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Review

Cyclophosphazene-based multi-site coordination ligands

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Contents

Abstract

This review deals with the recent developments in the design, assembly and utility of cyclophosphazene-based ligands. The reactive periphery of the chlorocyclophosphazenes allows their ready elaboration into a variety of multi-site coordination ligands such as pyrazolylcyclophosphazenes, cyclophosphazene hydrazides, pyridyloxycyclophosphazenes, pyridylaminocyclophosphazenes, phosphine-containing cyclophosphazenes, etc. The versatile coordination behavior of these diverse ligand systems is described. The extension of the small-molecule chemistry to the more complex polymer systems, which has been done in a few systems, is described. The utility of aminocyclophosphazenes for preparing multi-metallic architectures is also discussed.

Keywords: Cyclophosphazenes; Cyclophosphazene ligands; Multi-site coordination ligands; Polymeric ligands; Aminocyclophosphazenes; Metal complexes; Heterobimetallic complexes

1. Introduction

Cyclophosphazenes are inorganic heterocyclic rings containing a $[N=PX_2]$ repeat unit. Among this family of compounds, the chlorocyclophosphazenes $N_3P_3Cl_6$ (**1**) and $N_4P_4Cl_8$ (**2**) (Chart 1) have received maximum attention [1–10].

Traditionally the chemistry of cyclophosphazenes has revolved around two main themes:

(1) Nucleophilic substitution reactions of halogenocyclophosphazenes;
(2) Ring-opening polymerization of $N_3P_3Cl_6$ (**1**) to the linear polydichlorophosphazene, $[N=PCl_2]_n$. The versatility of the latter lies in its ready elaboration to various poly(organophosphazene)s by utilizing the nucleophilic substitution of the reactive P–Cl bonds [11–14].

In addition to these two main areas of research, cyclophosphazenes have also been attracting interest as possible ligands in coordination and organometallic chemistry [1,3,4,8–10,15–19]. The ring nitrogen atoms of cyclophosphazenes have sufficient basicity and can interact with Lewis acids. Further, the

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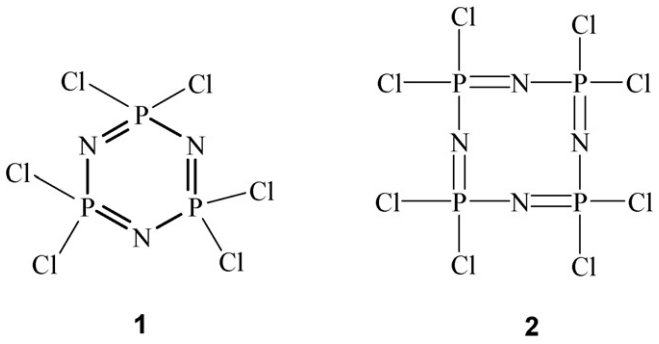
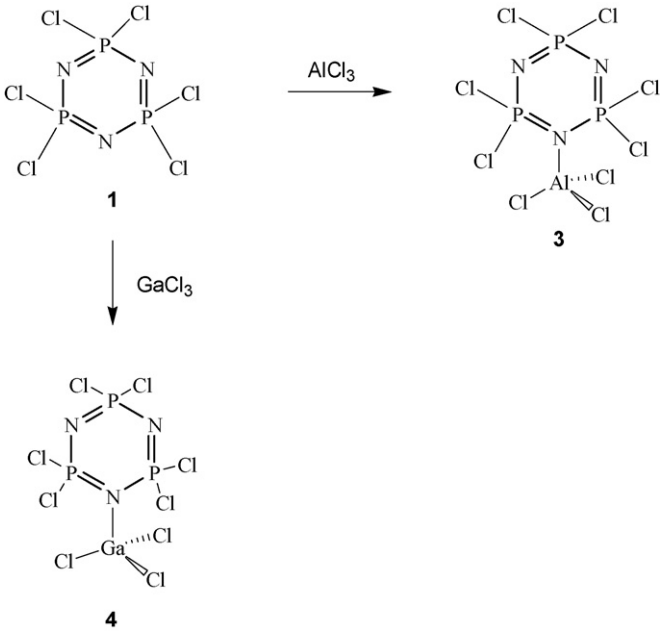


Chart 1. Representative examples of chlorocyclophosphazenes.

Lewis basicity of these ring nitrogen atoms can be modulated by a proper choice of substituents on phosphorus atom [6,15,16,20–24]. Also, increasing the ring size of the cyclophosphazenes can enhance their versatility as ligands owing to greater ring flexibility [15–17,19]. Many protonated cyclophosphazenes as well as metalated cyclophosphazenes have been prepared using this approach [6,15,16,20–24]. This aspect has been recently reviewed [16]. More recently, Lewis acid adducts of $N_3P_3Cl_6$ (**1**) have been isolated and characterized. Thus, 1:1 adducts, $N_3P_3Cl_6{\cdot}AlCl_3$ (**3**) and $N_3P_3Cl_6{\cdot}GaCl_3$ (**4**) were isolated (Scheme 1) [25]. Compounds **3** and **4** show dative N–Al (1.997(5) Å) and N–Ga (2.049(3) Å) bonds. Further, as a result of coordination, the P–N bonds flanking the site of coordination are lengthened considerably [average P–N distance: (1.658(2) Å for **3** and 1.643(3) Å for **4**)] in comparison to other P–N distances [average P–N distance: (1.565(4) Å for **3** and 1.570(4) Å for **4**)]. Such an increase in P–N bond lengths is consistent with the non-availability of the ring nitrogen lone pair for skeletal bonding. The cyclophosphazene ring undergoes substantial puckering upon the formation of **3** and **4** indicating the structural influence of coordination on the cyclophosphazene ring.



Scheme 1. Lewis acid adducts of $N_3P_3Cl_6$ with $AlCl_3$ and $GaCl_3$ [25].

Relying on the ring nitrogen basicity of cyclophosphazenes as the sole ingredient of ligand design severely restricts the utility of these ring systems as ligands. If on the other hand, additional coordination sites are provided on the cyclophosphazene platform, the versatility of such ligands enhances dramatically. The facile substitution of P–Cl bonds allows ready construction of cyclophosphazenes where suitable coordinating groups are placed on the phosphorus centers. The beauty of this approach lies in the ability to tailor the type, number and orientation of the coordinating units. In principle a library of multi-site coordination ligands can be readily accessed using this approach. This review will focus on such sigma donating cyclophosphazene ligands and their coordination chemistry.

2. Pyrazolylcyclophosphazenes

The pyrazole ligand is known for its versatile coordination behavior. The –NH unit of the pyrazole group allows it to be linked to other atoms such as boron [26–42], carbon [35,43–52], or phosphorus [53–62]. This strategy allows the synthesis of ligands containing multiple pyrazole units. Anionic and neutral ligands can be readily prepared. Thus, boron-based pyrazole ligands, viz., poly(pyrazolyl)borates (**5**) (Chart 2), first introduced by Trofimenko, have become extremely popular as multidentate ligands and have carved a niche for themselves in several areas of coordination, organometallic and bioinorganic chemistry [26–42].

More recently neutral analogues of poly(pyrazolyl)borates are also being studied. Thus, carbon-based (such as **6**) [35,43–52] and phosphorus-based pyrazole ligands (such as **7**) [53–62] (Chart 2) have been receiving attention. The synthesis of **7**, for example is readily carried out by the reaction of 3,5-dimethylpyrazole with $MeP(S)Cl_2$ in the presence of triethylamine (Scheme 2) [55].

The reaction shown in Scheme 2 involves nucleophilic substitution at phosphorus and proceeds by the replacement of the chloride by the pyrazolyl group generating new P–N bonds. Triethylamine acts as a hydrogen chloride scavenger in the reaction. Utilizing a similar approach several pyrazolyl-

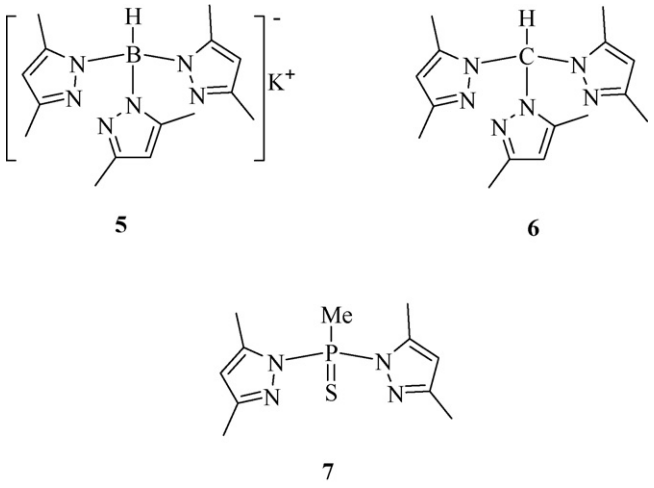
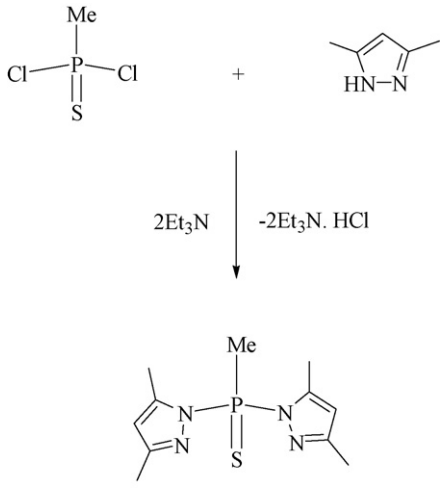


Chart 2. Boron-, carbon- and phosphorus-based polypyrazolyl ligands [26–62].



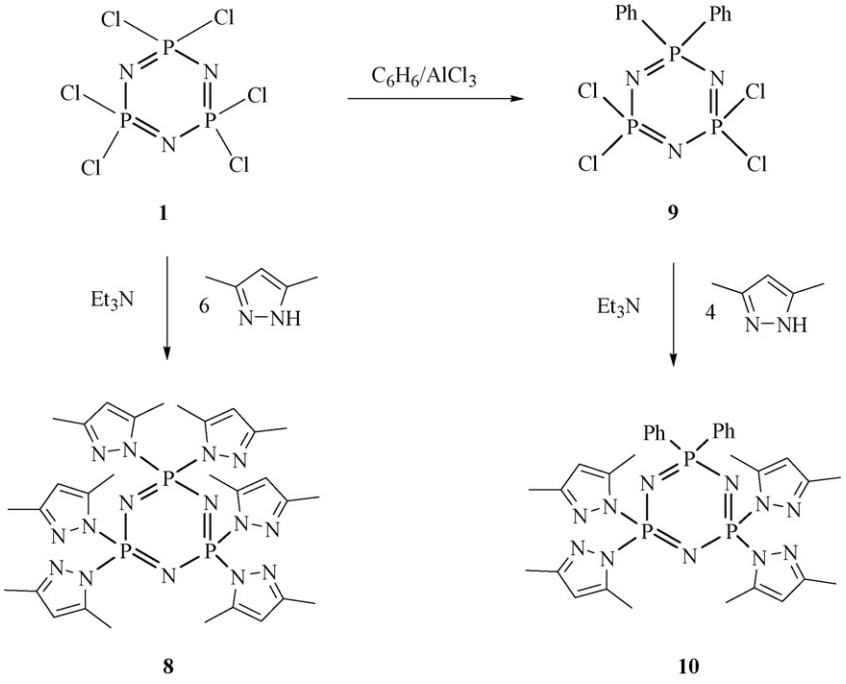
7

Scheme 2. Synthesis of phosphorus-based pyrazole ligands [55].

cyclophosphazenes have been synthesized. For example, the reaction of $N_3P_3Cl_6$ with 6 equiv. of 3,5-dimethylpyrazole in the presence of triethylamine affords $N_3P_3(3,5\text{-}Me_2Pz)_6$ (**8**) (Scheme 3) [63,64]. Site-differentiated ligands can be prepared by "blocking" some sites [65–78] and building the coordination manifold on other sites. This is based on the known regio- and stereo-selectivities involved in the nucleophilic substitution reactions of chlorocyclophosphazenes. For example, the reaction of $N_3P_3Cl_6$ with benzene in presence of $AlCl_3$ leads to the formation of *gem*-$N_3P_3Ph_2Cl_4$ (**9**) [65].

In **9** two sites on a phosphorus center are blocked by the phenyl substituents. The other two phosphorus centers are available for elaboration. Accordingly the reaction of **9** with 4 equiv. of 3,5-dimethylpyrazole affords *gem*-$N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4$ [63,72] (**10**) (Scheme 3). Several approaches for generation of site-differentiated ligands are available [65–81]. For example the reaction of $N_3P_3Cl_6$ with several difunctional reagents such as *N*-methylethanolamine [66], *N*,*N*-dialkylethylenediamine [67,73] or 2,2′-biphenol [68,69] leads to spirocyclic products containing two or four geminal P–Cl bonds. Similarly the reaction of $N_3P_3Cl_6$ with 4 equiv. of ammonia leads to a geminal product $N_3P_3Cl_4(NH_2)_2$ (**14**) [70,71]. On the other hand stoichiometric reaction of $N_3P_3Cl_6$ with phenols can afford various products including $N_3P_3Cl_5(OPh)$ (**18**) [81], *non-gem-cis* $N_3P_3(OPh)_4Cl_2$ (**19**) [81], and $N_3P_3(OPh)_5Cl$ (**20**) [68]. Representative examples of such site-differentiated cyclophosphazenes are shown in Charts 3 and 4. These compounds have been utilized for preparing various pyrazolylcyclophosphazenes (Charts 5–9) [16,17,66,72,73,75,78–95]. Pyrazolylcyclophosphazenes show rich and varied coordination chemistry [16,17]. Several types of coordination modes have been observed for this family of cyclophosphazene ligands. The participation of pyrazolyl moieties along with (or without) the cyclophosphazene ring nitrogen atoms leads to diverse coordination modes [16,17,64,72–74,78,79,82–95]. Representative types of complexes formed and the coordination response of the pyrazolylcyclophosphazene ligands are shown in Chart 10. A brief summary of this coordination behavior is as follows:

1. $N_3P_3(3,5\text{-}Me_2Pz)_6$ forms 1:1 and 1:2 complexes such as $N_3P_3(3,5\text{-}Me_2Pz)_6{\cdot}CuCl_2$ (**42**) [64], $[\{N_3P_3(3,5\text{-}Me_2Pz)_5O\}{\cdot}2CuCl_2]\{3,5\text{-}Me_2PzH\}$ (**42a**) [82], $N_3P_3(3,5\text{-}Me_2Pz)_6{\cdot}2CuI$ (**42b**) [87] and $N_3P_3(3,5\text{-}Me_2Pz)_6{\cdot}2ZnCl_2$ (**42c**) [87]. In **42**, **42a**, **42b** and **42c** the coordination



1 9 8 10

Scheme 3. Synthesis of pyrazolylcyclophosphazenes [63–65,72].

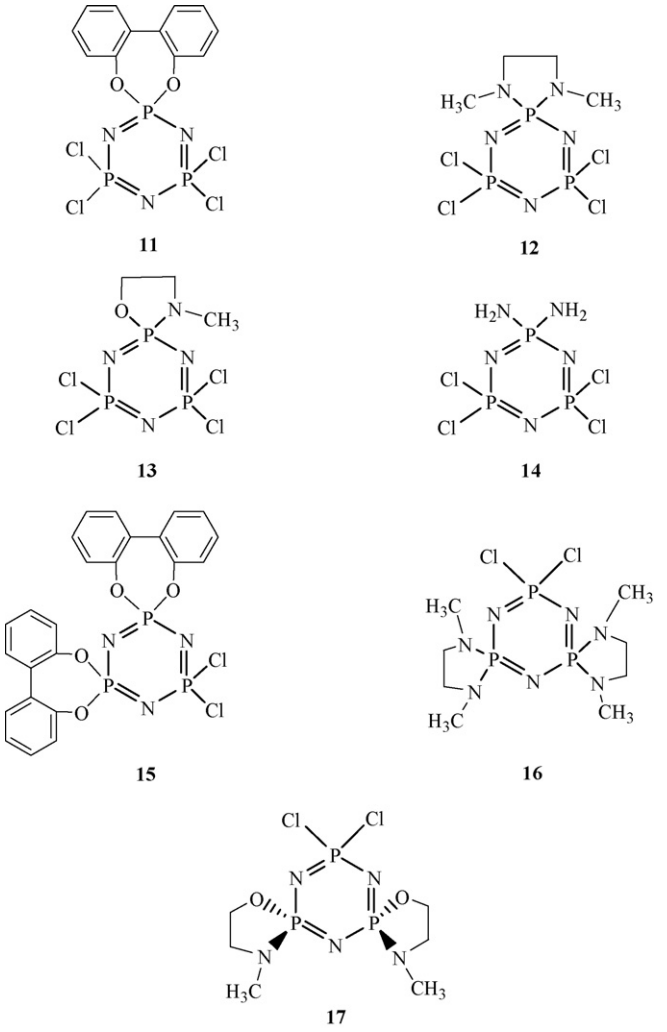


Chart 3. Representative examples of site-differentiated cyclophosphazenes [66–71].

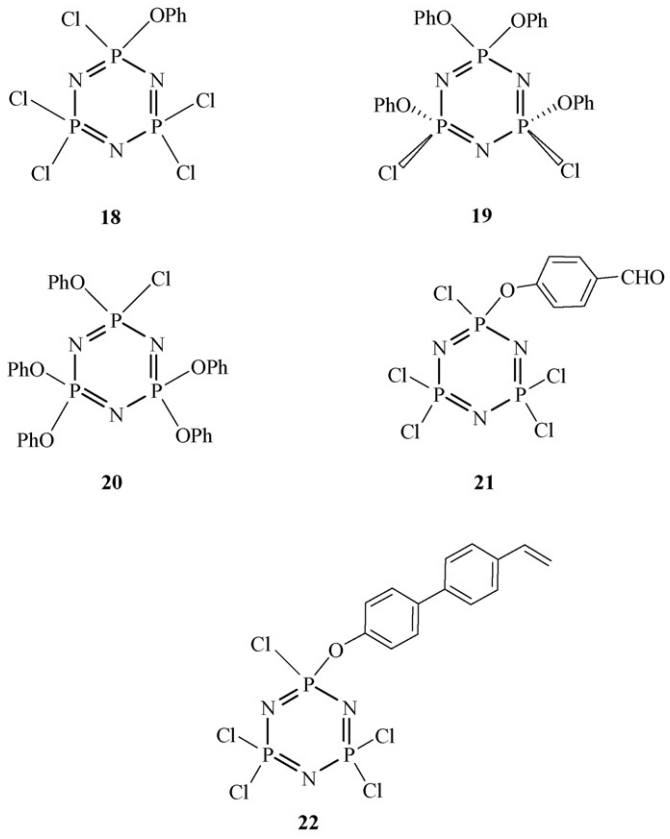


Chart 4. Further examples of site-differentiated cyclophosphazenes [68,74,77,78].

to the metal ion occurs in a *non-gem*-N_3 mode. This is illustrated for **42** in Chart 10. In this mode two non-geminal pyrazolyl nitrogen atoms along with the cyclophosphazene ring nitrogen atom act in a concerted coordination action to bind the metal ion. This generates two five-membered chelate rings. Maximum utilization of coordination sites by $N_3P_3(3,5\text{-}Me_2Pz)_6$ occurs in the samarium complex $N_3P_3(3,5\text{-}Me_2Pz)_6{\cdot}SmCl_3$ (**43**) [88] (Chart 10). Around the $SmCl_3$ unit five nitrogen atoms from the ligand (*gem*-N_5) are involved in coordination. $N_3P_3(3,5\text{-}Me_2Pz)_6$ can also be used to form heterobimetallic complexes such as **44** [89] (Chart 10). In **44** two types of coordination response are exhibited by the ligand. While Cu(II) solicits a *non-gem*-N_3 mode, Pd(II) is bound by a *gem*-N_2 mode. A similar coordination behavior is found for the homobimetallic complex, $N_3P_3(3,5\text{-}Me_2Pz)_6{\cdot}2ZnCl_2$ [87]. Interestingly 1:3 complexes have not been isolated, thus far, with pyrazolylcyclophosphazenes.

2. In ligands where some sites are blocked, the coordination response varies depending on the metal ion in question. Thus, tetrakis(pyrazolyl)cyclophosphazenes form 1:1 complexes of the type $N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4{\cdot}NiCl_2$ [72], $N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4{\cdot}Cu(ClO_4)_2{\cdot}2H_2O$ [83], $N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4{\cdot}Cu(ClO_4)_2{\cdot}2ImH$ [83], $N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4{\cdot}CuCl_2$ [90], $N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4{\cdot}CoCl_2$ [90] and $N_3P_3(NH_2)_2(3,5\text{-}Me_2Pz)4{\cdot}CoCl_2$ [84]. In all of these compounds a *non-gem*-N_3 coordination mode is observed. In contrast in $N_3P_3Ph_4(3,5\text{-}Me_2Pz)_2{\cdot}Mo(CO)_3$ (**45**) [94] a *gem*-N_3 mode is found (Chart 10). A rare *non-gem*-N_2 coordination action is seen in $N_3P_3(OPh)_4(3,5\text{-}Me_2Pz)_2{\cdot}PdCl_2$ (**46**) [86] (Chart 10).

Recent developments in the chemistry of pyrazolylcyclophosphazenes are as follows.

