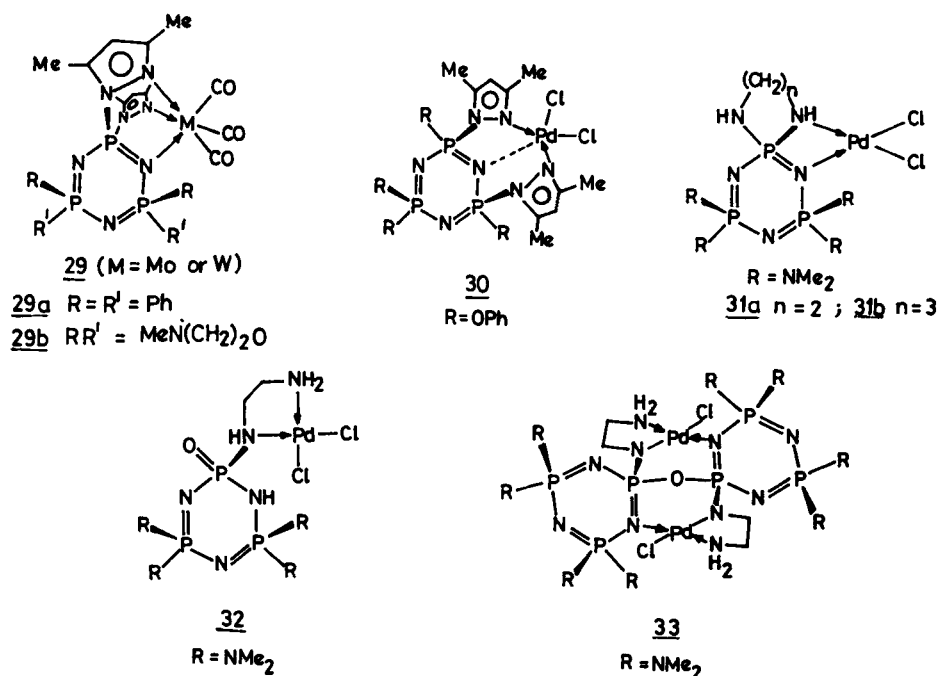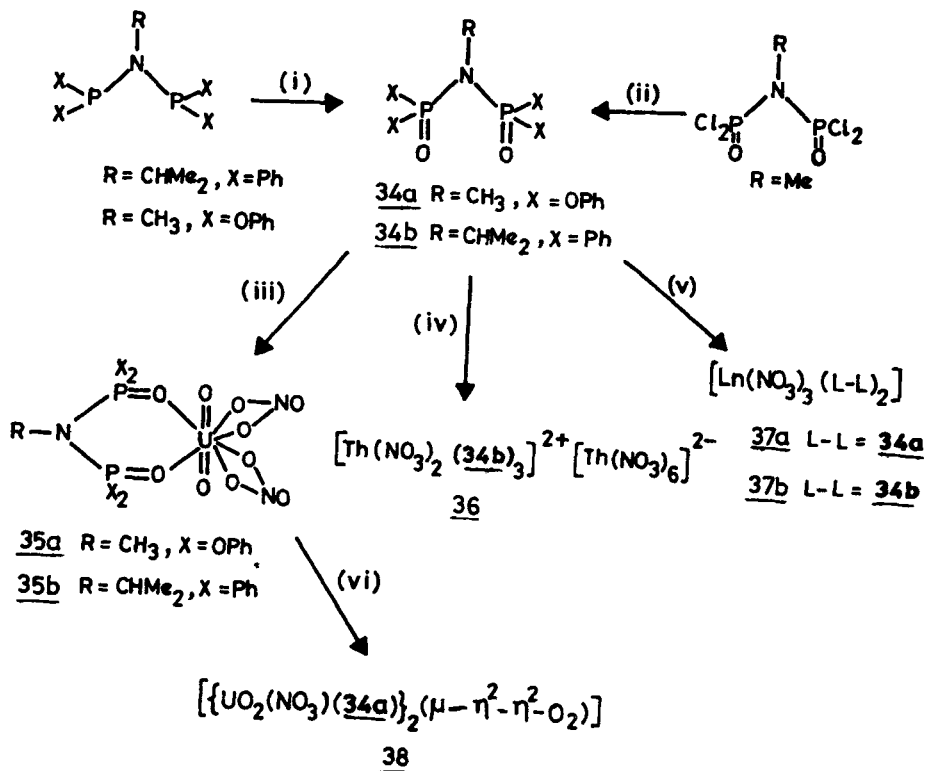
Figure 2. Some complexes of cyclotriphosphazenes.

