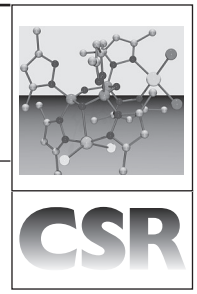
Phosphazenes as scaffolds for the construction of multi-site coordination ligands



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Chlorocyclophosphazenes containing a reactive periphery and a robust framework offer an ideal platform for the construction of a large variety of multi-site coordination ligands. Various types of neutral or (multi)anionic multi-site coordinating ligands can be assembled containing different numbers, type and stereochemical orientations of coordination sites reflecting the ease of modulation of these ligand types. Also it is possible to construct new types of macrocyclic ligands using cyclophosphazenes as scaffolds. The interaction of these ligands with transition and main group metals leads to a number of different complex types showing the rich diversity that is present in this family of compounds. A study of these ligands in principle also allows the assembly of the corresponding polymeric ligands.

1 Introduction

Cyclophosphazenes are an important family of inorganic ring systems, which traditionally have attracted attention for two main reasons. The substitution of P–X bonds in $[NPX_2]_n$ (X = Cl or F; n = 3 or 4) by many nucleophilic reagents has been studied in detail as this forms the principal route to synthesise a variety of organocyclophosphazenes containing exocyclic P–N, P–O, P–S or P–C bonds.[1,2] The sequential substitution of the P–X bonds from $[NPX_2]_n$ by nucleophiles has also been of great interest in view of the stereo- and regioselectivities that are involved in these reactions.[3] A second reason of interest in these compounds stems from the close relationship that exists between these ring systems with the high molecular weight polyphosphazenes, the largest family of inorganic polymers known. In fact the reactions carried out on the halogenocyclophosphazenes to a large extent serve as models for similar reactions on the polymeric analogues.[4]

A third facet of the chemistry of cyclophosphazenes which was known earlier but which has only received attention in recent years is the ability of these ring compounds to engage in coordination to transition metals.[5] Cyclophosphazenes can interact with transition and main group metals in several different ways.

1) The skeletal nitrogen atoms in these rings can act as Lewis bases towards suitable Lewis acids. The basicity of the ring nitrogens can be enhanced by the presence of electron releasing substituents on phosphorus. However, it has been observed that the mere presence of electron releasing substituents does not ensure that the cyclophosphazenes function effectively as ligands. Increasing the ring size enhances the skeletal flexibility of the inorganic rings and allows greater and more effective interaction with transition metal ions. Many protonated cyclophosphazenes such as $[HN_3P_3(NMe_2)_6]_2^+ [X]^{2-}$,(X = $CoCl_4$; Mo_6O_{19}), $[N_4P_4Me_8H_2][X]^{2-}$ (X = $PtCl_4$; $CoCl_4$) as well as compounds containing a M–N covalent bond such as $N_4P_4(NHMe)_8.PtCl_2$, $[N_8P_8(CH_3)_{16}CoNO_3]^+NO_3^-$, and compounds containing an exocyclic and a ring nitrogen coordination such as $N_4P_4(NMe_2)_8.W(CO)_4$ have been isolated using this approach.[5]

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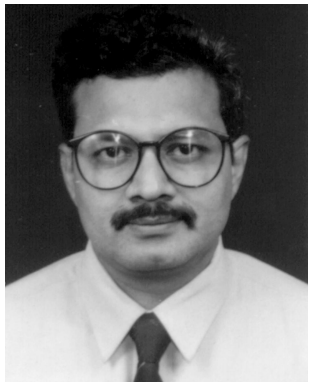

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2) The ring phosphorus atom of the cyclophosphazene can be involved in a direct metal linkage either through a covalent or a coordinate bond. The former is achieved by the substitution of the halogen by an organometallic nucleophilic reagent.[5,6] The coordinate mode of interaction of the ring phosphorus of cyclophosphazenes with metals occurs in certain instances. Thus, hydridocyclophosphazenes containing a P–H bond tautomerise in favourable situations and the resulting P(III) centre can be involved in interacting with soft metal centres.[5,6]

Fig. 1 summarises some of the examples that represent the above modes of interactions. These aspects have been the subjects of two critical and comprehensive reviews.[5,6]The ability of cyclophosphazenes to function as ligands is dramatically enhanced by the incorporation of suitable coordinating groups on phosphorus. This allows the assembly of potentially multi-site coordinating ligands. In this approach the cyclophosphazene rings can be conveniently utilised as building blocks for the construction of a large variety of ligands containing multiple centres for coordination. The main advantage of this approach is that a library of ligand systems with varying coordination capabilities in terms of number, nature and stereochemical disposition of the coordinating groups can be quite readily generated. Additionally this approach can be easily translated to the corresponding polyphosphazenes or polyolefin-supported cyclophosphazenes. This article summarises some of the new developments in this area.

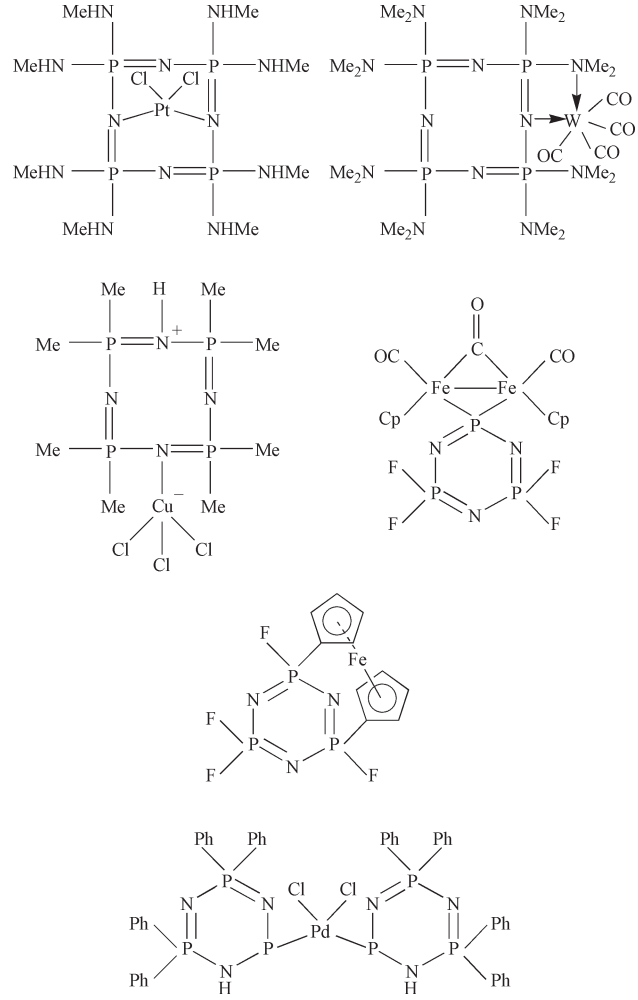
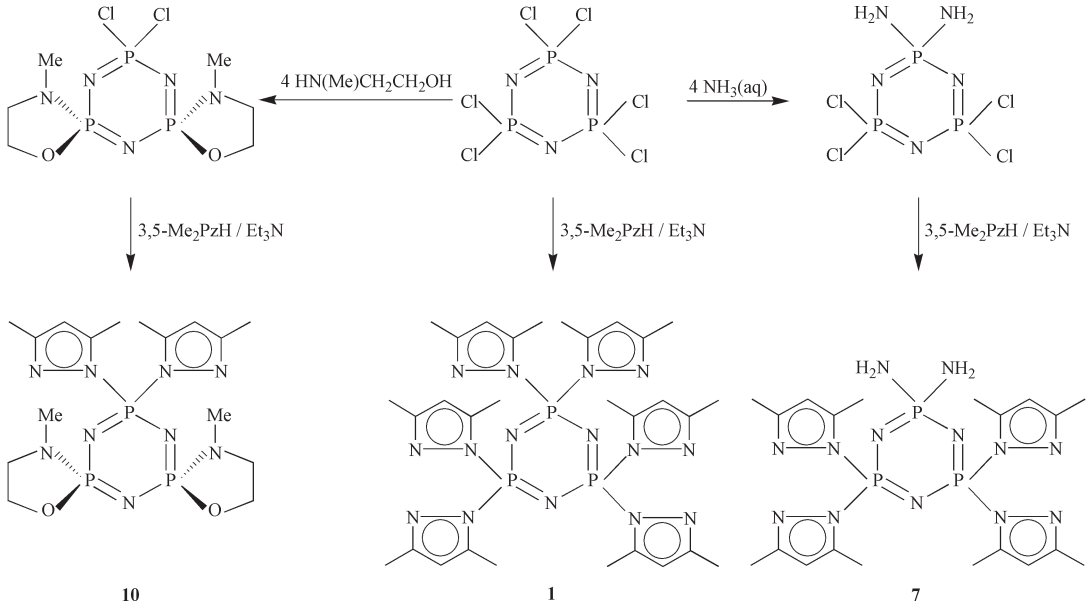


