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REVIEW

Coordination and organometallic chemistry of cyclophosphazenes and polyphosphazenes

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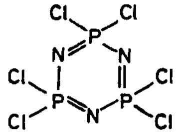
This review describes the chemistry of cyclophosphazene and polyphosphazene ligand systems and their transition and organometallic complexes. The structures of the ligands and the complexes are discussed.

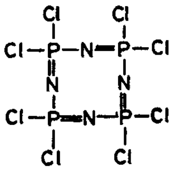
Keywords: Cyclophosphazene, polyphosphazene, coordination, organometallic, structure, X-ray, review

1 INTRODUCTION

Cyclophosphazenes constitute an important class of inorganic heterocyclic ring systems. The ring system is made up of alternating phosphorus and nitrogen atoms. Phosphorus is pentavalent and tetracoordinate while nitrogen is trivalent and dicoordinate. The phosphorus atom has two exocyclic substituents but the ring nitrogen atom has none. The two best-studied examples are the chlorocyclophosphazenes, $N_3P_3Cl_6$ (**1**) and $N_4P_4Cl_8$ (**1a**).



(1)

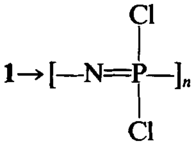


(1a)

Nucleophilic substitution reactions involving replacement of the labile P–Cl bonds in **1** and **1a** by nucleophiles such as aliphatic and aromatic amines, alcohols, phenols and organometallic reagents have been extensively studied and comprehensively reviewed.[1-5]

The substitution pattern in **1** and **1a** beyond the mono stage becomes complex because of the possibility of several positional and geometric isomers. These possibilities have been reviewed elsewhere.[2,3] Several examples have been thoroughly studied and the substitution preferences in terms of role of the nucleophile vis-à-vis the substrate are now reasonably well understood.

Another reason for the interest in the study of cyclophosphazenes stems from the ring-opening polymerization of $N_3P_3Cl_6$ (**1**):[6]



$$\mathbf{1} \rightarrow [-N{=}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}-]_n$$

(**1c**)

The linear polymer **1c**, although of high molecular weight, is not useful by itself because of its extreme hydrolytic susceptibility. However, this disadvantage has been quickly turned around: the reactive polymer (**1c**) can be reacted with several nucleophiles that have been studied on the prototype (**1**), thereby affording a route to structurally diverse macromolecules.[6-10]

Another important facet of the chemistry of cyclophosphazenes is their interaction with transition metals.[3,11,12] This aspect has been receiving much attention in recent years. Since substitution of P–Cl bonds by a variety of groups is relatively facile, wide-ranging ligands can be prepared from cyclophosphazenes. The possibility of coordination through ring nitrogen atoms or through exocyclic substituents on phosphorus has been explored[11] and some aspects of this study has been extended to the high-molecular-weight polyphosphazenes also.[12] This review will focus on the versatility of phosphazene–ligand systems, with emphasis on the design of ligands and on the structures of the transition-metal compounds formed from them. For the sake of convenience the subject is treated under the following headings:

2 Skeletal ring nitrogen cordination and salts and ionics.

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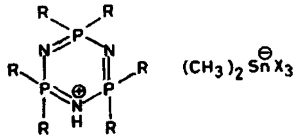
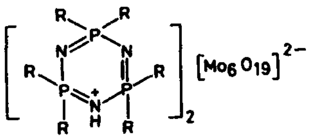
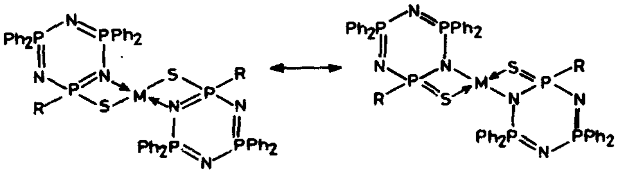
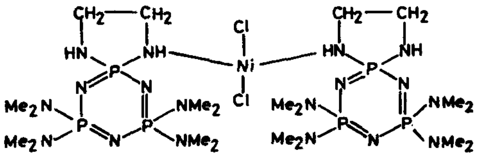
Table 1 Complexes formed from ring nitrogen coordination

Cyclophosphazene	Complex formed	Information about structure	Ref.
(1)	(2)	(3)	(4)
$N_3P_3Cl_6$ (**1**)	$N_3P_3Cl_6 \cdot AlCl_3$ (**18**) $N_3P_3Cl_6 \cdot AlBr_3$ (**19**)	$[N_3P_3Cl_5]^+[AlCl_4]^-$. Intermediate in Friedel–Crafts reaction on $N_3P_3Cl_6$	14
$N_3P_3Cl_6$ (**1**)	$N_3P_3Cl_6 \cdot Cr(CO)_3$ (**20**)	Postulated to be anaiogous to η^6-C_6H_6—$Cr(CO)_3$. Structure proposal unsubstantiated.	35
$N_3P_3Br_6$ (**2**)	$N_3P_3Br_6 \cdot AlBr_3$ (**21**) $N_3P_3Br_6 \cdot 2AlBr_3$ (**22**) $N_3P_3Br_6 \cdot AlCl_3$ (**23**)	Covalent structures. Coordination to Al through ring nitrogen atoms.	15
$N_3P_3(CH_3)_6$ (**3**)	$N_3P_3(CH_3)_6 \cdot MCl_4$ (**24**) (M = Ti, Sn)	Coordination from ring nitrogen atoms to metal. Five- or six-coordinate structures proposed.	36
$N_3P_3(CH_3)_6$ (**3**)	$[N_3P_3(CH_3)_6H]^+[(CH_3)_2SnX_3]^-$ (**25**) (X = Cl, Br)		37
$N_3P_3L_6$ (**4**) L = —NC_5H_{10}, —HNC_6H_{11}, —NC_4H_8O	$N_3P_3L_6 \cdot Mo(CO)_3$ (**26**)	π-complexes (η^6) proposed. IR evidence.	38
$N_3P_3(NMe_2)_6$ (**5**)	$[N_3P_3(NMe_2)_6H^+]_2\ [Mo_6O_{19}]^{2-}$ (**27**)		17
(**5**)	$[N_3P_3(NMe_2)_6H^+]_2[CoCl_4]^{2-}$ (**28**)	Structure as above. $[CoCl_4]^{2-}$ is hydrogen-bonded to both the phosphazene rings.	18
$N_3P_3Ph_4(R)(SH)$ (**6**) R = CH_3, C_6H_5, *p*-OMe	$[N_3P_3Ph_4RS]_2M$ (**29**) M = Ni, Pd, Pt		27
$N_3P_3(NMe_2)_4$ $[HNCH_2CH_2NH]$ (**7**)	$L_2 \cdot NiCl_2$ (**30**)		11

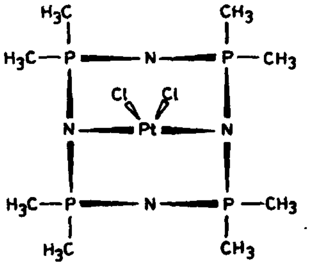
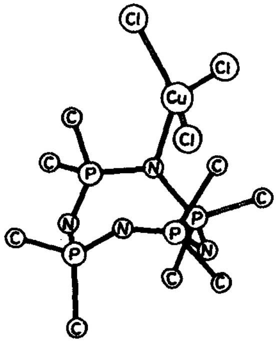
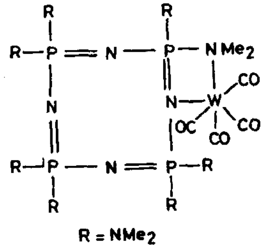
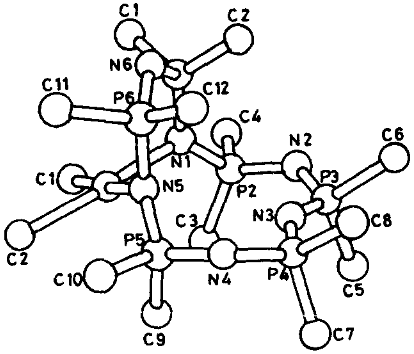
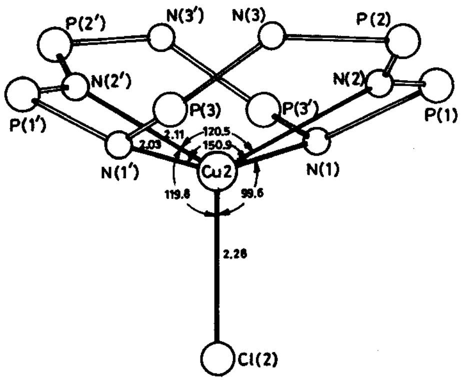
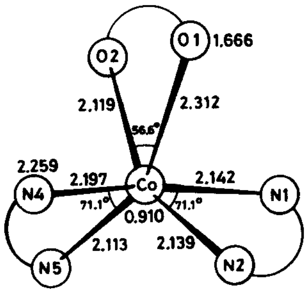
$N_4P_4(CH_3)_8$ (**8**)	$N_4P_4(CH_3)_8 \cdot M(CO)_3$ (**31**) $M = Mo, W$	Structure uncertain. Involvement of both π-system and ring nitrogens proposed.	24
8	$N_4P_4(CH_3)_8 \cdot PtCl_2 \cdot CH_3CN$ (**32**)	 Pt in a square planar geometry. Chlorines *cis* to each other.	21
8	$[N_4P_4(CH_3)_8H_2]^{2+}[MCl_4]^{2-}$ $M = Pt$ (**33**), Co (**34**)	Antipodal nitrogen atoms of the ring protonated. H-bonding between $[MCl_4]^{2-}$ and the ring N—H.	20, 21
8	$[N_4P_4Me_8H]^+[CuCl_3]^-$ (**35**)		19
8	$N_4P_4(CH_3)_8 \cdot 2HgCl_2$ (**36**)	Polymeric structure. Details not known.	39
	$N_4P_4(CH_3)_8 \cdot 4AgNo_3$ (**37**)	Structure uncertain.	
	$N_4P_4(CH_3)_8 \cdot 2AgCO_2CF_3$ (**38**)	Structure uncertain.	
$[N_4P_4(CH_3)_9]^+I^-$ (**9**)	$[N_4P_4(CH_3)_9]^+[M(CO)_5I]^-$ $M = Cr$ (**39**), Mo (**40**)	Ionic structure.	22
$N_4P_4(NHMe)_8$ (**10**)	$N_4P_4(NHMe)_8 \cdot PtCl_2$ (**41**)	Structure analogous to $N_4P_4(CH_3)_8 \cdot PtCl_2$. Two antipodal ring nitrogens involved in coordination to Pt. Pt in a square planar geometry. Chlorines are *cis*.	23
10	$N_4P_4(NHMe)_8 \cdot 2HgCl_2$ (**42**)	Polymeric structure. Details uncertain.	11
10	$N_4P_4(NHMe)_8 \cdot NiCl_2$ (**43**)	Two antipodal nitrogens of the ring proposed to coordinate to Ni which is in a tetrahedral geometry.	11

Table 1 (continued)

Cyclophosphazene (1)	Complex formed (2)	Information about structure (3)	Ref. (4)
$N_4P_4(NMe_2)_8$ **(11)**	$N_4P_4(NMe_2)_8 \cdot WCO)_4$ **(44)**		26
$N_4P_4L_8$ **(12)** L = —NC_5H_{10}, —NC_4H_8, —HNC_6H_{11}	$N_4P_4L_8 \cdot Mo(CO)_4$ **(45)**	*Analogous structure to the above proposed on the basis of IR.*	38
$N_5P_5(CH_3)_{10}$ **(13)**	$[N_5P_5(CH_3)_{10}H_2]^{2+}[CuCl_4]^{2-} \cdot H_2O$ **(46)**	Ring nitrogens protonated. H-bonding between $CuCl_4^{2-}$ and the NH of the phosphazene ring.	28
(13)	$N_5P_5(CH_3)_{10} \cdot M(CO)_3$ **(47)** M = Mo, W	Structure uncertain.	24
$N_6P_6(CH_3)_{12}$ **(14)**	$N_6P_6(CH_3)_{12} \cdot MCl_2$ M = Pd **(48)**, Pt **(49)**	 Pd in a square planar geometry, forms a six- and a ten-membered chelate ring with cyclophosphazene.	29

$N_6P_6(NMe_2)_{12}$ **(15)**	$[N_6P_6(NMe_2)_{12}]\cdot 2MCl_2$ **(50)** M = Mn, Fe, Co, Cu, Zn $[N_6P_6(NMe_2)_{12}CuCl]^+[CuCl_2]^-$ **(51)** $[N_6P_6(NMe_2)_{12}CoCl]_2^+[Co_2Cl_6]^{2-}$ **(52)**	 M (Co or Cu) coordinated to four ring nitrogen atoms. Metal in a distorted TBP geometry.	31, 32
(15)	$[N_6P_6(NMe_2)_{12}]\cdot M(NO_3)_2$ **(53)** M = Co, Ni, Cu, Zn, Mn	Structure postulated to be of the type $[N_6P_6(NMe_2)_{12}MNO_3]^+[NO_3]^-$.	30
$N_8P_8(CH_3)_{16}$ **(16)**	$[N_8P_8(CH_3)_{16}\cdot Co(NO_3)]^+[NO_3]^-$ **(54)**	Six-coordinate trigonal prismatic configuration for cobalt. Metal environment consists of two oxygens from one nitrato group and four nitrogens from cyclophosphazene group. 	33
$N_9P_9(NMe_2)_{18}$ **(17)**	$N_9P_9(NMe_2)_{18}\cdot CoCl_2$ **(55)**	Structure uncertain.	30

3 Exocyclic group interactions with transition metals.

4 Direct metal–(ring) phosphorus atom interactions.

2 SKELETAL RING NITROGEN COORDINATION AND SALTS AND IONICS

The cyclophosphazene ring nitrogen atoms possess a lone pair of electrons and therefore can be used as classical coordination ligands. Basicity studies on several cyclophosphazenes have shown that the ring nitrogen atoms are basic.[13] Also, electron-donating substituents on phosphorus atoms enhance the ring nitrogen atom basicity. An additional feature that governs the ligating properties of cyclophosphazenes is the ring size. Thus, larger-sized rings (8-, 10- and 12-membered, etc.) are puckered and therefore preferential coordination geometries are possible.[3] The various cyclophosphazene ligands used and the metal complexes formed are summarized in Table 1.

Two types of interaction have been realized: (a) where the cyclophosphazene merely forms a counter-cation to the transition-metal anionic species; and (b) where the ring nitrogen atoms are involved in coordination to the metals.