The introduction of amino groups on the cyclophosphazene ring enhances the donor ability of the ring nitrogen atoms but their binding to the transition metals may be impeded by steric factors. This difficulty can be overcome by the use of amino spirocyclic substituents. The spirocyclotriphosphazene derivatives, $N_3P_3(NMe_2)_4[NH(CH_2)_nNH]$ ($n = 2, 3$), readily form complexes with palladium chloride (31). The (1,2-diaminoethan) cyclotriphosphazene complex (31a) undergoes facile hydrolytic cleavage of the five-membered diazaphospholane ring to give novel mono- and bimetallic complexes 32 and 33 (figure 2) which have been structurally characterized. The monometallic complex may be regarded as a palladium chloride complex of a mono-N-substituted derivative of ethylenediamine, $[PdCl_2(H_2NCH_2CH_2NHR)]$ (R = oxophosphazadienyl). The dimetallic complex consists of an oxobridged bi(cyclotriphosphazene) acting as a hexadentate ligand in its dianionic form. Both the complexes show interesting packing in the crystal lattice through a network of inter- and intramolecular hydrogen bonds (Chandrasekaran *et al* 1994b).

6. Synthesis of linear diphosphazane dioxides and their complexes with *f*-block elements

There has been a renaissance in the fundamental chemistry of *f*-block elements in view of its implications in various technological applications (Cotton 1994; Soloveichik 1994). Keeping in mind that organophosphate esters form strong complexes with both lanthanides and actinides and are used for separation of these elements by solvent extraction, we have synthesized several new diphosphazene dioxides and investigated their complexes with lanthanides and actinides. Two synthetic approaches have been developed for diphosphazene dioxides. One of these involves the oxidation of phosphorus(III)

R = CHMe$_2$, X = Ph
R = CH$_3$, X = OPh

R = Me

34a R = CH$_3$, X = OPh
34b R = CHMe$_2$, X = Ph

35a R = CH$_3$, X = OPh
35b R = CHMe$_2$, X = Ph

$[Ln(NO_3)_3 (L-L)_2]$

37a L-L = **34a**
37b L-L = **34b**

$[Th(NO_3)_2 (\underline{34b})_3]^{2+} [Th(NO_3)_6]^{2-}$
36

$[\{UO_2(NO_3)(\underline{34a})\}_2(\mu-\eta^2-\eta^2-O_2)]$
38

Scheme 7. (i) H_2O_2/acetone; (ii) PhONa/toluene; (iii) $UO_2(NO_3)_2$/EtOH–CH_2Cl_2; (iv) Th$(NO_3)_4$/EtOH–CH_2Cl_2; (v) Ln$(NO_3)_3$/acetone; (vi) O_2(air)/methanol/25°C/several days.

diphosphazanes (see §2); the other method starts from a phosphorus(V) precursor (scheme 7). Treatment of the diphosphazane dioxides (34a, b) with uranyl nitrate affords the chelate complexes (35a, b) in which the metal is octacoordinated; on the other hand, thorium nitrate reacts with 34b to give a dinuclear complex (36) consisting of a ten-coordinated cationic $[Th(NO_3)_2(\underline{34b})]^{2+}$ and a twelve-coordinated anionic moiety $[Th(NO_3)_6]^{2-}$ (Aparna et al 1995a). The uranyl complex $[UO_2(\underline{34a})(NO_2)_2]$ in methanol on exposure to the atmosphere gives the dinuclear μ-peroxo complex $[\{UO_2(\underline{34a})(NO_3)\}_2(\mu-\eta^2-\eta^2-O_2)]$ (38). All these complexes have been structurally characterized (K Aparna, unpublished results).

Reaction of lanthanum nitrate with $X_2P(O)NPr^i)P(O))X_2(L-L)$ gives the *bis* chelate complexes $[Ln(NO_3)_3(L-L)_2$ (37a, 37b)]. The structure of the praseodymium complex (37a, M = Pr) has been determined by single crystal X-ray diffraction. It crystallises in the rare space group $P3_2$. There are two independent molecules in the unit cell which differ in the orientation of the phenyl groups. The lanthanide ion is ten-coordinated (Aparna et al 1995b).