The reaction of $N_3P_3(3,5\text{-}Me_2Pz)_6$ with 3 equiv. of $ReCl(CO)_5$ afforded a cationic mononuclear complex, *fac*-$[Re(CO)_3\{N_3P_3(3,5\text{-}Me_2Pz)_6\}]^+[Re_2Cl_3(CO)_6]^-$ (**47**) [95]. In the cationic unit of the complex, Re(I) is present in a distorted octahedral geometry with a *fac*-coordination sphere. Two pyrazole nitrogen atoms and one cyclophosphazene ring nitrogen atom are involved in coordination to the Re center (*non-gem*-N_3 coordination mode) (Chart 11).

The rhenium atom in **47** is displaced by 0.70 Å from the mean plane of the cyclophosphazene ring. The coordinating nitrogen atom of the cyclophosphazene ring also suffers a displacement of 0.17 Å from the phosphazene ring mean plane. The P–N ring bond lengths involving the coordinating nitrogen atom are longer than other cyclophosphazene P–N bond

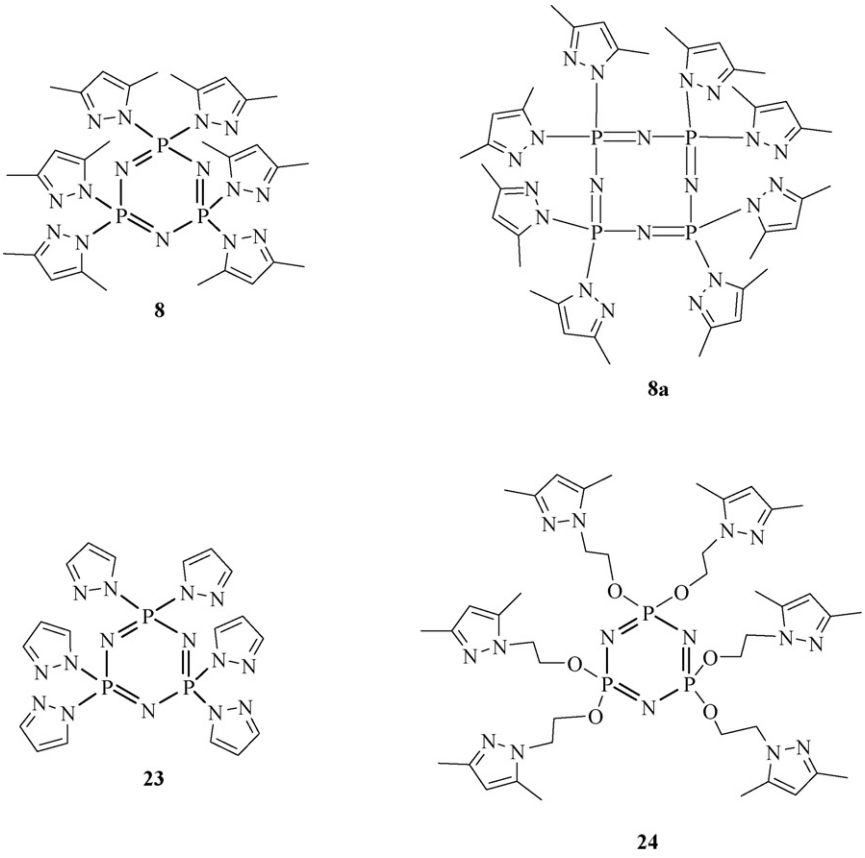


Chart 5. Cyclophosphazenes containing six- and eight-pyrazolyl arms [63,64,93].

lengths. These trends are in keeping with the features observed in other pyrazolylcyclophosphazene metal complexes. Site-differentiated ligands $N_3P_3(MeNCH_2CH_2NMe)_2(Pz)_2$ (**35**) or $N_3P_3(O_2C_{12}H_8)_2Pz_2$ (**32**) afford 1:1 Re complexes $[N_3P_3(MeNCH_2CH_2NMe)_2(Pz)_2{\cdot}Re(CO)_3]^+[SbF_6]^-$ (**48**) and $N_3P_3(O_2C_{12}H_8)_2Pz_2{\cdot}ReCl(CO)_3$ (**49**) (Scheme 4) [95].

Replacing the pyrazolyl group by pyridylpyrazole (Pypz) increases the number of coordination sites. Such ligands are suitable for binding metal ions that prefer higher coordination numbers. Accordingly the reaction of $N_3P_3(MeNCH_2CH_2NMe)_2(Pypz)_2$ (**36**) [73] with $La(NO_3)_3{\cdot}6H_2O$ affords a neutral complex $[N_3P_3(MeNCH_2CH_2NMe)_2(Pypz)_2{\cdot}La(NO_3)_3]$ (**50**) (Scheme 5) [73]. The La(III) ion in **50** is decacoordinate. Six

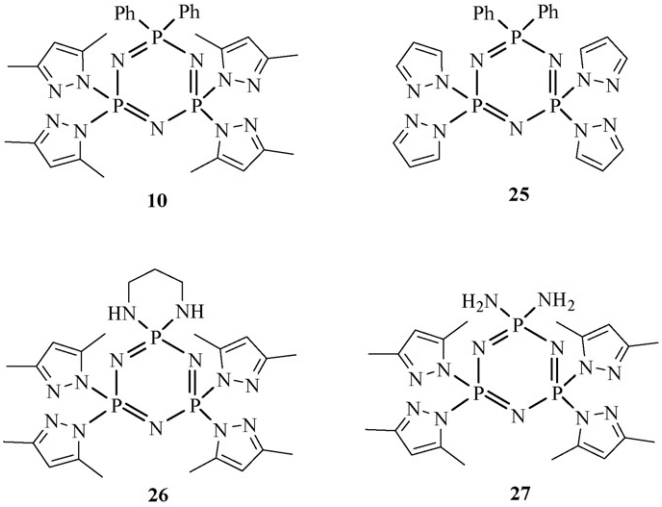


Chart 6. Tetrakis(pyrazolyl)cyclophosphazenes [72,83,90,93].

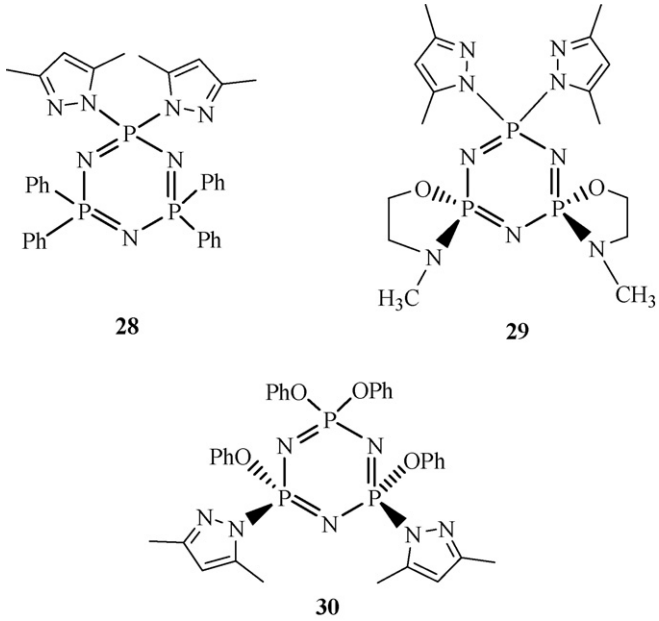


Chart 7. Bis(pyrazolyl)cyclophosphazenes, **28**–**30** [86,94].

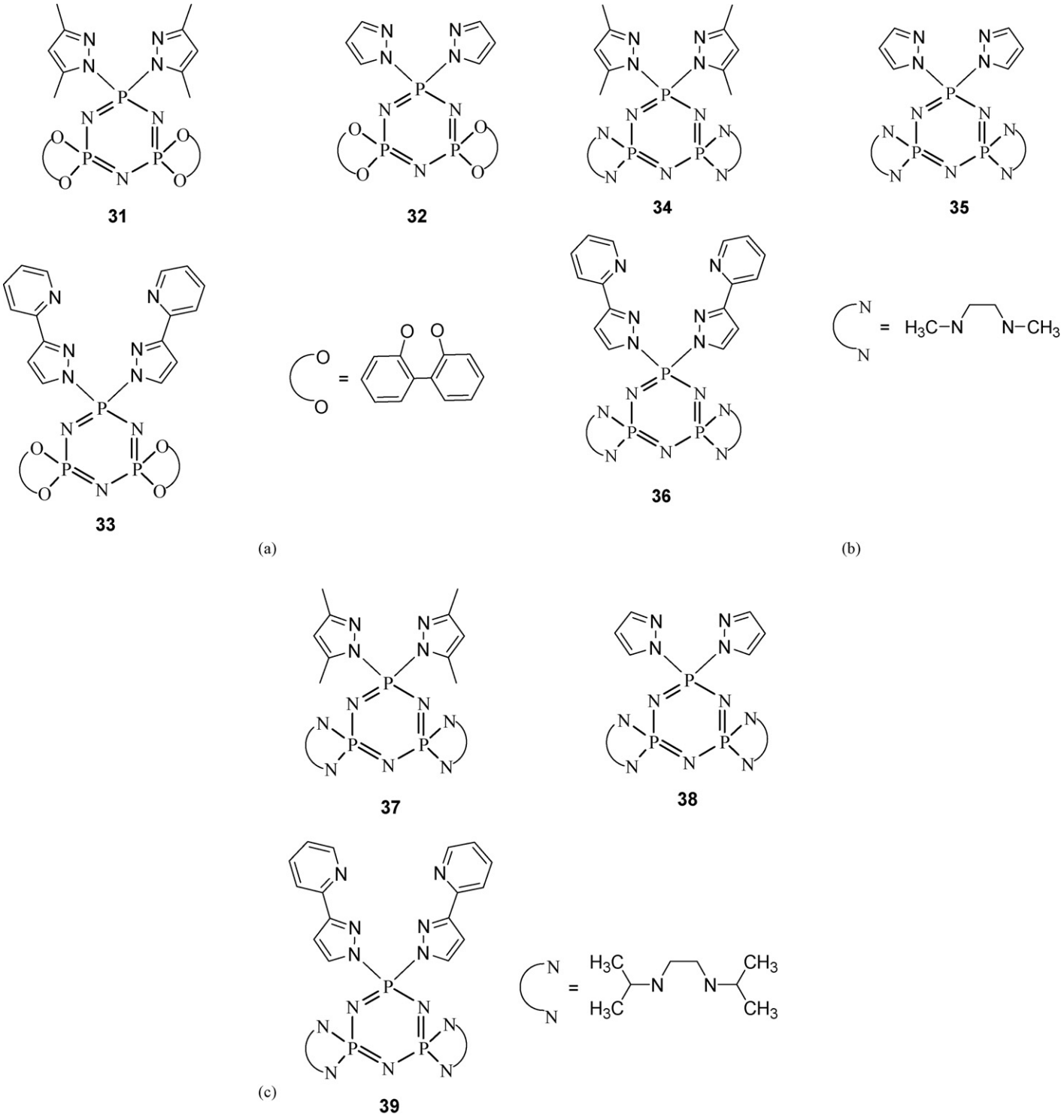
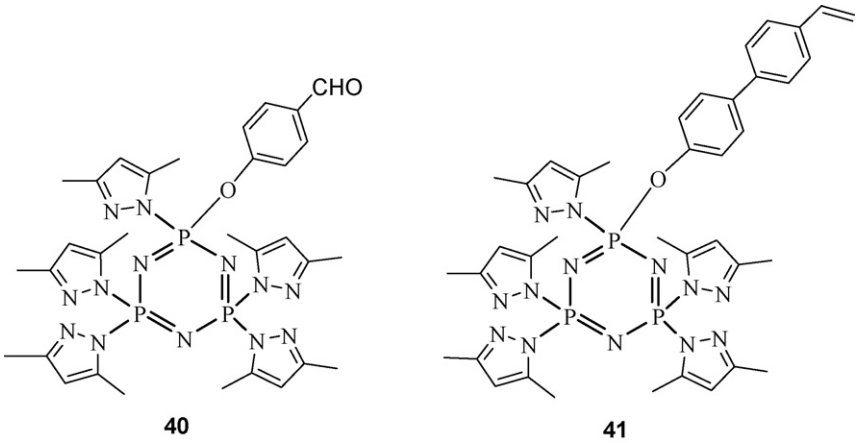


Chart 8. (a) Bis(pyrazolyl)cyclophosphazenes **31**–**33** [73,95], (b) bis(pyrazolyl)cyclophosphazenes **34**–**36** [73,95] and (c) bis(pyrazolyl)cyclophosphazenes **37**–**39** [73,95].

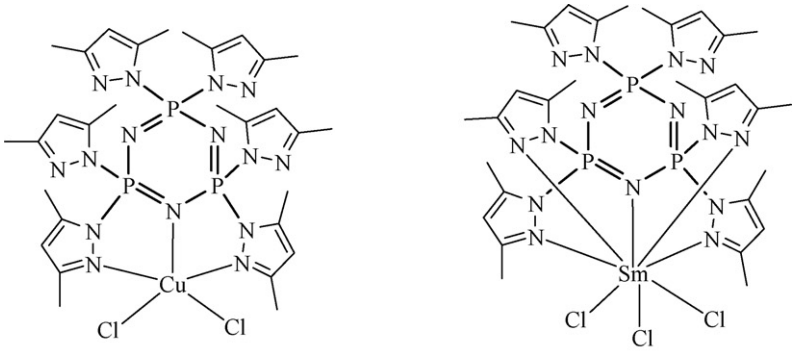
of these coordinating atoms are the oxygen atoms from the three chelating nitrate ligands. The remaining four coordinating atoms are the pyridylpyrazole nitrogen atoms. Perhaps, because of steric reasons, the cyclophosphazene ring nitrogen atoms do not participate in coordination to the lanthanide metal ion.

One of the advantages of the cyclophosphazene-based ligands is that they can be readily adapted to polymeric systems. This can be done in two ways: (A) linear polydichlorophosphazene can be modified so that suitable ligands can be anchored on the polymer backbone and (B) an intact cyclophosphazene can be anchored as a pendant group on a conventional organic polymer back



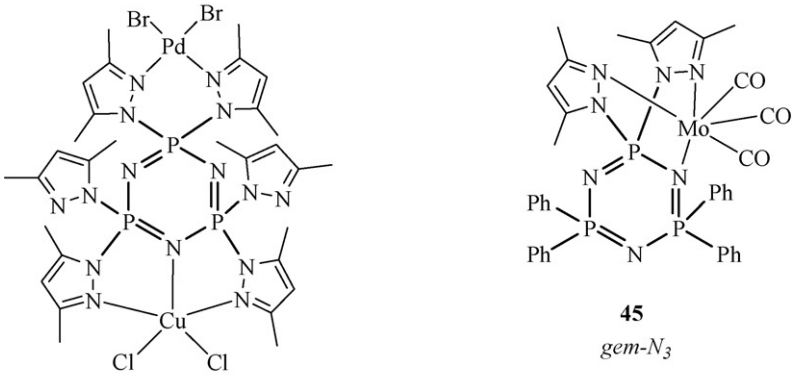
40 **41**

Chart 9. Pentakis(pyrazolyl)phosphazenes [78–80].



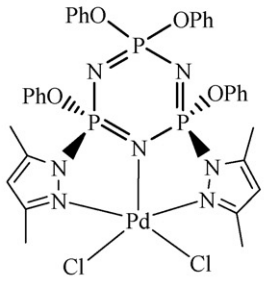
42
non-gem-N_3

43
gem-N_5



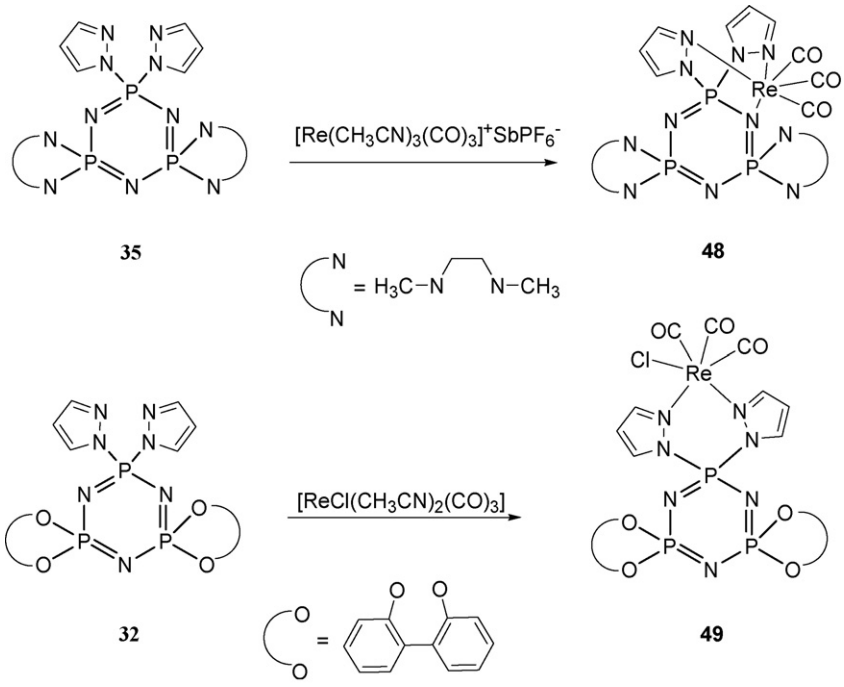
44
non-gem-N_3 (around $CuCl_2$)
gem-N_2 (around $PdBr_2$)

45
gem-N_3



46
non-gem-N_2

Chart 10. Different coordination modes of pyrazolylcyclophosphazenes [64,86,88,89,94].



Scheme 4. Organometallic Re(I) complexes (**48** and **49**) formed from ligands **35** and **32** [95].

bone [78–80]. The latter is usually accomplished by polymerizing a cyclophosphazene monomer, $N_3P_3R_5P$ (P = polymerizable functional group). This approach has been utilized in preparing polymeric compounds containing pyrazolylcyclophosphazenes as pendant groups.

The pentachlorocyclophosphazene, $N_3P_3Cl_5$(O–C_6H_4–*p*-C_6H_4–*p*-CH=CH_2) (**22**) reacts in a facile manner with 3,5-dimethylpyrazole to afford N_3P_3(3,5-Me_2Pz)$_5$(O–C_6H_4–*p*-C_6H_4–*p*-CH=CH_2) (**41**) [78–80]. A model compound for this in the form of N_3P_3(3,5-Me_2Pz)$_5$(O–C_6H_4–*p*-CHO) (**40**) was also prepared (Scheme 6) [79].

Both **40** and **41** can be readily metalated with $CuCl_2$ to afford 1:1 complexes **51** and **52** (Chart 12) [79].

Complex **51** was structurally characterized. It reveals a *non-gem*-N_3 coordination mode to the $CuCl_2$ group. The P–N bond distances flanking the site of coordination (N_2) are slightly elongated. Among the Cu–N distances, the bond distance Cu–N_1 involving the cyclophosphazene ring nitrogen is longer in comparison to Cu–N_4 or Cu–N_5. The geometry around Cu(II) in **51** is distorted trigonal bipyramidal. The effect of metalation on the cyclophosphazene ring is to distort the latter into a non-planar conformation, with N_2 and P_2 being displaced from the mean plane of the cyclophosphazene ring by +0.15 and −0.13 Å, respectively.

Polymerization of **41** in the presence of 1,4-divinylbenzene affords the cross-linked polymeric ligand **53** [79]. The latter can be metalated to afford the Cu(II)-containing polymer **53a** (Scheme 7) [79].