Interaction of $N_3P_3Cl_6$ with $AlCl_3$ leads to the cation–anion structure[14] $[N_3P_3Cl_5]^+[AlCl_4]^-$, whilst its complexes with $N_3P_3Br_6$ are believed to be covalent.[15] Non-ionic fluorine-bridged structures have been proposed for the complexes $(NPF_2)_n.2SbF_5$ ($n=3$ to 6).[16] Reaction of $N_3P_3(NMe_2)_6$ with molybdenum oxide[17] or cobalt chloride[18] affords ring-protonated species $[N_3P_3(NMe_2)_6H]^+$, with $Mo_6O_{19}^{2-}$ or $CoCl_4^{2-}$ as the counter-anion. The eight-membered ring $N_4P_4(CH_3)_8$ reacts with cupric chloride to give a product in which one ring nitrogen atom is protonated while the opposite ring nitrogen atom is

Table 2 X-ray crystallographic data for metal complexes formed by ring nitrogen coordination

Compound	Ring conformation	Ring bond lengths[a] (Å)	Average bond length[b] (Å)	Ring bond angles (deg.)[c]		Ref.
				P–N–P	N–P–N	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
$[HN_3P_3(NMe_2)_6]_2^+[Mo_6O_{19}]^{2-}$ (**27**)	Distorted chair	1.669, 1.598, 1.561	1.609	127.4	111.4	17
$[HN_3P_3(NMe_2)_6]_2^+[CoCl_4]^{2-}$ (**28**)	Non-planar	1.68, 1.58, 1.56	1.61[c]	128.3	111.0	18
$[N_3P_3Ph_4(Me)(S)]_2Ni$ (**29**)	Boat	1.64, 1.59, 1.58	1.60	123.9	116.0	27
$[N_4P_4(CH_3)_8]\cdot PtCl_2\cdot CH_3CN$ (**32**)	Saddle	1.658, 1.594	1.626[d]	128.2	115.3	21
$[H_2N_4P_4(CH_3)_8]^{2+}[PtCl_4]^{2-}$ (**33**)	Distorted chair	1.664, 1.600	1.612	137.4	111.4	21
$[H_2N_4P_4(CH_3)_8]^{2+}[CoCl_4]^{2-}$ (**34**)	Tub[e]	1.694, 1.612, 1.568, 1.537	1.603	128.8	114.6	
	Saddle	1.696, 1.616, 1.594, 1.534	1.610	130.7	116.5	20
$[HN_4P_4(CH_3)_8]^+\cdot CuCl_3$ (**35**)	Tub	1.668, 1.635, 1.597, 1.559	1.615	129.0	114.0	19
$[N_4P_4(CH_3)_9]^+[Cr(CO)_5I]^-$ (**39**)	Distorted tub	1.68, 1.60, 1.56, 1.51	1.60[f]	137.7	114.7	22
$N_4P_4(NHMe)_8\cdot PtCl_2$ (**41**)	Saddle	1.64, 1.58	1.61	126.9	115.2	23
$N_4P_4(NMe_2)_8\cdot W(CO)_4$ (**44**)	Non-planar	1.64, 1.62, 1.55	1.59[g]	133.0	118.1	26
$[H_2N_5P_5(CH_3)_{10}]^{2+}\cdot[CuCl_4]^{2-}\cdot H_2O$ (**46**)	Non-planar	1.67, 1.60, 1.55	1.61[h]	135.7	112.7	28
$[N_6P_6(CH_3)_{12}]\cdot PdCl_2$(**48**)	Non-planar	1.638, 1.583	1.600[i]	137.1	114.5	29
$[N_6P_6(NMe_2)_{12}CuCl]^+[CuCl_2]^-$ (**51**)	Non-planar	1.65, 1.61, 1.57, 1.53	1.60[j]	134.0	107.5	31
$[N_6P_6(NMe_2)_{12}CoCl]_2^+[Co_2Cl_6]^{2-}$ (**52**)	Non-planar	1.65, 1.63, 1.61, 1.59	1.62[j]	135.0	109.4	32
$[N_8P_8(CH_3)_{16}CoNO_3]^+NO_3^-$ (**54**)	Non-planar	1.64, 1.61, 1.58	1.60[k]	—	112.0	33

[a] The bond lengths given represent the average values of the most similar bond types. 1 A = 0.1 nm. [b] This value is the overall average value. [c] The average P–N ring bond length in $N_3P_3(NMe_2)_6$ is 1.588 Å; P–N–P bond angle is 123.0° and N–P–N angle is 116.7°.[40] [d] The values for $N_4P_4(CH_3)_8$ are: P–N bond length: 1.596 Å, P–N–P, 132.0°; N–P–N, 119.8°.[41] [e] Two molecules present in the unit cell, one with tub conformation and the other with saddle. [f] The mean Cr–CO distance 1.886 Å, C–O bond length: 1.135(22) Å, $\nu_{C-O} = 2052, 1972, 1923, 1866\ cm^{-1}$ in $CHCl_3$ solution.[42] [g] The values for $N_4P_4(NMe_2)_8$: P–N length: 1.58 Å, P–N–P, 133.0°; N–P–N, 120.1°.[43] [h] Values for $N_5P_5(Me)_{10}$: P–N bond length, 1.586 Å, P–N–P, 132.9°; P–N–P, 118.7°.[44] [i] Values for $N_6P_6(Me)_{12}$: P–N bond length 1.593 Å; P–N–P, 133.1°; N–P–N, 118.3°.[45] [j] Values for $N_6P_6(NMe_2)_{12}$: P–N bond length, 1.563 Å; P–N–P, 147.5°; N–P–N, 120.0°.[46] [k] Values for $N_8P_8(Me)_{16}$: P–N bond length, 1.590 Å; P–N–P, 139.9°; N–P–N, 117.2°.[47]

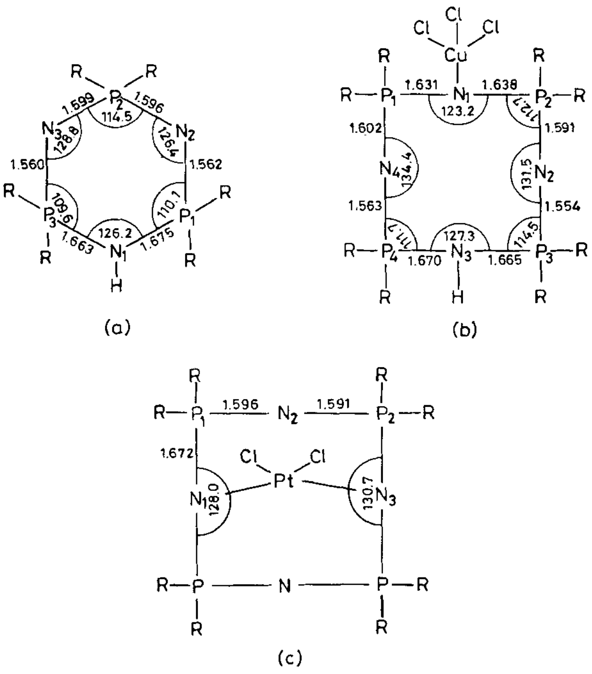


Figure 1 X-ray structure outlines for (a) cyclophosphazene ring of $[N_3P_3(NMe_2)_6H]_2^+[Mo_6O_{19}]^{2-}$ (27); (b) $[N_4P_4(CH_3)_8H][CuCl_3]$ (35); (c) $N_4P_4R_8\cdot PtCl_2$ (R = Me) (32).

coordinated to $CuCl_3$, copper being in a distorted square planar geometry.[19] Analogous reactions with chlorides of cobalt[20] or of platinum[21] afford only the diprotonated phosphazene, $[N_4P_4Me_8H]_2^+[CoCl_4]^{2-}$ or $[N_4P_4Me_8H]_2^+[PtCl_4]^{2-}$ $N_4P_4(CH_3)_8$ reacts with iodomethane (MeI) to afford the ring-quaternised iodide $[N_4P_4Me_8]^+I^-$, which forms an ionic salt with metal carbonyls.[22]

Allcock and co-workers have shown that in the eight-membered ring system it is possible to have a preferential coordination through skeletal nitrogen atoms. Thus, $N_4P_4R_8$ (R = CH_3 or NHMe) affords platinum complexes $N_4P_4R_8.PtCl_2$ (Table 1). In both these examples the platinum is present in a square planar geometry with two chlorines *cis* to each other.[21,23] Two antipodal ring nitrogen atoms complete the coordination sphere. The complex $N_4P_4(NHMe)_8.PtCl_2$ is water-soluble and shows good antitumour activity.[23] Although $N_4P_4Me_8$[24] and $N_3P_3Me_6$[25] form complexes with metal carbonyls, their structures are not known with any certainty; however, tenuous proposals involving the ring π-electrons in coordination to the metal have been made.

$N_4P_4(NMe_2)_8$ reacts with $W(CO)_6$,[26] with the loss of two carbon monoxide ligands. A distorted octahedral coordination around the metal is completed by one ring nitrogen atom and one exocyclic nitrogen atom of the phosphazene ring. Similar endo- and exo-cyclic coordination is also observed in the complexes $[N_3P_3Ph_4RS]_2M$ (R = Me, C_6H_5, anisyl; M = Ni, Pd, Pt).[27] The coordination around the metals is square planar, with an endocyclic nitrogen atom and an exocyclic sulphur atom from each ring involved in coordination to the metal.

Paddock and co-workers have studied interactions of higher-membered phosphazene ring systems ring $N_5P_5Me_{10}$ forms a protonated species $[N_5P_5Me_{10}H_2]^{2+}[CuCl_4]^{2-}$,[28] and a neutral complex $N_5P_5Me_{10}.M(CO)_3$ (M = Mo, W).[24] The structure of the latter is not certain although ring nitrogens are postulated to be involved in the coordination. The effect of ring puckering is seen with 12-membered rings. $N_6P_6(CH_3)_{12}$ forms 1:1 complexes with $PdCl_2$ and $PtCl_2$.[29] Two ring nitrogen atoms coordinate to the metal in a square planar geometry. As a result of coordination the ring forms a six- and a ten-membered chelate ring (Table 1).[29] In contrast, the other 12-membered ring, $N_6P_6(NMe_2)_{12}$ (DDPN), forms 1:2 complexes with several metals.[30-32] The X-ray structure of the cobalt and copper complexes shows that the metal is coordinated to four nitrogen atoms of the ring in a distorted trigonal bipyramidal geometry, the fifth position being occupied by a chloride.[31,32] The metal forms two six-membered and two four-membered chelate rings (Table 1). Four ring nitrogen atoms are also involved in coordination in the complex $[N_8P_8Me_{16}.Co(NO_3)]^+NO_3^-$, formed from the 16-membered ring $N_8P_8(Me)_{16}$ (Table 1).[33]

2.1 Effect of metal coordination on structure of cyclophosphazenes

Homogeneously substituted cyclophosphazenes, $N_3P_3R_6$, $N_4P_4R_8$ etc., possess uniform P–N bond lengths which are shorter (1.51–1.60 Å; 0.160 nm) than 'normal' P–N single bonds (1.77 Å; 0.177 nm).[3] Also, the ring P–N bond lengths decrease with increasing electronegativity of the exocyclic substituents on phosphorus. Bonding theories proposed by Craig, Paddock and Dewar suggest that the framework of the P–N ring skeleton is supplemented by a π-bond between a nitrogen p_z orbital and a phosphorus *d* orbital (Dewar's model involves equal contributions from d_{xz} and d_{yz} leading to three-centre P–N–P island π-bonds). This type of π-bonding (π_a) can be supplemented by an in-plane bonding between an sp^2 nitrogen lone pair with a suitable phosphorus

Table 3 Synthesis of exocyclic ligand-containing cyclophosphazenes

(a) Acetylenic functional group

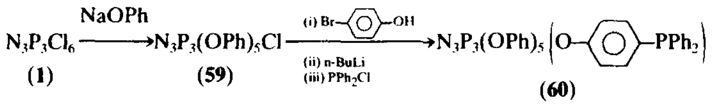
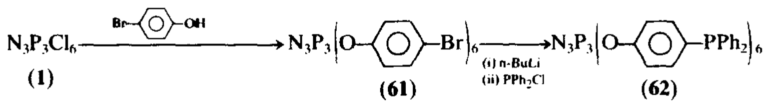
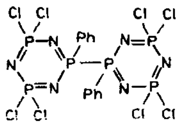
No.	Reaction	Ref.
1	$\underset{(\mathbf{1})}{N_3P_3Cl_6}\xrightarrow[\text{(ii) BrCH}_2\text{—C}\equiv\text{CH}]{\text{(i) RMgX/[n-Bu}_3\text{PCuI]}_4}\underset{(\mathbf{55})}{gem\text{-}N_3P_3Cl_4(R)(CH_2—C\equiv CH)}\xrightarrow{\text{MeLi}}\underset{(\mathbf{56})}{gem\text{-}N_3P_3Cl_4(R)(C\equiv C—CH_3)}$	53
2	$\underset{(\mathbf{1c})}{N_3P_3F_6}\xrightarrow{\text{(i) Ph—C}\equiv\text{C—Li}}\underset{(\mathbf{57})}{N_3P_3F_5(C\equiv C—Ph)}\xrightarrow{\text{PhC}\equiv\text{C—Li}}\underset{(\mathbf{58})}{gem\text{-}N_3P_3F_4(C\equiv C—Ph)_2}$	50
	(b) Phosphine attachment to phosphazenes	
3	 (1) (59) (60)	54
4	 (1) (61) (62)	54
5	 (63) $\xrightarrow[\text{(ii) EPh}_2\text{Cl}]{\text{(i) LiBEt}_3\text{H}}\underset{(\mathbf{64})}{gem\text{-}N_3P_3Cl_4(Ph)(EPh_2)}$ (E = As, P)	55

Table 3 (continued)
(c) Other exocyclic ligating attachments

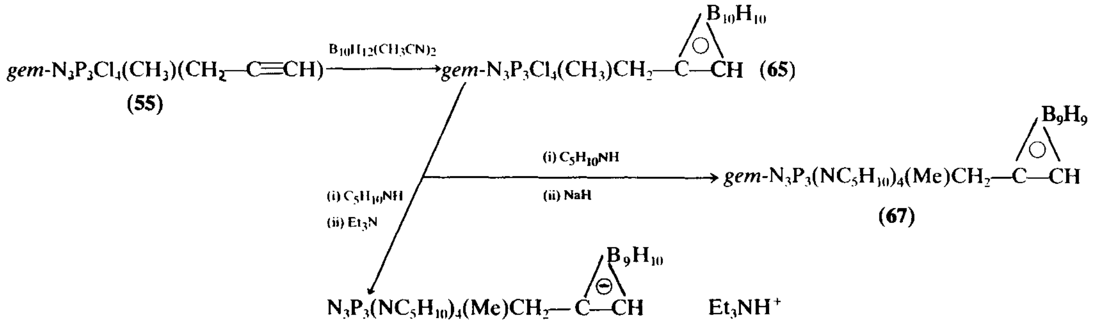
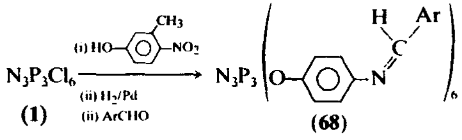
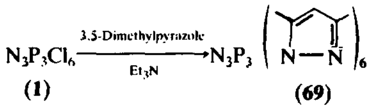
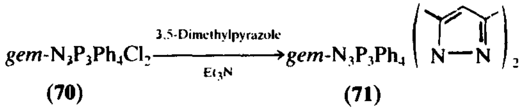
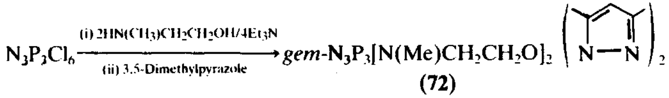
6	 (55) (65) (67) (66)	57
7	 (1) (68)	61
8	 (1) (69)	58
	 (70) (71)	58
10	 (72)	60