Fig. 1 Various coordination modes of cyclophosphazenes.

2 Pyrazolylcyclophosphazenes

2.1 Synthetic Aspects

The versatile coordination behaviour of pyrazoles as ligands in general and poly(pyrazolyl) borates in particular has prompted us to assemble and investigate the ligating behaviour of multi pyrazolyl cyclophosphazenes. Paddock and co-workers had previously reported the synthesis of some pyrazolylcyclophosphazenes.[7] Utilising an improved synthetic procedure we and others have synthesised several types of pyrazolylcyclotriphosphazenes with six,[8] four[9,10] and two pyrazolyl groups.[11,12] Although in most cases 3,5-dimethylpyrazole has been used, some examples with unsubstituted pyrazole are also known. The synthesis of the pyrazolylcyclophosphazenes is readily accomplished by the reaction of the corresponding chlorocyclophosphazene with stoichiometric amount of pyrazole using a tertiary amine for scavenging the hydrogen chloride formed in the reaction. Both geminal and non-geminal pyrazolylcyclophosphazenes are accessible by an appropriate choice of the corresponding chloro precursors. In most cases the yields are nearly quantitative. A typical synthetic strategy for the preparation of these compounds is illustrated in Scheme 1. The synthesis of simple pyrazolyl derivatives is readily extended to the polymeric analogues as shown in Scheme 2.[13] In this approach a functional cyclophosphazene $N_3P_3Cl_5(O\text{-}C_6H_4\text{-}$



10 **1** **7**

Scheme 1

p-C_6H_4-*p*-CH=CH_2) is synthesised containing one polymerisable olefin moiety (well separated from the σ-electron withdrawing cyclophosphazene group) and five reactive P–Cl bonds. The chlorine atoms on phosphorus are readily replaced by pyrazolyl substituents adopting the same procedure as was developed for the preparation of N_3P_3(3,5-Me_2Pz)$_6$. The resulting monomer N_3P_3(3,5-Me_2Pz)$_5$(O-C_6H_4-*p*-C_6H_4-*p*-CH=CH_2) can be homopolymerised or copolymerised (in the presence of divinylbenzene). The latter procedure affords a cross-linked polymeric resin containing multiple pyrazolyl moieties available for coordination. The ^{31}P NMR chemical shifts of the pyrazolyl cyclotriphosphazenes show that the phosphorus containing the pyrazolyl substituents is quite shielded and resonates between −5.4 and + 6.0 ppm (Table 1).

2.2 Coordination behaviour of pyrazolylcyclotriphosphazenes

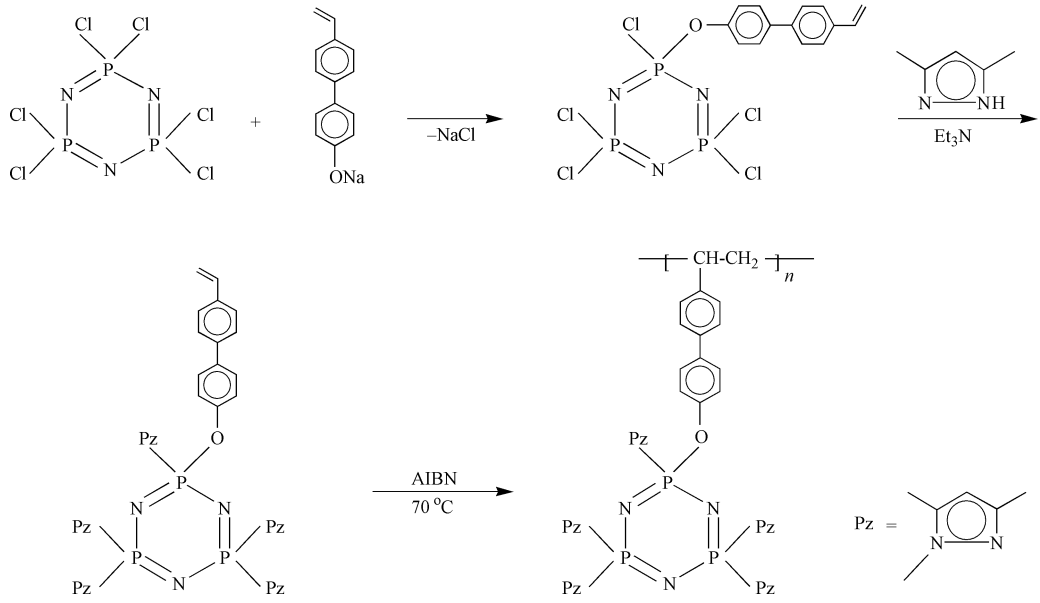
The following is the general summary of the coordination behaviour observed with these multi-site ligands.

1) Pyrazolylcyclotriphosphazenes are very effective coordinating ligands and readily bind a variety of metal ions ranging from first row transition metal ions to lanthanides. These ligands have been very effective to assemble monometallic and bimetallic derivatives. Sequential metallation to afford heterobimetallic derivatives is also possible (Scheme 3). Most of the studies have been carried out using 3,5-dimethylpyrazole as the substituent on phosphorus. The presence of the methyl groups on the pyrazole moiety apart from imparting favourable solubility properties on the metal complexes also allows isolation of discrete molecular entities.

2) The nature of the ligand can be very readily fine-tuned in terms of the number of pyrazolyl substituents and their stereochemical disposition. This is readily accomplished by assembling cyclophosphazenes containing the required number of reactive groups (in most instances chlorine substituents) in precise stereo and regiochemical disposition (notice the preparation of ligands **7** and **10**, for example, in Scheme 1).

3) Pyrazolylcyclotriphosphazenes belie the conventional wisdom about the non-suitability of the six-membered cyclotriphosphazenes as ligands. In fact they show a number of coordination modes. The pyrazolyl groups coordinate either exclusively or in conjunction with cyclotriphosphazene ring nitrogen atoms. The cyclophosphazene ring nitrogen atoms have not been found to coordinate exclusively in any metal complex so far, involving these ligands.