The polymeric complex **53a** was utilized as a phosphoesterase involving the hydrolysis of *p*-nitrophenyl phosphate (*p*NPP), bis(*p*-nitrophenyl) phosphate (*b*NPP) and 2-hydroxypropyl-*p*-nitrophenyl phosphate (*h*NPP) (Chart 13). While *p*NPP serves as a model for phosphomonoester, *b*NPP

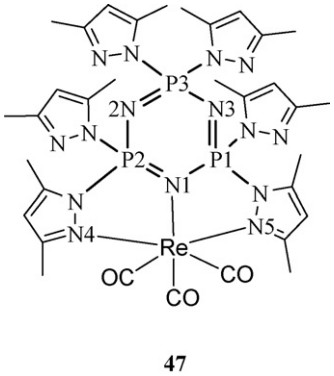
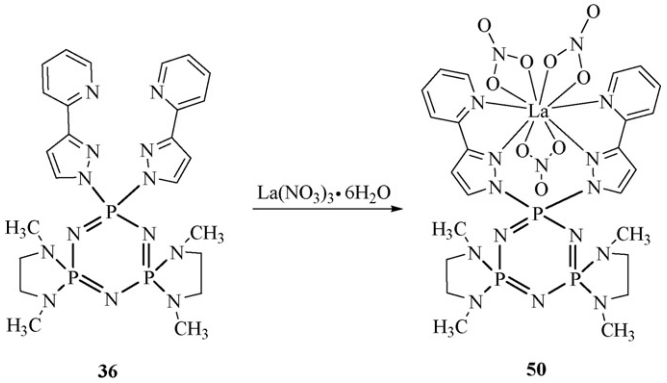
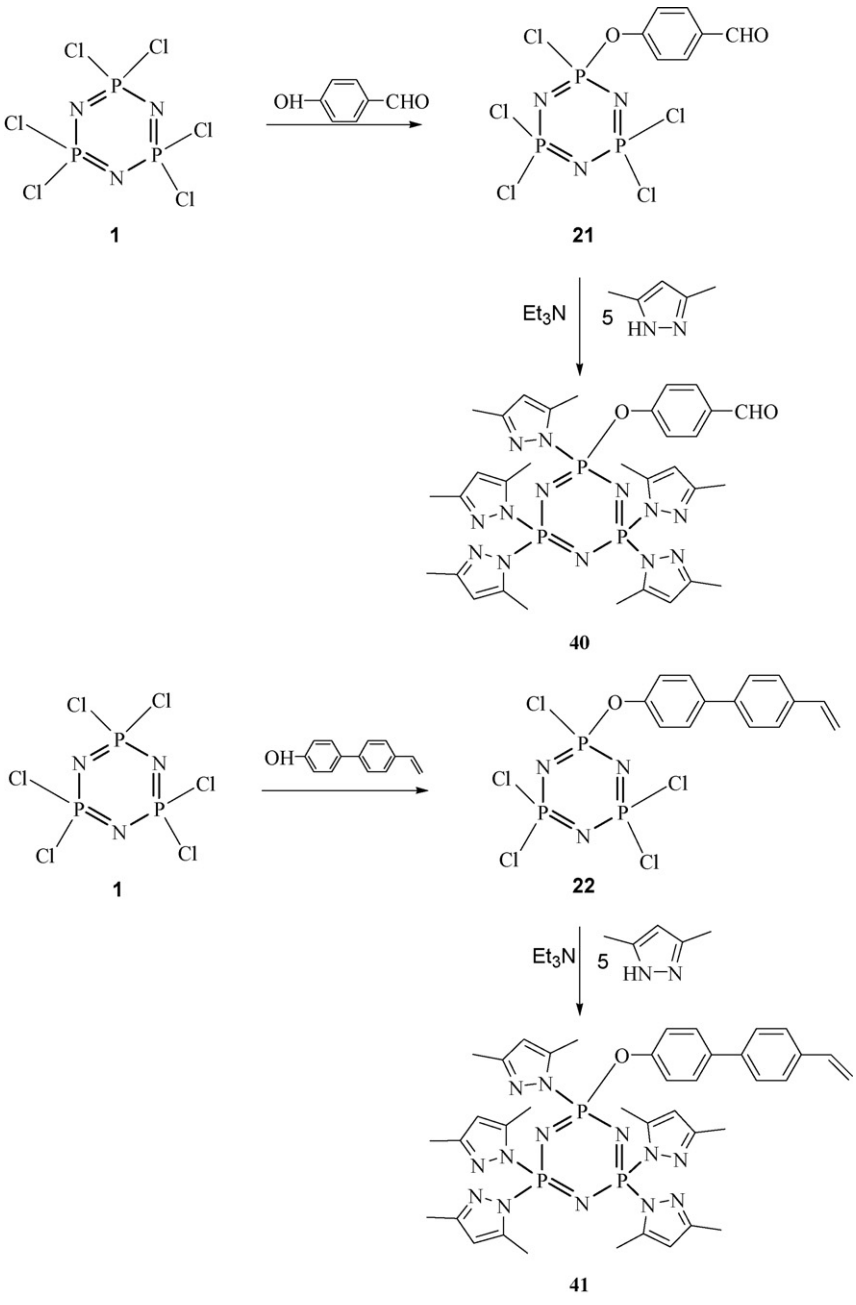


Chart 11. Mononuclear Re(I) complex (**47**) [95]. Metric parameters in the cationic portion of **47**: Re–N1, 2.247(12) Å; Re–N4, 2.216(11) Å; Re–N5, 2.183(11) Å; P1–N1, 1.596(11) Å; P2–N1, 1.634(12) Å; P1–N3, 1.573(12) Å; P2–N2, 1.555(12) Å; P3–N2, 1.592(11) Å; P3–N3, 1.583(12) Å.



Scheme 5. Synthesis of the La(III) complex **50** [73].



Scheme 6. Synthesis of **40** and **41** [78,79].

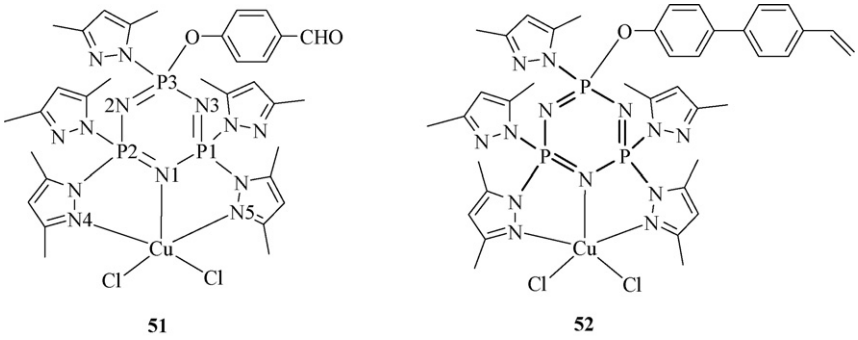
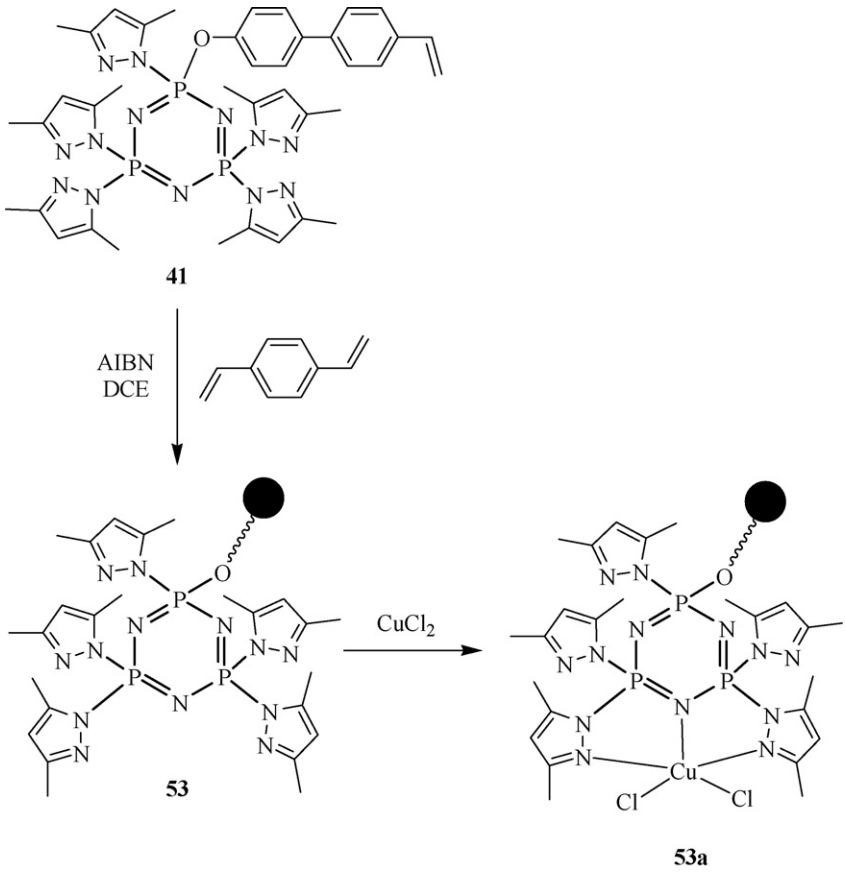


Chart 12. Cu(II) complexes **51** and **52** [79]. Metric parameters in the complex **51**: Cu–N1, 2.295(3) Å; Cu–N4, 2.010(3) Å; Cu–N5, 1.993(3) Å; P1–N1, 1.598(3) Å; P1–N3, 1.569(3) Å; P2–N1, 1.594(3) Å; P2–N2, 1.572(3) Å; P3–N2, 1.580(3) Å; P3–N3, 1.590(3) Å.



Scheme 7. Synthesis of cross-linked polymeric ligand and its metal complex (**53a**) [79].

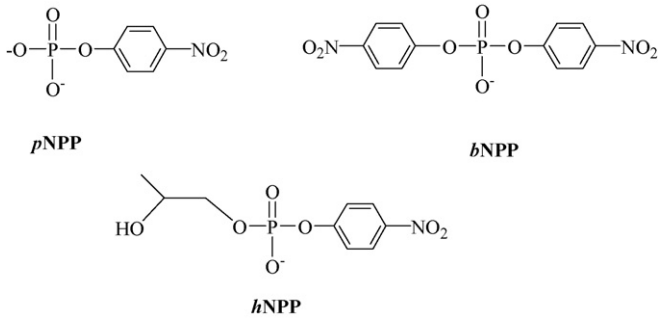


Chart 13. Activated phosphate esters [79].

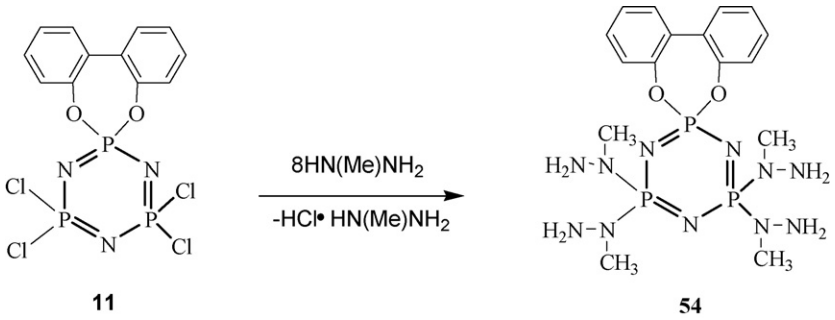
serves as a model for a phosphodiester; *h*NPP is a phosphosdiester model which is also a RNA model [79].

The kinetics of hydrolysis of all the three substrates by **53a** reveals a Michaelis–Menten behavior. Substantial rate enhancements, *p*NPP (8.98×10^2), *b*NPP (2.81×10^5) and *h*NPP (2.68×10^2) were observed. Remarkably **53a** can be recycled several times, indicating that it is a robust catalyst.

3. Cyclophosphazene hydrazides

Phosphohydrazides of the type $P(E)[N(Me)NH_2]_3$ (E = O, S), $RP(E)[N(Me)NH_2]_2$ and $R_2P(E)[N(Me)NH_2]$ have gained in importance in recent years as substrates for the construction of macrocycles, cryptands and dendrimers, as well as ligands in coordination chemistry [96–105]. Analogues cyclophosphazene hydrazides have been prepared and utilized for the assembly of several multiferrocene assemblies [106,107].

The terminal $–NH_2$ groups of the cyclophosphazene hydrazides can also be utilized for coordination to metal ions. The cyclophosphazene hydrazide $N_3P_3[O_2C_{12}H_{18}][N(Me)-NH_2]_4$ (Scheme 8) (**54**) [108] has been used in coordination to Co(III), Ni(II), Zn(II) and Cd(II). Interestingly in all cases two cyclophosphazene hydrazide molecules are involved in coordination to a central metal ion (2:1, L:M). Homoleptic complexes of the type $[L_2M]^{2+}\cdot 2[NO_3]^-$ (M = Ni, Zn, Cd) and $[L_2M]^{3+}\cdot 3[Cl]^-$ are readily formed (Scheme 9) [108]. No complex involving only one cyclophosphazene ligand is formed. In all cases the cyclophosphazene ligand interacts with the metal ion through one ring nitrogen atom and two $–NH_2$ nitrogen atoms belonging to the *non*-geminal N-methylhydrazine groups that flank the coordinating cyclophosphazene nitrogen atom. The coordination environment around the metal ion is distorted octahedral in a *fac*-stereochemistry. In comparison to the situation in metal complexes of pyrazolylcyclophosphazenes, where the cyclophosphazene ring is severely distorted, in the complexes formed with the hydrazides the cyclophosphazene ring does not deviate substantially from planarity. The summary of the structural parameters of the complexes **55–58** is given in Table 1.

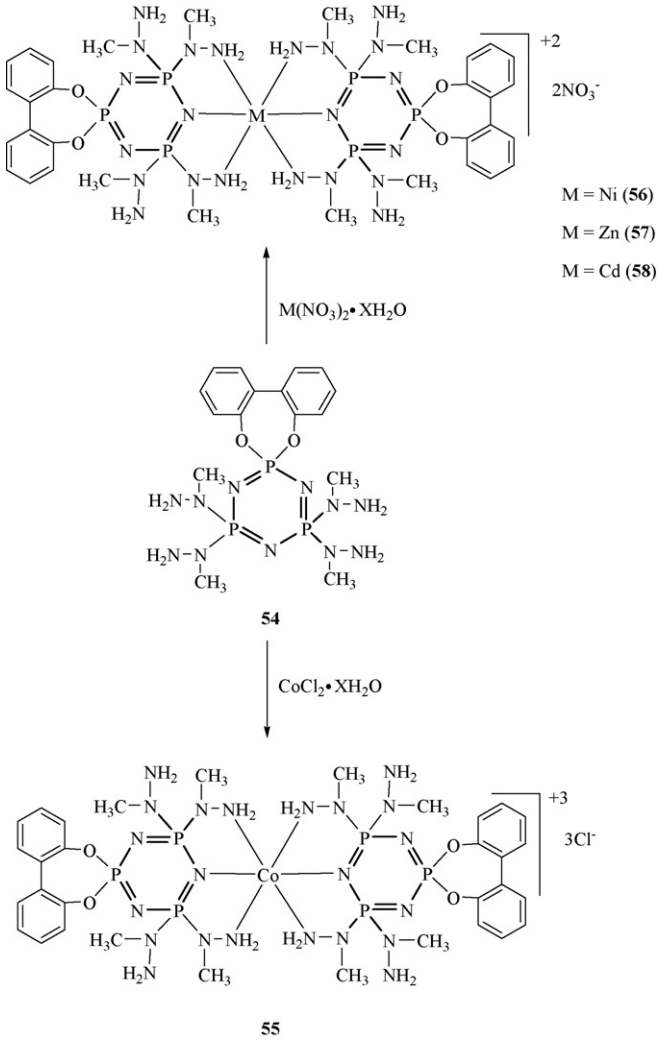


11 54

Scheme 8. Synthesis of cyclophosphazene tetrahydrazides.

A structural comparison of the complexes **55**–**58** with that of **54** reveals the following:

1. The average P–N distance in the segment P2–N1/P1–N1 in all the complexes is longer than that found in the parent cyclophosphazene hydrazide (**54**). The longest P–N distance is found for the Co(III) complex (**55**).
2. The three M–N bond distances in each complex are nearly similar indicating the flexibility of the hydrazide arm. It may be noted that in the metal complexes formed from pyrazolylcyclophosphazenes, in general, the M–N distances are not equivalent (in the *non-gem*-N_3 coordination mode).



Scheme 9. 2:1 (L:M) complexes formed with the ligand **54** [108].

4. Pyridyloxycyclophosphazenes

Pyridyloxycyclophosphazenes are multi-site coordination ligands where the coordinating pyridine ligand is attached to the phosphorus atom of the cyclophosphazene ring by means of a "spacer" oxygen atom. Representative examples of pyridyloxycyclophosphazenes are shown in Charts 14–16 [19,109–114]. These also include compounds where bipyridyl groups are attached to cyclophosphazenes [113]. Typically the synthesis of these ligands involves the reaction of chlorocyclophosphazenes with hydroxypyridines in the presence of a base like K_2CO_3 (see Scheme 10, for example, for the synthesis of **70**) [109]. However, the synthesis of **71** has been carried out by the reaction of the corresponding chlorocyclophosphazenes with the sodium salt of substituted hydroxypyridines (Scheme 11) [115].

Octakis(2-pyridyloxy)cyclophosphazenes **72** and **73** were prepared by the reaction of $N_4P_4Cl_8$ with the corresponding sodium salts of the hydroxypyridines (Scheme 12) [116].

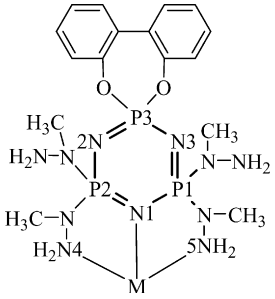
Compound **73** could be crystallized with dichloromethane (**73**·$2CH_2Cl_2$) or water (**73**·H_2O) as the solvent of crystallization. The crystal structures of **73**·$2CH_2Cl_2$ and **73**·H_2O reveals the presence of tunnels which entrap the solvent molecules [116].

Although the coordination chemistry of pyridyloxycyclophosphazenes was explored earlier, the versatile coordination behavior of these ligands became more evident in recent years. Ainscough and Brodie have reported that the reaction of 2 equiv. of $CuCl_2$ with **70** afforded the complex **74** which contained a trinuclear cationic part along with $[Cu_2Cl_6]^{2-}$ counter anion (Scheme 13) [117].

The trinuclear cation of **74** is a $CuCl_2$-bridged dimer. Each monomeric unit binds to a Cu(II) by a *gem*-N_5 mode. The six-coordinate Cu(II) ions are present in an elongated rhombic octahedral geometry. Of the remaining two pyridyloxy groups present in the ligand, one each from the two monomers is involved in linking the central $CuCl_2$ unit.

Recently we have observed that the reaction of **70** with 1 equiv. of $CuCl_2$ followed by a reaction with $Co(NO_3)_2{\cdot}6H_2O$ results in the formation of the complex, $[\{N_3P_3(OC_5H_4N)_5(O){\cdot}CuCl\}_2\{CoNO_3\}][Cl]$ (**75**) (Scheme 14) [118].

Table 1
Selected bond distances (Å) for **54–58**



	P1–N1/P2–N1	P1–N3/P2–N2	P3–N2/P3–N3	M–N1	M–N4	M–N5
54	1.572(6)	1.591(5)	1.550(6)	–	–	–
55	1.649(12)	1.582(15)	1.569(14)	1.993(12)	1.940(12)	1.946(11)
56	1.622(4)	1.593(4)	1.566(4)	2.135(30)	2.100(40)	2.106(4)
57	1.617(16)	1.596(16)	1.572(17)	2.189(15)	2.155(17)	2.159(17)
58	1.612(3)	1.584(4)	1.576(4)	2.428(30)	2.309(4)	2.367(4)

The cationic part of compounds **74** and **75** have structural similarities. Thus, the molecular structure of **75** contains two copper-metalated cyclophosphazene units which are bridged by a central Co(II). Remarkably the formation of **75** involves a P–O bond scission leading to the expulsion of one pyridyloxy unit. The coordination environment around the two Cu(II) ions is distorted rhombic octahedral and is similar to that found in

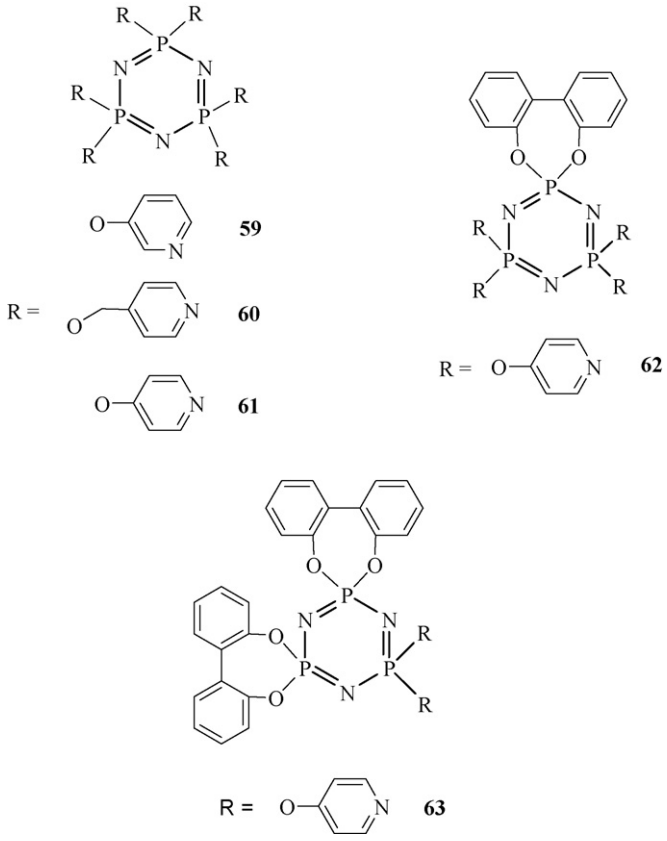


Chart 14. Examples of pyridyloxy derivatives of cyclophosphazenes [19,109–114].

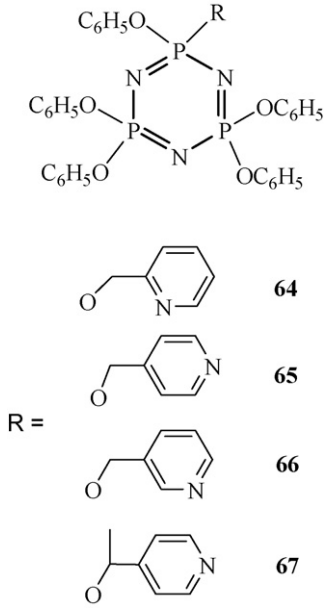


Chart 15. Examples of mono pyridyloxycyclophosphazenes [19].

74. The bridging Co(II) is hexacoordinate and contains a 2N, 4O coordination environment. This arises from a chelating nitrate ligand, two P–O groups (generated by the hydrolytic scission of the P–O–C_5H_4N group) and two pyridyloxy nitrogen atoms.