7. Summary and outlook

The versatile chemistry of linear and cyclic phosphorus-nitrogen compounds offers enormous opportunities for designing novel multidentate ligands for complexation

with both transition and inner transition elements. The use of short-bite diphosphazanes of the type $X_2 PN(R)PX_2$ for building metal clusters by reductive carbonylation of metal chlorides, the applications of chiral diphosphazane complexes in enantioselective catalysis, amination reactions of chlorophosphanes coordinated to transition metals to generate P–N rings and the potential utility of diphosphazane dioxide complexes for separation of lanthanides are some of the attractive topics for future investigations.

Acknowledgements

References

Allcock H R, Desorcie J L and Riding G H 1987 *Polyhedron* **6** 119
Aparna K, Krishnamurthy S S and Nethaji M 1995a *J. Chem. Soc., Dalton Trans.* 2991
Aparna K, Krishnamurthy S S and Nethaji M 1995b *Z. Anorg. Allg. Chem.* **621** 1913
Babu R P K 1995 *Synthetic, spectroscopic and structural investigations on transition metal complexes of unsymmetrical and chiral diphosphazane ligands*, Ph D thesis, Indian Institute of Science, Bangalore
Babu R P K and Krishnamurthy S S 1994 *Proc. Indian Acad. Sci. (Chem. Sci.)* **106** 37
Babu R P K, Krishnamurthy S S and Nethaji M 1993 *J. Organomet. Chem.* **454** 157
Babu R P K, Aparna K, Krishnamurthy S S and Nethaji M 1995a *Phosphorus, Sulfur Silicon* **103** 39
Babu R P K, Krishnamurthy S S and Nethaji M 1995b *Tetrahedron: Asymmetry* **6** 427
Babu R P K, Krishnamurthy S S and Nethaji M 1995c *Organometallics* **14** 2047
Balakrishna M S, Reddy V S, Krishnamurthy S S, Nixon J F and Burckett St. Laurent J C T R 1994 *Coord. Chem. Rev.* **129** 1
Chandrasekhar V and Thomas K R J 1993 *Appl. Organomet. Chem.* **7** 1
Chandrasekaran A, Krishnamurthy S S and Nethaji M 1993 *Inorg. Chem.* **32** 6102
Chandrasekaran A, Krishnamurthy S S and Nethaji M 1994a *J. Chem. Soc., Dalton Trans.* 63
Chandrasekaran A, Krishnamurthy S S and Nethaji M 1994b *Inorg. Chem.* **33** 3085
Cotton S A 1994 In *Encyclopedia of inorganic chemistry* (ed.) R B King (Chichester: John Wiley) vol. 7, pp 3595–3618
Fantucci P 1992 *Comments Inorg. Chem.* **31** 241
Gallicano K D and Paddock N L 1982 *Can. J. Chem.* **60** 521
Katti K V, Reddy V S and Singh P R 1995 *Chem. Soc. Rev.* 97
Mague J T 1995 *Inorg. Chim. Acta* **229** 17
Murugavel R, Krishnamurthy S S, Nethaji M and Chandrasekhar J 1993 *Inorg. Chem.* **32** 5447
Murugavel R, Kumaravel S S, Krishnamurthy S S, Nethaji M and Chandrasekhar J 1994 *J. Chem. Soc., Dalton Trans.* 847
Pacchioni G and Bagus P S 1992 *Inorg. Chem.* **31** 4391
Reddy V S, Krishnamurthy S S and Nethaji M 1992 *J. Organomet. Chem.* **438** 99
Reddy V S, Krishnamurthy S S and Nethaji M 1994 *J. Chem. Soc., Dalton Trans.* 2661
Reddy V S, Krishnamurthy S S and Nethaji M 1995 *J. Chem. Soc., Dalton Trans.* 1933
Reed A E and Schleyer P V R 1990 *J. Am. Chem. Soc.* **112** 1434
Soloveichik G L 1994 In *Encyclopedia of inorganic chemistry* (ed.) R B King (Chichester: John Wiley) vol. 1, pp 1–19
Thomas K R J, Chandrasekhar V, Scott S R and Cordes A W 1995 *Polyhedron* **14** 1607