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Pyridyloxy Cyclophosphazenes and Carbophosphazenes: Inorganic Ring-supported Coordination Platforms

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Abstract: This review deals with the utility of cyclophosphazenes and carbophosphazenes as supports for the construction of multi-site coordination platforms. The rich nucleophilic substitution chemistry of the chlorocyclophosphazenes and the analogous carbocyclophosphazenes can be utilized to replace chlorine atoms from these inorganic rings with coordinating side arms. This leads to the assembly of interesting compounds that have the capability to bind to multiple transition metal ions. Using this strategy several coordination ligands have been constructed. After a brief introduction to such ligands, this review deals with pyridyloxy cyclophosphazenes and carbophosphazenes. These ligands, in addition to possessing multiple coordinating arms, are also considered to be structurally flexible systems. This is because the pyridyl substituents are connected to the inorganic ring skeleton through flexible oxygen spacer atoms. The coordination chemistry of these pyridyloxy systems is discussed particularly in light of the work that has emanated from our laboratories in India.

Keywords: Cyclophosphazene · Carbophosphazene · Heterometallic compounds · Multi-site coordination ligands · Pyridyloxy carbophosphazene · Pyridyloxy cyclophosphazene · Pyridyloxy ligands

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Introduction

Cyclophosphazenes are inorganic heterocyclic rings that contain alternating phosphorus and nitrogen atoms in the ring skeleton.[1] While the phosphorus atoms bear exocyclic substituents, the nitrogen atoms do not possess any. The phosphorus atom is pentavalent and tetracoordinate, while the nitrogen atom is trivalent and dicoordinate. The most well-studied example of the cyclophosphazene family is the hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**). Replacing two phosphorus atoms with carbon affords the ring system, $N_3PC_2Cl_4$ (**2**).[2] The relationship between **1** and **2** can be readily understood by examining the structure of cyanuric chloride, $C_3N_3Cl_3$, (**3**) which is another heterocyclic ring where the ring system contains alternate carbon and nitrogen atoms.[3] Thus, the carbophosphazene **2** is a hybrid between $N_3P_3Cl_6$ and $C_3N_3Cl_3$ (Fig. 1).[2] In this review we will discuss the utility of **1** and **2** to support multi-site coordination platforms.

Before discussing the utility of **1** and **2** to support coordination ligands, it may be relevant to briefly discuss the chemistry of these rings as represented by $N_3P_3Cl_6$.

The chemistry of chlorocyclophosphazenes has been dominated by nucleophilic substitution reactions involving the replacement of the chlorine substituents on phosphorus by appropriate nucleophiles such as alkyl/aryl amines,[1f,4,5] alcohols/phenols[1f,4,5] or even organometallic reagents,[1f,4–6] although the latter also cause skeletal degradation. These reactions have served as the principal means to prepare diverse members of the cyclophosphazene family. Additionally, detailed studies on the nucleophilic substitution reactions have helped to unravel the various mechanisms that operate in these reactions and the factors that govern them.[1f,4]

Another facet of the chemistry of $N_3P_3Cl_6$ involves its ring-opening polymer-

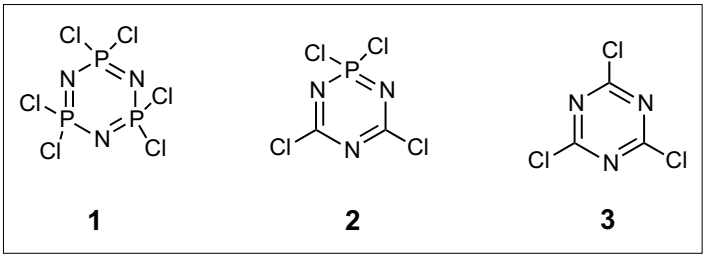

Fig. 1.

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ization to the open-chain polymer, $[NPCl_2]_n$ (**4**).[1a,7,8] Although the latter is hydrolytically extremely sensitive, macromolecular substitution on it by appropriate nucleophiles affords hydrolytically stable polymers (Scheme 1).[1a,7,8] These polymers represent the largest family of inorganic polymers. The polymer properties in this family can be readily altered by a modulation of the substituent on the polymer backbone. Thus, while polymers such as $[NP(OCH_2CF_3)_2]_n$ are extremely hydrophobic and possess very low glass transition temperatures (–66 °C), polymers such as $[NP(NHPh)_2]_n$ possess high glass transition temperatures (+91 °C).[1a,8]

Another way of preparing polymers from cyclophosphazenes involves incorporating them as pendants in organic linear polymers (Scheme 2).[9] This procedure involves the incorporation of a suitable substituent (containing a remote polymerizable group such as $–CH=CH_2$) on the cyclophosphazene framework and then polymerizing it. Various types of homo- and copolymers could be accessed by this methodology.[1a] Monomers such as **7** were also utilized to prepare cross-linked polymeric ligands (**9**, **10**) whose metal complexes could be utilized in heterogeneous catalysis (Fig. 2).[10]

With this background, it may be appropriate to first describe the utility of cyclophosphazenes to support coordination ligands before embarking on the topic of this review.