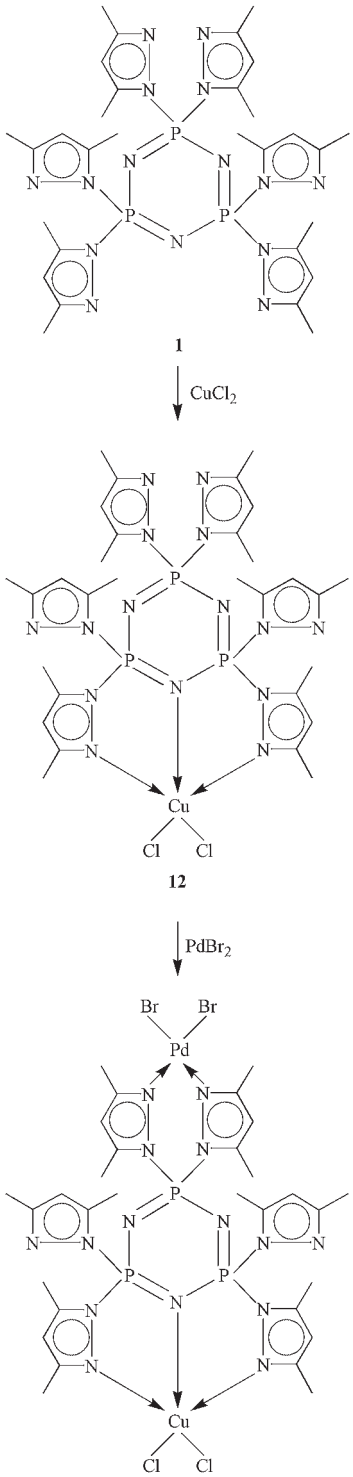
4) The observed modes of coordination with these ligands are (Fig. 2): A) *gem* N_2—two geminally substituted *pyrazolyl* ring nitrogens are involved in coordination to the metal; there is no interaction of the cyclotriphosphazene ring nitrogen atom. This leads to the formation of a six-membered metallacycle. B) *gem* N_3—two geminally substituted *pyrazolyl* nitrogens and one adjacent *ring* nitrogen. This type of coordination leads to the formation of two five-membered metallacycles. C) *gem* N_5—four *pyrazolyl* nitrogens and one *ring* nitrogen atom present in between them. This represents the situation where the largest number of coordinating sites (five) is provided by the cyclotriphosphazene ligand system. D) *non-gem* N_2—two non-geminally substituted *pyrazolyl* nitrogens. This mode leads to a relatively large seven-membered metallacycle. However, it may be noted that even in the only example where this coordination



Scheme 2

Table 1 ^{31}P NMR Data for pyrazolylcyclophosphazenes

Compound	δ P(Pz)$_2$	δ PR_2	^2J(*P*-N-*P*)	Ref
N_3P_3(3,5-Me_2Pz)$_6$ **1**	−3.4	—	—	8
N_3P_3(Pz)$_6$ **2**	1.2	—	—	15
N_4P_4(3,5-Me_2Pz)$_8$ **3**	5.4	—	—	7
N_3P_3(1-CH_2CH_2O- 3,5-Me_2Pz)$_6$ **4**	—	17.5	—	15
gem-$N_3P_3Ph_2$(3,5-Me_2Pz)$_4$ **5**	−5.4	20.3	25.2	9
gem-$N_3P_3Ph_2$(Pz)$_4$ **6**	−2.0	24.1	30.5	14
gem-$N_3P_3(NH_2)_2$(3,5-Me_2Pz)$_4$ **7**	1.5	18.2	66.3	10
gem-$N_3P_3(NH(CH_2)_3NH)$(3,5-Me_2Pz)$_4$ **8**	1.9	13.0	50.7	10
gem-$N_3P_3Ph_4$(3,5-Me_2Pz)$_2$ **9**	−5.2	18.2	20.0	7, 12
gem-cis-N_3P_3[N(Me)CH_2 CH_2O]$_2$(3,5-Me_2Pz)$_2$ **10**	6.0	31.2	68.0	11
non-gem-cis-$N_3P_3(OPh)_4$(3,5-Me_2Pz)$_2$ **11**	6.3	6.3	—	11



Scheme 3

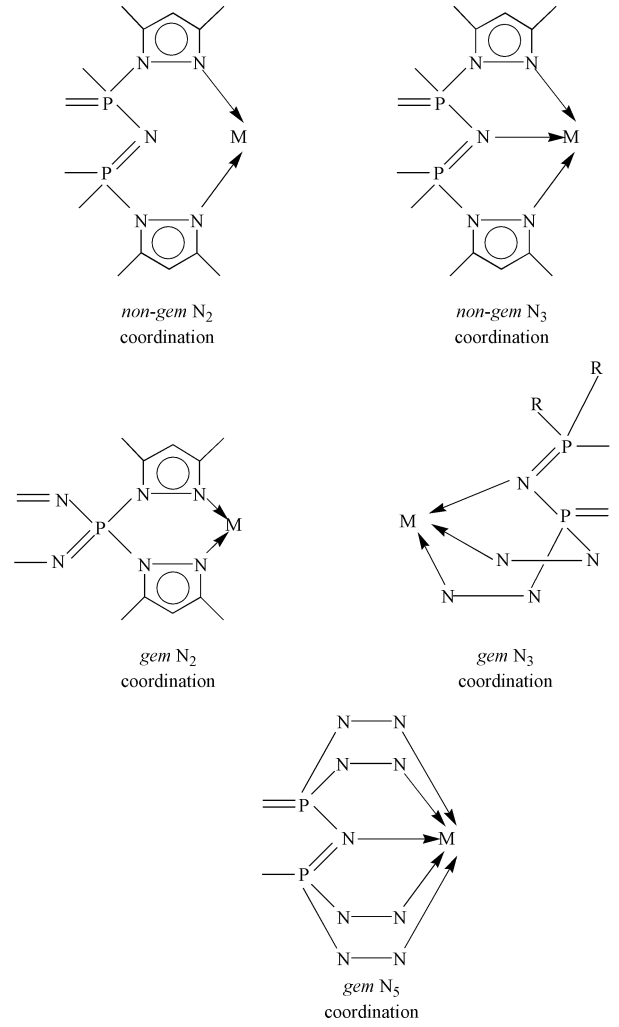


Fig. 2 Coordination modes observed with various pyrazolylcyclophosphazenes. (In all cases only part of the cyclophosphazene frame-work is shown. In the case of *gem* N_3 and *gem* N_5 modes only part of the pyrazolyl substituent is shown.)

mode is observed *viz*., in *non-gem-cis*-$N_3P_3(OPh)_4(3,5\text{-}Me_2Pz)_2.PdCl_2$ a weak interaction between the cyclophosphazene ring nitrogen and the metal ion is observed.[11] E) *non-gem* N_3—two non-geminally substituted *pyrazolyl* nitrogens and the *ring* nitrogen atom present *in between* them. This mode leads to the formation of two five-membered metallacycles and appears to be the most common type of coordination response exhibited by these classes of ligands.

The X-ray crystal structures of a number of metal derivatives derived from these ligands are now known[8–22] (Table 2). In situations where the cyclophosphazene nitrogen and the pyrazole nitrogen are simultaneously involved in coordination to the metal ion usually the $M–N_{CTP}$ bond distance is longer than the $M–N_{Pz}$(CTP = cyclotriphosphazene; pz = pyrazolyl). However, in some cases as in $N_3P_3(3,5\text{-}Me_2Pz)_6.SmCl_3$ the $Sm–N_{CTP}$ distance is smaller (2.499 Å) than the $Sm–N_{Pz}$ distance (2.832 Å). A general consequence of the coordination of the ligand to the metal ion is the distortion in the cyclophosphazene ring planarity; in most instances the ring nitrogen involved in coordination to the metal is displaced from the mean plane of the remaining cyclophosphazene atoms. However, this also points out the relative ease with which the cyclophosphazene ring can adapt itself in providing a flexible ligand environment to meet the needs of the metal ion. Another general result of the coordination of the cyclophosphazene to the metal ion is the lengthening of the P–N bonds flanking the site of the coordination. The bond length and angle variations in the cyclophosphazene ring upon interaction with metal is illustrated in Fig. 3 for the complex $N_3P_3(3,5\text{-}Me_2Pz)_6.CuCl_2$ **12**. The bond length differences observed are consistent with the bonding model of Craig and Paddock.[1–3] Accordingly when the lone pair on the ring nitrogen is involved in coordination to the metal ion it is not available for π-bonding within the ring with a consequent increase in the corresponding P–N bond length. The coordination environment around the metal in most instances also deviates from regular geometry to accommodate the ligation mode of the pyrazolylcyclophosphazene ligand. Typically for complexes showing a trigonal bipyramidal coordination environment (from a *non-gem* N_3 mode of coordination) substantial deviations from the regular geometry are observed around the metal ion (Table 2, Fig 3).