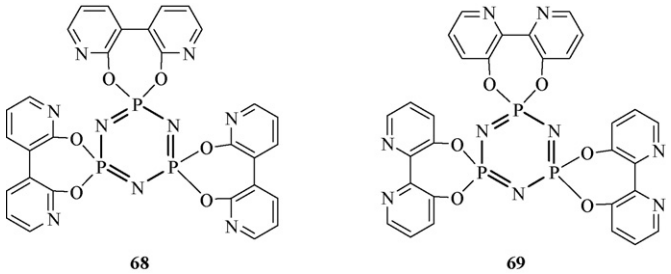
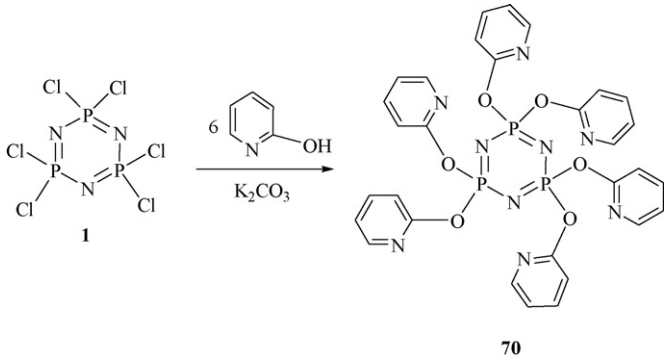
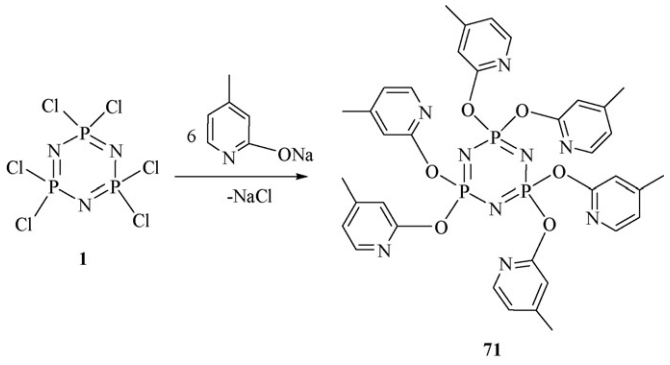


Chart 16. Spirocyclic phosphazenes containing bipyridyl ligands [114].



1 70

Scheme 10. Synthesis of **70** [109].



1 71

Scheme 11. Synthesis of **71** [115].

Sequential metalation of hexakis(pyridyloxy)cyclophosphazenes affords homo- and hetero-bimetallic complexes (**76**–**82**) (Scheme 15) [118,119].

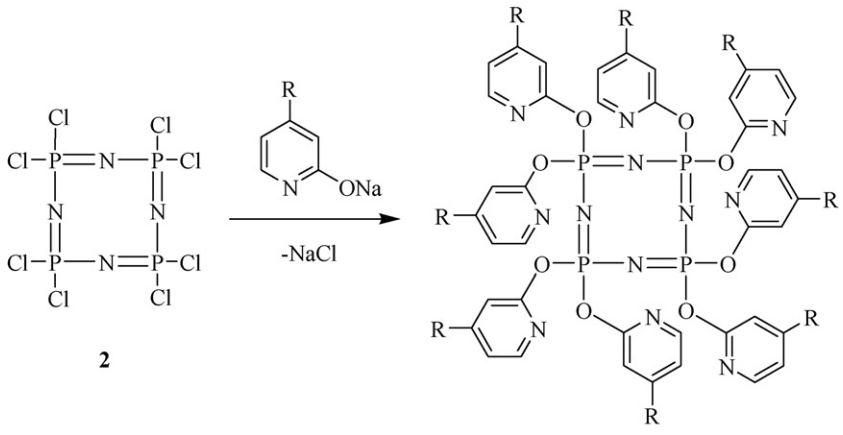
Complexes **76**–**82** exhibit two types of coordination environment. In each one of these, M_a is bound by a *gem*-N_5 manner and is six-coordinate. On the other hand M_b is tetracoordinate and is bound by one pyridyloxy nitrogen atom. It has been reported that a 1:1 reaction of **70** or **71** with $CuCl_2$ or $CoBr_2$ yielded neutral complexes **83** and **84** (Scheme 16) [118,119]. In these complexes the metal ion is five-coordinate (3N, 2Cl). The cyclophosphazene ligand binds to the metal ion in a *non-gem*-N_3 mode. Interestingly a 1:1 reaction of **70** with MX_2 followed by treatment with $[Ag(MeCN)_4]PF_6$ affords cationic complexes **85**–**88** (Scheme 17) [115,119]. Here, the metal ion is six-coordinate and possesses a 5N, 1Cl coordination environment.

A neutral 1:2 complex (**89**) has been reported in the reaction of **71** with $CuCl_2$ (Scheme 18) [115]. Both the copper ions are pentacoordinate (3N, 2Cl; *non-gem*-N_3). An interesting feature of the structure of this complex is that two pyridyloxy groups emanating from a single phosphorus atom are involved in coordination to two different copper centers.

On the other hand, reaction of **70** with 2 equiv. of $ZnCl_2$ affords the dinuclear complex **90** (Scheme 19) [118,119]. In this case while one of the $ZnCl_2$ units is bound by a *non-gem*-N_3 mode the other $ZnCl_2$ unit is bound by a *gem*-N_2 mode.

In an interesting case of structural isomerism the reaction of **70** with $NiCl_2$ afforded a hexacoordinate Ni(II) complex (green) (**91**) and a pentacoordinate Ni(II) complex (red) (**92**) (Chart 17) [119]. In the former three pyridyloxy nitrogen atoms and a cyclophosphazene ring nitrogen atom are coordinated to a $NiCl_2$ group. In the red complex two pyridyloxy nitrogen atoms and a cyclophosphazene ring nitrogen atom are involved in coordination to the $NiCl_2$ unit.

Interestingly coordination polymers $\{[\mathbf{70}\cdot Ag]^+[PF_6]^-\}_\infty$ (**93**) and $\{[\mathbf{71}\cdot Ag]^+[NO_3]^-\}$ (**94**) are formed through the interaction of Ag(I) with the ligands **70** and **71** [120]. The Ag(I) ions assists in linking successive cyclophosphazenes through coordinative interactions to generate a one-dimensional polymer. Each Ag(I) ion in **93** is pseudo-five-coordinate with a 5N coordination environment. Essentially every Ag(I) ion is bound by two cyclophosphazene ligands. One of the cyclophosphazene ligands binds through a ring nitrogen atom and a pyridyloxy nitrogen atom. The other ligand binds through two geminal pyridyloxy nitrogen atoms and an adjacent ring nitrogen atom (Chart 18) [120]. The structure of **94** is grossly similar to that of **93** except for minor variations.

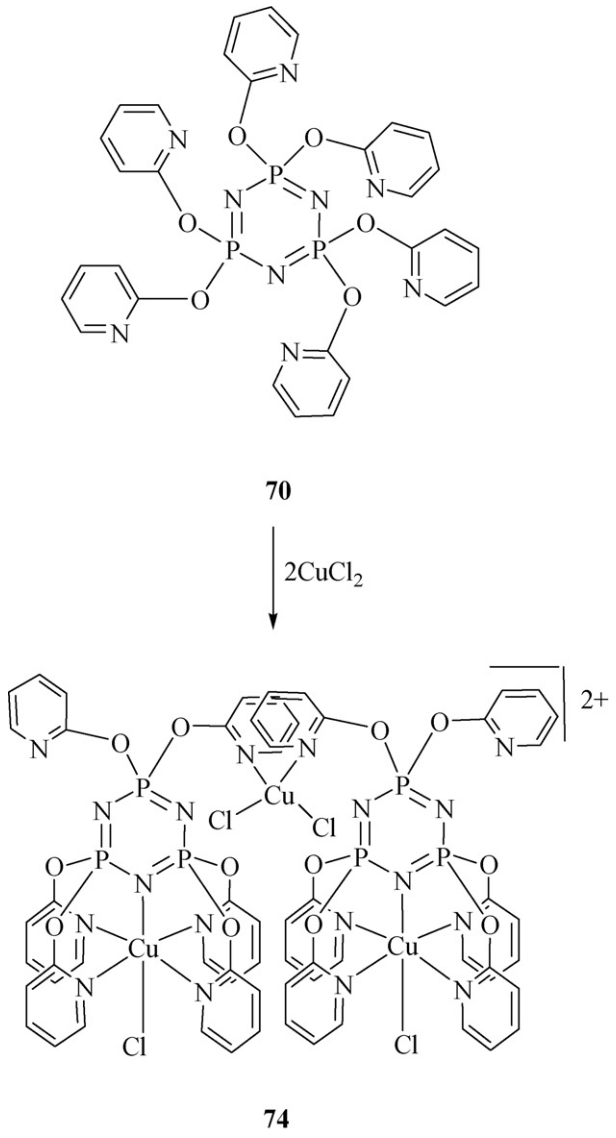


2

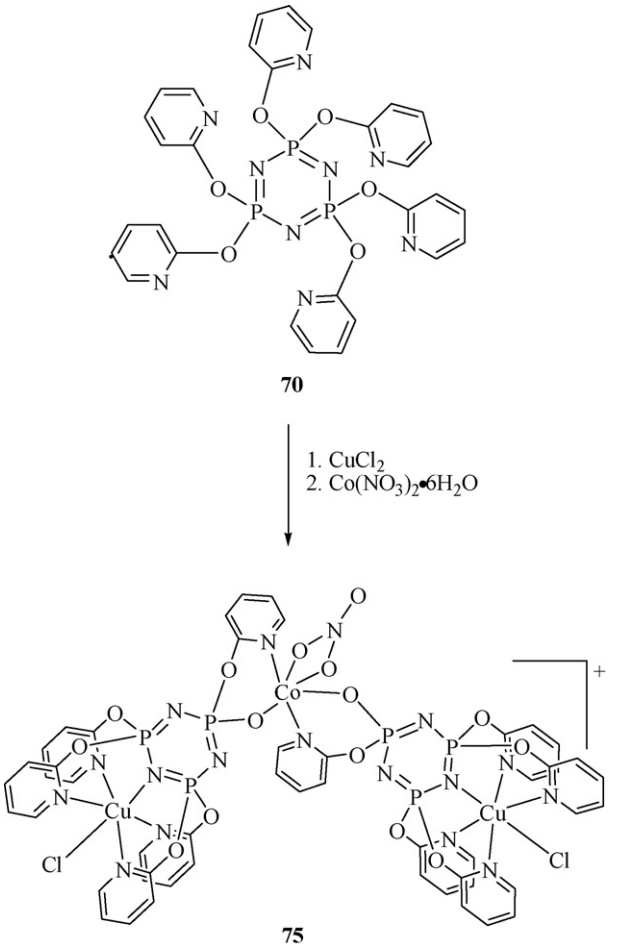
R = H (**72**)

R = Me (**73**)

Scheme 12. Synthesis of **72** and **73** [116].



Scheme 13. Trinuclear Cu(II) complex **74** (only the cationic portion is shown) [117].



Scheme 14. Assembly of the heterobimetallic trinuclear metal complex **75** [118].

Attempts to prepare Cu(I) analogues of **93** resulted in an oxidized Cu(II) product **95**. Compound **95** is a dicopper derivative, where the two Cu(II) ions are bridged a μ-OH and a pyridyloxy ligand. The latter is speculated to arise from an oxidation/hydrolysis reaction of the initial product, viz., {[**71**·Cu][PF_6]} (Scheme 20) [120].

The structural features of the metal complexes formed by pyridyloxycyclophosphazenes are summarized in Table 2. The summary of the coordination behavior of these ligands is as follows:

1. Pyridyloxycyclophosphazenes enable the assembly of mono- and di-nuclear complexes. In two instances trinuclear derivatives were obtained. One of these also involves the assembly of a heterobimetallic (2Cu, 1Co) derivative. Coordination polymers have been reported with Ag(I) salts.
2. Almost in all cases the cyclophosphazene ring remains planar. This is in contrast to the situation found for other cyclophosphazene ligands such as pyrazolylcyclophosphazenes, where the ring undergoes puckering upon coordination. The planar cyclophosphazene geometry found in the metal complexes of pyridyloxycyclophosphazenes is probably due to the flexible oxygen spacer that separates the pyridyl group from the cyclophosphazene ring and allows a *strain-free* coordination to the metal ions.

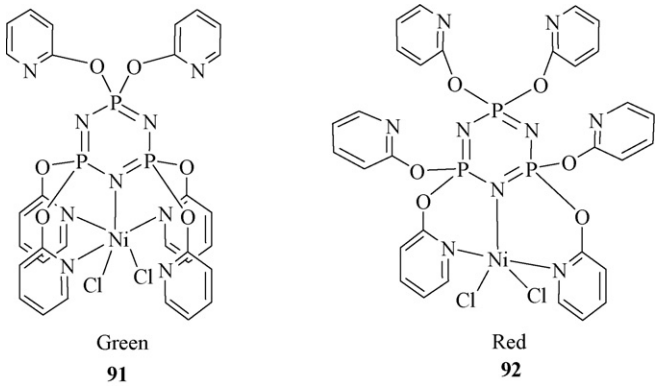
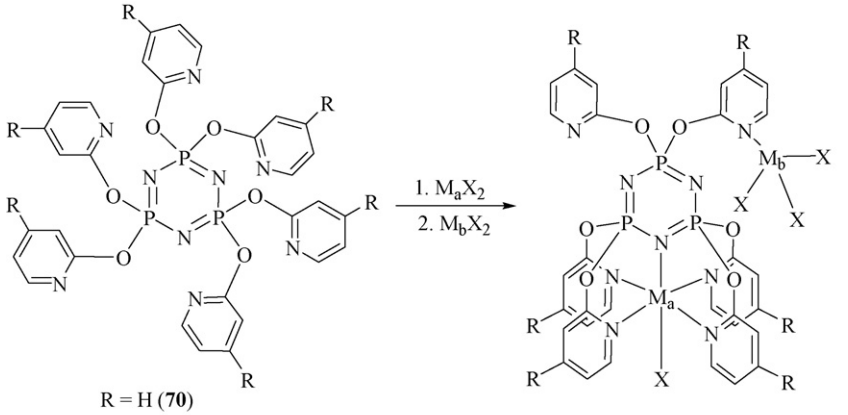


Chart 17. Structural isomerism in the Ni(II) complex of **70** [119].



R = H (**70**)

R = Me (**71**)

M_a = Cu; M_b = Co; X = Cl ; R = H (**76**)

M_a = Cu; M_b = Zn; X = Cl ; R = H (**77**)

M_a = Co; M_b = Zn; X = Cl; R = H (**78**)

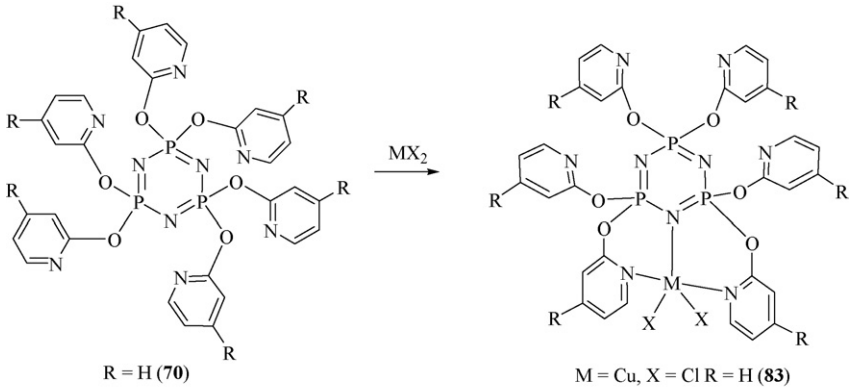
M_a = M_b = Co; X = Cl; R = H (**79**)

M_a = M_b = Co; X = Br; R = H (**80**)

M_a = M_b = Co; X = Cl; R = Me (**81**)

M_a = M_b = Co; X = Br; R = Me (**82**)

Scheme 15. Hetero- and homo-bimetalic complexes of **70** and **71** [118,119].



R = H (**70**)

R = Me (**71**)

M = Cu, X = Cl R = H (**83**)

M = Co, X = Br R = Me (**84**)

Scheme 16. Pentacoordinate mononuclear metal complexes **83** and **84** formed from hexakis(pyridyloxy)cyclophosphazenes **70** and **71** [115,119].

3. The metal ions (in complexes involving only one ligand) are bound by *non-gem*-N_3, *gem*-N_3 or N_1 modes.
4. In all cases the P–N bonds (in the cyclophosphazene ring) flanking the coordinating nitrogen atom are elongated.

5. Pyridylaminocyclophosphazenes

Pyridylaminocyclophosphazenes are ligands where the pyridine groups are linked to the cyclophosphazene ring by a *spacer* –NH unit. Charts 19–23 list a number of pyridylaminocylcophosphazene ligands that are known in literature [19,114,121–123]. Chart 24 lists a few illustrative examples of metal complexes obtained from these ligands [19]. This subject has been recently reviewed [19]. The developments that have occurred since are presented here.

Solvent-free synthetic methodology has been used for the successful assembly of the bis(2-pyridyl)aminocyclophosphazenes **122** and **123** (Scheme 21) [73].

Reaction of $N_3P_3(PyNH)_2(MeNCH_2CH_2NMe)_2$ (**123**) with $[ReCl(CH_3CN)_2(CO)_3]$ resulted in the elimination of acetonitrile and the formation of a 1:2 (L:M) complex $[\{ReCl(CO)_3\}_2\{N_3P_3(PyNH)_2(MeNCH_2CH_2NMe)_2\}]$ (**124**)

70

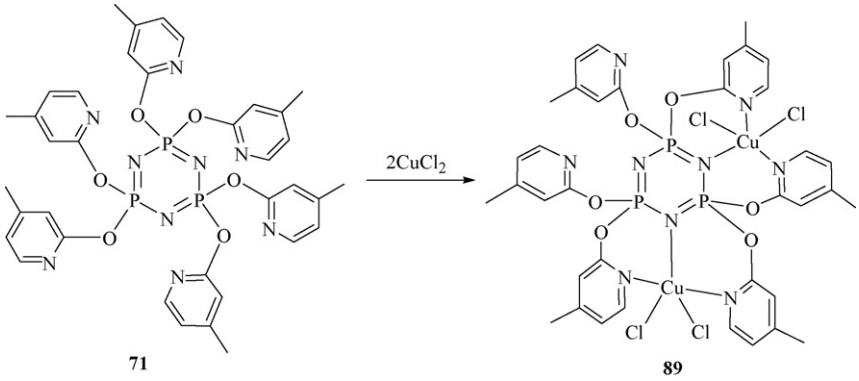
M = Co; X = Cl, (**85**)

M = Co; X = Br (**86**)

M = Ni; X = Cl (**87**)

M = Cu; X = Cl (**88**)

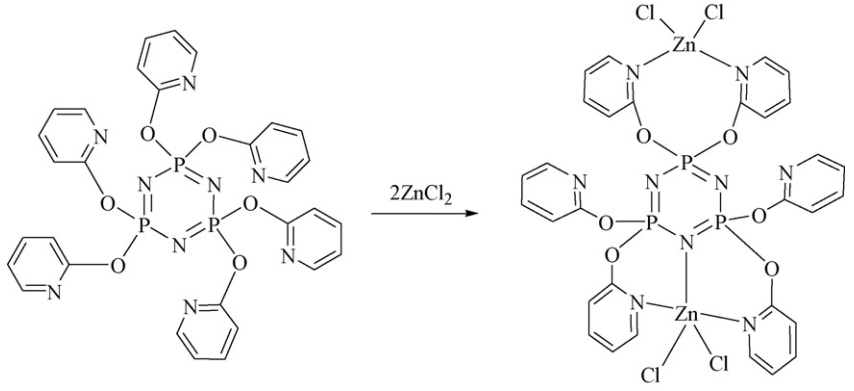
Scheme 17. Hexacoordinate mononuclear metal complexes formed from **70** [115,119].



71 **89**

Scheme 18. Dinuclear Cu(II) complex (**89**) formed from the reaction of **71** with $CuCl_2$ [115].

(Scheme 22) [73]. The ^{31}P NMR spectrum of this compound is of the AX_2 type with chemical shifts, δ_A at 15.9 and δ_X at 17.6 ppm. While δ_X in the ligand also is seen at 29.1 ppm, δ_A in the ligand appears at 6.3 ppm. Further the ^2J(P–N–P) value decreases from 55.4 Hz (ligand) to 48.5 Hz (complex). Dinuclear metal complexes (**125** and **126**) were also obtained with Fe(II) and Pd(II). An interesting aspect of the synthesis of the dinuclear Fe(II) complex (**125**) is the in situ generation of FeI_2 which is then allowed to react with the ligand. All the dinuclear complexes are bound by the cyclophosphazene ligand in a nearly similar manner [73]. Each metal atom in a given dinuclear complex is bound by a pyridyl nitrogen and a cyclophosphazene



70 **90**

Scheme 19. Dinuclear zinc complex (**90**) formed from the ligand **70** [118,119].