Cyclophosphazene-based Coordination Ligands

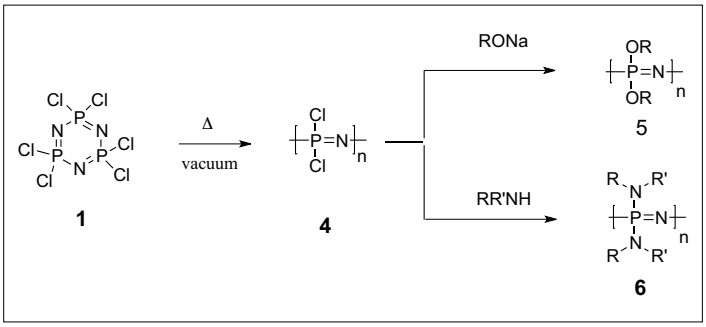
Although the presence of the lone electron pair on the skeletal nitrogen atoms of the cyclophosphazene ring has always intrigued coordination chemists to utilize them in dative bonding to transition metal ions, this aspect did not really take off in spite of sporadic examples of metal complexes. Part of the problem was that to some extent the lone pair on the ring nitrogen atom was involved in a skeletal pπ-dπ bonding. Increase of the basicity of the ring nitrogen atoms by incorporation of electron-releasing groups and therefore increasing the capability of the nitrogen atoms to engage in coordination to metal ions was a strategy with limited success, partly because the resulting ligands would often still have an inadequate number of effective coordination sites or are sterically very hindered.[5,11] The utility of cyclophosphazenes as ligands was dramatically enhanced by the realization that the reactive chlorine atoms on chlorocyclophosphazenes such as $N_3P_3Cl_6$ can be replaced by coordinating arms.[11] Such ligands had a sufficient number of viable coordination sites and therefore could be used very effectively in coordination chemistry. Among the successful ligands prepared by this approach are the pyrazolyl cyclophosphazenes.[12,13] A representative example of this family is hexakis (3,5-dimethylpyrazolyl)cyclotriphosphazene, $N_3P_3(3,5\text{-}Me_2Pz)_6$ (**11**) (Fig. 3). The coordination chemistry of **11** and related ligands has been widely explored.[13] Among the important modes of coordination of this ligand is the η^3-*non-geminal*-N_3 mode and the η^2-*geminal*-N_2 mode. Both of these modes are exhibited simultaneously in the heterobimetallic complex, $N_3P_3(3,5\text{-}Me_2Pz)_6{\cdot}CuCl_2{\cdot}PdBr_2$ (**12**) (Fig. 3).[13e]

Another representative family of cyclophosphazene ligands are the cyclophosphazene hydrazides.[14] These can be prepared by the regiospecific nucleophilic substitution reaction involving *N*-methylhydrazine and an appropriate chlorocyclophosphazene. For example, the reaction of *spiro*-$N_3P_3Cl_4(O_2C_{12}H_8)$ with *N*-methylhydrazine afforded $N_3P_3(O_2C_{12}H_8)_4[N(Me)NH_2]_4$ (**13**) which on reaction with metal salts afforded 2:1 complexes, such as **14**–**16** (Scheme 3).[14]

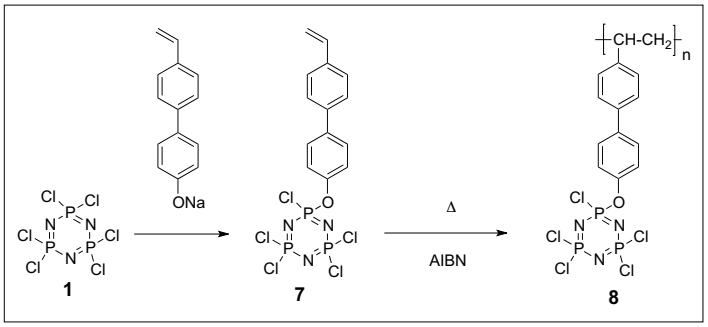
An analogous tetrahydrazide such as *gem*-$N_3P_3Ph_2[N(Me)NH_2]_4$ upon condensation with *o*-hydroxybenzaldehyde afforded the tetrakis hydrazone, *gem*-$N_3P_3Ph_2[N(Me)N=CH\text{-}C_6H_4\text{-}2\text{-}OH]_4$ (**17**), which upon reaction with $Cu(OAc)_2$ afforded the neutral tetranuclear derivative (**18**) (Scheme 4).[15]

The hexakis cyclophosphazene hydrazide, $N_3P_3[N(Me)NH_2]_6$ (**19**) has been utilized, particularly by the research group of J. P. Majoral and co-workers, to prepare novel dendrimeric derivatives such as **20** (Fig. 4).[16]

Similar to cyclophosphazenes, cyclo-



Scheme 1.



Scheme 2.

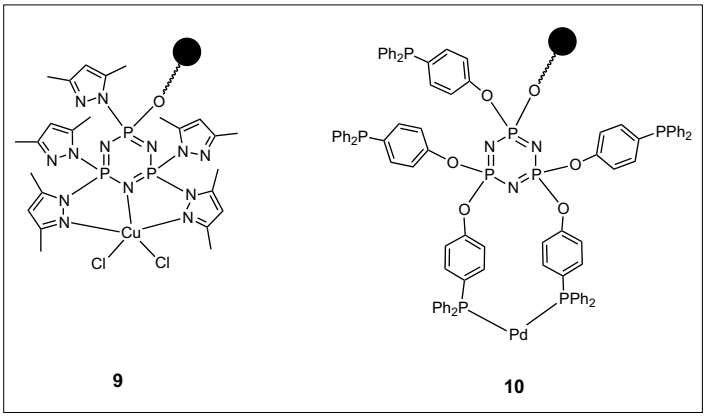


Fig. 2.