Electronic spectra of many of the metal complexes obtained from pyrazolylcyclophosphazenes are characterised by pyrazole–metal charge transfer bands in addition to d–d transitions as observed in the case of simple pyrazole–metal complexes.[8–10] This suggests that the overall electronic nature of the pyrazole moiety is unaffected by the cyclophosphazene ring.

EPR spectra of a number of Cu(II) complexes such as **12**, **14**, **17**, **19** , **20** and **21** as frozen glasses were either of the rhombic or axial symmetry.[8,9,14,17,19,21] In the latter instance the spectra are characterized by $g_{||} > g_{\perp}$ and with $A_{||}$ values in the range of 130–170 $\times$ 10^{-4} cm^{-1}.

There have not been many reactivity studies on the metal complexes derived from these cyclophosphazene ligands. In the limited examples that are known, reactions with other nitrogen bases leads to the substitution of the labile ligands and not the cyclophosphazene as illustrated for the complex **19** (Scheme 4). The electrochemical studies carried out on a few Cu(II) complexes **12**, **17**, **19** and **20** show quasi-reversible one electron metal centred oxidations and reductions.[8,9,17,19]

Although most of the metal complexes of pyrazolylcyclophosphazenes are quite stable the dinuclear copper complex **14** results from a hydrolysis reaction involving a P–N bond cleavage of a pyrazolyl substituent from the initially formed complex $N_3P_3(3,5\text{-}Me_2Pz)_6.2CuCl_2$.[17] It has been suggested that the hydrolysis occurs to relieve the steric crowding. It is noted that metal activated P–N bond cleavage occurs also in the

Table 2 X-ray structure parameters of some metal complexes derived from pyrazolyl cyclophosphazenes

Entry	Coordination Mode (geometry around metal)	Bond Distances Å				Ref
		M–N_{CTP}	M–N_{Pz}	P–N(M)–P	Other P–N	
$N_3P_3(3,5\text{-}Me_2Pz)_6.CuCl_2$ **12**	*non-gem* N_3(distorted TBP)	2.360	1.984 1.974	1.596 1.589	1.572	8
$N_3P_3(3,5\text{-}Me_2Pz)_6.SmCl_3$ **13**	*gem*-N_5(hendecahedral)	2.499	2.859 2.771 2.860 2.839	 1.592 1.593	1.564 1.574 1.577	16
$[[N_3P_3(3,5\text{-}Me_2Pz)_5.O].2CuCl_2][3,5\text{-}Me_2PzH_2]$ **14**	*non-gem* N_3–N_3(distorted TBP)	2.366 2.317	1.982 1.969 1.978 1.998	1.601 1.576 1.630 1.577	1.600 1.522	17
$N_3P_3(3,5\text{-}Me_2Pz)_6.2CuI$ **15**	*non-gem* N_3–N_3 (distorted tetrahedral)	2.461 2.472	2.065 1.983 2.048 2.000	1.577 1.589 1.587 1.583	1.564 1.573	18
$N_3P_3(3,5\text{-}Me_2Pz)_6.2ZnCl_2$ **16**	*non-gem* N_3–*gem* N_2(distorted TBP and distorted tetrahedral)	2.333	2.141 2.200 2.081 2.092	1.596 1.596 	1.574 1.580 1.556 1.587	18
$N_3P_3(3,5\text{-}Me_2Pz)_6.CuCl_2.PdBr_2$ **17**	*non-gem* N_3– *gem* N_2 [distorted TBP(Cu) and square-planar(Pd)]	2.362	2.003 1.997	1.585 1.586	1.552 1.554 1.558 1.591	19
$N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4.NiCl_2$ **18**	*non-gem* N_3 (distorted TBP)	2.079	2.080 2.089	1.590 1.591	1.537 1.537 1.611 1.600	20
$N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4.Cu(ClO_4)_2.2H_2O$ **19**	*non-gem* N_3 (elongated octahedral)	2.383	2.037 2.010	1.593 1.589	1.568 1.558 1.617 1.615	9
$N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4Cu(ClO_4)_2.2ImH$ **20**	*non-gem* N_3 (distorted square pyramidal)	2.325	2.076 2.014	1.590 1.605	1.569 1.558 1.600 1.607	9
$N_3P_3Ph_2(3,5\text{-}Me_2Pz)_4.CuCl_2$ **21**	*non-gem* N_3 (distorted TBP)	2.320	1.984 1.974	1.601 1.600	1.561 1.552 1.610 1.614	21
$N_3P_3Ph_2(Pz)_4.CoCl_2$ **22**	*non-gem* N_3 (distorted TBP)	2.419	2.062 2.038	1.586 1.592	1.548 1.551 1.621 1.615	22
$N_3P_3(NH_2)_2(3,5\text{-}Me_2Pz)_4.CoCl_2$ **23**	*non-gem* N_3 (distorted TBP)	2.115	2.113 2.112	1.608 1.625	1.558 1.560 1.611 1.619	10
$N_3P_3Ph_4(3,5\text{-}Me_2Pz)_2.W(CO)_3$ **24**	*gem* N_3(distorted trigonal anti prism)	2.310	2.250 2.274	1.579 1.628	1.569 1.545 1.586 1.593	12
$N_3P_3Ph_4(3,5\text{-}Me_2Pz)_2.Mo(CO)_3$ **25**	*gem* N_3(distorted trigonal anti prism)	2.394	2.299 2.312	1.594 1.636	1.569 1.586 1.593 1.545	12
cis-$N_3P_3(OPh)_4(3,5\text{-}Me_2Pz)_2.PdCl_2$ **26**	*non-gem* N_2(square planar)	2.86	2.060 2.051	1.581 1.577	1.585 1.586 1.585 1.580	11

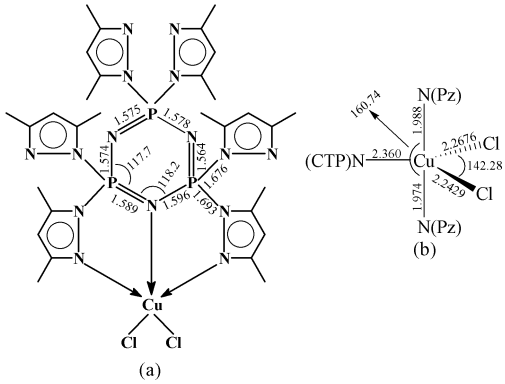


Fig. 3 (a) The metric parameters of the cyclophosphazene ring in the complex $N_3P_3(3,5\text{-}Me_2Pz)_6.CuCl_2$ **12**. (b) The coordination environment around Cu(II) in the complex **12**. Pz = pyrazolyl; CTP = cyclotriphosphazene.

metal complexes of other aminocyclophosphazenes (*vide infra*) and is also documented with acyclic phosphorus pyrazolides such as $P(O)(3,5\text{-}Me_2Pz)_3$ and $MeP(S)(3,5\text{-}Me_2Pz)_2$.[23]