Table 4 Transition-metal interaction with exocyclic ligands on cyclophosphazenes

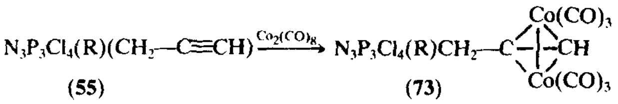
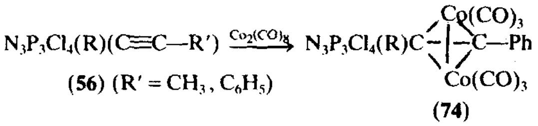
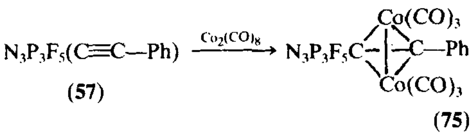
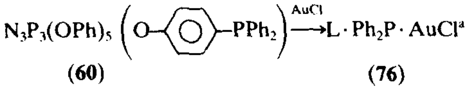
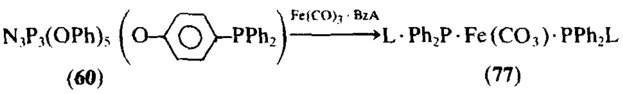
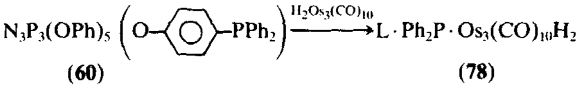
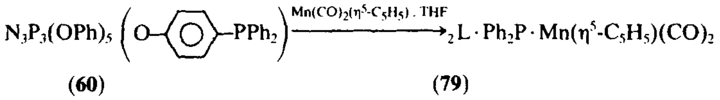
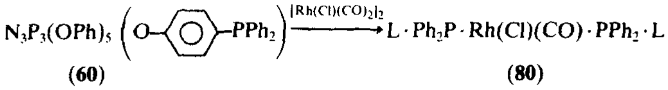
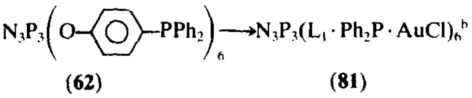
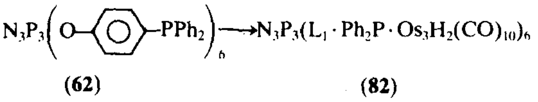
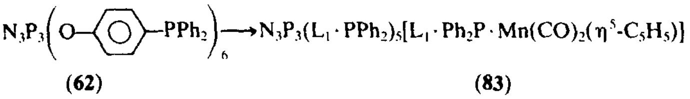
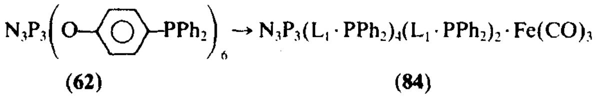
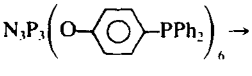
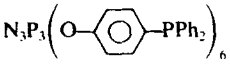
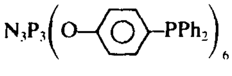
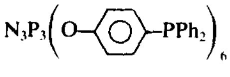
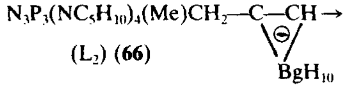
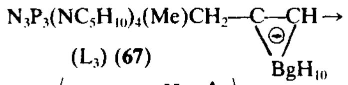
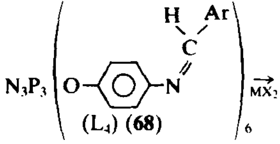
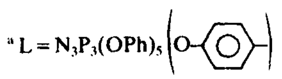
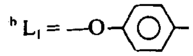
	Reaction	Ref.
1	 (55) (73)	53
2	 (56) (R′ = CH_3, C_6H_5) (74)	53
2a	 (57) (75)	50
3	 (60) (76)	54
4	 (60) (77)	54
5	 (60) (78)	54
6	 (60) (79)	54
7	 (60) (80)	54
8	 (62) (81)	54
9	 (62) (82)	54
10	 (62) (83)	54
11	 (62) (84)	54

Table 4 (continued)

	Reaction	Ref.
12	 $\rightarrow N_3P_3(L_1 \cdot PPh_2)_4(L_1 \cdot PPh_2)_2 \cdot Rh(Cl)(CO)$ **(85)**	54
13	 $\rightarrow N_3P_3(L_1 \cdot PPh_2)_6 \cdot [Rh(Cl)(CO)]_3$ **(86)**	54
14	 $\rightarrow N_3P_3(L_1 \cdot PPh_2)_4(L_1 \cdot PPh_2)_2 \cdot Mn(\eta^5\text{-}C_5H_5)(CO)$ **(87)**	54
15	 $\rightarrow N_3P_3(L_1 \cdot PPh_2)_6 \cdot Mn(\eta^5\text{-}C_5H_5)(CO)$ **(88)**	54
16	$N_3P_3Cl_4(Ph)(PPh_2) \rightarrow N_3P_3Cl_4(Ph)(Ph_2P \cdot M)$ $M = Cr(CO)_5, Fe(CO)_4, Ru_3(CO)_4$ **(64)** **(89)** **(90)** **(91)**	55
	$N_3P_3Cl_4(Ph)(PPh_2) \rightarrow [N_3P_3Cl_4(Ph)(Ph_2P)]_n \cdot Ru_3(CO)_{12-n}$ **(92)** ($n = 2, 3$)	55
18	 $N_3P_3(NC_5H_{10})_4(Me)CH_2\text{—}C\text{—}CH$ ($\ominus$, BgH_{10}) $\rightarrow L_2 \cdot Rh(H)(PPh_3)_2$ (L_2) **(66)** **(93)**	57
19	 $N_3P_3(NC_5H_{10})_4(Me)CH_2\text{—}C\text{—}CH$ ($\ominus$, BgH_{10}) $\rightarrow L_3 \cdot M(CO)_3$ (L_3) **(67)** **(94)** ($M = Mo, W$)	57
20	 (L_4) **(68)** $\xrightarrow{MX_2} L_4 \cdot 6MX_2$ **(95)** ($M = Pt, Zn$; $X = Cl$ $M = Zn, Pd$; $X = CH_3\text{—}C\text{—}O$)	61
21	$N_3P_3Ph_4(3,5\text{-}Me_2Pz)_2 \xrightarrow{Mo(CO)_6} L_5 \cdot Mo(CO)_3$ L_5 **(71)** **(96)**	60
22	$N_3P_3[N(CH_3)CH_2CH_2O]_2(3,5\text{-}Me_2Pz)_2 \xrightarrow{M(CO)_6} L_6 \cdot M(CO)_3$ (L_6) **(72)** **(97)** ($M = Mo, W$)	60
23	$N_3P_3(3,5\text{-}Me_2Pz)_6 \rightarrow L_7 \cdot nMCl_2$ (L7) **(69)** **(98)** ($M = Pt$; $n = 2$ $M = Pd$; $n = 2$ or 3)	59
24	$N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4 \rightarrow L_8 \cdot PdCl_2$ (L_8) **(69a)** **(99)**	59

[a] $L = N_3P_3(OPh)_5$ 

[b] $L_1 =$ 

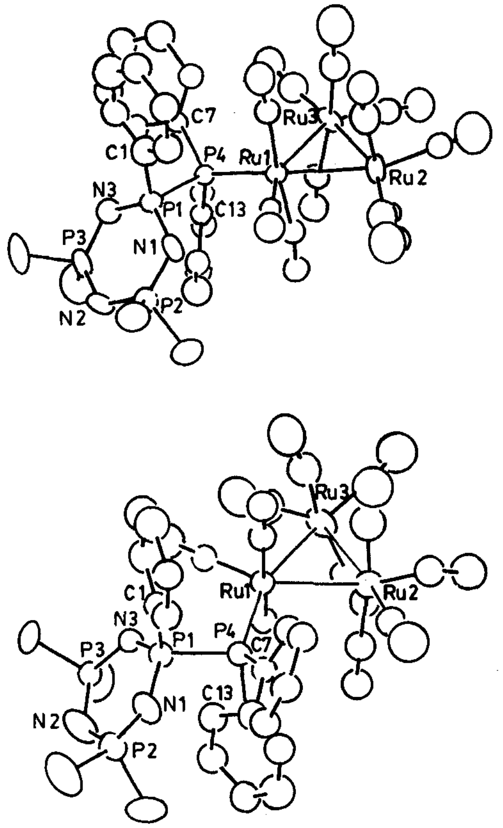


Figure 2 X-ray structure of $N_3P_3Cl_4(Ph)(PPh_2)\cdot Ru_3(CO)_{11}$ (**91**). Two molecules present in the asymmetric unit are shown. [Reprinted from Allcock *et al.*[55] with permission from the American Chemical Society (1990)].

orbital ($d_{x^2-y^2}$ or d_{xy}) (π_s).[3,34] Electron-withdrawing substituents on phosphorus can accentuate the π_s bonding by contracting the phosphorus *d* orbitals and facilitating the donation of a nitrogen sp^2 lone pair. If on the other hand mesomeric electron-releasing substituents are present on phosphorus, the π_s contribution would be less, but would be replaced by an exocyclic π-bond between phosphorus (d_{z^2}) and the exocyclic substituent. The effect of this would be to localise the lone pair on the ring nitrogen. The effects of ring protonation or metal coordination are easily understood with the help of the above theories. X-ray structural data for this class of cyclophosphazenes are summarized in Table 2. Three examples are shown to illustrate the effect (Fig. 1). The principal effect of metal coordination to the ring nitrogen atom in terms of bond lengths seems to be a lengthening of the immediate P–N bond length. A proton is more effective; thus in $[N_3P_3(NMe_2)_6H^+]_2[Mo_6O_{19}]^{2-}$ the P–N bond lengths increase to 1.670 and 1.665 Å (0.167 and 0.1665 nm).[17] This lengthening is understood by considering that the lone pair on a ring nitgrogen (sp^2 orbital) is now not available for 'in-plane' π_s-bonding. The ring bond angles are not affected to the same extent although in the example in Fig. 1(b) the angles at a nitrogen atom which is coordinated to copper or protonated are much closer to 120° than the other two angles.

Increase of ring size in cyclophosphazenes is accompanied by a greater ring puckering, which allows for a preferential arrangement of coordination sites to meet the requirements of the interacting transition metal. Thus, in the example of $N_4P_4R_8.PtCl_2$ (R = NHMe or Me), the ring is puckered in such a manner that the antipodal nitrogens are coplanar and coordinate leading to a *cis* geometry at the metal.[21,23] In the larger rings (12- or 16-membered) as many as four ring nitrogens are involved from the phosphazene ring in coordination to the transition metal, as seen in, for example, $[N_6P_6(NMe_2)_{12}CuCl]^+[CuCl_2]^-$,[31,32] or $[N_8P_8(CH_3)_{16}.CO(NO_3)]^+[NO_3]^-$.

3 EXOCYCLIC GROUPS PARTICIPATING IN COORDINATION

In the last section it was shown how the basicity of the ring nitrogen atoms was used in coordination

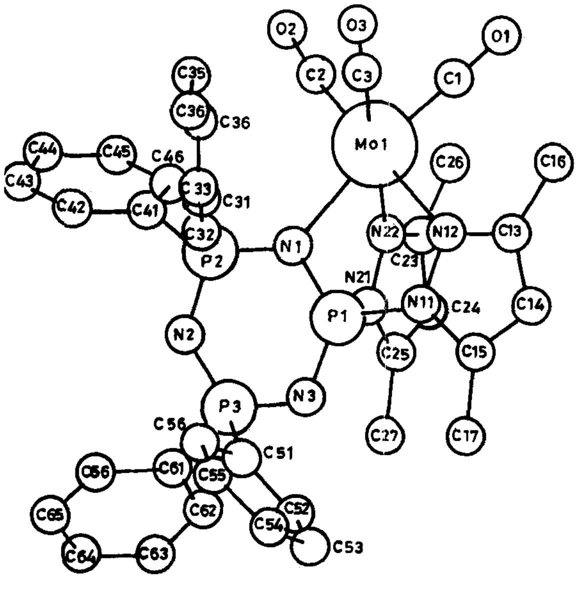


Figure 3 X-ray structure of $N_3P_3Ph_4(Me_2Pz)_2Mo(CO)_3$ (**96**).

to transition metals or to form protonated species. The variations in ligand were brought about by increasing the ring size and/or changing the substituents on phosphorus. Increases in the number and versatility of ligand systems that can be formed from cyclophosphazenes can be achieved by use of a strategy where the exocyclic substituent on phosphorus can participate in interaction with transition metals. The other advantage of this method is that it can be more readily translated to macromolecular chemistry, thereby opening a route for synthesis of polyphosphazenes which can interact with metals.

Several types of exocyclic ligating groups have been substituted on cyclophosphazenes. Most of the work has been on six-membered ring systems. Table 3 summarizes the synthesis of the ligands and Table 4 summarizes the interaction of these ligands with transition metals.

3.1 Acetylenic functionality

There are two ways of synthesizing cyclophosphazenes containing acetylenic substituents (Eqns [1], [2]):

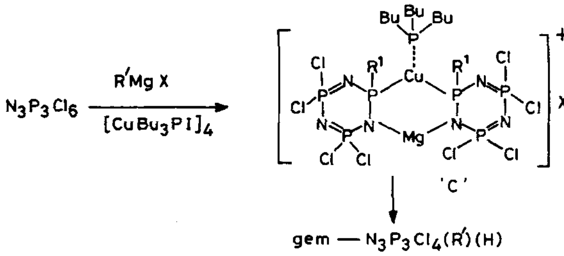
$$N_3P_3Cl_6 + nHX{-}CH_2{-}C{\equiv}CH \rightarrow$$
$$(X = NH_2 \text{ or } OH)$$
$$N_3P_3Cl_{6-n}(X{-}CH_2{-}C{\equiv}CH)_n + nHCl \quad [1]$$
$$\mathbf{A} \qquad \text{(Ref. 48)}$$

$$N_3P_3X_6 + n^-C{\equiv}C{-}R \rightarrow$$
$$(X = F \text{ or } Cl;\ R = \text{phenyl or alkyl})$$
$$N_3P_3X_{6-n}(C{\equiv}CR)_n + nX^- \quad [2]$$
$$\mathbf{B} \qquad \text{(Refs 49, 50)}$$

The compounds of the type **A** contain a nitrogen or oxygen spacer atom separating the organic unit from the cyclophosphazene ring. These are synthesized by conventional nucleophilic substitution reactions at phosphorus by amines or alcohols. Recently, using this methodology, several propargylalkoxy cyclotriphosphazenes, $N_3P_3Cl_{6-n}(OCH{-}C{\equiv}CH)_n$ ($n = 1$–6), have been synthesized.[48] However, there are no studies on the reactivity of the acetylenic functionality in these compounds towards transition metals.

Chivers and co-workers have synthesized compounds of the type **B**. $N_3P_3F_5(C{\equiv}C{-}Ph)$ and *gem*-$N_3P_3F_4(C{\equiv}CPh)_2$ have been synthesized (Table 3). The mono-derivative $N_3P_3F_5(C{\equiv}CPh)$ reacts readily with dicobalt octacarbonyl, $Co_2(CO)_8$. Two molecules of CO are lost and $Co_2(CO)_6$ binds to the triple bond of the acetylenic group[50] (Table 4, Reaction 2a).