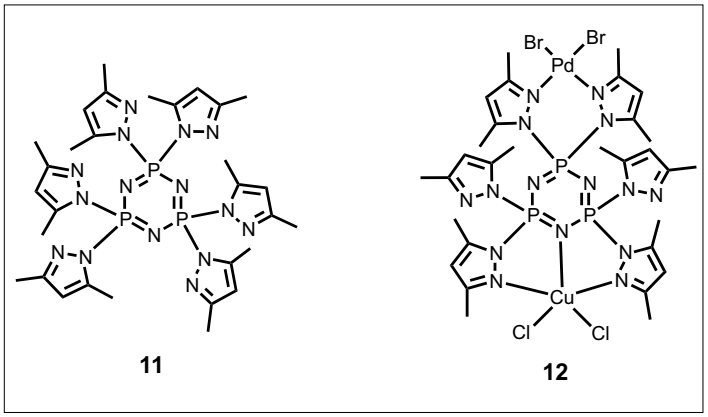


Fig. 3.

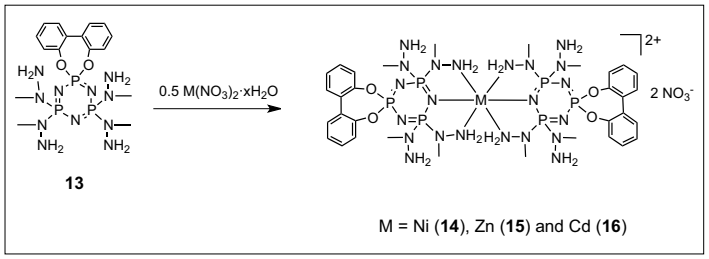
carbophosphazenes have also been used to prepare pyrazolyl derivatives such as [{NC(3,5-Me_2Pz)}$_2$NP(3,5-Me_2Pz)$_2$] (**21**).[17] This compound on reaction with $CuCl_2$ or $CuBr_2$ displays a regiospecific P–N bond hydrolysis. On the other hand, the C-pyrazole motif remains intact and binds to Cu(II). The overall result is the formation of tetranuclear Cu(II) ensembles **22** and **23** (Scheme 5).

More recently, such a P–N bond hydrolysis, as discussed above, has also been observed in another metalation reaction involving a pyrazolyl carbophosphazene and Pd(II) chloride affording the complex **24** (Fig. 5).[18] In this case, one of the P–N bonds, involving the pyrazolyl linkage is cleaved. In this complex the Pd(II) is bound to a ring nitrogen atom, a C-pyrazole motif, a chloride ligand and a free pyrazole. The latter is presumably generated *in situ* by the metal-assisted hydrolysis of the ligand.

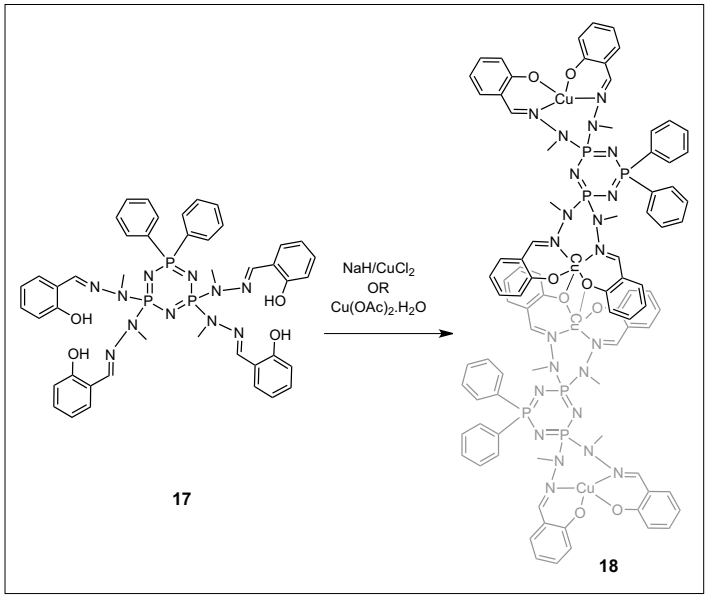
Carbophosphazene ligands **25**, containing guanidine substituents have been prepared.[18] Unlike pyrazolylcarbophosphazenes discussed above, the reaction of **26** with $PdCl_2$ does not lead to P–N bond scission. A robust, hydrolytically stable Pd(II) complex has been isolated in this instance (Scheme 6).

Pyridyloxy Cyclophosphazenes

Cyclophosphazene ligands such as pyrazolylcyclophosphazenes, while being undoubtedly versatile, are structurally rigid and lack the plasticity that is sometimes needed in a ligand to adjust to the coordination requirements of various types of metal ions. This rigidity is primarily due to the fact that the pyrazole group is directly attached to the phosphorus atom of the cyclophosphazene ring through the pyrazole nitrogen atom.[11] In contrast, if a coordinating group is attached to the cyclophosphazene ring by means of a spacer group or a hinge atom the overall coordination motif is far more flexible. Pyridyloxy cyclophosphazenes, where the pyridyl ring is separated from the cyclophosphazenes by means of the spacer oxygen atom, offer the possibility of structurally plastic and flex-



Scheme 3.