2.3 Fluxional behaviour

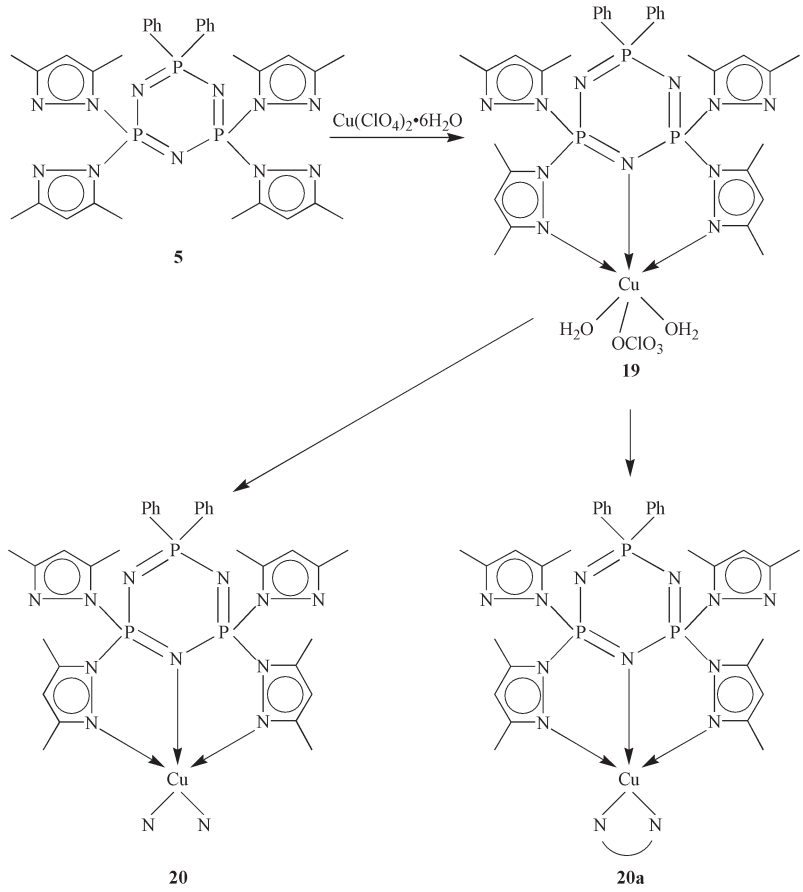
Many diamagnetic d^{10} compounds of pyrazolylcyclophosphazenes show complex dynamic behaviour in solution, which can be monitored by ^{31}P NMR.[18] Both conformational changes as well as change in coordination geometry have been detected. These are possible primarily due to the multiple sites that are available for binding with the metal ion. An example of such a fluxional behaviour for the dinuclear Cu(I) complex **15** is shown in Scheme 5. Fluxional behaviour has also been noted in the palladium complex **26** where a coordination and conformation change (from *non-gem* N_2 boat to *gem* N_2 chair) has been detected in solution.[11] In view of these findings it is possible that the metal complexes involving paramagnetic ions are also stereochemically non-rigid in solution.

3 Other types of nitrogen donor ligands constructed on cyclophosphazene scaffolds

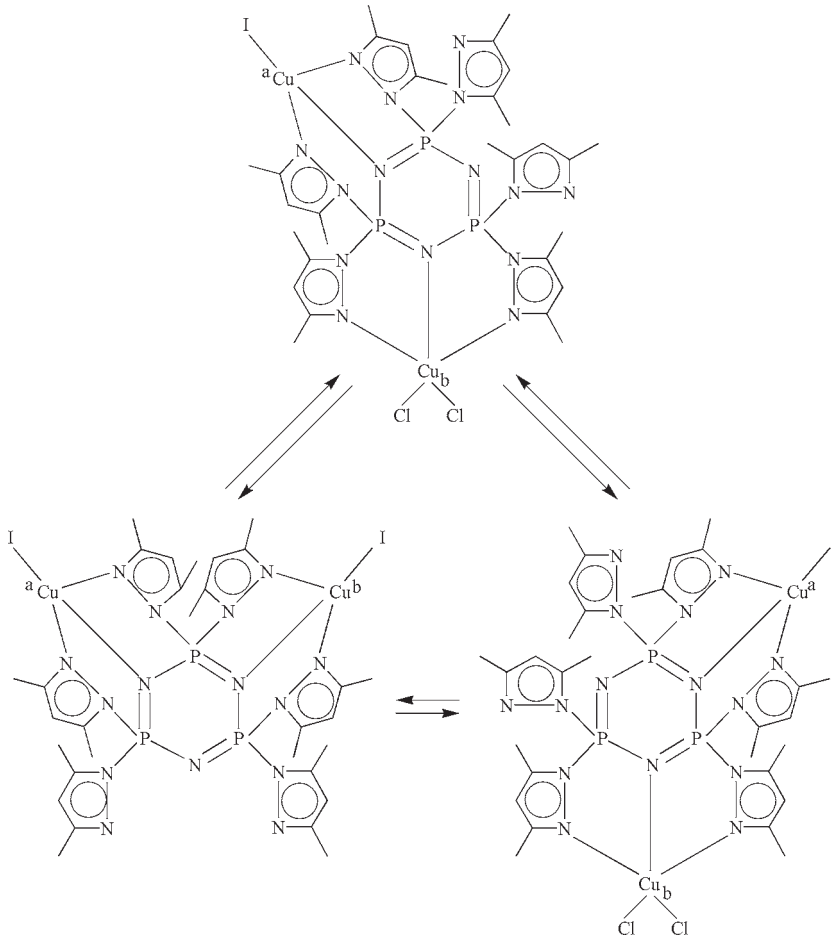
The efficacy of the cyclophosphazene ring as a building block for the construction of multi-site ligand systems is demonstrated by some of the examples[24–28] shown in Scheme 6. Other earlier examples that are known include phosphines, acetylinic moieties, carboranyl derivatives, schiff base linkages *etc*.[5,6]

The coordination chemistry of the ligands shown in Scheme 6 is still in its infancy. However, the few examples known, point to the exciting potential of these cyclophosphazene based ligands. Thus, the hexakis(2-pyridinoxy)cyclotriphosphazene **27** reacts with $CuCl_2$ and affords a trinuclear complex.[29] In this derivative a $CuCl_2$ unit bridges two cyclophosphazene units; each of the cyclophosphazene ligands is coordinated to Cu(II) in a *gem* N_5 mode involving one cyclophosphazene ring nitrogen and four pyridine nitrogens (Fig. 4).

The mono pyridylamino cyclophosphazene derivative **30** has been shown to have a varied coordination response, which is dependent upon the type of metal ion used.[26] The ligand



Scheme 4



Scheme 5

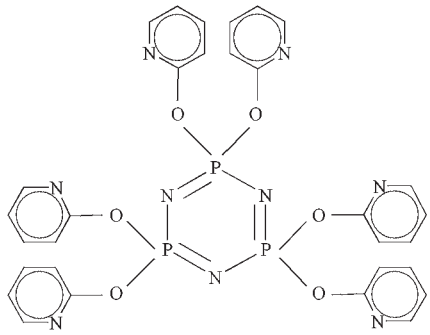
coordinates either exclusively through the pyridylamino nitrogens (compounds **32** and **34**) or through a conjunction of the cyclophosphazene ring nitrogen and the pyridylamino nitrogens (compound **33**) (Scheme 7).

Most of the nitrile-containing cyclophosphazene derivatives are involved in coordination only through the remote nitrile nitrogen centres. The ring nitrogen atoms of the cyclophosphazene skeleton do not participate in interaction with the transition metal involved.[27]

Mixed amino cyclophosphazenes, particularly those containing a spirocyclic diamino substituent and dimethylamino groups such as the compound **31** have been shown to interact with transition metals.[28] The structures of the palladium complexes have been determined. The coordination to palladium occurs through one of the nitrogen atoms of the diaminoalkane moiety and an adjacent ring nitrogen atom of the phosphazene skeleton as shown for **35**. However, **35** undergoes spontaneous hydrolysis to afford monometallic and bimetallic complexes. A plausible mechanism for the hydrolysis reaction is given in Scheme 8. The isolation and X-ray structural characterisation of **36** and **39** lends credence to the proposed mechanism (Scheme 8).