Chivers' method of introducing the acetylenic group on cyclophosphazenes involves the reaction of the $R{-}C{\equiv}C^-$ as the nucleophile.[49] This method is useful only for the fluorocyclophosphazenes. Reactions of the chlorocyclophosphazenes with organometallic reagents in general and organolithium reagents in particular leads to a complex mixture of products including several ring degradation reactions.[3] To circumvent this difficulty Allcock and co-workers have used the organocopper reagent $[CuBu_3PI]_4$ in conjunction with a Grignard reagent.[51] The reaction is now believed to proceed through the intermediate **C** in which copper and magnesium are bound to ring phosphorus or nitrogen atoms of the cyclophosphazene ring.[52] If this reaction intermediate is allowed to be reacted with isopropanol as shown in Eqn [3] the product obtained is a

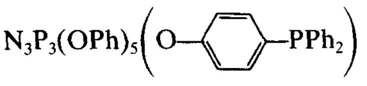


[3]

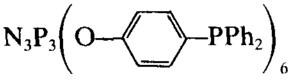
hydridophosphazene, *gem*-$N_3P_3Cl_4(R)(H)$, in which the hydrogen is geminally attached to the phosphorus containing the alkyl group. If on the other hand the intermediate **C** is allowed to react with $BrCH_2C{\equiv}CH$, the propynyl cyclophosphazene *gem*-$N_3P_3Cl_4(R)(CH_2C{\equiv}CH)$ is obtained. this compound can isomerize to the product containing an internal triple bond, *gem*-$N_3P_3Cl_4R(C{\equiv}C{-}CH_3)$[53] (Table 3, Reaction 1). Both of these products form π-complexes with dicobalt octacarbonyl with the loss of two carbon monoxide molecules (Table 4, Reactions 1 and 2). X-ray structures (see Table 5) of the dicobalt complexes show that only the acetylenic unit is involved in interaction with the metal, and ring nitrogens are not participating in coordination. The catalytic utility of these complexes has been examined. It is found that they are active catalysts for the cyclotrimerization of phenylacetylene and diphenylacetylene as well as for the self-trimerization of the propynyl phosphazenes themselves.[53]

3.2 Phosphine units on cyclophosphazenes

Two types of attachment of the diphenylphosphino unit Ph_2P on to cyclophosphazenes has been accomplished, as shown in Table 3 (Reactions 3 and 4). In the first method a spacer group such as an aryloxy separates the phosphino unit from the phosphazene ring. The derivatives



and



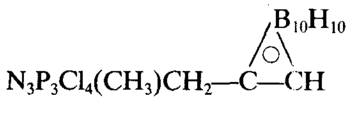
containing one terminal phosphine and six phosphine units, respectively, have been synthesized.[54] Metal complexes are formed readily with AuCl, $H_2Os_3(CO)_{10}$, $Mn(CO)_3(\eta^5\text{-}C_5H_5)$, $Fe(CO)_3(PhCH{=}CHCOCH_3)$ and $[RhCl(CO)_2]_2$ (Table 4, Reactions 3–15). Coordination to metals occurs through the pendant phosphines only and skeletal nitrogen atoms do not interact. The coordination behaviour resembles simple trialkyl or triaryl phosphines. Both intra- and inter-molecular complexation occurs in situations where the metal could accept two phosphine ligands, as seen for example in the reactions with $Fe(CO)_3(PhCH{=}CHCOCH_3)$ and $[RhClCO]_2$[54] (Table 4, Reactions 4, 7, 11–14).

The second method of attachment of phosphines to cyclophosphazenes involves direct P–P bond formation. Synthesis of these derivatives is accomplished by the cleavage of the P–P bond in the bicyclic phosphazene $[N_3P_3Cl_4Ph]_2$ with $LiBEt_3H$.[55] The resulting cyclophosphazene anion reacts readily with Ph_2PCl or Ph_2AsCl giving $N_3P_3Cl_4(Ph)(EPh_2)$ (Table 3, Reaction 5). Here the trivalent phosphorus or arsenic is attached directly to the pentavalent phosphorus of the phosphazene ring. The directly attached phosphino group reacts with $Cr(CO)_6$ or $Fe_2(CO)_9$ affording simple mononuclear complexes $N_3P_3Cl_4(Ph)PPh_2.Cr(CO)_5$ and $N_3P_3Cl_4(Ph)Ph_2\text{-}PFe(CO)_4$, respectively.[55] If the reaction is carried out with the polynuclear metal carbonyl cluster $Ru_3(CO)_{12}$, one of the carbon monoxides is lost and the phosphine coordinates to one of the ruthenium atoms in the trinuclear cluster (Table 4, Reaction 16), as shown in Fig. 2.

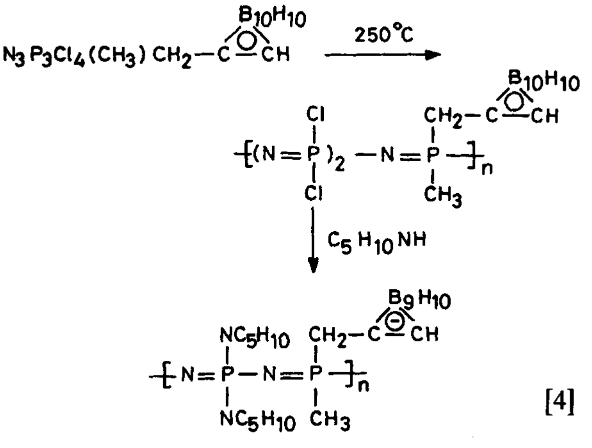
Both types of phosphine attachment method have been extended to the polyphosphazenes. However, polyphosphazenes bearing directly bound phosphines were not very stable and no complexes could be isolated although, in solution, complex formation could be detected.[55] In contrast, the phosphine bearing poly(aryloxy)phosphazenes, $[NP(OC_6H_4PPh_2)_x(OPh)_{2-x}]_n$ ($x = 0.3$ or 0.6) could be synthesized and used as high-polymeric ligands for binding to transition metals.[54] The metal interaction leads to coordinative crosslinking in the polymers. A catalytic study was carried out using the cobalt hexacarbonyl complex of $[NP(OPh)_{1.7}\text{-}(OC_6H_4PPh_2)_{0.3}]_n$. It was found that these hydroformylation catalysts were more stable than the analogous phosphine-bearing polystyrene systems. The polyphosphazene catalyst functions with an initial activity equal to that of the homogeneous analogue. It appears that a cleavage of the crosslinking P–Co–P sites in the high polymer occurs to generate the active catalytic species $HCo(CO)_3PR_3$, which is soluble, and therefore the catalytic activity is high.[56]

3.3 Carboranyl phosphazenes

Nido-anion species prepared from pendant carboranyl phosphazenes (Table 3, Reaction 6) have been used as ligands. Interaction with $Rh(PPh_3)_3Cl$ or $Mo(CO)_6$ or $W(CO)_6$ affords complexes (Table 4, Reactions 18, 19).[57] As in the previous examples of pendant group coordination, only the carborane anion participates in coordination. The neutral nido carboranyl phosphazene,

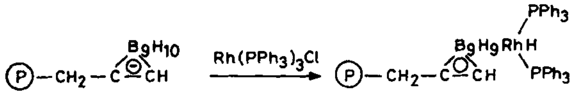


polymerizes by ring-opening polymerization at 250 °C (Eqn [4]):

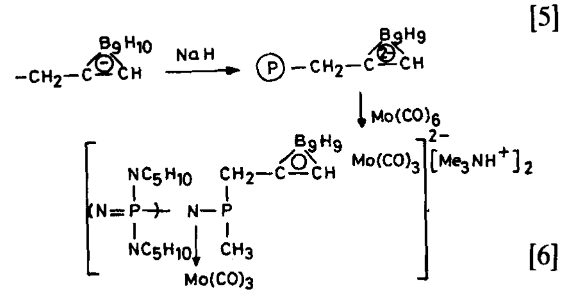


[4]

The polymeric nido carboranyl anion forms complexes with Rh and Mo (Eqns [5] and [6]):



[5]



[6]

3.4 Exocyclic nitrogen atom coordination

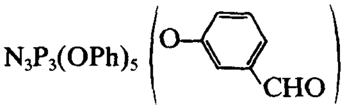
Basicity studies have shown that in aminocyclophosphazenes $N_3P_3(NRR')_6$, the ring nitrogen atoms are more basic than the exocyclic nitrogen atoms.[13] However, by a proper choice of exocyclic nitrogen-containing substituents it is possible to involve the exocyclic nitrogen atoms in coordination to transition metals.

Paddock and co-workers have synthesized a number of pyrazolyl-substituted cyclophosphazenes (Table 3, Reactions 8, 9).[58,59] The X-ray structure of $N_4P_4(Me_2Pz)_8$ (Me_2Pz = 3,5-dimethyl-1-pyrazolyl) shows that the mean ring P–N bond length is 1.557 Å (0.1557 nm). This value is comparable with the average P–N bond length of $N_4P_4Cl_8$ itself, indicating that electron release from the exocyclic groups to the phosphazene ring is negligible.[58] Also, the exocyclic P–N bond length in $N_4P_4(Me_2Pz)_8$ (1.691 Å; 0.1691 nm) is compared with $N_4P_4(NMe_2)_8$ (1.678 Å; 0.1678 nm), again substantiating the poor π-electron release from the pyrazole ring to the phosphazene ring. In the light of this X-ray evidence, it is expected that the N(2) of the pyrazole ring with the lone pair is expected to participate in coordination to transition metals. This has been confirmed by the synthesis of $N_3P_3(Me_2Pz)_6.2MCl_2$ (M = Pd, Pt) and *gem*-$N_3P_3Ph_2(Me_2Pz)_4.PdCl_2$[59] (Table 4, Reactions 23, 24). In these complexes the exocyclic pyrazole nitrogens are involved in coordination to the metal. However, more recently it has been shown that *gem*-$N_3P_3Ph_4(Me_2Pz)_2$ reacts with $Mo(CO)_6$ to afford a 1:1 complex, $N_3P_3Ph_4(ME_2Pz)_2.Mo(CO)_3$ (Table 4, Reaction 22). The X-ray structure shows that two exocyclic pyrazole nitrogen atoms and a ring nitrogen are involved in completing the coordination around molybdenum[60] (Fig. 3).

Cyclophosphazenes containing exocyclic Schiff base linkages have been synthesized (Table 3, Reaction 7).[61] These also coordinate to several transition metals through the exocyclic CH═N linkage (Table 4, Reaction 20). Ring nitrogen coordination is not involved.[61]

3.5 Macrocycles linked with cyclophosphazenes

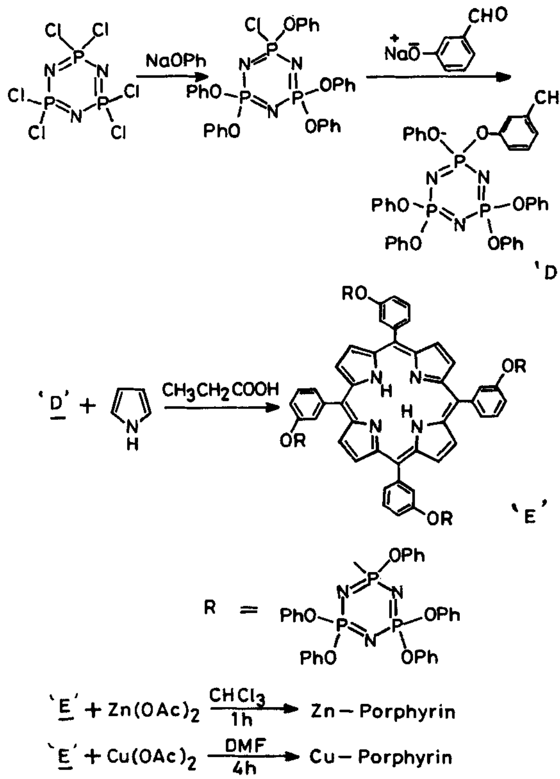
Suitable reactive exocyclic groups on cyclophosphazenes have been converted into macrocycles. For example the phosphazene



containing the aldehydic functionality has been converted into a tetraphenylporphyrin which takes up transition metals in the porphyrin core[62] (Scheme 1). Similarly cyclophosphazene-linked phthalocyanines have been synthesized.[63] An interesting haem complex has been synthesized by first attaching a picket-fence haemin and protohaemin chloride to a water-soluble polyaminophosphazene, $[NP(NHCH_3)_x(NCH_3CH_2CH_2CH_2NH_2)_4]_n$, and then reducing with dithionate.[64]

3.6 Metallocenyl cyclophosphazenes

Recently there have been investigations into the incorporation of metallocenyl units in the cyclophosphazene skeleton. Reactions of monolithiobis(cyclopentadienyl)metallocenes (M = Fe and



Scheme 1 Synthesis of cyclophosphazene—containing porphyrin and its metallo derivatives [reprinted from Selvaraj *et al.*[62] with permission from the Japan Institute of Heterocyclic Chemistry (1991)].

Ru) with hexafluorocyclotriphosphazene affords mono- and bis- (non-*gem*) substituted derivatives [Scheme 2, Reaction (1)]. In these, one end of the cyclopentadienyl unit is attached to the phosphorus.[65] Similar reactions with $N_3P_3Cl_6$ lead to poor yields and a greater number of products[65] [Scheme 2, Reaction (2)]. This behaviour is analogous to that observed in other reactions of halogenocyclophosphazenes with alkyl or aryl lithium derivatives.[3]

Reactions of 1,10-dilithio derivatives of metallocenes with $N_3P_3F_6$ affords substitution of fluorines present on two different phosphorus atoms, leading to intramolecularly bridged products. The ruthenium metallocene affords, in addition, the intermolecularly bridged product (Scheme 3).[65] Again, these reactions with $N_3P_3Cl_6$ become more complex, leading to several products (Scheme 4). An interesting feature of this reaction is that one of the end-products contains a chlorine attached to the cyclopentadienyl ring. The mechanism proposed (Scheme 5) involves abstraction of a chlorine by $LiC_5H_4MC_5H_4Li$ to afford a phosphazene anion which on further reaction with $N_3P_3Cl_6$ affords the end-products with chlorines on the cyclopentadienyl groups.

The reactions of metallocenyl reagents has been extended to the eight-membered ring system. The reactions of the fluoro derivative $N_4P_4F_8$ are more facile than those of $N_4P_4Cl_8$ (Schemes 6 and 7). $N_4P_4F_8$ reacts with a lithiometallocene $LiC_5H_4{-}M{-}C_5H_5$ (M = Fe or Ru) to give the mono-substituted derivative and 2,6-disubstituted derivative[65] (Scheme 6, Reaction 1). Analogous reactions with $N_4P_4Cl_8$ gives a ring-degraded product (Scheme 6, Reaction 2).[66] A 1:1 mixture of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ reacts in an interesting manner with monolithio- or dilithioferrocenes giving bicyclic products in which the six-membered and the eight-membered rings are joined by a P–P bond (Scheme 6, Reaction 3).

The dilithiometallocene $LiC_5H_4{-}M{-}C_5H_4Li$ (M = Fe or Ru) reacts with $N_4P_4F_8$ giving both the 2,4 and the 2,6- substituted products (Scheme 7). An interesting feature of this reaction is that with the dilithioruthenocene a bis-*trans*-annular ruthenocenyl derivative, $N_4P_4F_4[C_5H_4RuC_5H_4]_2$, is isolated.[67]

Further reactions of these cyclopentadienyl derivatives are summarized in Schemes 2–4, 7 and 8.