Scheme 4.

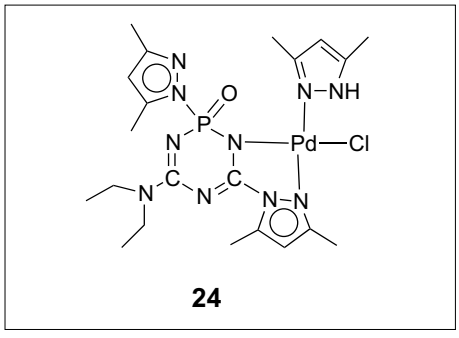


Fig. 5.

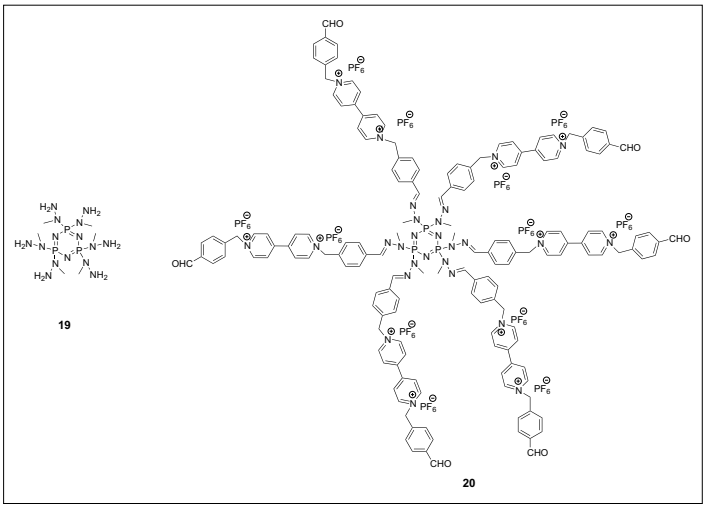
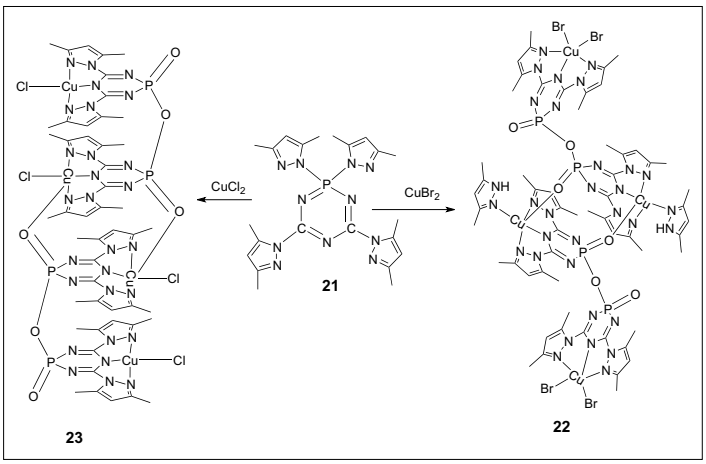
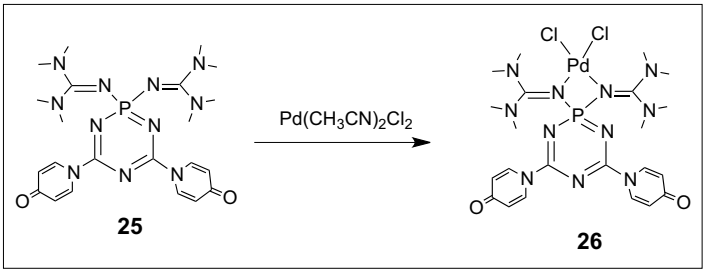


Fig. 4.



Scheme 5.



Scheme 6.

ible coordination ligands. Representative examples of this family of ligands are illustrated in Fig. 6.[19,20]

The first of these ligands, **27** and **32**, were prepared by Carriedo and coworkers by the reaction of the hexachlorocyclophosphazene, $N_3P_3Cl_6$ with the corresponding hydroxypyridines using acetone as solvent in the presence of potassium carbonate as base.[19a] Initial exploration of the coordination chemistry of these compounds was carried out with metal carbonyls. However, many of the products that were isolated could not be characterized by single crystal X-ray crystallography.

The interest in pyridyloxy cyclophosphazenes was stimulated by a communication by Brodie and coworkers who reported the isolation of a trinuclear Cu(II) complex (**33**).[20a] The unusual feature of this compound was the fact that two mononuclear metalated cyclophosphazenes were bridged by a $CuCl_2$ unit. Interestingly, each of the cyclophosphazene rings bind to one Cu(II) center in a η^5-*geminal*-N_5 manner; the nitrogens required for this coordination mode are provided by the four nitrogen atoms of the geminally substituted pyridyloxy groups and the cyclophosphazene ring nitrogen atom that is present in between. The flexible nature of the ligand is indicated by the fact that in spite of the coordination action of four of its arms, the cyclophosphazene ring does not show any distortion in its structure (Fig. 7). This is in contrast to the situation in pyrazolyl cyclophosphazenes where the inorganic ring deviates from planarity upon binding to transition metal ions.