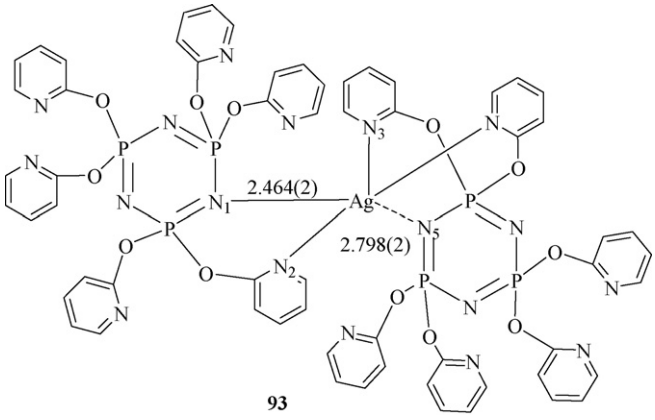


Chart 18. Basic structural unit of the silver coordination polymer $\{[\mathbf{70}\cdot Ag]^{+}\text{-}[PF_6]^{-}\}_{\infty}$ [120].

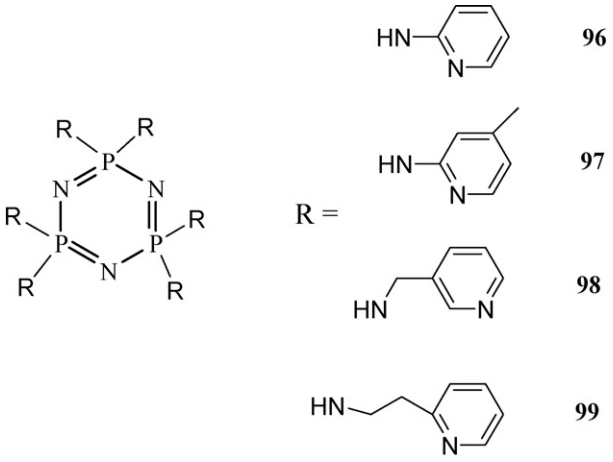


Chart 19. Hexakis(pyridylamino)cyclophosphazenes **96–99** [19].

ring nitrogen affording a six-membered chelate ring. In the rhenium(I) complex the rest of the coordination sites are taken up by three facial CO and one chloride ligands. Interestingly the effect of coordination is minimal on the cyclophosphazene ring in terms of its conformation. Presumably because the pyridyl units are linked to the cyclophosphazene by the "spacer –NH group", their interaction with the metal ion does not demand structural deformation of the inorganic heterocyclic ring. The structural parameters of the complexes **124–126** are summarized in Table 3.

The formation of the dinuclear complexes also affects the chemical shift of the phosphorus atom bearing the coordinating pyridyl groups. Thus, the free ligand displays an AX_2 spectrum [$\delta_A = 6.3$ (t) and $\delta_c = 29.1$ (d)]. In **124** δ_A moves to 15.9 ppm while in the palladium complex δ_A resonates at 1.9 ppm.

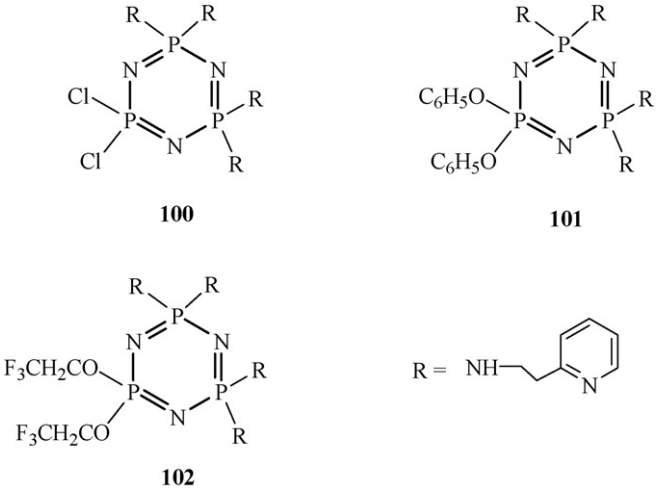
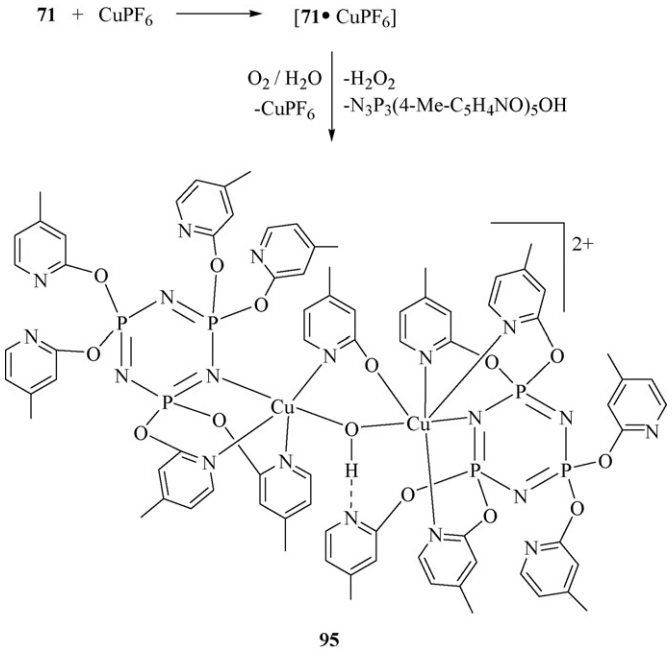


Chart 20. Tetrakis(pyridylamino)cyclophosphazenes **100–102** [19].



Scheme 20. μ-OH-bridged dicopper complex **95** [120].

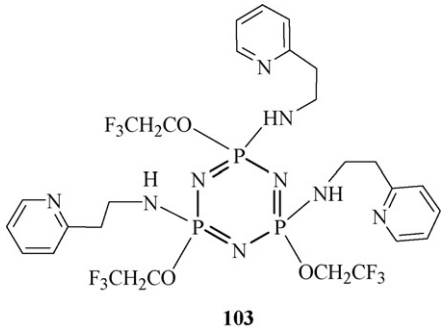


Chart 21. Tris(pyridylamino)cyclophosphazene **103** [19].

6. Aminocyclophosphazenes

Aminocyclophosphazenes, of the type $[NP(NHR)_2]_n$ and $[NP(NR_2)_2]_n$ were among the first cyclophosphazene ligands to be investigated for their coordination properties (it is noted that pyrazolylcyclophosphazenes and pyridylaminocyclophosphazenes, discussed vide supra, are a special class of aminocy-

Table 2
Summary of the structural features of the metal complexes obtained from pyridyloxycyclophosphazenes[a]

S. no.	Complexes	Geometry around metal ions[b]	Cyclophosphazene P–N bond distance (Å)[c]	M–N ring nitrogen distance (Å)[c]	Reference
1	$[L_2Cu_3Cl_4][Cu_2Cl_6]$ (**74**)	(a) Hexacoordinate [Cu(II)] (5N, 1Cl) η^5-*gem*-N_5, elongated rhombic octahedral. (b) Tetracoordinate [Cu(II)] (2N, 2Cl), compressed tetrahedral	1.600(2), 1.566(2), 1.584(2)	1.988(2)	[117]
2	$[\{(L''CuCl)_2Co(NO_3)\}Cl^-]$ (**75**)	(a) Hexacoordinate [Cu(II)] (5N, 1Cl) η^5-*gem*-N_5, distorted rhombic octahedral. (b) Hexacoordinate [Co(II)] (4O, 2N), distorted octahedral	1.601(3), 1.549(3), 1.606(3)	1.967(3)	[118]
3	$[LCuClCoCl_3]$ (**76**)	(a) Hexacoordinate [Cu(II)] (5N, 1Cl) η^5-*gem*-N_5, distorted rhombic octahedral. (b) Tetracoordinate [Co(II)] (1N, 3Cl), tetrahedral	1.600(2), 1.563(2), 1.582(2)	1.988(2)	[118]
4	$[LCuClZnCl_3]$ (**77**)	(a) Hexacoordinate [Cu(II)] (5N, 1Cl) η^5-*gem*-N_5, distorted rhombic octahedral. (b) Tetracoordinate [Zn(II)] (1N, 3Cl), tetrahedral	1.601(3), 1.564(3), 1.581(3)	1.982(3)	[118]
5	$[LCoClZnCl_3]$ (**78**)	(a) Hexacoordinate [Co(II)] (5N, 1Cl) η^5-*gem*-N_5, distorted rhombic octahedral. (b) Tetracoordinate [Zn(II)] (1N, 3Cl), tetrahedral	1.591(3), 1.564(3), 1.581(3)	2.048(3)	[118]
6	$[LCoClCoCl_3]$ (**79**)	(a) Hexacoordinate (5N, 1Cl) η^5-*gem*-N_5, elongated rhombic octahedral. (b) Tetracoordinate (1N, 3Cl), compresed tetrahedral	1.595(5), 1.555(5), 1.579(5)	2.032(5)	[119]
7	$[LCoBrCoBr_3]$ (**80**)	(a) Hexacoordinate (5N, 1Br) η^5-*gem*-N_5, elongated rhombic octahedral. (b) Tetracoordinate (1N, 3Br), compresed tetrahedral	1.583(5), 1.555(5), 1.579(5)	2.034(5)	[119]
8	$[L'CoClCoCl_3]$ (**81**)	(a) Hexacoordinate (5N, 1Cl) η^5-*gem*-N_5, elongated rhombic octahedral. (b) Tetracoordinate (1N, 3Cl), compresed tetrahedral	1.586(4), 1.560(4), 1.577(4)	2.035(4)	[119]
9	$[LCuCl_2]$ (**83**)	Pentacoordinate (3N, 2Cl) η^3-*non-gem*-N_3, distorted TBP	1.592(3), 1.579(3), 1.580(3)	2.264(3)	[115]
10	$[L'CoBr_2]$ (**84**)	Pentacoordinate (3N, 2Br) η^3-*non-gem*-N_3, distorted TBP	1.626(2), 1.575(2), 1.593(2)	2.089(2)	[119]
11	$[LCoBr]PF_6$ (**86**)	Hexacoordinate (5N, 1Br) η^5-*gem*-N_5, elongated rhombic octahedral	1.590(3), 1.565(3), 1.586(3)	2.064(2)	[119]
12	$[LNiCl]PF_6$ (**87**)	Hexacoordinate (5N, 1Cl) η^5-*gem*-N_5, elongated rhombic octahedral	1.590(3), 1.560(3), 1.591(3)	2.027(3)	[119]
13	$[LCuCl]PF_6$ (**88**)	Hexacoordinate (5N, 1Cl) η^5-*gem*-N_5, elongated rhombic octahedral	1.599(3), 1.558(3), 1.585(3)	1.993(3)	[115]
14	$[L'(CuCl_2)_2]$ (**89**)	Pentacoordinate (3N, 2Cl) η^3-*non-gem*-N_3, distorted TBP	1.596(3), 1.573(3), 1.568(3)	2.214(3)	[115]
15	$[L(ZnCl_2)_2]$ (**90**)	(a) Pentacoordinate (3N, 2Cl) η^3-*non-gem*-N_3, distorted TBP. (b) Tetracoordinate (2N, 2Cl) η^2-*gem*-N_3, tetrahedral	1.607(3), 1.564(3), 1.566(3)	2.089(3)	[118,119]
16	$[LNiCl_2]$ (**91**)	Hexacoordinate (4N, 2Cl) η^4-*gem*-N_4, distorted octahedral	1.600(2), 1.571(2), 1.587(2)	2.107(2)	[119]
17	$[LNiCl_2]$ (**92**)	Pentacoordinate (3N, 2Cl) η^3-*non-gem*-N_3, distorted TBP	1.608(3), 1.581(4), 1.549(5)	2.023(6)	[119]
18	$[LAg]PF_6$ (**93**)	Pentacoordinate (5N)	1.581(1), 1.592(1), 1.571(1)	2.464(2), 2.798(1)	[120]
19	$[L'Ag]PF_6$ (**94**)	Pentacoordinate (5N)	1.585(3), 1.586(3), 1.575(3)	2.296(3), 2.768(3)	[120]
20	$[L'_2Cu_2(\mu\text{-OH})\text{–}(\mu\text{-4-MeOpy})][PF_6]_2$ (**95**)	(a) Pentacoordinate (4N, 1O) square-based pyramidal. (b) Hexacoordinate (4N, 2O) distorted rhombic	(a) 1.613(7), 1.574(3), 1.572(7); (b) 1.610(4), 1.577(6), 1.574(6)	2.047(2), 2.067(7)	[120]

The description of the geometry around the metal ions in the complexes is made according to the different types of metal ions present.

[a] L is $N_3P_3(2\text{-}OC_5H_4N)_6$ (**70**) [115,117–120], L′ is $N_3P_3(2\text{-}OC_5H_3N\text{–}4\text{-}Me)_6$ (**71**) [115,119,120] and L″ is $N_3P_3(2\text{-}OC_5H_4N)_5(O)$ [118].

[b] The description of the geometry around the metal ions in the complexes is made according to the different types of metal ions present.

[c] Average bond distances.

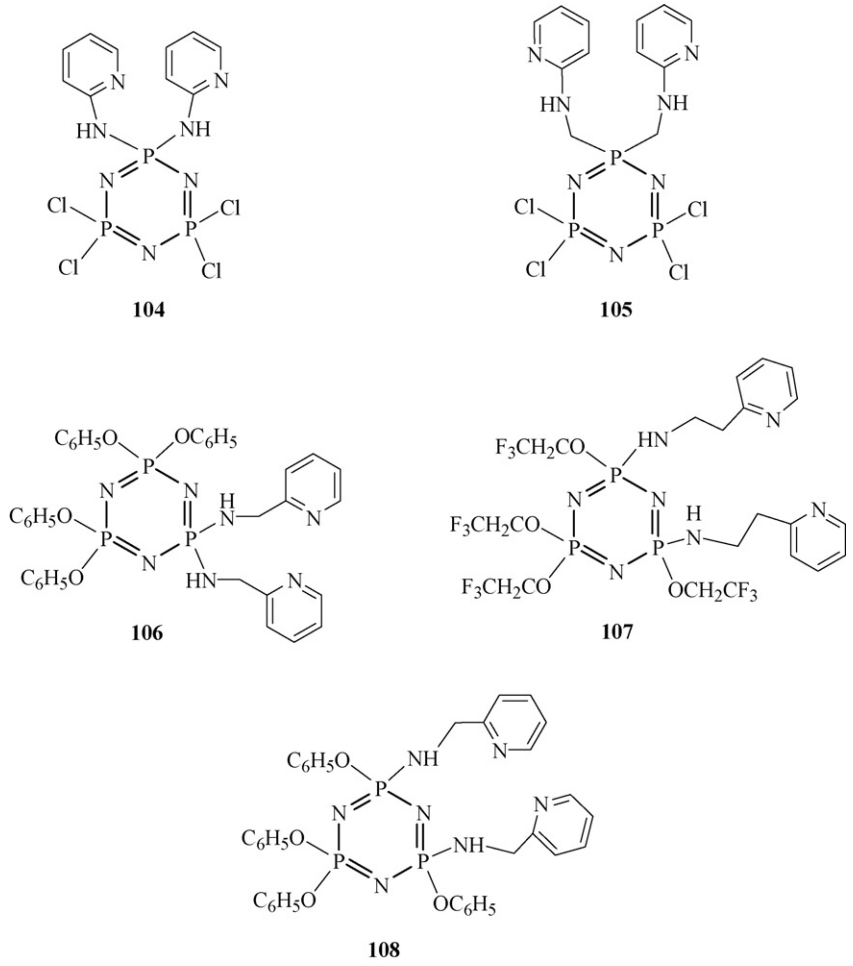
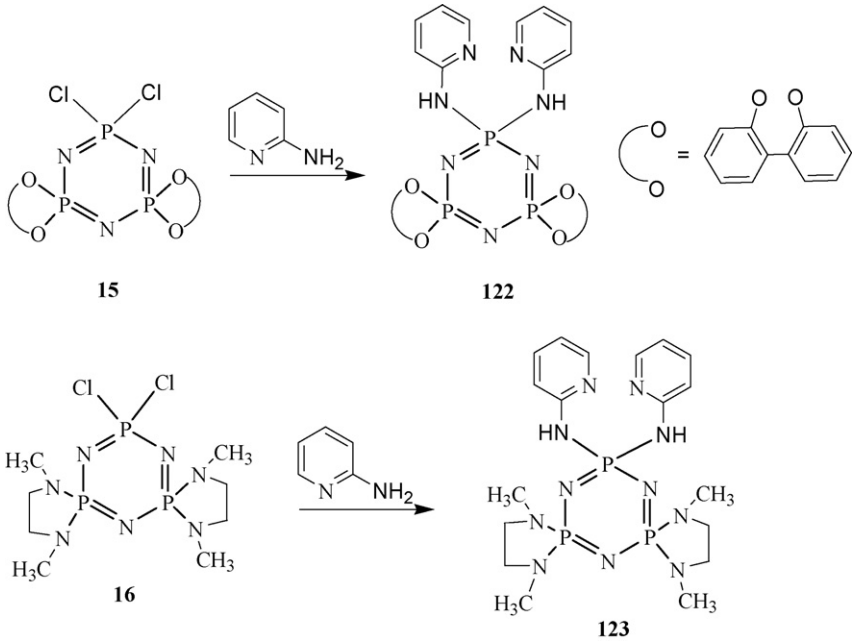


Chart 22. Bis(pyridylamino)cyclophosphazenes **104**–**108** [19].



Scheme 21. Synthesis of **122** and **123** [73].

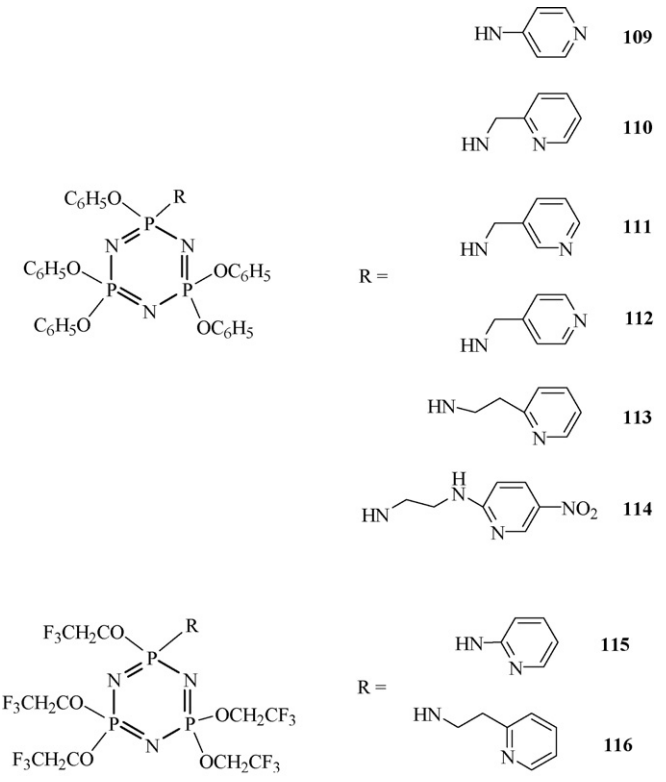
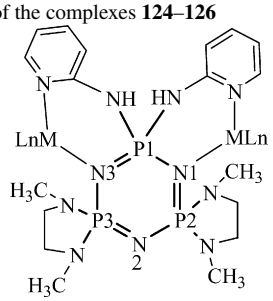


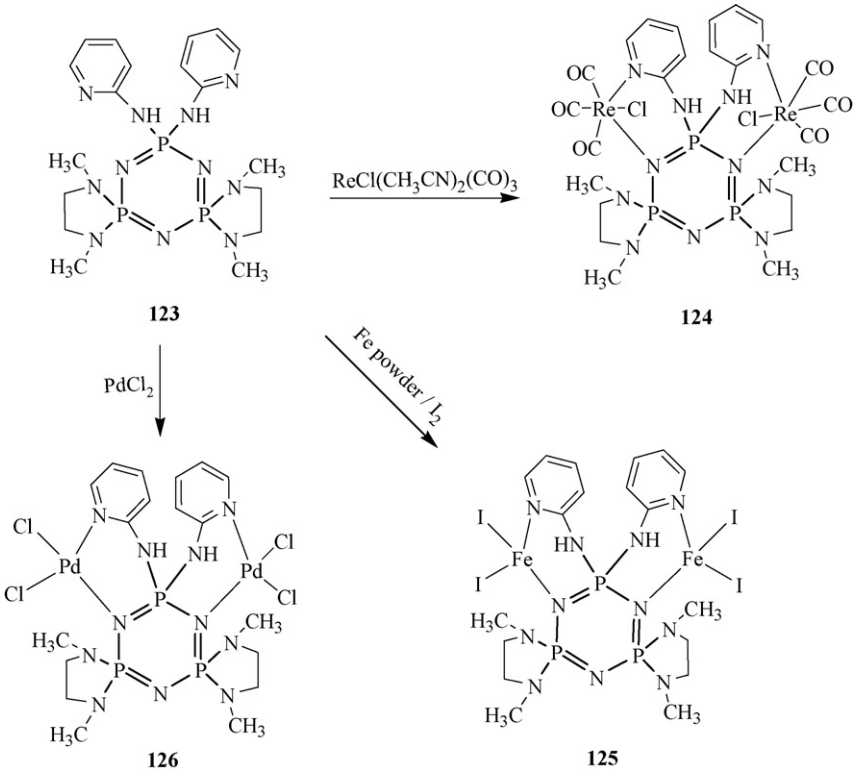
Chart 23. Monopyridylaminocyclophosphazenes **109–116** [19].

clophosphazenes in that they have other coordinating atoms besides the amino nitrogen atom). For example $N_4P_4(NHMe)_8$ is known to form a water soluble complex $N_4P_4(NHMe)_8{\cdot}PtCl_2$ (**127**) (Chart 25). In the latter the platinum atom is bound to two antipodal nitrogen atoms of the cyclotetraphosphazene ring [23]. Octakis(dimethylamino)cyclophosphazene $N_4P_4(NMe_2)_8$ reacts with $W(CO)_6$ to afford $N_4P_4(NMe_2)_8{\cdot}W(CO)_4$ (**128**) (Chart 25) [124]. In the latter the tungsten atom is coordinated both by an exocyclic (NMe_2) nitrogen atom as well as a ring nitrogen atom. Spirocyclic phosphazenes have been used as ligands, and interesting metalated products **129** and **130** (Chart

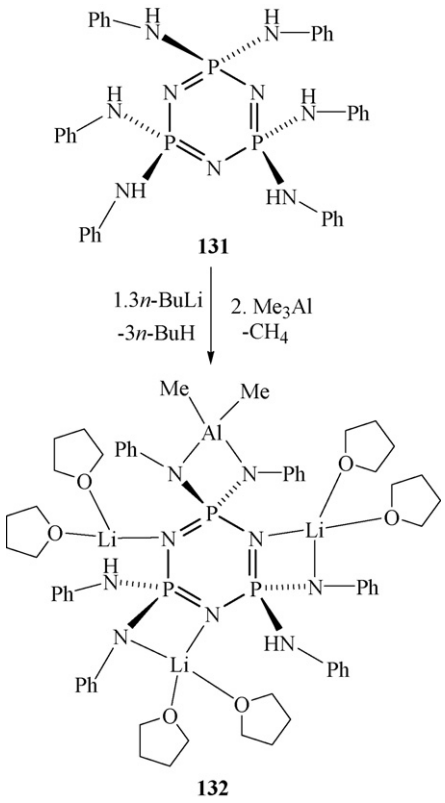
Table 3
Structural parameters of the complexes **124–126**



S. no.	MLn	Geometry around metal	Average P–N distances (Å)
1	$Re(CO)_3Cl$	Distorted octahedral	P1–N1/P1–N3 1.609(7) P2–N1/P3–N3 1.658(7) P3–N2/P2–N2 1.576(7)
2	FeI_2	Pseudo tetrahedral	P1–N1/P1–N3 1.604(5) P2–N1/P3–N3 1.653(5) P3–N2/P2–N2 1.585(5)
3	$PdCl_2$	Distorted square planar	P1–N1/P1–N3 1.611(6) P2–N1/P3–N3 1.652(6) P3–N2/P2–N2 1.582(6)



Scheme 22. Synthesis of the dinuclear metal complexes **124–126** from the pyridylaminocyclophosphazene **123** [73].