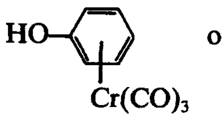
Recently, η^6-arene chromium tricarbonyl derivatives of cyclophosphazenes have been reported. Two strategies have been described[68] (Scheme 8; Eqns [7], [8]):

$$N_3P_3F_5Ph \xrightarrow{Cr(CO)_6} N_3P_3F_5C_6H_5Cr(CO)_3 \quad [7]$$

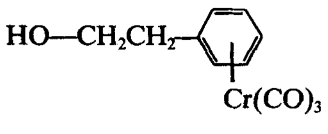
$$N_3P_3Cl_6 \xrightarrow[\mathrm{Na[RCr(CO)_3]}]{} N_3P_3Cl_{6-n}[RCr(CO)_3]_n \quad [8]$$

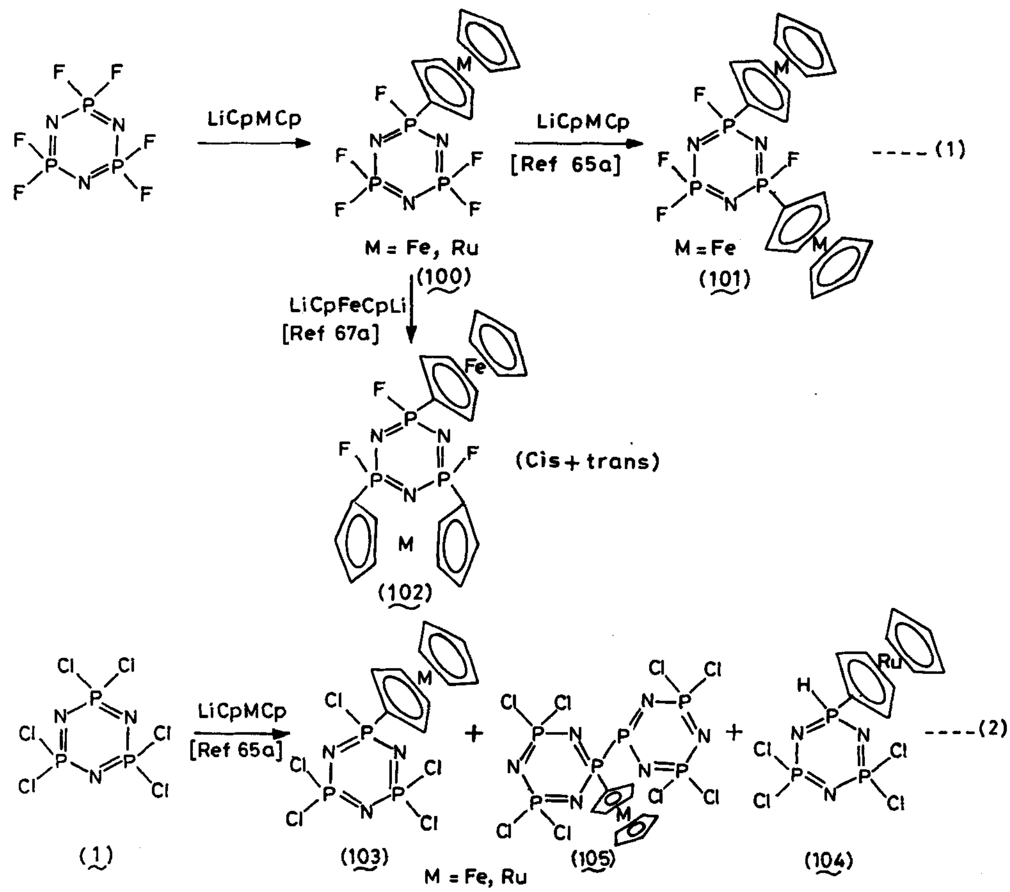
$$(n = 1 \text{ or } 6)$$

In the first method, a preformed cyclophosphazene containing an aryl or an aryloxy substituent is treated with $Cr(CO)_6$. Three molecules of carbon monoxide are expelled and the aryl or aryloxy group functions as an η^6 (six-electron donor) ligand. In the second method, phenol or phenoxyethanol is first treated with $Cr(CO)_6$ affording the reagents



or



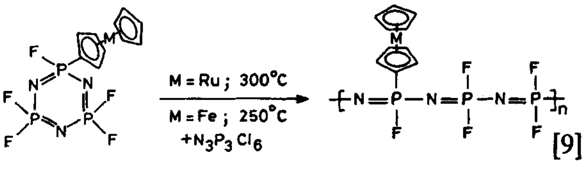


Scheme 2 Reactions of $N_3P_3F_6$ and $N_3P_3Cl_6$ with monolithio metallocenes.

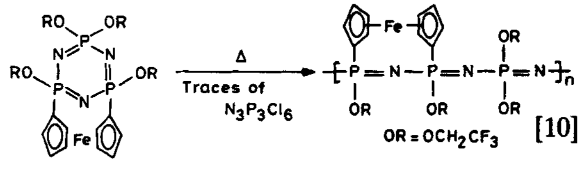
These reagents can react with $N_3P_3Cl_6$. Using this method a loading of up to six chromium atoms per cyclophosphazene unit has been achieved.[68]

3.7 Polymerization of metallocenyl cyclophosphazenes

Metallocenyl phosphazenes can undergo ring-opening polymerization[69] (Eqns [9], [10] and [12])



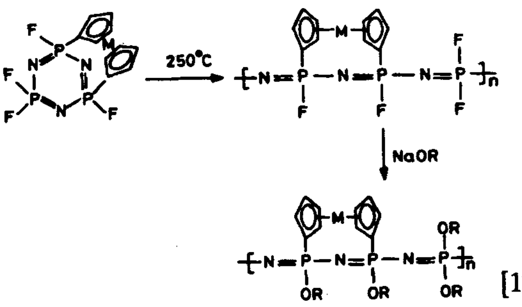
[9]



[10]

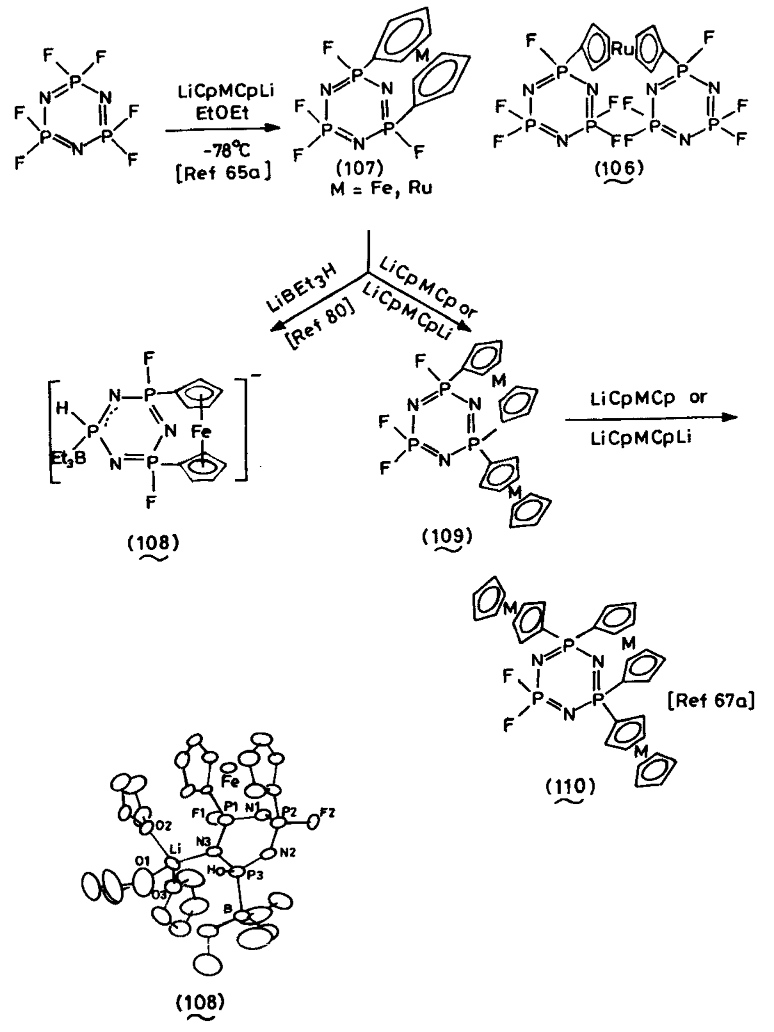
An interesting feature of the polymerization of the metallocenyl phosphazenes is the apparent role of ring strain on ring opening of the six-membered cyclophosphazene ring[70] (viz. Eqns [10], [11]).

$$N_3P_3(OCH_2CF_3) \xrightarrow[\text{of } N_3P_3Cl_6]{} \text{No polymer} \qquad [11]$$
$_{\text{6 or traces of}}$

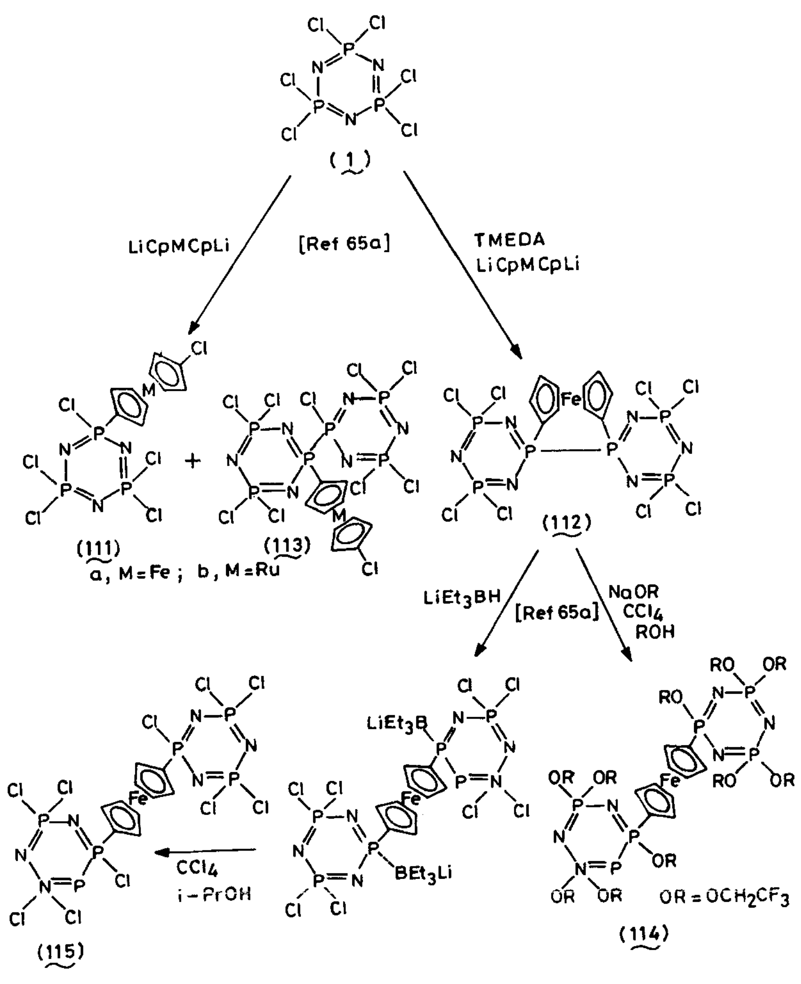


[12]

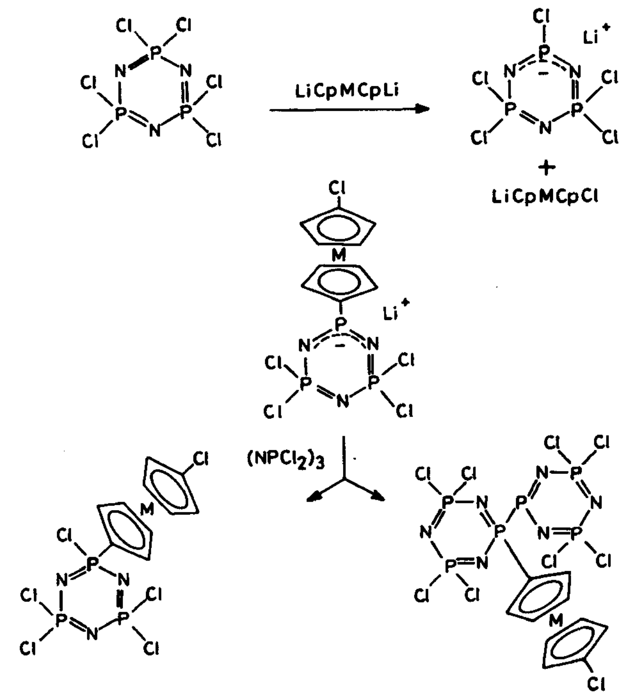
The hexak(trifluoroethoxy) derivative does not undergo polymerization. In contrast, the 2,4-metallocenyl derivative containing a strained ring



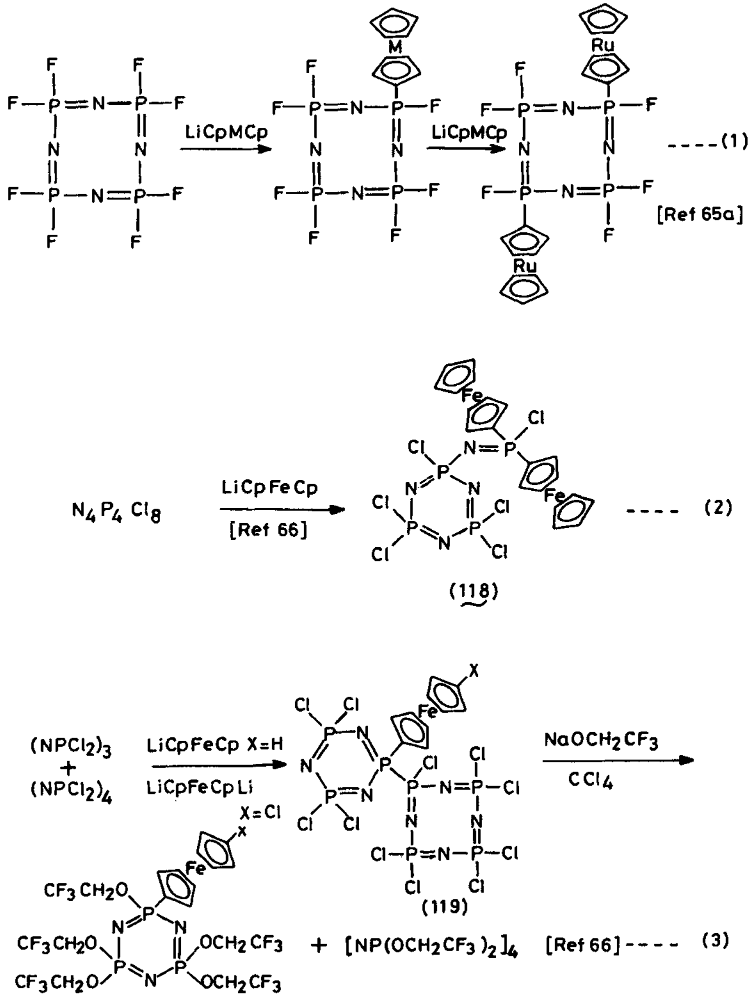
Scheme 3 Reactions of $N_3P_3F_6$ with dilithio metallocenes. X-ray structure of $[N_3P_3(H)(BEt_3)F_2(C_5H_4FeC_5H_4)]$ (**108**) reprinted from Manners *et al.*,[80] with permission from the American Chemical Society (1989).