We investigated the reactions of hexakis(2-pyridyloxy)cyclophosphazene and were able to isolate homo and heterobimetallic compounds: [L(CuCl)($CoCl_3$)] (**34**), [L(CuCl)($ZnCl_3$)] (**35**), [L(CoCl)($ZnCl_3$)] (**36**) and [L($ZnCl_2$)$_2$] (**37**) (Figs 8 and 9).[21a] In the heterobimetallic compounds **34**, **35**, and **36** one face of the pyridyloxycyclophosphazene ligand binds in a η^5-*geminal*-N_5 manner to either a CuCl or a CoCl unit. The resulting coordination environment around the metal ion is distorted octahedral. The other face of the cyclophosphazene ring binds to a MCl_3 unit in a η^1-N_1 fashion. Thus, in these heterobimetallic compounds, all except one pyridyloxy arm of the ligand are involved in binding to the metal ion. Remarkably, even upon formation of such heterobimetallic compounds, the cyclophosphazene ring does not suffer any structural distortion and remains planar.

The homobimetallic compound L($ZnCl_2$)$_2$ (**37**), shows two types of coordination responses. One face of the ligand binds to Zn(II) in a η^3-*non-geminal*-N_3 mode. Here, two different pyridyloxy arms along with a cyclophosphazene ring nitrogen atom bind to a $ZnCl_2$ unit; the latter shows a distorted trigonal bipyramidal coordination geometry. The second face of the ligand binds to Zn(II) in a η^2-*geminal*-N_2 mode (Fig. 9). Here, the two geminally substituted pyridyloxy arms are involved in coordination to Zn(II) which is present in a distorted tetrahedral coordination environment. While fluxional behavior was not experimentally probed in this compound latter reports have suggested the existence of such a possibility in related mononuclear Zn(II) compounds (Scheme 7).[22]

A sequential reaction of $N_3P_3(OC_5H_4N\text{-}2)_6$ with $CuCl_2$ followed by $Co(NO_3)_2{\cdot}6H_2O$ resulted in an unusual heterometallic trinuclear compound **41**.[21a] The latter contains two copper-bound cyclophosphazene structural units [(CuCl)$N_3P_3(OC_5H_4N\text{-}2)_5$(O)] that are bridged to each other by a central cobalt(II) ion (Fig. 10). Remarkably, in this reaction a P–O bond scission is observed, which occurs after the addition of $Co(NO_3)_2{\cdot}6H_2O$.

In contrast to the formation of di- and trinuclear complexes in the reactions of $N_3P_3(OC_5H_4N\text{-}2)_6$ with M(II)

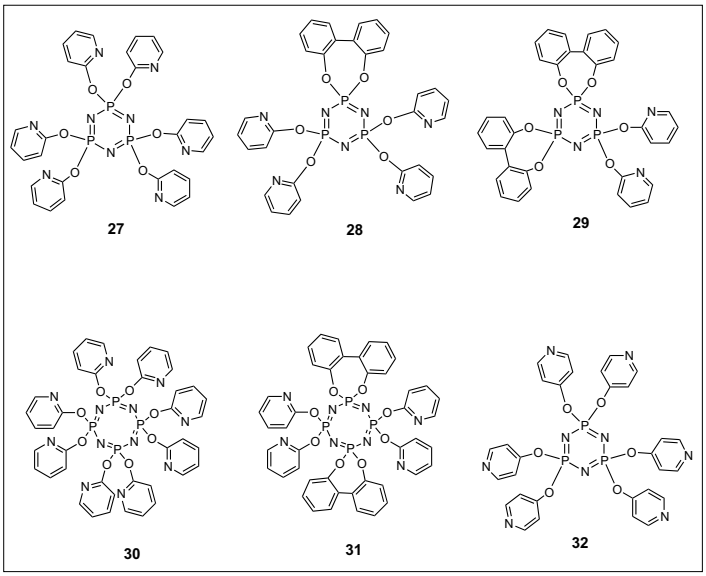


Fig. 6.

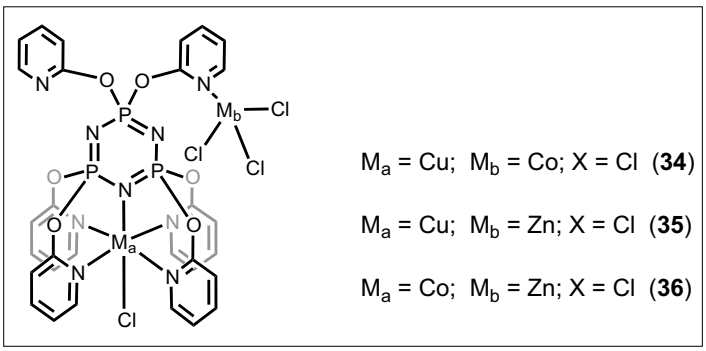


Fig. 8.