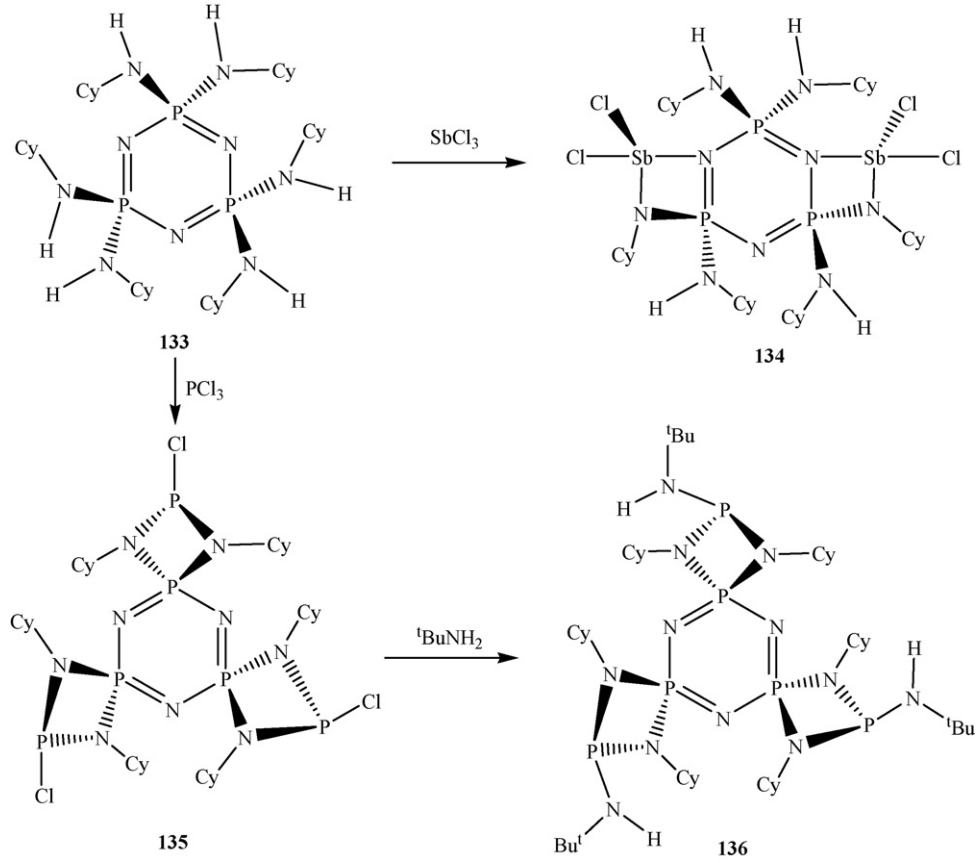


Scheme 23. Synthesis of mixed-metal derivatives from aminocyclophosphazenes [131].

25) have been isolated [125]. The formation of these complexes involved a hydrolysis of the P–N bond.

Fully substituted (organoamino)cyclophosphazenes have become available recently. These show a rich supramolecular chemistry in their solid state [126]. These (organoamino)-cyclophosphazenes can be readily deprotonated by strong bases such as *n*-BuLi. Recently such deprotonation chemistry of aminocyclophosphazenes has been utilized to generated multi-anionic phosphazenates [127–132]. Compounds such as $[N_3P_3(NR)_6]^{6-}[Li^+]_6$ (R = cyclohexyl), *non-gem-cis*-$[N_3P_3(NHR)_3(NR)_3]^{3-}[Li^+]_3$ (R = cyclohexyl, phenyl) have been prepared [127–129].

The Li^+ ions are bound to the anionic cyclophosphazene ligands in a variety of ways. Deprotonation reactions have also been utilized to prepare metal-amido complexes involving cyclophosphazenes. For example, the reaction of a primary amino derivative such as $N_3P_3(NHR)_6$ (R = cyclohexyl) with trimethylaluminum or diethylzinc has been shown to proceed by the elimination of methane to afford multi-nuclear derivatives $[\{N_3P_3(NR)_6\}(thf{\cdot}MeAl)(Me_2Al)_4]$ or $[\{N_3P_3(NR)_6\}(EtZn)_6]$ [130]. Similarly $N_4P_4(NHR)_8$ affords a hexazinc derivative $[\{N_4P_4(NHR)_2(NR)_6\}(EtZn)_6]$ [130]. Recently, sequential deprotonation reactions have been carried out on $N_3P_3(NHPh)_6$ (**131**), first with *n*-BuLi to afford *cis-non-gem*-$[N_3P_3(NHR)_3(NR)_3][Li(THF)_2]_3$. The latter upon reaction with Me_3Al leads to further deprotonation to afford the mixed-metal derivative, $[N_3P_3(NHPh)_2(NPh)_4][\{Li(THF)_2\}_3(AlMe_2)]$ (**132**) (Scheme 23) [131].



Scheme 24. Interaction of $N_3P_3(NHCy)_6$ (**133**) with PCl_3 and $SbCl_3$ [133].

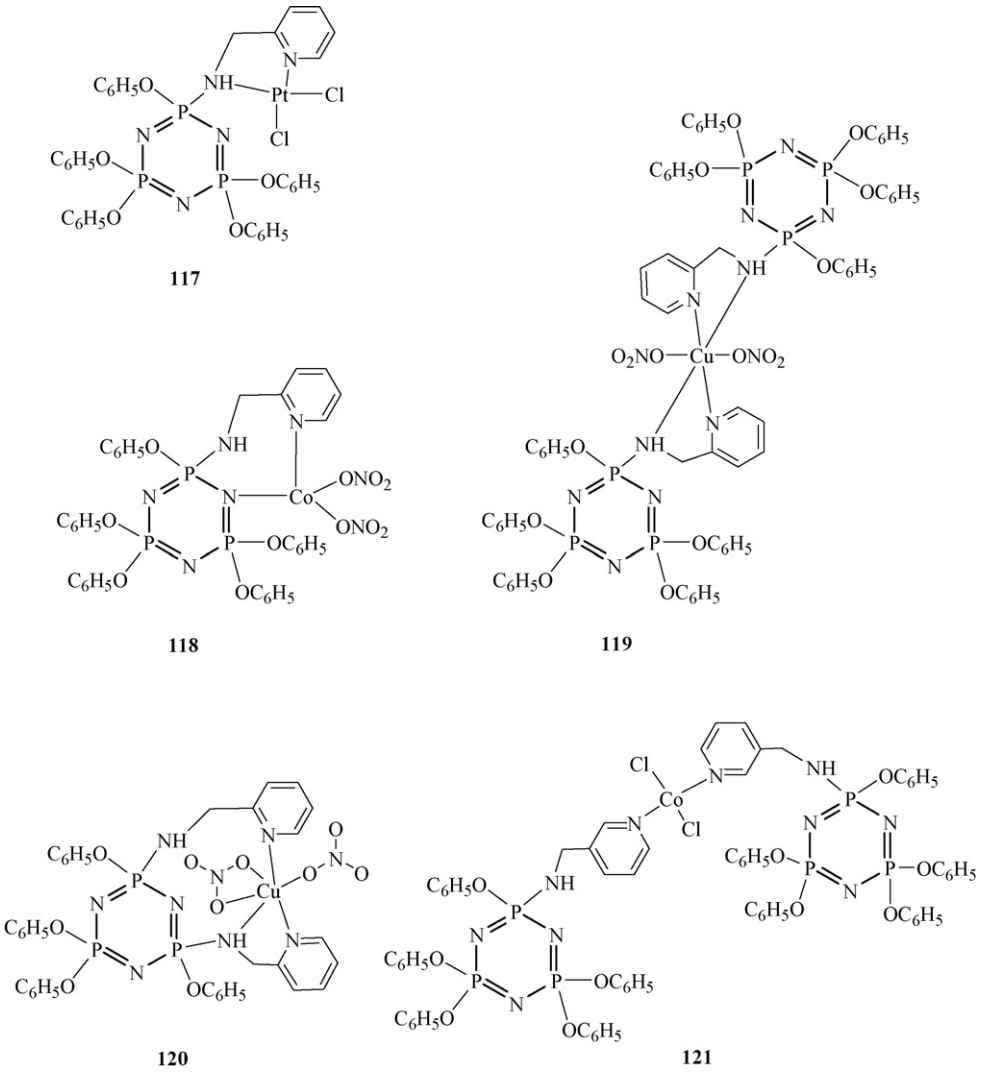
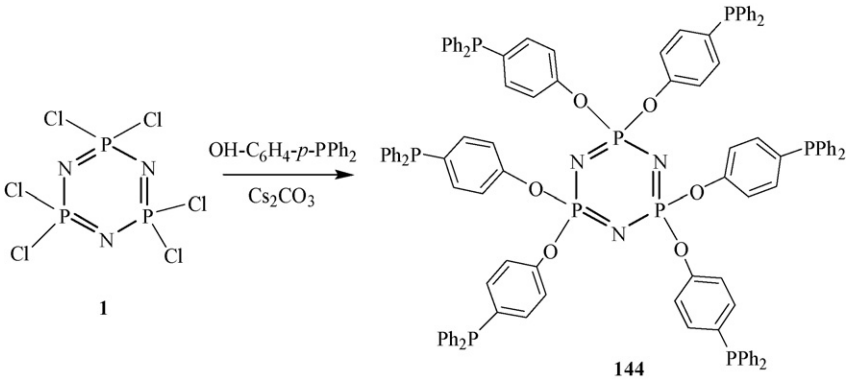


Chart 24. Examples of metal complexes obtained from pyridylaminocyclophosphazene ligands [19].

The structural features of the mixed-metal compound **132** can be summarized as follows:

a. it contains a planar PN_2Al ring as a result of the chelating action of the exocyclic N–P–N segment;
b. two four-membered rings PN_2Li are formed as a result of the coordination of exo/endo-cyclic N–P–N segments;
c. one lithium ion is bound solely by a ring nitrogen atom;
d. the cyclophosphazene ring adopts a half-chair conformation;



Scheme 25. Synthesis of $N_3P_3(OC_6H_4$–p-$PPh_2)_6$ (**144**) [136].

Table 4
Description of the supramolecular networks formed in the silver complexes of aminocyclophosphazenes

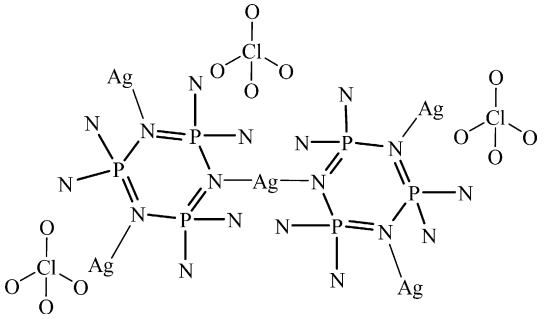
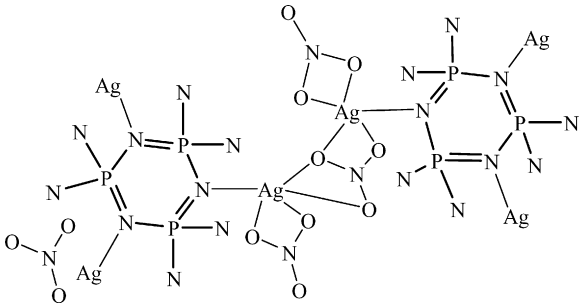
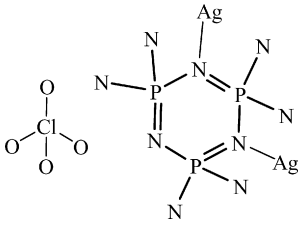
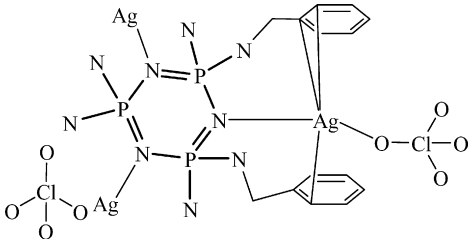
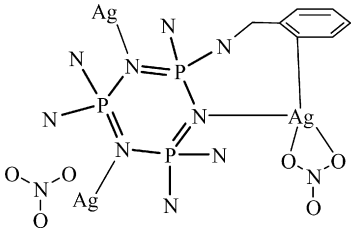
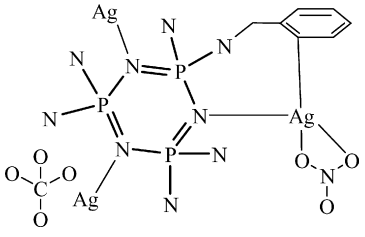
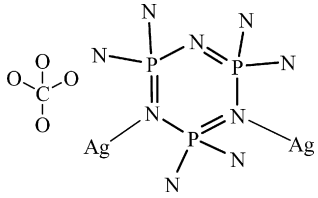
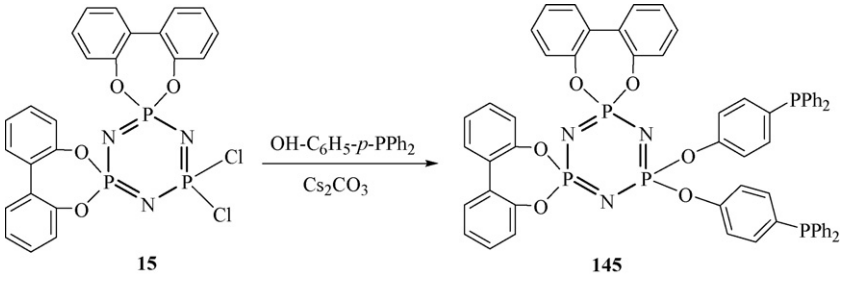
S. no.	Compound	Description of the structure	Basic unit of the supramolecular
1	$[\{N_3P_3(NHPr^n)_6\}_2\{AgClO_4\}_3]$ (**137**)	(1) Graphite type (6,3) network. (2) Each phosphazene binds through three ring nitrogen atoms. (3) Linear N–Ag–N linkages perpetuate the network. (4) The counter anions do not coordinate to Ag(I), but are found do H-bond with the NH groups of the amino substituent	
2	$[\{N_3P_3(NHPr^n)_6\}\{AgNO_3\}_2]$ (**138**)	(1) Two-dimensional sheet. (2) All three ring nitrogen atoms are involved in coordination. Two of these are involved to form intermolecular N–Ag–N linkages. The third is involved in forming N–Ag(μ-NO_3)–Ag–N links. (3) Nitrate counter anion binds in a chelating mode to Ag(I)	
3	$[\{N_3P_3(NHCy)_6\}\{AgClO_4\}]$ (**139**)	(1) One-dimensional coordination polymer. (2) Two ring nitrogen atoms coordinate to Ag(I) ions to form intermolecular N–Ag–N linkages. One ring nitrogen atom remains non-coordinating. (3) The perchlorate counter anions are non-coordinating, but form NH···O linkages	
4	$[\{N_3P_3(NHCH_2Ph)_6\}\{AgClO_4\}_2]$ (**140**)	(1) Zig-zag chain arrangement. (2) Ag(I) ions in both bridging and terminal. Two nitrogen atoms of cyclophosphazenes form N–Ag–N links. (3) Aryl-Ag(I) terminal contacts present in supramolecular structure	
5	$[\{N_3P_3(NHCH_2Ph)_6\}\{AgNO_3\}_2]$ (**141**)	Supramolecular structure similar to $[\{N_3P_3(NHCH_2Ph)_6\}\{AgClO_4\}_2]$	
6	$[\{N_3P_3(NHCH_2Ph)_6\}(AgNO_3)(AgClO_4)]$ (**142**)	(1) Supramolecular structure similar to above. (2) Two distinct anion binding sites. While NO_3 binds to the metal ion, ClO_4^- is found hydrogen bonded to the NH groups	

Table 4 (*Continued*)

S. no.	Compound	Description of the structure	Basic unit of the supramolecular
7	$[N_3P_3(C_4H_8N)_6{\cdot}AgClO_4]$ (**143**)	Supramolecular structure similar to $[\{N_3P_3(NHCy)_6\}\{AgClO_4\}]$	



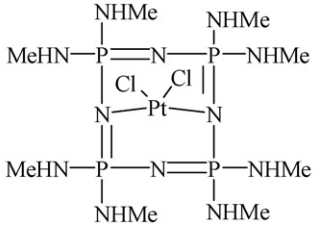
15 145

Scheme 26. Synthesis of $N_3P_3(O_2C_{12}H_8)_2(OC_6H_4{-}p{-}PPh_2)_2$ (**145**) [136].

e. the ring P–N bond lengths are consistently longer than that found in aminocyclophosphazenes with the average distance being 1.615(3) Å.

Interestingly the ^{31}P NMR spectrum of **132** shows a fluxional behavior. A concerted oscillation of lithium ions around the coordination sphere of the ligand has been reported [131].