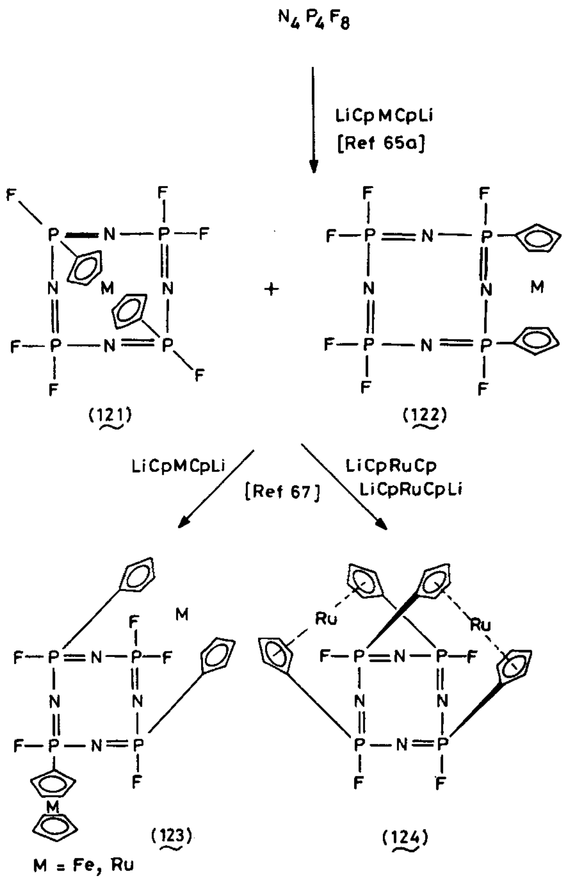
Scheme 4 Reactions of $N_3P_3Cl_6$ with dilithio metallocenes.



Scheme 5 Metal-halogen exchange mechanism observed in the reactions of $N_3P_3Cl_6$ with dilithio metallocenes [reprinted from Allcock *et al.*[65a] with permission from the American Chemical Society (1984)].



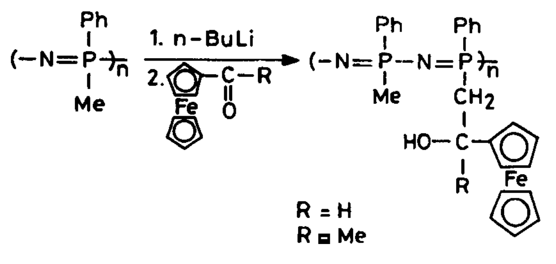
Scheme 6 Reactions of $N_4P_4F_8$ and $N_4P_4Cl_8$ with monolitthio metallocenes.



Scheme 7 Reactions of $N_4P_4F_8$ with dilithio metallocenes.

polymerizes readily due to a release of ring strain. (Eqn [12]). However, if instead of the trifluoroethoxy group, a phenoxy group is the substituent, only low amounts of polymer are formed.[70]

An alternative route towards the synthesis of ferrocenyl-containing polyphosphazenes consists of deprotonation of poly(methylphenylphosphazene) by n-butyllithium followed by reaction of ferrocene carboxaldehyde or acetylferrocene[71] (Eqn. [13]):

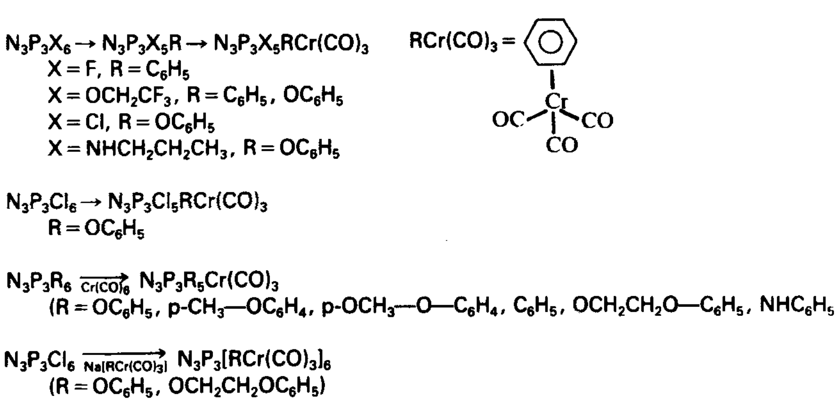


[13]

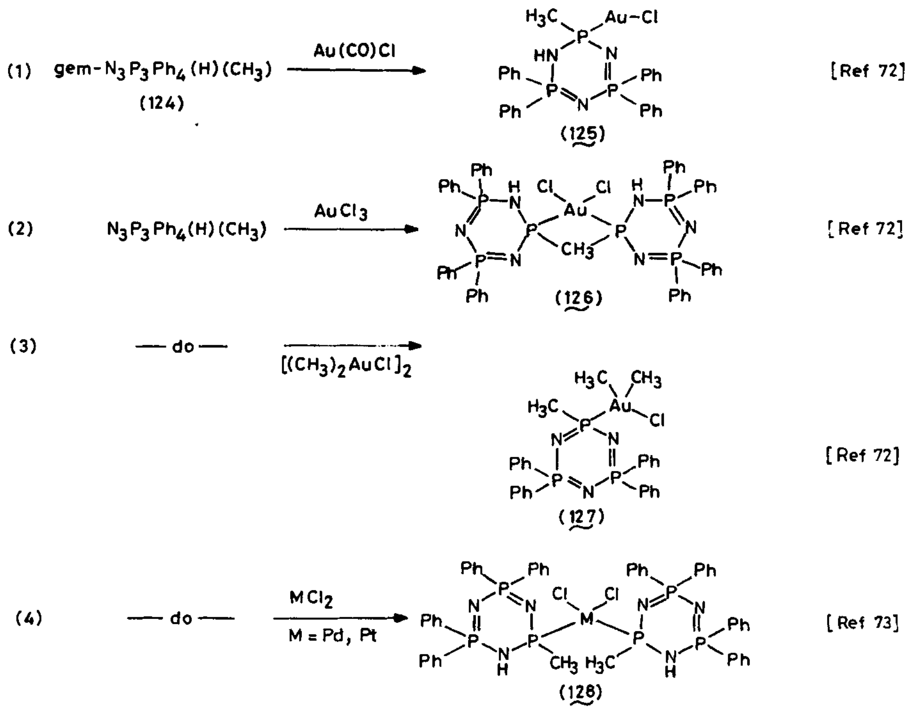
The properties of many of these polymetallocenyl phosphazenes remain largely unexplored so far, although it is speculated that with their high metal content they could behave as electrically conducting polymers.

4 DIRECT METAL–PHOSPHORUS ATOM INTERACTIONS

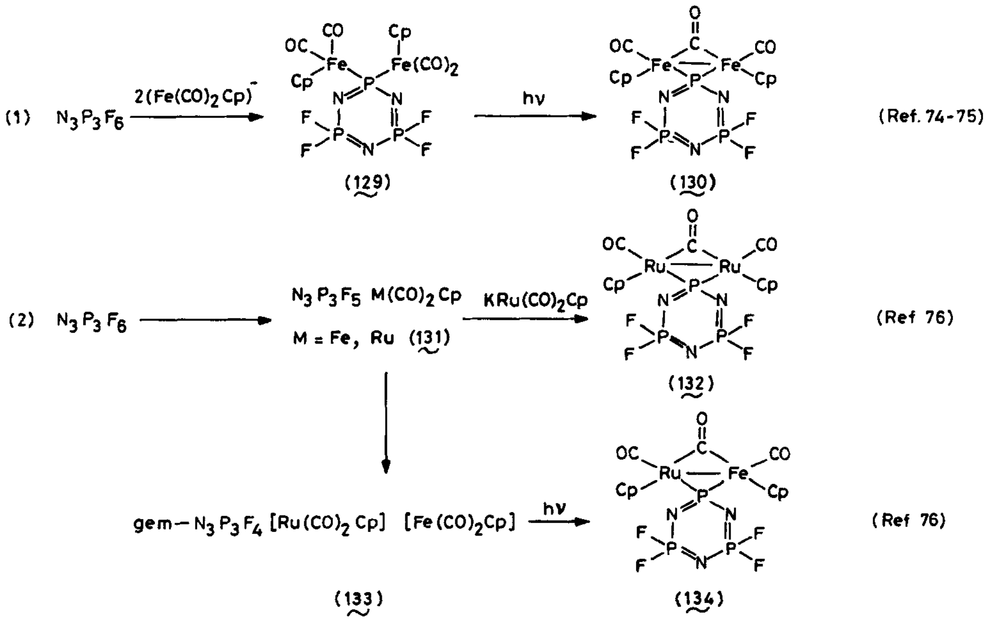
One of the earliest synthetic methods of linking the phosphorus atom of the cyclophosphazene ring directly to a metal involves the use of the hydridocyclophosphazene, *gem*-$N_3P_3Ph_4(CH_3)(H)$. Two resonance forms are possible (Eqn [14]).



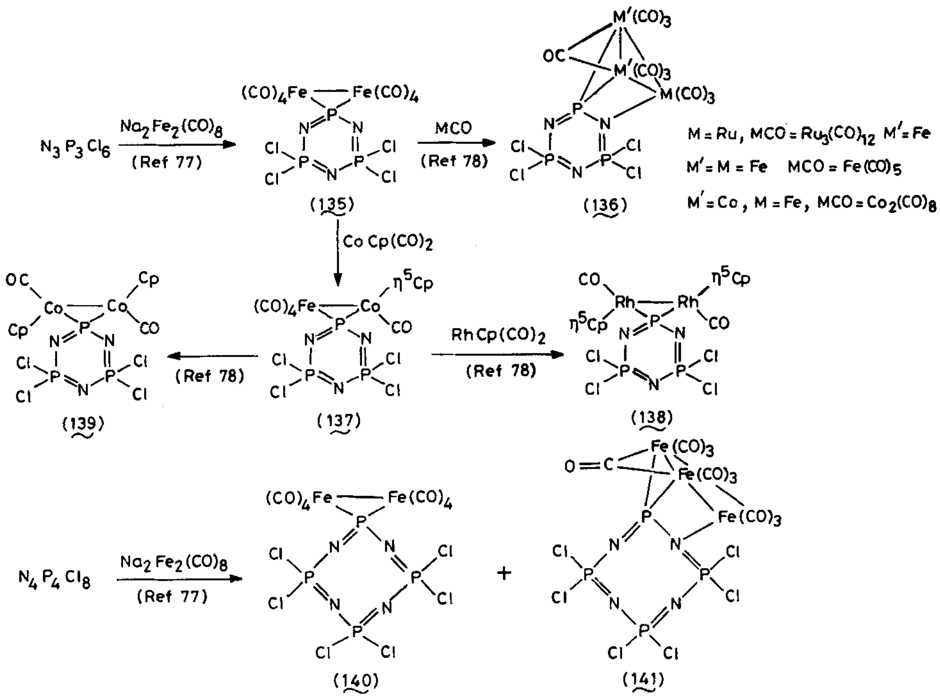
Scheme 8 Cyclophosphazenes attached to η^6(–C$_6$H$_4$–Cr(CO)$_3$) [Ref 68]



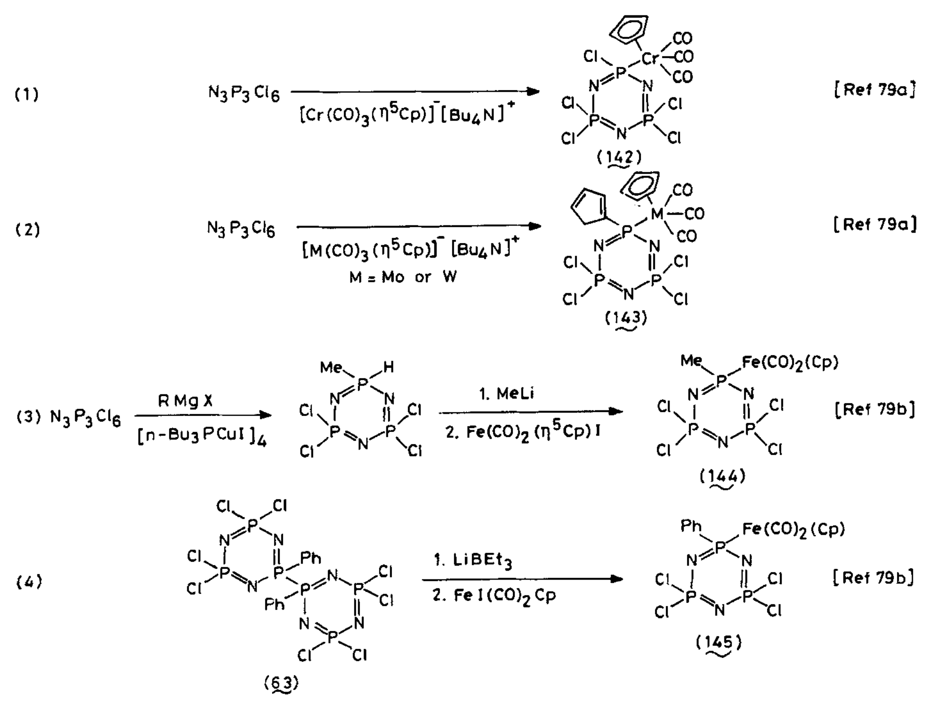
Scheme 9 Reactions of the hydridophosphazene $N_3P_3Ph_4(H)(CH_3)$ with transition metals.



Scheme 10 Reactions of $N_3P_3F_6$ with $[M(CO)_2(C_5H_5)]^-$; M = Fe, Ru.



Scheme 11 Reactions of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with $Na_2Fe_2(CO)_8$ and formation of metal clusters on cyclophosphazene templates.



Scheme 12 Direct metal–phosphorus bond derivatives involving metallocenes.