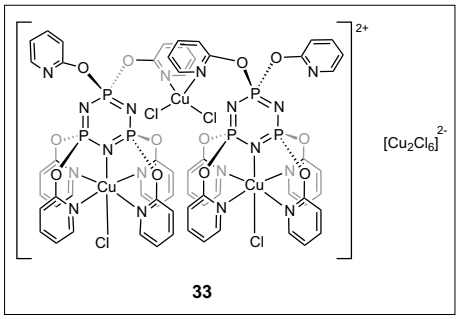


Fig. 7.

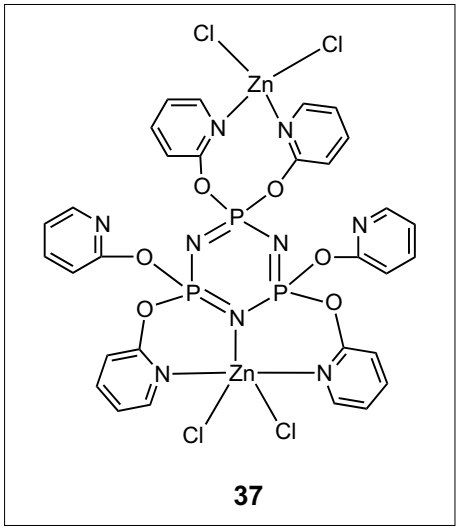
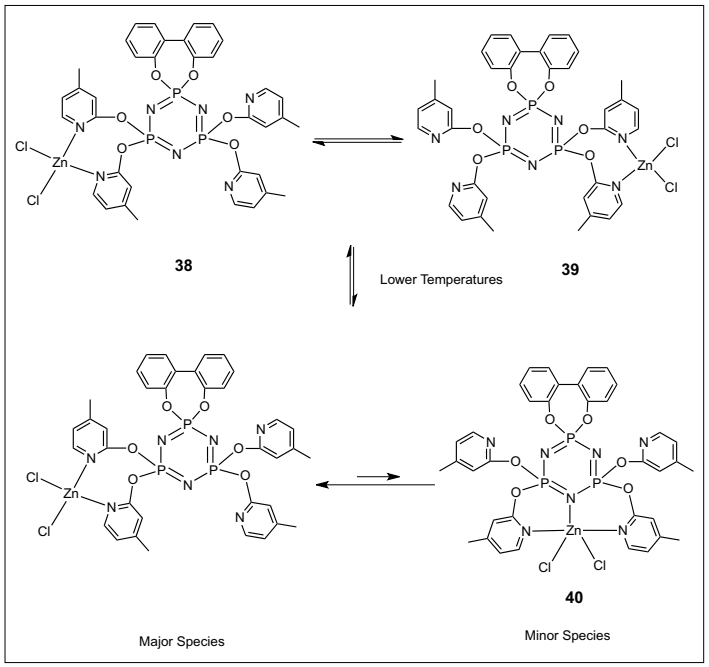
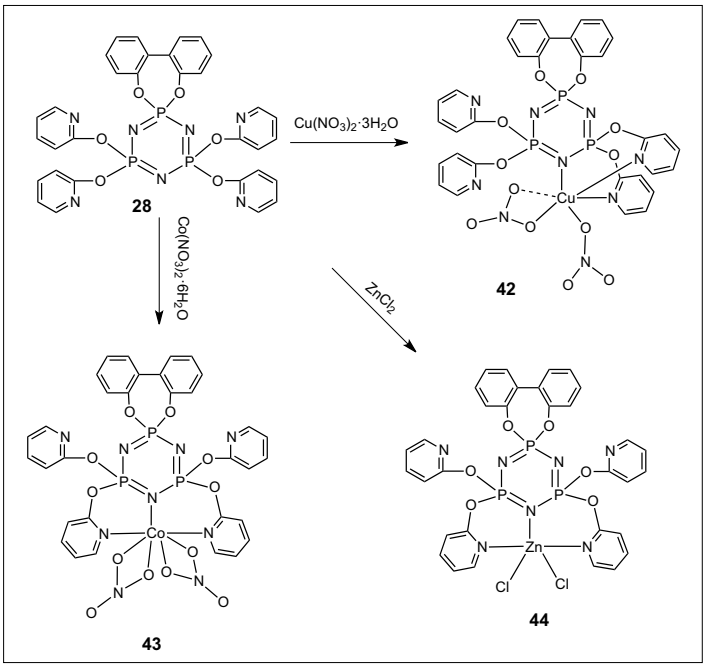


Fig. 9.



Scheme 7.



Scheme 8.