Recently it has been shown that the hydrates of aminophosphazenes $N_3P_3(NHPr^n)_6{\cdot}1.5H_2O$ and $N_3P_3(NHCy)_6{\cdot}8H_2O$ react with 4.5 and 8 equiv. of diethylzinc, respectively, to afford molecular complexes. In the first instance a planar Zn_3O_3 six-membered ring is sandwiched between two $N_3P_3(NHPr^n)_3(NPr^n)_3(EtZn)_3$ segments [132]. In the second compound a hexagonal $(ZnO)_6$ prism is sandwiched between two $N_3P_3(NHCy)_3(NCy)_3(EtZn)_3$ segments



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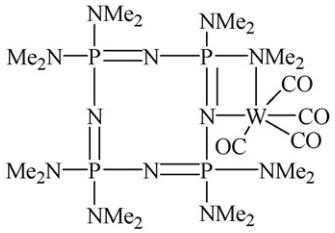

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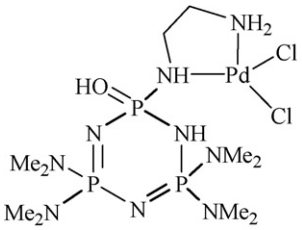

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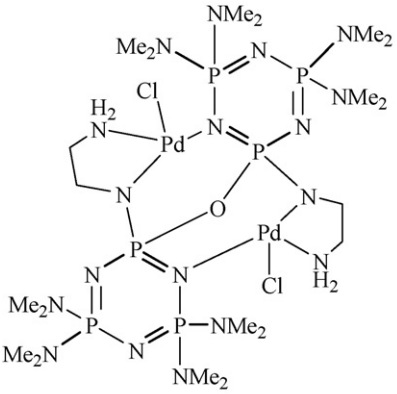

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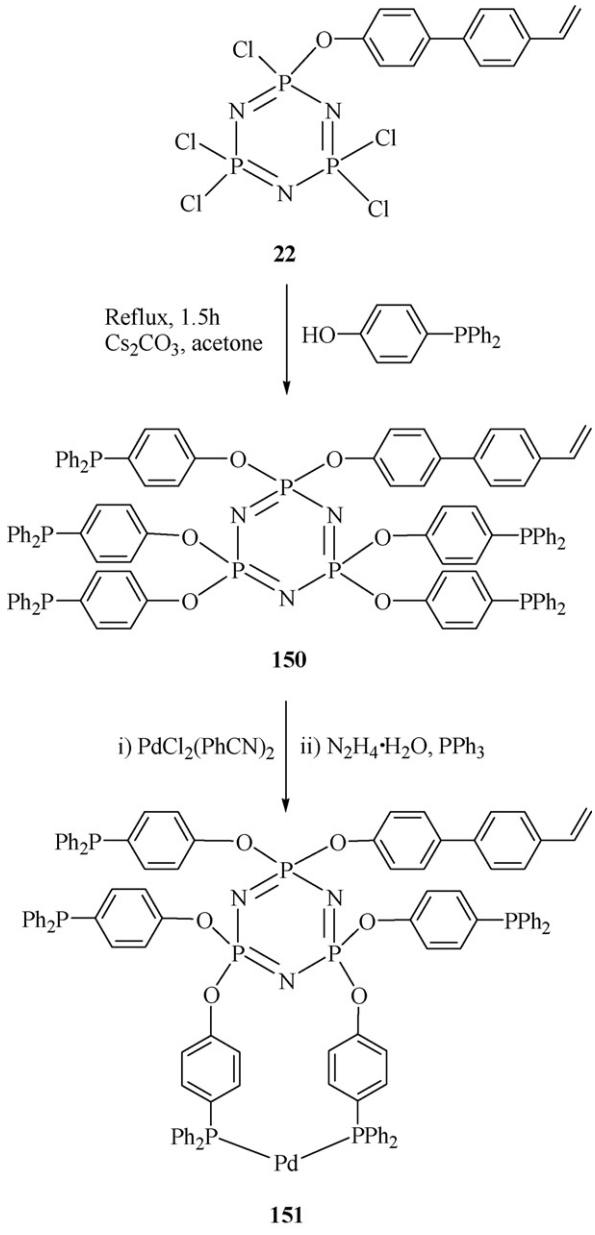
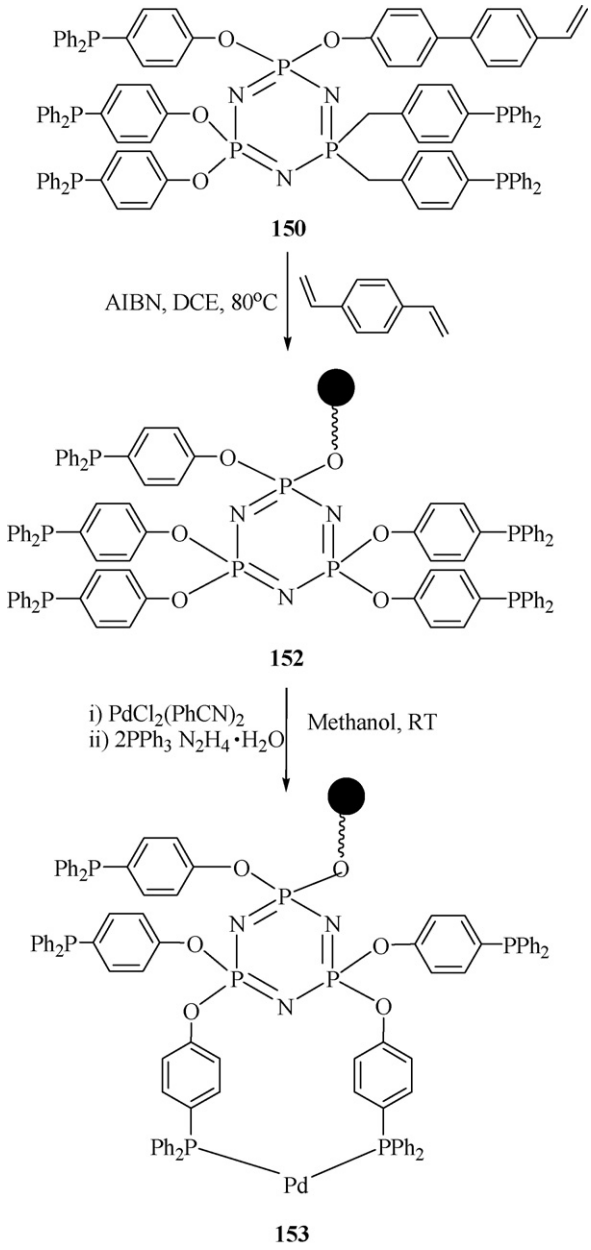
Chart 25. Examples of metal complexes formed from aminocyclophosphazenes [23,124,125].



Scheme 27. Preparation of Pd(0) complexes of phosphine-linked cyclophosphazenes [138].

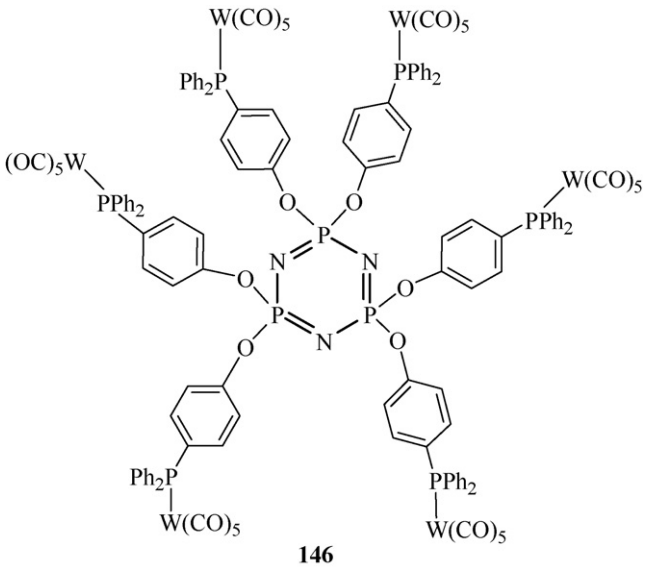


Scheme 28. Synthesis of cross-linked polymers containing Pd-metalated cyclophosphazene pendant groups [138].

[132]. In these compounds, it has been shown that tris(ethylzinc)phosphazenates, owing to their bowl-shaped coordination surface as well as due to the presence of both Lewis acidic and Lewis basic sites are able to act as templates for trapping molecular zinc oxides [132].

Hexakis(cyclohexylamino)cyclophosphazene $N_3P_3(NHCy)_6$ (**133**) reacts with PCl_3 in the presence of Et_3N to give the compound **135** (Scheme 29) [133]. Reaction of **135** with *t*-$BuNH_2$ affords **136** (Scheme 24). Both **135** and **136** are trispirocyclic systems and contain a central six-membered phosphazene core which supports three four-membered phosphazene rings. The presence of lone pairs on the phosphorus centers of the phosphazane periphery renders these molecules to exist as C_{3h} and C_s isomers. The coordination chemistry of these ligands should be interesting. In contrast to the reactions with PCl_3, those of $N_3P_3(NHCy)_6$ (**133**) with $SbCl_3$ affords a dinuclear complex, *non-gem-trans*-$N_3P_3(NHCy)_4(NCy)_2(SbCl_2)_2$ (**134**) (Scheme 24) [133]. In this case each $SbCl_2$ is bound in a covalent manner by a deprotonated NCy unit. Further coordinative interaction with an adjacent ring nitrogen atom affords a four-membered ring.

It was mentioned vide supra that pyridyloxycyclotriphosphazenes functioned as multi-site coordinating bridging ligands to form one-dimensional coordination polymers of Ag(I). More complex supramolecular coordination network formations were realized in the Ag(I) complexes of various aminocyclophosphazenes, $N_3P_3(NHR)_6$ (R = *n*-Pr, Cy. benzyl) and $N_3P_3(C_4H_8N)_6$ [134]. Primarily the driving force for these supramolecular networks is the formation of linear N–Ag–N



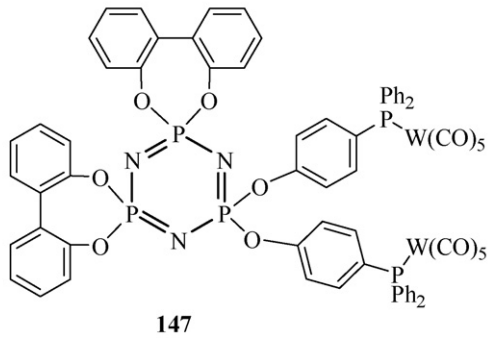
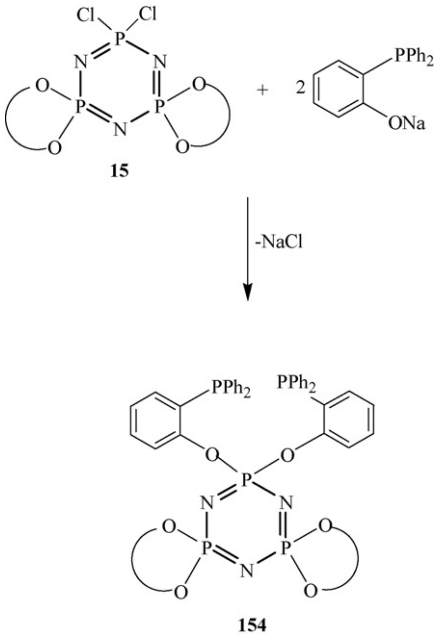
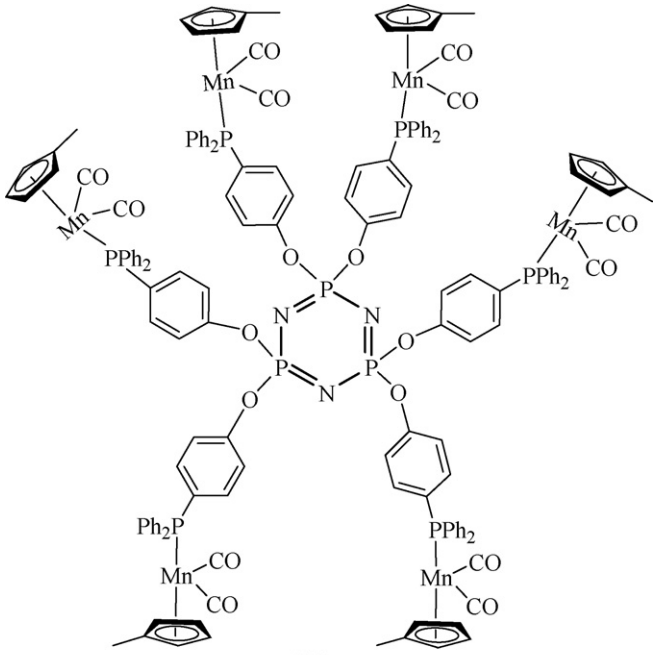


Chart 26. Metal carbonyl derivatives of cyclophosphazenes [136].



Scheme 29. Synthesis of a cyclophosphazene containing chelating phosphine groups **154** [139].



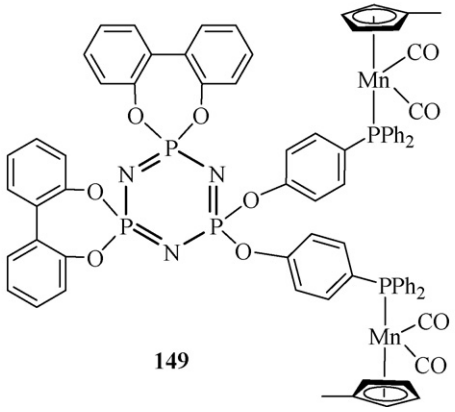
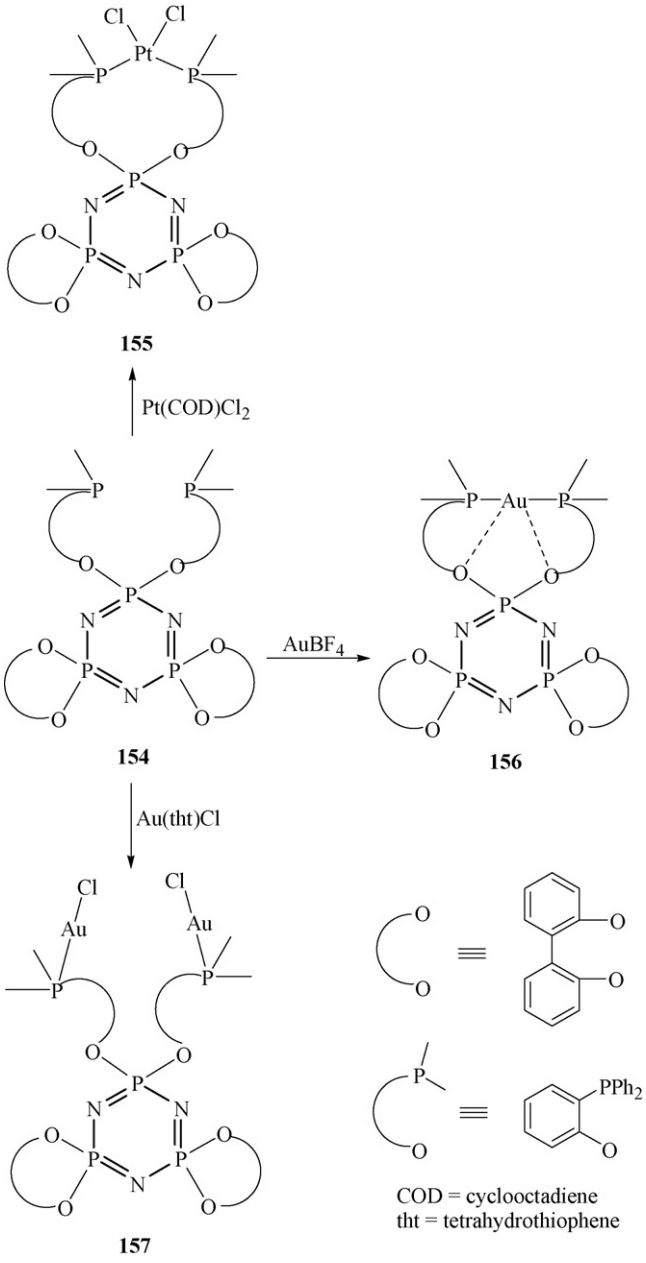


Chart 27. Half-sandwich organometallic complexes prepared from cyclophosphazene ligands [137].

bonds which occur through the cyclophosphazene ring nitrogen atoms. Both two-dimensional networks as well as one-dimensional zig-zag chain arrangements are realized. Thus, for example, the complex $[\{N_3P_3(NHPr^n)_6\}_2\cdot\{AgClO_4\}_3]$ (**137**) forms a graphite-like (6,3) network. The supramolecular structural description of the Ag(I)-coordination networks of aminocyclophosphazenes is summarized in Table 4. In addition to their interesting coordination chemistry, recently it has been shown that aminocyclophosphazenes can be converted into various types of phosphazene cations with potential utility in polyelectrolytes, membranes and drug delivery systems [135].

7. Miscellaneous ligands

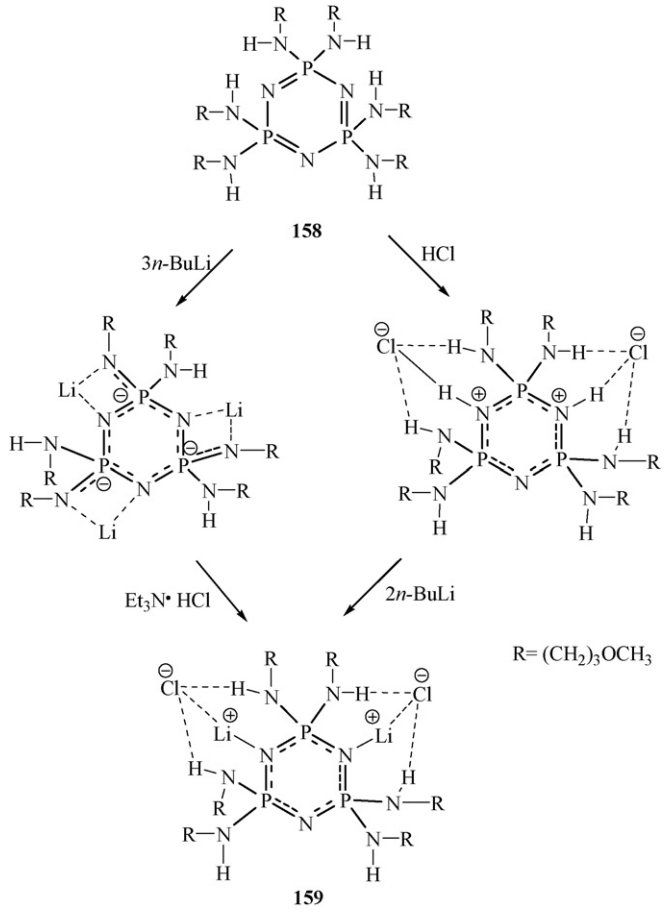
Phosphine-linked cyclophosphazenes have been of interest as ligands towards metals in low oxidation states as well as towards metals belonging to the second and third transition series. Carriedo and co-workers have reacted $N_3P_3Cl_6$



Scheme 30. Pt(II) and Au(I) complexes prepared from $N_3P_3(O_2C_{12}H_8)_2$ (O–C_6H_4–*o*-PPh_2)$_2$ [139].

(**1**) or $N_3P_3(O_2C_{12}H_8)_2Cl_2$ (**15**) with OH–C_6H_4–*p*-PPh_2 in presence of Cs_2CO_3 to afford $N_3P_3(OC_6H_4$–*p*-$PPh_2)_6$ (**144**) [136] and $N_3P_3(O_2C_{12}H_8)_2(OC_6H_4$–*p*-$PPh_2)_2$ (**145**) [136] (Schemes 25 and 26).

Similarly the reaction of the tungsten carbonyl complex OH–C_6H_4–*p*-PPh_2·$W(CO)_5$ with $N_3P_3Cl_6$ or $N_3P_3(O_2C_{12}H_8)_2Cl_2$ afforded the hexanuclear (**146**) and dinuclear (**147**) metal carbonyl derivatives, respectively (Chart 26) [136]. The reaction of $N_3P_3Cl_6$ or $N_3P_3(O_2C_{12}H_8)_2Cl_2$ with [HO–C_6H_4–*p*-PPh_2·$Mn(CO)(\eta^5$-$C_5H_4Me)$] afforded the corresponding hexanuclear (**148**) and dinuclear (**149**) derivatives, respectively (Chart 27) [137]. The synthetic approaches used in these small-molecule preparation could be extended to the linear polyphosphazenes as well.



Scheme 31. LiCl complexes of aminocyclophosphazenes [140].

The reaction of $N_3P_3Cl_5$[O–C_6H_4–*p*-CH=CH_2] with OH–C_6H_4–*p*-PPh_2 afforded N_3P_3(OH–C_6H_4–*p*-$PPh_2)_5$(O–C_6H_4–*p*-CH=CH_2) (**150**). The latter has been found to metalate Pd(0) to afford **151** (Scheme 27) [138]. Compound **150** has been polymerized in presence of 1,4-divinylbenzene to afford a cross-linked polymer **152** which contains phosphine-linked cyclophosphazene units as pendant groups. Metalation of **152** with Pd(0) afforded **153** (Scheme 28) [138]. Both **151** and **153** could be used as catalysts in the Heck arylation reaction. The advantage of **153** is that it could be recycled up to at least four cycles without significant loss of activity [138].

Recently the reactions of phosphine-linked phenols have been extended to prepare a chelating ligand system. Accordingly, the reaction of $N_3P_3(O_2C_{12}H_8)_2Cl_2$ (**15**) with $NaOC_6H_4$–*O*–PPh_2 afforded the ligand **154** (Scheme 29) [139]. The ligand **154** reacts with $AuBF_4$ to give a mononuclear Au(I) complex **156** (Scheme 30) [139]. In **156** the formally dicoordinate Au(I) is in a near linear geometry being bound by the two phosphino groups. Short Au···O contacts (∼3.00–3.12 Å) are also present. The phosphine-linked ligand **154** affords a dinuclear Au(I) complex **157** (Scheme 30) upon reaction with Au(tht)Cl where the two AuCl units are coordinated by each of the phosphine arms of the cyclophosphazene ring. The ligand **154** also reacts with $Pt(COD)Cl_2$ to afford a square planar Pt(II) complex **155**

(Scheme 30) [139]. In this complex the two geminal phosphine groups act in a concerted chelating coordination to the Pt(II) center.

Among other cyclophosphazene ligands to have been investigated recently include $N_3P_3[CH_3O(CH_2)_3NH]_6$ (**158**). The latter has been shown to form complexes with LiCl by a clever synthetic method involving an initial deprotonation followed by treatment of $Et_3N{\cdot}HCl$ to afford $N_3P_3[CH_3O(CH_2)_3NH]_6{\cdot}2LiCl$ (**159**). The latter can also be obtained by initial protonation of **158** followed by deprotonation by *n*-BuLi (Scheme 31) [140].

The crystal structure of **159** shows that each phosphazene molecule binds two lithium ions through two ring nitrogen atoms. Compounds such as **159** lend credence to the belief that in polymer electrolytes involving polyphosphazene–LiX complexes it is reasonable to assume that the back bone nitrogen atoms play an important role in binding to lithium ions [140].