4 Multi-anionic phosphazenates

Primary amino substituted cyclophosphazenes such as $N_3P_3(NHR)_6$ contain reactive NH groups that can be deprotonated to afford multi-anionic phosphazene derivatives $[N_3P_3(NR)_6]^{6-}$ (R = cyclohexyl or phenyl).[30,31] These systems are formally isoelectronic with the cyclotrisilicate ion $[Si_3O_9]^{6-}$. Quite remarkably the hexaanionic derivatives are soluble in a number of non-polar aprotic organic solvents. The deprotonation is accompanied by a large down field shift in the phosphorus chemical shifts[31] (Table 3). Trianionic derivatives have also been synthesised from two different routes. The first of these involves a *direct deprotonation* of three NH moieties as is found for $N_3P_3(NHPh)_6$. In the second route the hexaanionic derivatives $[N_3P_3(NR)]^{6-}$ (R = cyclohexyl **41** or phenyl **44**) can be *protonated* at three exocyclic nitrogens (Scheme 9). Remarkably, the trianionic derivatives **42** and **45** contain the protonated amino substituents (NHR) in a stereospecific non-geminal *cis* orientation. Further, the X-ray structure of the lithiated derivatives reveal that the cyclophosphazene ring adopts a chair conformation and the three NHR groups are found exclusively as the axial substituents on the three phosphorus atoms. The X-ray structure of the hexaanion **41** shows that it is dimeric with a molecular formula $[\{N_3P_3(NLi\text{-}Cyc)_6\}(thf)_2]_2$. 2.5 THF,(*Cyc* = cyclohexyl). The two phosphazene rings in the dimer are non-planar and show a chair conformation (Fig. 5). Most important, however, is the observation that the P–N distances throughout the whole anion are in the same range (Table 3). This suggests that the negative charge is delocalised over the entire molecule involving six exocyclic nitrogens, three ring nitrogens and three ring phosphorus atoms. This may be contrasted with the primary amino cyclophosphazenes where the $P–N_{exo}$ distance involving the exocyclic amino substituent is substantially longer than the corresponding P–N bonds present in the cyclophosphazene ring. The variation of the $P–N_{exo}$ distances in the trianionic derivatives ($P–NH_{exo}$ *vs* $P–N_{exo}$) (Table 3) further confirms the delocalisation of the negative charge among the P–N bonds. Analogous to the hexaanion **41**, the trianion **42** is also dimeric



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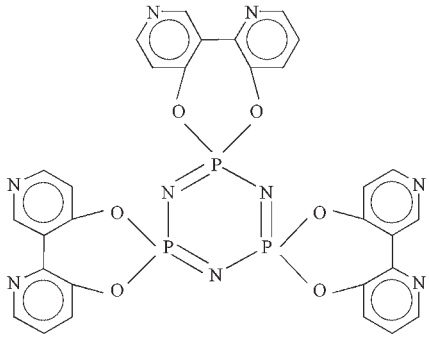

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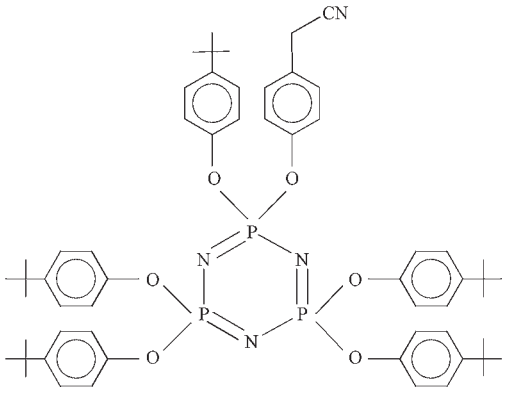

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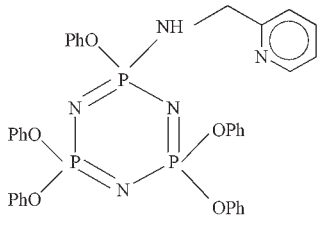

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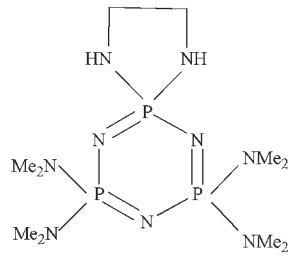

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Scheme 6

in the solid state. In contrast the trianion **42** has a monomeric structure(Fig. 5). The dimeric structures **40** and **41** contain an array of six lithium ions sandwiched between the two phosphazene motifs; each lithium in this sandwich core is coordinated by a bidentate N(ring)–P–N(eq) chelating segment from one anion and by a further N(eq) interaction from the other anion. In the case of **40** the other lithium cations are coordinated by the open ends of the remaining N_3P_3 faces. In **42,** which is a monomer, the deprotonation occurs exclusively from the equatorial nitrogens. Coordination to the lithium cations occurs in a similar way as found for **41** (Fig 5). The eight membered ring ß-*trans*-2,4,6,8-$N_4P_4Ph_4(NHCyc)_4$ has also been deprotonated to afford the tetraanionic derivative, $[N_4P_4Ph_4(NCyc)_4]^{4-}$. The interesting aspect of this tetraanionic derivative is that this system shows two separated tetradentate coordination sites.[32] The deprotonation of these cyclic primary amino compounds suggests that the corresponding polymeric derivatives $[NP(NHR)_n]$[33] would be good candidates for the preparation of highly charged macromolecules.

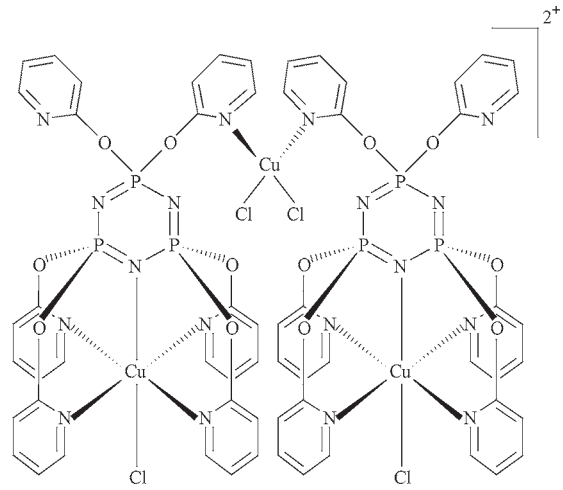


Fig. 4 Structure of the trinuclear complex.

The NH protons of primary amino cyclophosphazenes can also be deprotonated in reactions with metal alkyls to generate phosphazene complexes with a high metal loading [Eqns. (1) and (2)].