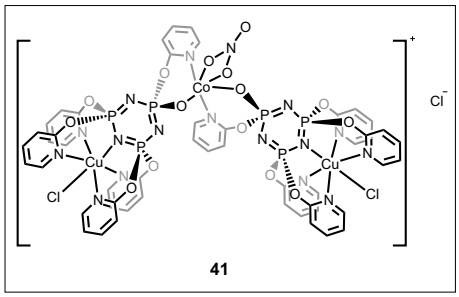
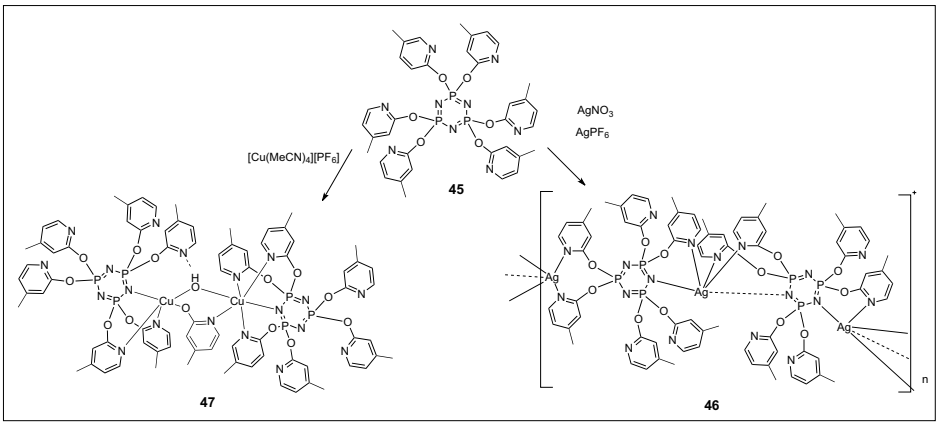


Fig. 10.



Scheme 9.

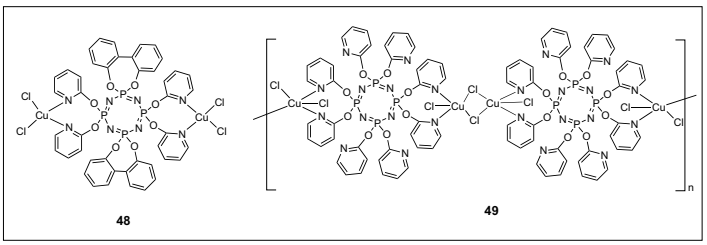


Fig. 11.

salts, the analogous reactions with *spiro*-$N_3P_3(O_2C_{12}H_8)(OC_5H_4N\text{-}2)_4$ (**28**) afforded mononuclear compounds, $[LCu(NO_3)_2]$ (**42**), $[L(Co(NO_3)_2]$ (**43**) and $[LZnCl_2]$ (**44**). Remarkably, the cobalt(II) ion is heptacoordinate in a pentagonal bipyramidal geometry (Scheme 8) .[21b]

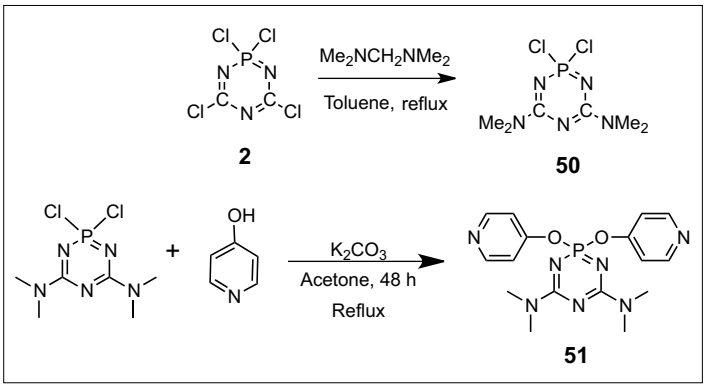
In contrast to the reactions of $N_3P_3(O\text{-}C_5H_4N\text{-}2)_6$ with M(II) salts the reaction of the ligand and its analogous congener $N_3P_3(O\text{-}4(Me)C_5H_3N\text{-}2)_6$ (**45**), containing the 4-methyl-2-pyridyloxy substituent with Ag(I) salt afforded the formation of a coordination polymer **46** (Scheme 9).[20c] In this case the bifacial coordination of the cyclophosphazene ligand in a *non-geminal-*N_2 mode on one side and a *geminal-*N_3 mode on the other leads to formation of a silver-containing coordination polymer chain. On the other hand, the reaction with a Cu(I) salt led to the formation of a dinuclear Cu(II) complex **47**, where two Cu(II) centers are bridged by a μ-OH (Scheme 9).

Among other examples of pyridyloxy cyclophosphazenes, ligand **31** should be mentioned. This ligand binds to two Cu(II) ions through its two opposite coordination faces to form **48**. Metal complexes of octakis(2-pyridyloxycyclophosphazenes) have been reported which include a coordination polymer bridged by a Cu_2Cl_2 unit (compound **49**) (Fig. 11).[20g]

Pyridyloxy Carbophosphazenes

As mentioned in the introduction, carbophosphazenes also afford the opportunity to be used as supports for multi-site coordinating platforms. We wanted to use only the phosphorus atom to bear the coordinating arms. Accordingly, the carbophosphazene **2** was C-protected by a de-alkylation reaction involving $(CH_3)_2NCH_2N(CH_3)_2$. This was followed by its reaction with 4-hydroxypyridine in the presence of K_2CO_3 to afford **51** (Scheme 10).[23a] The reaction of **51** with $CdCl_2$ afforded two compounds $L_2(CdCl_2)_3.H_2O$ (**52**) and $[L_2(CdCl_2)_2]\cdot4H_2O\cdot CHCl_3$ (**53**) respectively. The former was a 3D-coordination polymer containing two different types of $CdCl_2$ subunits (**54**, **55**, Fig. 12). In the latter, which is also a 3D coordination polymer, four-membered inter-connected Cd_2Cl_2 units are present.