8. Conclusion

Cyclophosphazenes continue to attract interest and remain the most important family of inorganic ring systems. These inorganic heterocyclic rings are particularly well-suited, as described vide supra, for being used as scaffolds or platforms for the construction of multi-site coordination ligands. This feature stems from the fact that chlorocyclophosphazenes, important starting materials for this group of compounds, have a fairly robust skeleton and a reactive periphery. The latter comprised of P–Cl bonds is susceptible for nucleophilic substitution reactions. Utilizing this reactive behavior a library of multi-site coordination ligands have been designed and assembled in recent years. The coordination chemistry of these ligands is quite exciting and several structurally diverse metal complexes have been synthesized and structurally characterized. Metal ions ranging from first row transition ion metal ions to lanthanide metal ions have been involved in complex formation utilizing cyclophosphazene-based ligands. The coordination behavior of cyclophosphazene ligands can be modulated by the type, number and orientation of the coordinating groups that are attached to the cyclophosphazene skeleton.

Recent paradigms in cyclophosphazene-based ligands include their use in a deliberate design to generate robust metal-mediated supramolecular networks as well as in the assembly of heterometallic derivatives. Site-differentiation is readily accomplished in cyclophosphazenes and serves as an important tool for ligand modification.

In spite of the large number of cyclophosphazene-based metal complexes that have been synthesized and structurally characterized, their utility in catalytic reactions has remained largely unexplored. Recently there have been a few efforts in this regard and it is anticipated that future research will prove rewarding in this area. The symbiosis that exists between cyclophosphazenes and the corresponding polymeric systems will ensure that small-molecule developments will be readily translated to the more complex macromolecules.

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References

[1] V. Chandrasekhar, V. Krishnan, Adv. Inorg. Chem. 53 (2002) 159.
[2] C.W. Allen, Chem. Rev. 91 (1991) 119.
[3] V. Chandrasekhar, K.R. Justin Thomas, Struct. Bonding (Berlin) 81 (1993) 41.
[4] M. Gleria, R. De Jaeger (Eds.), Applicative Aspects of Cyclophosphazenes, Nova Science Publishers, New York, 2004.
[5] A.J. Elias, J.M. Shreeve, Adv. Inorg. Chem. 52 (2001) 335.
[6] S.S. Krishnamurthy, A.C. Sau, M. Woods, Adv. Inorg. Chem. Radiochem. 21 (1978) 41.
[7] C.W. Allen, Coord. Chem. Rev. 130 (1994) 137.
[8] M. Witt, H.W. Roesky, Chem. Rev. 94 (1994) 1163.
[9] L. Mahalakshmi, D. Stalke, Struct. Bonding (Berlin) 103 (2002) 85.
[10] A. Steiner, S. Zacchini, P.I. Richards, Coord. Chem. Rev. 227 (2002) 193.
[11] V. Chandrasekhar, Inorganic and Organometallic Polymers, Springer-Verlag, Heidelberg, Germany, 2005.
[12] J.E. Mark, H.R. Allcock, R. West, Inorganic Polymers, Prentice-Hall, New Jersey, 1992.
[13] H.R. Allcock, Chemistry and Applications of Polyphosphazenes, Wiley, Hoboken, NJ, USA, 2003.
[14] M. Gleria, R. De Jaeger, Phosphazenes—A World Wide Insight, Nova Science, New York, 2004.
[15] V. Chandrasekhar, K.R. Justin Thomas, Appl. Organomet. Chem. 7 (1993) 1.
[16] V. Chandrasekhar, S. Nagendran, Chem. Soc. Rev. 30 (2001) 193.
[17] V. Chandrasekhar, V. Krishnan, in: M. Gleria, R. De Jaeger (Eds.), Applicative Aspects of Cyclophosphazenes, Nova Science, New York, 2004, p. 159.
[18] H.R. Allcock, J.L. Desorcie, G.H. Riding, Polyhedron 6 (1987) 119.
[19] U. Diefenbach, in: M. Gleria, R. De Jaeger (Eds.), Applicative Aspects of Cyclophosphazenes, Nova Science, New York, 2004, p. 185.
[20] H.R. Allcock, E.C. Bissell, E.T. Shawl, Inorg. Chem. 12 (1973) 2963.
[21] H.R. Allcock, R.W. Allen, J.P. O'Brien, J. Am. Chem. Soc. 99 (1977) 3984.
[22] J.P. O'Brien, R.W. Allen, H.R. Allcock, Inorg. Chem. 18 (1979) 2230.
[23] R.W. Allen, J.P. O'Brien, H.R. Allcock, J. Am. Chem. Soc. 99 (1977) 3987.
[24] J. Trotter, S.H. Whitlow, J. Chem. Soc. A (1970) 455.
[25] A.J. Heston, M.J. Panzner, W.J. Youngs, C.A. Tessier, Inorg. Chem. 44 (2005) 6518.
[26] S. Trofimenko, Scorpionates—The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999.
[27] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[28] D.D. Wick, K.I. Goldberg, J. Am. Chem. Soc. 121 (1999) 11900.
[29] S. Reinartz, P.S. White, M. Brookhart, J.L. Templeton, J. Am. Chem. Soc. 123 (2001) 6425.
[30] M.C. Kuchta, J.B. Bonanno, G. Perkin, J. Am. Chem. Soc. 118 (1996) 10914.
[31] J.P. Lee, K.A. Pittard, N.J. DeYonker, T.R. Cundari, T.B. Gunnoe, J.L. Petersen, Organometallics 25 (2006) 1500.
[32] S.A. Sproules, H.T. Morgan, C.J. Doonan, J.M. White, C.G. Young, Dalton Trans. (2005) 3552.
[33] W.H. Myers, K.D. Welch, P.M. Graham, A. Keller, M. Sabat, C.O. Trindle, W.D. Harman, Organometallics 24 (2005) 5267.

[34] A.J. Vetter, C. Flaschenriem, W.D. Jones, J. Am. Chem. Soc. 127 (2005) 12315.
[35] D.L. Reger, J.R. Gardinier, S. Bakbak, R.F. Semeniuc, U.H.F. Bunz, M.D. Smith, New J. Chem. 29 (2005) 1035.
[36] D.A. Delafuente, W.H. Myers, M. Sabat, W.D. Harman, Organometallics 24 (2005) 1876.
[37] P. Yuan, S.H. Liu, W. Xiong, J. Yin, G.-A. Yu, H.Y. Sung, I.D. Williams, G. Jia, Organometallics 24 (2005) 1452.
[38] P.M. Graham, C.J. Mocella, M. Sabat, W.D. Harman, Organometallics 24 (2005) 911.
[39] D.J. Darensbourg, D.R. Billodeaux, L.M. Perez, Organometallics 23 (2004) 5286.
[40] C.J. Mocella, D.A. Delafuente, J.M. Keane, G.R. Warner, L.A. Friedman, M. Sabat, W.D. Harman, Organometallics 23 (2004) 3772.
[41] J.M. Keane, M.D. Chordia, C.J. Mocella, M. Sabat, C.O. Trindle, W.D. Harman, J. Am. Chem. Soc. 126 (2004) 6806.
[42] J. Jaffart, M.L. Cole, M. Etienne, M. Reinhold, J.E. McGrady, F. Maseras, Dalton Trans. (2003) 4057.
[43] I. Krummenacher, H. Rüegger, F. Breher, Dalton Trans. (2006) 1073.
[44] E.T. Papish, M.T. Taylor, F.E. Jernigan III, M.J. Rodig, R.R. Shawhan, G.P.A. Yap, F.A. Jové, Inorg. Chem. 45 (2006) 2242.
[45] C.S. Tredget, S.C. Lawrence, B.D. Ward, R.G. Howe, A.R. Cowley, P. Mountford, Organometallics 24 (2005) 3136.
[46] L. Wang, J.-C. Chambron, Org. Lett. 6 (2004) 747.
[47] D.L. Reger, T.C. Grattan, Synthesis 8 (2003) 1306.
[48] D.L. Reger, C.A. Little, M.D. Smith, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, I.A. Guzei, Inorg. Chem. 41 (2002) 19.
[49] D.L. Reger, T.D. Wright, C.A. Little, J.J.S. Lamba, M.D. Smith, Inorg. Chem. 40 (2001) 3810.
[50] D.L. Reger, C.A. Little, A.L. Rheingold, M. Lam, L.M. Liable-Sands, B. Rhagitan, T. Concolino, A. Mohan, G.J. Long, V. Briois, F. Grandjean, Inorg. Chem. 40 (2001) 1508.
[51] D.L. Reger, T.C. Grattan, K.J. Brown, C.A. Little, J.J.S. Lamba, A.L. Rheingold, R.D. Sommer, J. Organomet. Chem. 607 (2000) 120.
[52] D.L. Reger, R.F. Semeniuc, B. Captain, M.D. Smith, Inorg. Chem. 44 (2005) 2995.
[53] S. Fischer, L. Peterson, J. Nixon, Can. J. Chem. 52 (1974) 3981.
[54] D.D. LeCloux, C.J. Tokar, M. Osawa, R.P. Houser, M.C. Keyes, W.B. Tolman, Organometallics 13 (1994) 2855.
[55] V. Chandrasekhar, S. Kingsley, A. Vij, K.C. Lam, A.L. Rheingold, Inorg. Chem. 39 (2000) 3238.
[56] S. Kingsley, A. Vij, V. Chandrasekhar, Inorg. Chem. 40 (2001) 6057.
[57] C.J. Tokar, P.B. Kettler, W.B. Tolman, Organometallics 8 (1992) 2737.
[58] S.K. Chowdhury, V.S. Joshi, A.G. Samuel, V.G. Puranik, S.S. Tavale, A. Sarkar, Organometallics 13 (1994) 4092.
[59] V. Chandrasekhar, S. Nagendran, S. Kingsley, V. Krishnan, R. Boomishankar, Proc. Ind. Acad. Sci. (Chem. Sci.) 112 (2000) 171.
[60] V.S. Joshi, V.K. Kale, K.M. Sathe, A. Sarkar, S.S. Tavale, C.G. Suresh, Organometallics 10 (1991) 2898.
[61] E. Psillakis, J.C. Jaffery, J.A. McCleverty, M.D. Ward, J. Chem. Soc., Dalton Trans. (1997) 1645.
[62] J.S. Fleming, E. Psillakis, J.C. Jeffery, K.L.V. Mann, J.A. McCleverty, M.D. Ward, Polyhedron 17 (1998) 1705.
[63] K.D. Gallicano, N.L. Paddock, Can. J. Chem. 60 (1982) 521.
[64] K.R. Justin Thomas, V. Chandrasekhar, P. Pal, S.R. Scott, R. Hallford, A.W. Cordes, Inorg. Chem. 32 (1993) 606.
[65] E.T. McBee, K. Okuhara, C.J. Morton, Inorg. Chem. 4 (1965) 1672.
[66] V. Chandrasekhar, S.S. Krishnamurthy, H. Manohar, A.R.V. Murthy, R.A. Shaw, M. Woods, J. Chem. Soc., Dalton Trans. (1984) 621.
[67] T. Chivers, R. Hedgeland, Can. J. Chem. 50 (1972) 1017.
[68] G.A. Carriedo, L. Fernández-Catuxo, F.J.G. Alonso, P. Gómez-Elipe, P.A. González, Macromolecules 29 (1996) 5320.
[69] I. Dez, R. De Jaeger, Phosphorus Sulfur Sillicon 130 (1997) 1.
[70] G.R. Feistel, T.J. Moeller, Inorg. Nucl. Chem. 29 (1967) 2731.
[71] W. Lehr, Z. Anorg, Allg. Chem. 350 (1967) 18.
[72] K.R. Justin Thomas, P. Tharmaraj, V. Chandrasekhar, E.R.T. Tiekink, J. Chem. Soc., Dalton Trans. (1994) 1301.
[73] M. Harmjanz, I.M. Piglosiewicz, B.L. Scott, C.J. Burns, Inorg. Chem. 43 (2004) 642.
[74] I.I. Selvaraj, D. Reddy, V. Chandrasekhar, T.K. Chandrashekar, Heterocycles 32 (1991) 703.
[75] V. Chandrasekhar, S.S. Krishnamurthy, A.R.V. Murthy, R.A. Shaw, M. Woods, Inorg. Nucl. Chem. Lett. 17 (1981) 181.
[76] C.V. Depree, E.W. Ainscough, A.M. Brodie, A.K. Burrell, C. Lensink, B.K. Nicholson, Polyhedron 19 (2000) 2101.
[77] K. Inoue, M. Takagi, M. Nakano, H. Nakamura, T. Tankgaki, Makromol. Chem. Rapid Commun. 9 (1988) 345.
[78] V. Chandrasekhar, A. Athimoolam, K. Vivekanadan, S. Nagendran, Tetrahedron Lett. 40 (1999) 1185.
[79] V. Chandrasekhar, A. Athimoolam, S.G. Srivatsan, P.S. Sundaram, S. Verma, A. Steiner, S. Zacchini, R. Butcher, Inorg. Chem. 41 (2002) 5162.
[80] V. Chandrasekhar, A. Athimoolam, V. Krishnan, R. Azhakar, C. Madhavaiah, S. Verma, Eur. J. Inorg. Chem. (2005) 1482.
[81] B. Dell, B.W. Fitzsimmons, R.A. Shaw, J. Chem. Soc. (1965) 4070.
[82] K.R. Justin Thomas, V. Chandrasekhar, S.R. Scott, R. Hallford, A.W. Cordes, J. Chem. Soc., Dalton Trans. (1993) 2589.
[83] K.R. Justin Thomas, P. Tharmaraj, V. Chandrasekhar, C.D. Byan, A.W. Cordes, Inorg. Chem. 33 (1994) 5382.
[84] K.R. Justin Thomas, V. Chandrasekhar, K. Vivekanandan, G.T. Senthil Andavan, S. Nagendran, S. Kingsley, E.R.T. Tiekink, Inorg. Chim. Acta 286 (1999) 127.
[85] K.R. Justin Thomas, V. Chandrasekhar, P. Zanello, F. Laschi, Polyhedron 16 (1991) 1003.
[86] A. Chandrasekaran, S.S. Krishnamurthy, M. Nethaji, Inorg. Chem. 32 (1993) 6102.
[87] Y. Byun, D. Min, J. Do, H. Yun, Y. Do, Inorg. Chem. 35 (1996) 3981.
[88] B.H. Koo, Y. Byun, E. Hong, Y. Kim, Y. Do, Chem. Commun. (1998) 1227.
[89] K.R. Justin Thomas, V. Chandrasekhar, C.D. Bryan, A.W. Cordes, J. Coord. Chem. 35 (1995) 337.
[90] K.R. Justin Thomas, V. Chandrasekhar, S.R. Scott, A.W. Cordes, Polyhedron 14 (1995) 1607.
[91] K.R. Justin Thomas, P. Tharmaraj, V. Chandrasekhar, S.R. Scott, A.W. Cordes, Polyhedron 14 (1995) 977.
[92] K.D. Gallicano, N.L. Paddock, Can. J. Chem. 60 (1982) 321.
[93] K.R. Justin Thomas, Cyclophosphazenes as transition metal carriers: synthesis and characterization of Cu(II), Ni(II) and Co(II) complexes of pyrazylcyclophosphazenes, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India, 1993.
[94] A. Chandrasekaran, S.S. Krishnamurthy, M. Nethaji, J. Chem. Soc., Dalton Trans. (1994) 63.
[95] M. Harmjanz, B.L. Scott, C.J. Burns, Chem. Commun. (2002) 1386.
[96] J.P. Majoral, R. Kraemer, J. Navech, F. Mathias, Tetrahedron 32 (1976) 2633.
[97] K.V. Katti, V.S. Reddy, P.R. Singh, Chem. Soc. Rev. 24 (1995) 97.
[98] A.M. Caminade, J.P. Majoral, Acc. Chem. Res. 37 (2004) 341.
[99] A.M. Caminade, J.P. Majoral, Chem. Rev. 94 (1994) 1183.
[100] M. Badri, J.P. Majoral, A.M. Caminade, M. Delmas, A. Gaset, A. Gorgues, J. Jaud, J. Am. Chem. Soc. 112 (1990) 5618.
[101] J.P. Majoral, M. Badri, A.M. Caminade, A. Gorgues, M. Delmas, A. Gaset, Phosphorus Sulphur Silicon 49–50 (1990) 413.
[102] J. Mitjaville, A.M. Caminade, J.C. Daran, B. Donnadieu, J.P. Majoral, J. Am. Chem. Soc. 117 (1995) 1712.
[103] M. Wang, E.W. Volkert, P.R. Singh, K.K. Katti, P. Lusiak, K.V. Katti, C.L. Barnes, Inorg. Chem. 33 (1994) 1184.
[104] P.R. Singh, H. Jimenez, K.V. Katti, W.A. Volkert, C.L. Barnes, Inorg. Chem. 33 (1994) 736.
[105] K.V. Katti, P.R. Singh, C.L. Barnes, Inorg. Chem. 31 (1992) 4588.
[106] V. Chandrasekhar, V. Krishnan, G.T. Senthil Andavan, A. Steiner, S. Zacchini, CrystEngComm. 5 (2003) 245.
[107] V. Chandrasekhar, G.T. Senthil Andavan, S. Nagendran, V. Krishnan, R. Azhakar, R.J. Butcher, Organometallics 22 (2003) 976.

[108] V. Chandrasekhar, V. Krishnan, A. Steiner, J.F. Bickley, Inorg. Chem. 43 (2004) 166.
[109] G.A. Carriedo, P.G. Elipe, F.J.G. Alonso, L.F. Catuxo, M.R. Diaz, S.G. Granda, J. Organomet. Chem. 498 (1995) 207.
[110] Y. Cho, H. Baek, Y.S. Sohn, Macromolecules 32 (1999) 2167.
[111] Y.S. Sohn, Y.H. Cho, H. Baek, O.-S. Jung, Macromolecules 28 (1995) 7566.
[112] K. Inoue, T. Itaya, N. Azuma, Supramol. Sci. 5 (1998) 163.
[113] O.S. Jung, Y.T. Kim, Y.A. Lee, Y.J. Kim, H.K. Chae, Inorg. Chem. 38 (1999) 5457.
[114] U. Diefenbach, P. Adamaszek, M. Bloy, M. Kretschman, S. Scholz, Z. Anorg, Allog. Chem. 624 (1998) 1679.
[115] E.W. Ainscough, A.M. Brodie, C.V. Depree, B. Moubaraki, K.S. Murray, C.A. Otter, Dalton Trans. 20 (2005) 3337.
[116] E.W. Ainscough, A.M. Brodie, A. Derwahl, Polyhedron 22 (2003) 189.
[117] E.W. Ainscough, A.M. Brodie, C.V. Depree, J. Chem. Soc., Dalton Trans. (1999) 4123.
[118] V. Chandrasekhar, B. Murugesa Pandian, R. Azhakar, Inorg. Chem. 45 (2006) 3510.
[119] E.W. Ainscough, A.M. Brodie, C.V. Depree, C.A. Otter, Polyhedron 25 (2006) 2341.
[120] E.W. Ainscough, A.M. Brodie, C.V. Depree, G.B. Jameson, C.A. Otter, Inorg. Chem. 44 (2005) 7325.
[121] U. Diefenbach, M. Kretschmann, B. Stromburg, Chem. Ber. 129 (1996) 1573.
[122] U. Diefenbach, H.R. Allcock, Inorg. Chem. 33 (1994) 4562.
[123] U. Diefenbach, M. Kretschmann, B. Stromburg, Phosphorus Sulfur Silicon 124–125 (1997) 143.
[124] H.P. Calhoun, N.L. Paddock, J. Trotter, J. Chem. Soc. A (1973) 2708.
[125] A. Chandraskaran, S.S. Krishnamurthy, M. Nethaji, Inorg. Chem. 33 (1994) 3085.
[126] J.F. Bickley, R. Bonar-Law, G.T. Lawson, P.I. Richards, F. Rivals, A. Steiner, S. Zacchini, Dalton Trans. (2003) 1235.
[127] A. Steiner, D.S. Wright, Angew. Chem. Int. Ed. Engl. 35 (1996) 636.
[128] F. Rivals, A. Steiner, Chem. Commun. (2001) 1426.
[129] G.T. Lawson, F. Rivals, M. Tascher, C. Jacob, J.F. Bickley, A. Steiner, Chem. Commun. (2000) 341.
[130] G.T. Lawson, C. Jacob, A. Steiner, Eur. J. Inorg. Chem. (1999) 1881.
[131] F. Rivals, A. Steiner, Eur. J. Inorg. Chem. (2003) 3309.
[132] R. Boomishankar, P.I. Richards, A. Steiner, Angew. Chem. Int. Ed. 45 (2006) 4632.
[133] P.I. Richards, A. Steiner, Inorg. Chem. 44 (2005) 275.
[134] P.I. Richards, A. Steiner, Inorg. Chem. 43 (2004) 2810.
[135] M.A. Benson, A. Steiner, Chem. Commun. (2005) 5026.
[136] G.A. Carriedo, F.J.G. Alonso, P.A. González, P.G.-Elipe, Polyhedron 18 (1999) 2853.
[137] G.A. Carriedo, F.J.G. Alonso, P.A. Gonzálaz, C.D. Valenzuela, N.Y. Sáez, Polyhedron 21 (2002) 2579.
[138] V. Chandrasekhar, A. Athimoolam, Org. Lett. 4 (2002) 2113.
[139] E.W. Ainscough, A.M. Brodie, A.B. Chaplin, J.M. O'Connor, C.A. Otter, Dalton Trans. (2006) 1264.
[140] P.I. Richards, M.A. Benson, A. Steiner, Chem. Commun. (2003) 1392.