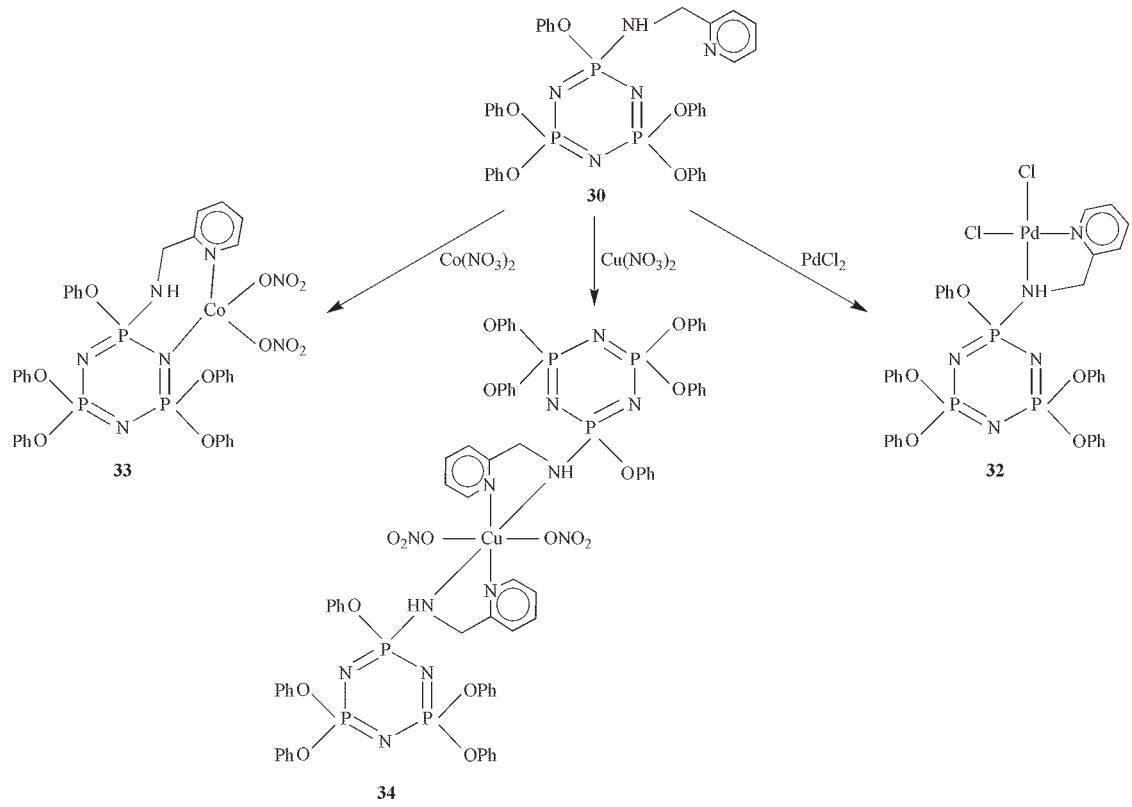
$$N_3P_3(NHCyc)_6 + 5\ Me_3Al \rightarrow \underset{\mathbf{40}}{} \underset{\mathbf{46}}{[\{N_3P_3(NCyc)_6(thfMeAl)(Me_2Al)_4] + 6\ CH_4} \quad (1)$$

$$N_3P_3(NHCyc)_6 + 6\ Et_2Zn \rightarrow \underset{\mathbf{40}}{} \underset{\mathbf{47}}{[\{N_3P_3(NCyc)_6\}(EtZn)_6] + 6\ C_2H_6} \quad (2)$$

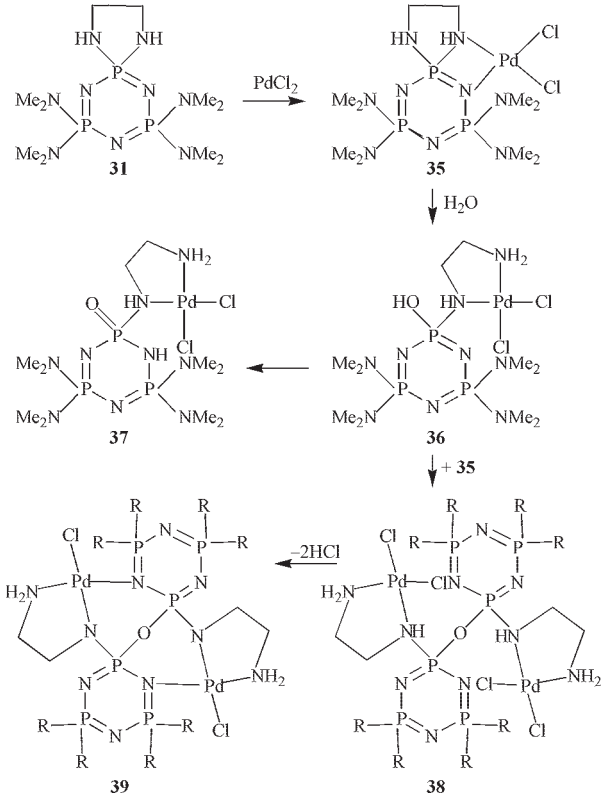
The X-ray structures of these metal-rich cyclophosphazene derivatives are extremely interesting (Fig. 6). The cyclophosphazene ring in both of these complexes is highly puckered and is involved in a complex coordination mode. Thus in the pentaaluminium complex **46** the coordination to the various aluminium atoms occur in the bidentate manner shown in **I**, **II** and **III** of Fig. 7 while in the hexazinc complex **47** the various zinc atoms are coordinated in the bidentate manner **II** as well as in the tridentate manner **IV** and **V**. It may be noted that the tridentate mode of coordination **VI** occurs in the lithium complex of the hexaanion, **41.** The P–N bond length variations in these compounds parallels that observed in the lithium derivatives of the multi-anionic phosphazenates discussed *vide supra*. In contrast to the complete deprotonation observed in the reaction of diethyl zinc with $N_3P_3(NHCyc)_6$ the corresponding reaction with $N_4P_4(NHCyc)_8$ affords a hexazinc derivative $[\{N_4P_4(NHCyc)_2(NCyc)_6\}(EtZn)_6]$ involving the deprotonation of six amino groups out of the total eight.[34]

5 Cyclophosphazene supported crown-ethers

The utility of the cyclophosphazene ring as a support for constructing macrocyclic ligands is only slowly being realised. An important step in this direction is the assembly of several new crown ethers supported on the phosphazene skeleton. It has been observed that the reaction of $N_3P_3Cl_6$ with long chain diols



Scheme 7



Scheme 8

such as tetraethylene glycol or pentaethylene glycol affords a mixture of products where the substitution of the glycol has occurred at the same phosphorus (spirocyclic) or at two different phosphorus atoms (ansa) within the cyclophosphazene ring (Scheme 10). Elaboration of these products into other types of macrocyclic compounds is possible.[35] Although the coordination chemistry of these new types of macrocyclic systems has not yet been delineated, clearly these have great potential in complexing alkali and transition metal ions. Further, they offer applications in areas such as phase-transfer catalysis.

6 Conclusions

Chlorocyclophosphazenes by virtue of their multifunctional nature and the reactive P–Cl bonds that they possess offer great potential in terms of being amenable to facile synthetic manipulations. A multitude of multi-site ligands can be constructed taking advantage of the above special features as has been shown *vide supra*. The cyclophosphazene framework in most instances serves as an excellent scaffold to hold the various coordinating groups together. Design of ligands, which contain a specified number and type of ligating motifs, is possible. Additionally the stereochemical orientation of the ligand sites can be designed by appropriate choice of the cyclophosphazene precursor. Another important advantage of this methodology is the ability to translate this chemistry readily to the macromolecular system with the possibility of generating a variety of polymeric ligands catering to the coordination needs of specific metal ions.