Table 5 Structural parameters for organometallics formed by exocyclic donor groups and P-M bonded systems

No.	Compound	Structure description	Mean P-N ring bond length (Å)	Total average bond length (Å)	Ring bond angles (deg.) P-N-P	Ring bond angles (deg.) N-P-N	Ref.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	$N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ **(72)**	$Cr(CO)_3$ bound in a η^6 manner to the phenyl group attached to phosphorus of the phosphazene ring.	1.569, 1.562, 1.548	1.560	121.3	118.6	68
2	$N_3P_3Cl_4(CH_3)[C_3H_3Co_2(CO)_6]$ **(73)**	Terminal acetylene unit. Dicobalt unit attached to acetylenic triple bond.	1.606, 1.574, 1.559	1.580	121.9	117.9	53
3	$N_3P_3Cl_4(CH_3)[C_3H_3Co_2(CO)_6]$ **(74a)**	Internal acetylene unit attached to dicobalt hexacarbonyl.	1.616, 1.581, 1.550	1.582	121.3	117.3	53
4	$N_3P_3Cl_4(C_3H_7)[C_3H_3Co_2(CO)_6]$ **(74b)**	Terminal acetylene unit attached to dicobalt hexacarbonyl.	1.582, 1.552, 1.517	1.550	121.3	118.3	53
5	$N_3P_3Cl_4(Ph)(PPh_2)\cdot Cr(CO)_5$ **(89)**	Phosphine attached to cyclophosphazene by P-P bond. Phosphine acts as a 2e donor.	1.605, 1.584, 1.556[a]	1.582	121.9	117.7	55
6	$N_3P_3Cl_4(Ph)(PPh_2)\cdot Ru_3(CO)_{11}$ **(91)**	Ruthenium cluster attached to terminal phosphine.	1.60, 1.58, 1.57[b] 1.63, 1.55	1.58 1.58	120.9 121.5	118.6 117.9	55
7	$N_3P_3Ph_4(3,5\text{-}Me_2Pz)_2\cdot Mo(CO)_3$ **(96)**	Molybdenum attached to two exocyclic nitrogens of the pyrazole substituents and one ring nitrogen.	1.632, 1.593, 1.557	1.600	122.2	117.6	60
8	$N_3P_3F_5(C_5H_4\text{—}Fe\text{—}C_5H_5)$ **(100a)**	Covalent linkage between a cyclopentadienyl group of ferrocene and cyclophosphazene.	1.586, 1.556, 1.501	1.548	120.8	119.1	65
9	$N_3P_3F_4(C_5H_4\text{—}Fe\text{—}C_5H_4)$ **(107a)**	Cyclopentadienyl groups of metallocene attached to two different phosphorus atoms of the phosphazene ring.	1.394, 1.593, 1.559	1.582	115.8	117.1	67
10	$N_3P_3F_4(C_5H_4\text{—}Ru\text{—}C_5H_4)$ **(107b)**	Cyclopentadienyl groups of metallocene attached to two different phosphorus atoms of the phosphazene ring.	1.601, 1.587, 1.557	1.582	116.5	117.6	65
11	$[N_3P_3Cl_4]_2[C_5H_4\text{—}Fe\text{—}C_5H_4]$ **(112)**	Two cyclophosphazenes containing a P-P bond linked by the ferrocenyl unit.	1.601, 1.575, 1.555[c] 1.604, 1.576, 1.556	1.577 1.579	121.0 121.1	118.7 118.7	65
12	$2,4,6\text{-}N_3P_3F_3(C_5H_4\text{—}Fe\text{—}C_5H_5)(C_5H_4\text{—}Fe\text{—}C_5H_4)$ **(102)**	One metallocenyl unit attached to one phosphorus. The other metallocenyl unit bridges the other two phosphorus atoms of the cyclophosphazene (ANSA type).	1.600, 1.596, 1.592	1.596	115.8	116.8	67
13	$[2,4\text{-}N_3P_3F_2(C_5H_4\text{—}Fe\text{—}C_5H_4)2,2(H)(BEt_3)]^-Li^+$ **(108)**	Phosphazene anion. Metallocenyl unit bridges two P(F) atoms. Lithium coordinated to a ring nitrogen.	1.674, 1.626, 1.592, 1.588, 1.572	1.607	117.3	115.7	80
14	$N_3P_3Cl_5[N{=}P(Cl)(C_5H_4\text{—}Fe\text{—}C_5H_5)_2]$ **(118)**	Phosphazenyl phosphazene. Exocyclic phosphorus attached to metallocene units.	1.607, 1.584, 1.548 P=N (exo): 1.566	1.580	120.9	118.5	66

Table 5 (continued)

No.	Compound	Structure description	Mean P–N ring bond length (Å)	Total average bond length (Å)	Ring bond angles (deg.) P–N–P	Ring bond angles (deg.) N–P–N	Ref.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
15	$N_3P_3Cl_4[(C_5H_4)Fe(C_5H_5)]N_4P_4Cl_7$ **(119)**	The six-membered and eight-membered cyclophosphazene rings attached through a P–P bond. Metallocenyl unit attached to six-membered ring at the phosphorus junction.	Six-membered ring: 1.594, 1.568, 1.559 Eight-membered ring. Average value 1.562	1.574 1.562	120.4 133.8	118.5 121.4	66
16	2,6-$N_4P_4F_6[C_5H_4$—Fe—$C_5H_4]$ **(121a)**	The metallocenyl unit forms[d] a 2,6-*trans*-annular link in the eight-membered cyclophosphazene ring which is distorted into a boat conformation.	—	1.548	135.1	122.2	67
16a	2,6-$N_4P_4F_6(C_5H_4$—Ru—$C_5H_4)$ **(121b)**	The metallocenyl unit forms[d] a 2,6-trans-annular link in the eight-membered cyclophosphazene ring which is distorted into a boat conformation.	1.51, 1.53, 1.57	1.539	134.4	121.9	65a
17	2,6,4-8-$N_4P_4F_4[C_5H_4$—Ru—$C_5H_4]_2$ **(124)**	A bis (*trans*-annular) metallocenyl cyclophosphazene.	—	1.565	134.2	121.9	67
18	2,2-$N_3P_3F_4(Fe(C_5H_5)(CO)_2)_2$ **(129)**	Two geminal P–Fe bonds.	1.666, 1.576, 1.530[e]	1.591	122.5	117.3	74, 75
19	2,2-$N_3P_3F_4\{[Fe(C_5H_5)CO]_2CO\}$ **(130)**	Phosphazene with a three-membered spirocyclic ring at phosphorus.	1.635, 1.565, 1.542[f]	1.581	121.8	117.4	74, 75
20	2,2-$N_3P_3Cl_4[Fe(CO)_4]_2$ **(135)**	Phosphazene with a three-membered spirocyclic ring at phosphorus.	1.64, 1.61, 1.53[g] 1.64, 1.57, 1.55	1.59 1.59	122.3 122.6	117.5 117.1	77
21	2,2-$N_3P_3F_4\{[Ru(C_5H_5)CO][Fe(C_5H_5)CO]CO\}$ **(134)**	Three membered spirocyclic ring at phosphorus with a Fe—Ru bond.	1.65, 1.58, 1.55[h]	1.59	121.6	117.6	76
22	2,2-$N_3P_3Cl_4[Co(C_5H_5)CO]_2$ **(139)**	Three-membered spirocyclic ring with Co–Co bond.	1.641, 1.579, 1.564[i]	1.595	120.5	117.5	78
23	2,2-$N_3P_3Cl_4[Rh(C_5H_5)CO]_2$ **(138)**	Three-membered spirocyclic ring with Rh–Rh bond.	1.63, 1.60, 1.54[j] 1.65, 1.59, 1.55	1.59 1.60	120.6 120.8	117.0 117.1	78
24	2,2-$N_3P_3Cl_4\{(Fe(CO)_4)[Co(C_5H_5)CO]\}$ **(137)**	Three-membered spirocyclic ring with Fe–Co bond.	1.631, 1.587, 1.553[k]	1.590	121.1	117.6	78
25	$N_3P_3Cl_4(CH_3)[Fe(C_5H_5)(CO)_2]$ **(144)**	P–Fe bond geminal to P–CH_3.	1.638, 1.574, 1.546 Fe–P, 2.214	1.586	122.2	117.3	79b
26	$N_3P_3(OR)_5[Fe(C_5H_5)(CO)_2]$ R = OCH_2CF_3	P–Fe bond geminal to P–OR.	1.629, 1.580, 1.567 Fe–P, 2.196	1.592	121.8	117.4	81
27	$N_3P_3Cl_5[Cr(C_5H_5)(CO)_3]$ **(142)**	P–Cr bond.	1.61, 1.57, 1.57 Cr–P, 2.35	1.58	119.8	116.0	79a

28	2,2-$N_3P_3Cl_4(C_5H_4)[Mo(C_5H_5)(CO)_3]$ **(143a)**	P–Mo bond geminal to P–C_5H_4 unit.	1.65, 1.59, 1.55 Mo–P, 2.51	1.60	122.1	117.2	79a
29	$N_3P_3Cl_4[Co_2(CO)_6][Fe(CO)_3]$ **(136c)**	Dicobalt unit bound to phosphorus in a three-membered spirocyclic ring. $Fe(CO)_3$ linked to ring nitrogen and the dicobalt unit.	1.648, 1.582, 1.541[l]	1.590	122.7	115.3	78
30	$N_3P_3Cl_4[(Fe(CO)_3)_3CO]$ **(136b)**	Tri-iron cluster. Di-iron unit attached geminally to phosphorus. Third Fe bound to ring nitrogen.	1.63, 1.58, 1.56[m] 1.64, 1.58	1.59 1.60	124.3 124.7	114.3 114.6	77
31	$N_3P_3Cl_4[(Fe(CO)_3)_2Ru(CO)_3CO]$ **(136a)**	Di-iron ruthenium cluster. Di-iron unit attached geminally to phosphorus. Ru bound to ring nitrogen.	1.62, 1.59, 1.58[n] 1.67, 1.58, 1.56	1.60 1.60	125.0 122.7	114.3 115.6	77
32	$[N_3P_3Ph_4(CH_3)(H)]_2 \cdot PdCl_2$ **(128)**	Hydridophosphorus tautomerizes to P(III). Two ring P(III) atoms form a *cis* geometry around square planar Pd.	1.704, 1.652, 1.579[o]	1.645	125.0	111.1	73

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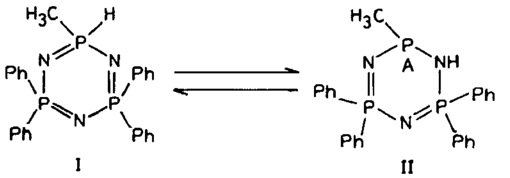
[a] P–P, 2.234 Å; P–Cr, 2.387 Å. [b] Two molecules in a symmetric unit cell. P–P, 2.25 Å; P–Ru, 2.343 Å. [c] Two molecules in a symmetric unit cell. P–P, 2.219 Å. [d] P–C_{cp} mean distances are 1.756 Å, 1.739 Å respectively in **121a** and **121b**. [e] Fe··· Fe, 3.922 Å; P–Fe, 2.272 Å; 2.277 Å; Fe–P–Fe, 119.1°. [f] Fe–Fe, 2.593 Å; P–Fe, 2.179 Å; 2.193 Å; Fe–P–Fe, 72.77°. [g] Two molecules in a symmetric unit cell. P–Fe, 2.241 Å, 2.211 Å; Fe–Fe, 2.746 Å. Fe–P–Fe, 76.2°. [h] P–Ru, 2.231 Å; P–Fe, 2.256 Å; Ru–P–Fe, 73.93°; Ru–Fe, 2.698 Å. [i] Co–Co, 2.552 Å; P–Co, 2.14 Å; Co–P–Co, 73.0°. [j] Rh–Rh, 2.748 Å; P–Rh, 2.23 Å; Ph–P–Rh, 75.9°. [k] Two molecules in a symmetric unit cell. Co–Co, 2.56 Å; Co–Fe, 2.647 Å; P–Co, 2.149 Å; P–Fe, 2.22 Å; Co–P–Fe, 74.5°. [l] Co–Co, 2.56 Å; Co–Fe, 2.65 Å, 2.64 Å; Co–P, 2.125 Å; Fe–N, 2.05 Å; Co–P–Co, 73.9°. [m] Two molecules in a symmetric unit cell. Fe–Fe, 2.62–2.68 Å; P–Fe, 2.19 Å; Fe–N, 2.04 Å; Fe–P–Fe, 73.5°. [n] Two molecules in a symmetric unit cell. Fe–Fe, 2.62 Å; Fe–Ru, 2.73 Å; Fe–P, 2.19 Å, Ru–N, 2.16 Å; Fe–P–Fe, 73.5°. [o] Pd–P, 2.242 Å; P–Pd–P, 87.4°.



[14]

In the tautomer **II** the phosphorus (A) is now trivalent and is expected to coordinate to a transition metal. This expectation is realized: monomeric complexes are formed with Au(CO)Cl and $[(CH_3)_2AuCl]_2$ (Scheme 9). An ionic product $[(N_3P_3Ph_4Me)_2AuCl_2]^+[AuCl_4]^-$ is also formed. In these examples a direct P–Au bond is present.[72]

Similarly the phosphorus(III) atoms of two such hydridophosphazenes are involved in coordination to palladium or platinum.[73] Scheme 9 summarizes these results.

Allcock and co-workers have found that the reaction of $N_3P_3F_6$ with $[Fe(CO)_2C_5H_5]^-$ affords the geminally substituted derivative, $N_3P_3F_4[Fe(CO)_2C_5H_5]_2$. Upon photolysis a three-membered spirocyclic product containing a Fe–Fe bond is formed[74, 75] (Scheme 10). The ruthenium analogue and a mixed iron–ruthenium derivative have been synthesized using similar synthetic methodology.[76]

Reaction of the disodium salt $Na_2Fe_2(CO)_8$ with $N_3P_3Cl_6$ affords the versatile spirocyclic

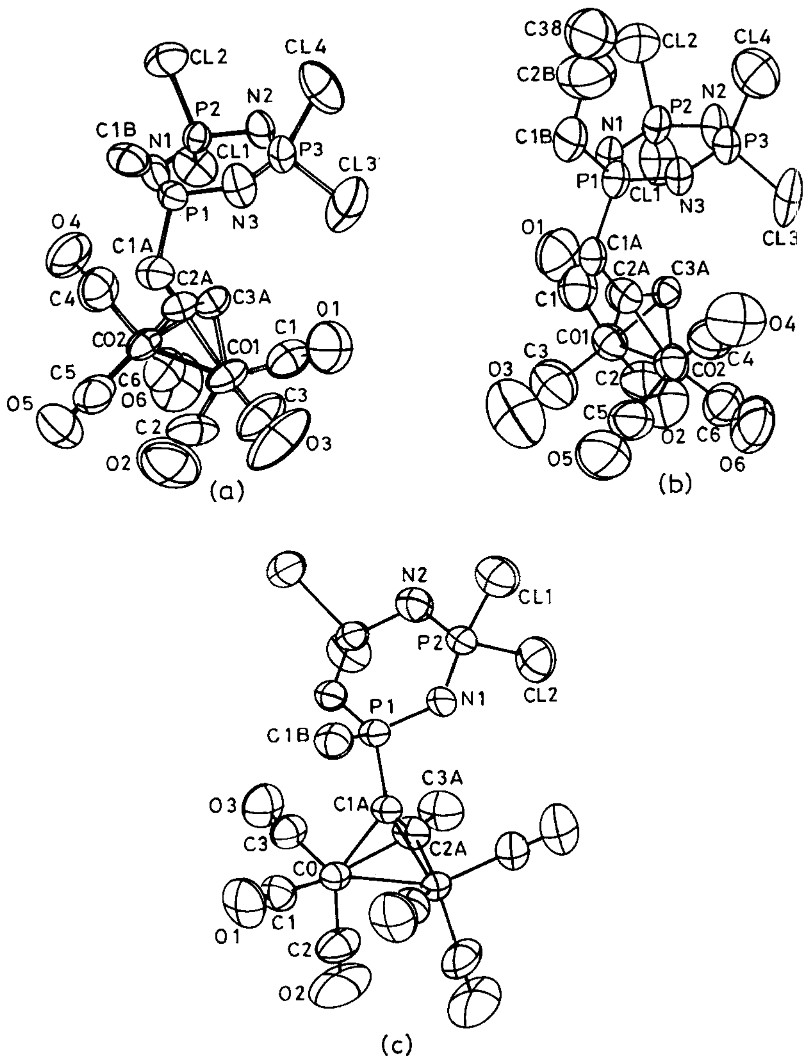


Figure 4 X-ray structures of (a) $N_3P_3Cl_4(CH_3)CH_2(C{\equiv}CH)\cdot Co_2(CO)_6$ (**73**); (b) $N_3P_3Cl_4(C_3H_7)(CH_2C{\equiv}CH)\cdot Co_2(CO)_6$ (**74b**); (c) $N_3P_3Cl_4(CH_3)(C{\equiv}C{-}CH_3)\cdot Co_2(CO)_6$ (**74a**) [reprinted from Allcock *et al.* with permission from the American Chemical Society (1984)].