The coordination chemistry of the various multi-site ligands derived from cyclophosphazenes is extremely interesting and as expected shows considerable variety. The participation of the ring nitrogen atoms of the cyclophosphazene ring in interaction with metals can be controlled by the choice of the ligand as well as the metal. The deprotonation methodology to generate multi-anionic phosphazenates is quite exciting and as shown *vide supra* several metal-rich cyclophosphazenes can be assembled using this approach. One of the important features that emerges out of the studies on the transition metal complexes of the multi-site coordinating cyclophosphazene ligands is the considerable

Table 3 ^{31}P NMR and X-ray structural parameters of multi-anionic phosphazenates and related metal complexes

		X-Ray structure parameters		
			Bond distances (Average values in Å)	
Compound	^{31}P ppm	Structure	P–N (ring)	P–N (exocyclic)
$N_3P_3(NHCyc)_6$[a], **40**	14.9	Planar	1.598	1.658
$[N_3P_3(NCyc)_6]^{6-}$, **41**	25.3	Dimeric cage; phosphazene ring puckered, chair shape	1.660	1.630 ($P–N_{eq}$) 1.640 ($P–N_{ax}$)
Non-gem-cis-$[N_3P_3(NHCyc)_3(NCyc)_3]^{3-}$, **42**	16.2	Dimeric cage; phosphazene ring puckered, chair shape	1.635	1.614 ($P–N_{eq}$) 1.665 ($P–NH_{ax}$)
$N_3P_3(NHPh)_6$, **43**	3.2	—	—	—
$[N_3P_3(NPh)_6]^{6-}$, **44**	16.2	—	—	—
Non-gem-cis-$[N_3P_3(NHPh)_3(NPh)_3]^{3-}$, **45**	5.0	Monomeric; phosphazene ring puckered, chair shape	1.617	1.592 ($P–N_{eq}$) 1.708 ($P–NH_{ax}$)
$[N_3P_3(NCyc)_6(thf\ MeAl)(Me_2Al)_4]$, **46**	—	Monomeric; phosphazene ring puckered, boat shape	1.640	1.640
$[\{N_3P_3(NCyc)_6\}(EtZn)_6]$, **47**	—	Monomeric phosphazene ring puckered, twist shape	1.640	1.640

[a] *Cyc* = cyclohexyl, C_6H_{11}

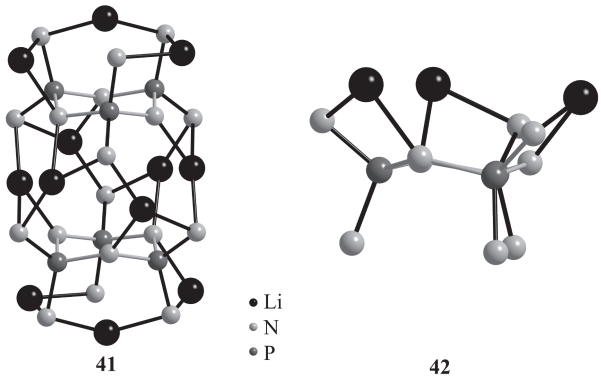


Fig. 5 Structure of the frame-work in $[\{N_3P_3(NLiCyc)_6\}(thf)_2]_2.2.5$ THF, **41** and *non-gem-cis* $[N_3P_3(NHCyc)_3(NLiCyc)_3]$, **42**. Only N, P and Li atoms are shown. The lighter colored bonds represent the P–N bonds within the cyclophosphazene ring.

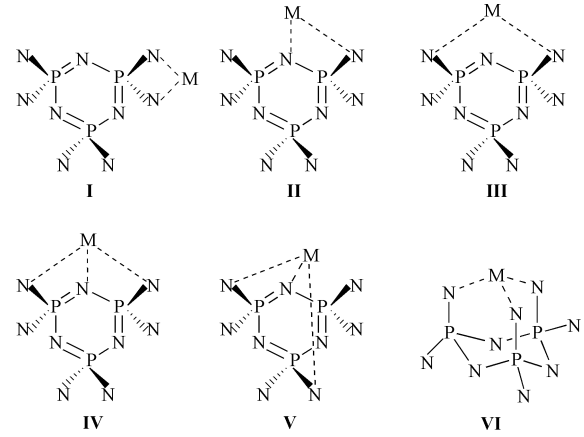


Fig. 7 Coordination modes of the deprotonated $N_3P_3(NHCyc)_6$ ligand.

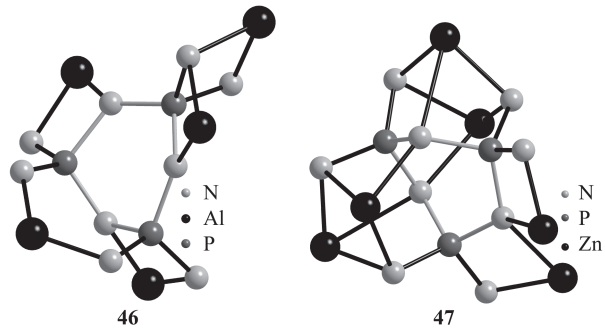
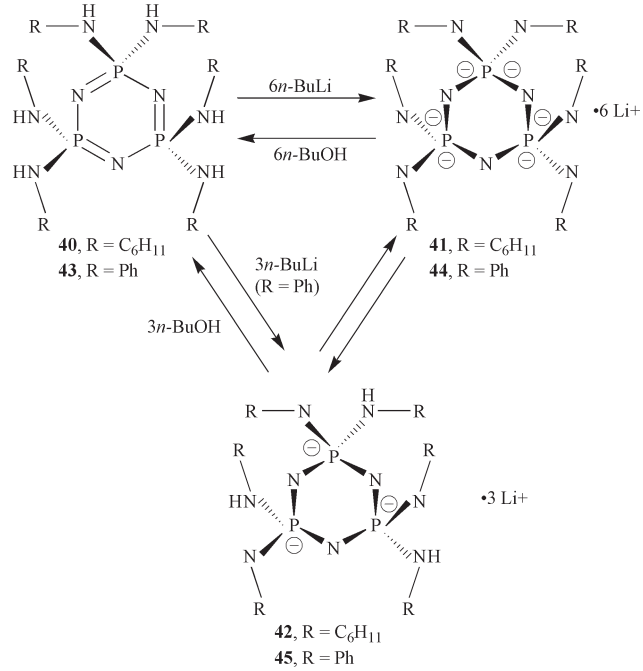
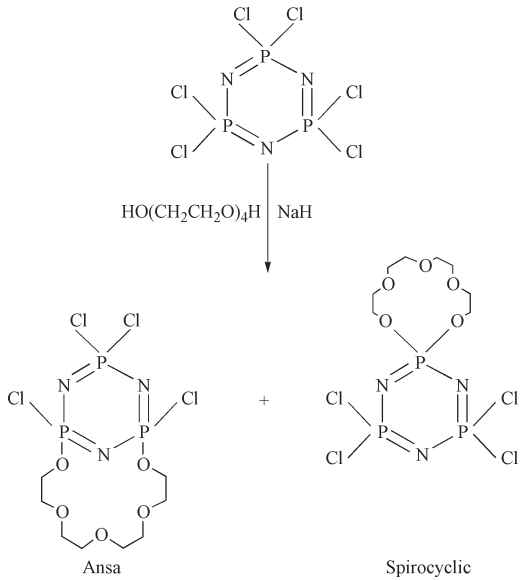


Fig. 6 Structure of the frame-work in $[N_3P_3(NCyc)_6(thf\ MeAl)(Me_2Al)_4]$, **46** and $[\{N_3P_3(NCyc)_6\}(EtZn_6\}(EtZn)_6]$, **47**. The bonds within the cyclophosphazene ring are represented by lighter colored bonds.



Scheme 9



Scheme 10

ease with which the six-membered cyclophosphazene rings adapt themselves to meet the coordination needs of the metal ion. Although higher membered cyclophosphazene rings have been known for their skeletal flexibility, the six-membered rings have been characterised by rigid, planar structures. The interaction with transition metals allows the six-membered rings also to adopt several puckered conformations, showing that ring size is not a prohibitive feature in the design of the ligands based on cyclophosphazene rings. The highly delocalised nature of the multi-anionic phosphazenates also points to the possibility of assembling new lipophilic polymeric materials bearing high negative charges. In view of all of the above features it appears that this aspect of the cyclophosphazene chemistry will receive considerable attention in the years to come.

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