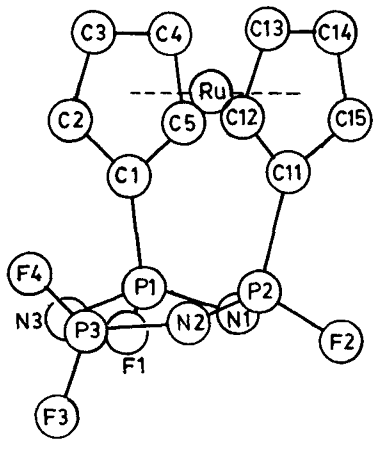


Figure 5 X-ray structure of $N_3P_3F_4(C_5H_4$—$RuC_5H_4)$ (**107b**) [reprinted from Allcock *et al.*[65a] with permission from the American Chemical Society (1984)].

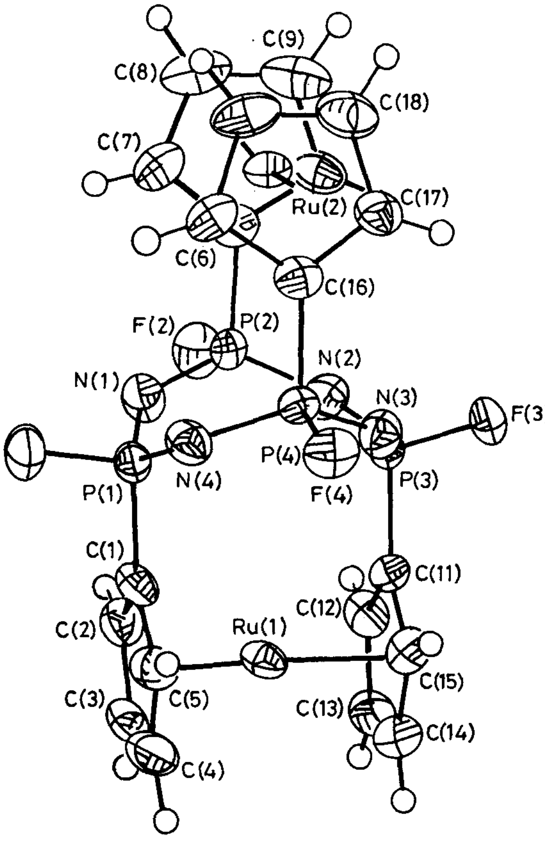


Figure 6 X-ray structure of $N_4P_4F_4(C_5H_4$—Ru—$C_5H_4]_2$ (**124**) [reprinted from Lavin *et al.*[67b] with permission from the Royal Chemical Society (1986)].

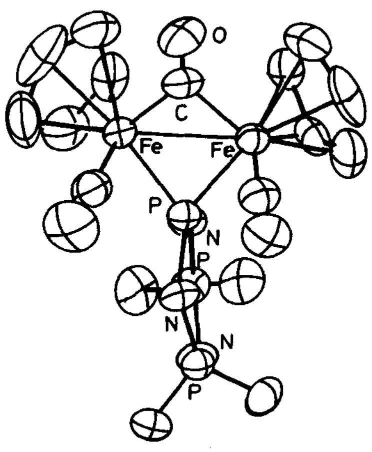


Figure 7 X-ray structure of $N_3P_3F_4[(Fe(C_5H_5(CO)_2CO]$ (**130**) [reprinted from Allcock *et al.*[74] with permission from the American Chemical Society (1979)].

di-iron octacarbonyl-bonded phosphazene, $N_3P_3Cl_4Fe_2(CO)_8$ (Scheme 11).[77] This compound acts as a template for the construction of transition-metal dimers or clusters.[78] Several such clusters have been isolated (Scheme 11). In contrast, the eight-membered ring $N_4P_4Cl_8$ reacts with $Na_2Fe_2(CO)_8$ to give a di-iron cluster along with the expected di-iron spirocyclic compound. Attachment of transition metals already bound to cyclopentadienyl ligands to cyclophosphazenes is accomplished as outlined in Scheme 12 (Reactions (1), (2)]. Accordingly, $N_3P_3Cl_6$ reacts with the anion $[Cr(CO)_3(C_5H_5)]^-[Bu_4N]^+$ to give the mono-derivative, $N_3P_3Cl_5[Cr(CO)_3(C_5H_5)]$.[79] Interestingly, analogous reaction with the molybdenum or analogue tungsten affords the compound $N_3P_3Cl_4(C_5H_4)[(M(CO)_3(C_5H_5)]$. Here a cyclopentadienyl group is directly attached to the phosphorus geminal to the metal.[79a] An alternative route [Scheme 12, Reactions (3), (4)] involves reactions of lithium 2-methyl-4,4,6,6-tetrachlorocyclotriphosphazenide and lithium 1-phenyl-2-triethylborata-4,4,6,6-tetrachlorocyclotriphosphazene with dicarbonyl cyclopentadienyliodoiron.

5 X-RAY STRUCTURES

The X-ray structural data for the transition-metal and organometallic complexes involving either exocyclic ligands on cyclophosphazenes or direct P–M bonds are summarized in Table 5. Descriptions by category are given below.

5.1 Acetylenic phosphazenes

Three X-ray structures are known (Fig. 4). In all of these the acetylenic moiety is linked to a dicobalt hexacarbonyl fragment in a tetrahedral fashion (Table 4, Reaction 1; Table 5).[53] The P–N ring bond lengths closest to the organic unit are longer than in $N_3P_3Cl_6$, the next adjacent bonds are the shortest, and those farthest apart from the organic group are of intermediate length. This trend is similar to the one observed when ring nitrogen atoms participate in coordination to transition metals, except that the longest bond length is only slightly longer than the 'normal' P–N bond length in $N_3P_3Cl_6$ (Table 5). The dicobalt-hexacarbonyl unit is bonded to the acetylenic site and the alkynyl groups are bent away from the dicobalt moiety in a *cis* geometry. The

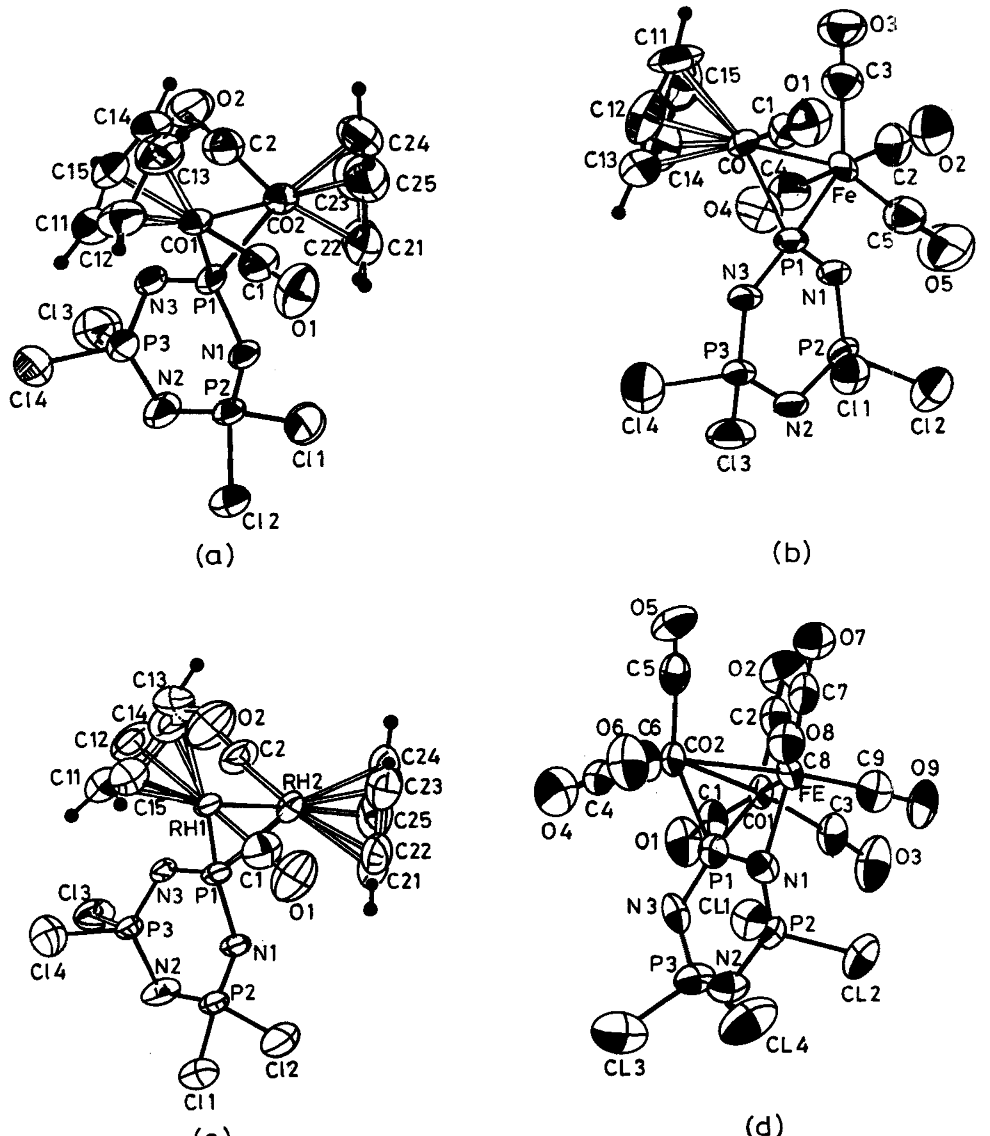


Figure 8 X-ray structures of (a) $N_3P_3Cl_4[Co(C_5H_5)CO]_2$ (**139**); (b) $N_3P_3Cl_4[Fe(CO)_4(Co(C_5H_5)CO)]$ (**137**); (c) $N_3P_3Cl_4[Rh(C_5H_5)CO]_2$ (**138**); (d) $N_3P_3Cl_4[Co_2(CO)_6][Fe(CO)_3]$ (**136c**) [reprinted from Allcock *et al.*[78] with permission from the American Chemical Society (1985)].

Co–Co bond distances are unexceptional (*ca* 2.454 Å; 0.2454 nm) and are comparable with literature values. No interference from phosphazene ring nitrogen atoms is seen.

5.2 Phosphinophosphazenes and pyrazolyl phosphazenes

X-ray structures of the compounds $N_3P_3Cl_4(Ph)(PPh_2).Cr(CO)_5$ and $N_3P_3Cl_4(Ph)(PPh_2).Ru_3(CO)_{11}$ are known (Fig. 2). In both of these compounds phosphino phosphorus acts as a normal two-electron donor and completes the geometry around chromium and ruthenium respectively.[55] The ring P–N bond length variations are similar to those in other compounds discussed earlier. The P–P bond length in the complexes is lengthened (2.22 Å; 0.22 nm) in the chromium complex, and in the ruthenium complex (2.24 Å; 0.224 nm) as compared with the parent phosphino phosphazene (2.119 Å; 0.2119 nm).

The pyrazolyl phosphazene $N_3P_3Ph_4(3,5\text{-}Me_2Pz)_2$ forms a 1:1 complex with $Mo(CO)_3$ (Fig. 3).[60] An interesting feature of this structure, as can be seen from the figure, is that two of the geminal exocyclic pyrozolyl pyridinic nitrogen atoms and a phosphazene ring nitrogen atom are involved in coordination to the metal.[60]

5.3 Metallocenyl phosphazenes

Several X-ray structures of metallocenyl phosphazenes are now known. These are summarized in Table 5.

The influence of the cyclophosphazene ring on the metallocene structure is negligible. In almost all instances the cyclopentadienyl rings are planar and the two cyclopentadienyl rings are coplanar. In contrast, the cyclophosphazene ring is influenced by the metallocenyl unit. While this influence is not significant in examples where the metallocenyl unit is attached to the phosphazene ring through one end of the cyclopentadienyl ring, the influence is considerably greater where the metallocenyl unit acts as an intramolecular bridge. Thus in $N_3P_3F_4(C_5H_4\text{—}RuC_5H_4)$ (Fig. 5) the phosphazene ring is distorted; N(1) between the bridging sites is displaced by nearly 0.51 Å (0.051 nm) from the remaining five atoms, the ring angle at N(1) is much smaller (113.1°) than other ring angles at nitrogen (average 118°).[65] Similarly the ring angles at P(1) and P(2), the bridge sites, are smaller than those observed elsewhere. The authors attribute these changes to an attempt by the phosphazene ring to relieve the ring strain imposed upon it by the bridging metallocenyl unit.

A remarkable distortion of the cyclophosphazene ring is seen in the bis(*trans*-annular diruthenocenyl) derivative $2\text{–}6,4\text{–}8\text{-}N_4P_4F_4\text{-}[(C_5H_4)_2Ru]_2$ (Fig. 6).[67] The ring adopts a boat conformation in comparison with the planar geometry observed for the parent cyclophosphazene $N_4P_4F_8$. The average bond angles at phosphorus and nitrogen are narrower (Table 5), indicating the adjustments required by the phosphazene ring to accommodate the steric constraints imposed by two *trans*-annular bridges.

5.4 Phosphorus–metal direct bonds

A number of examples of P–M bonded systems are known (Table 5). In these there are compounds that contain a three-membered spirocyclic ring involving the ring phosphorus atom and two metal–metal centres (Fe–Fe, Co–Co, Rh–Rh, Fe–Ru, or Fe–Co].[74–78] Figure 7 gives the structure of an Fe–Fe compound. The angle at the phosphorus contained in the spirocyclic ring is very narrow (*ca* 70 °; Table 5). The bond length and bond angle variations are similar to those observed in other derivatives described earlier. Trimetallic clusters are formed from cyclophosphazenes containing the three-membered spirocyclic units (Fig. 8). In all of these, the presence of the trimetallo unit disrupts the bond length symmetry of the cyclophosphazene skeleton. The longest bond lengths are those next to the nitrogen involved in coordination to the metal. The smallest endocyclic angles are associated with the phosphorus contained in the spirocyclic unit.

The average P–N bond lengths in the complex formed from the hydridophosphazene $[N_3P_3Ph_4(CH_3)(H)]_2.PdCl_2$ are much longer than any P–N bond lengths discussed here.[73] This is because, as discussed earlier, the hydridophosphazene forms a complex with the metal in its tautomeric form containing a P–N single bond. Therefore, the average P–N bond lengths involved are longer than in other examples where all the ring phosphorus atoms are pentavalent.

CONCLUSION

From the foregoing discussion it is abundantly clear that cyclophosphazene-based ligand systems are extremely versatile in their interactions with transition metals, resulting in a rich fare of coordination and organometallic chemistry. Both skeletal nitrogen participation and exocyclic group ligation are possible, depending on proper substituent choice. It is possible to develop an even larger variety of ligand systems because of the facile substitution reaction pathways available in cyclophosphazene chemistry. Thus, cyclophosphazenes can be used as structural motifs for generating ligand systems with specific numbers and types of coordination sites. These may find applications in the construction of model structures of active sites of metalloenzymes and in synthesis of heterometallic systems. Further, most of the small-molecule chemistry has not yet been fully translated to the more interesting polyphosphazenes. Polyphosphazene-based ligand systems are expected to be useful in such diverse applications such as conducting polymers, polymer catalysts for organic transformations, bioactive materials, and so on.

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