The ligand **51** upon reaction with cadmium acetate afforded a coordination poly-



Scheme 10.

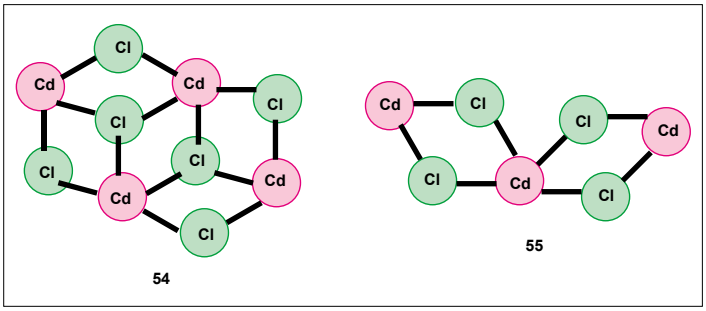


Fig. 12.

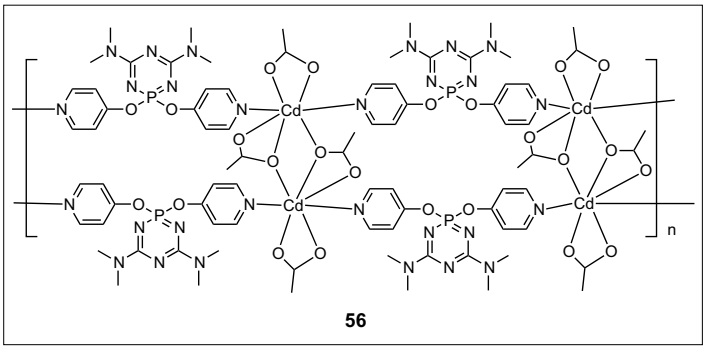
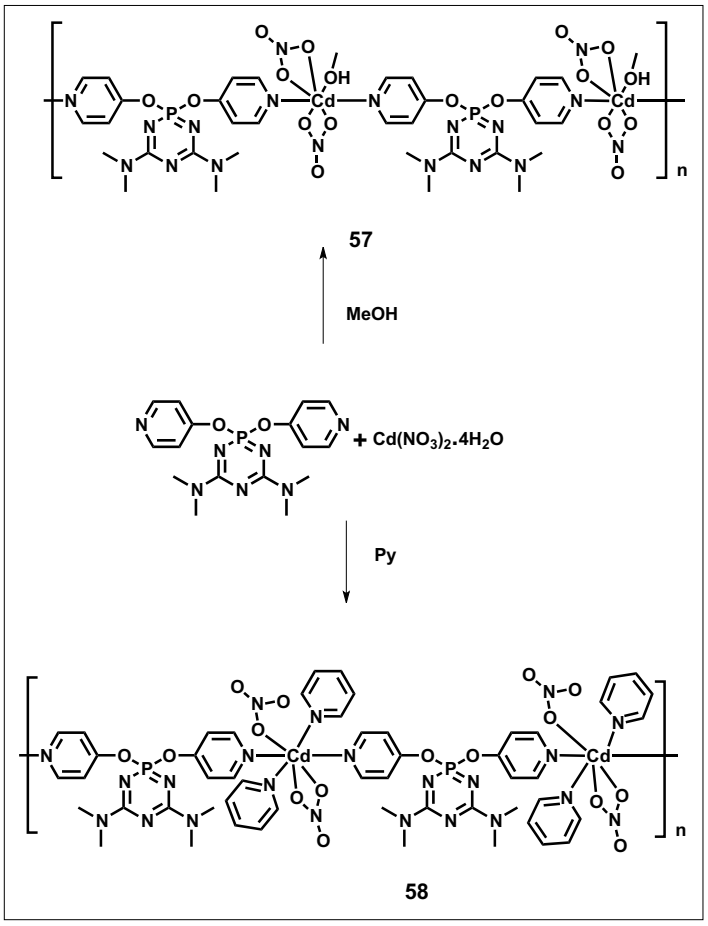


Fig. 13.



Scheme 11.

mer $\{[Cd(CH_3COO)_2(L)]\cdot CH_3OH\cdot 2H_2O]_n$ (**56**) (Fig. 13) while a similar reaction with cadmium nitrate afforded $[Cd(NO_3)_2(L)(MeOH)]_n$ (**57**). The latter reaction in the presence of pyridine gave the compound $[Cd(NO_3)_2(L)(Py)_2]_n$ (**58**).[23b] **56** is a railroad-like double strand coordination polymer (Fig. 13), where L functions as a bridging ligand to bridge successive cadmium(II) centers. The one-dimensional coordination polymers thus formed, are interlinked by the acetate ligands which results in the formation of the four-membered Cd_2O_2 rings. In contrast to the structure of **56**, the compounds **57** and **58** are single-strand one-dimensional coordination polymers (Scheme 11). In all of these compounds Cd(II) is seven coordinate in a pentagonal bipyramidal geometry.

The reaction of L with MCl_2 (M = Zn(II), Mn(II), Co(II)) results in the formation of $[(LZnCl_2)\cdot MeOH]_n$ (**59**), $[L_2MnCl_2]_n$ (**60**) and $[L_2CoCl_2]_n$ (**61**). While **59** is a 1D coordination polymer containing a tetrahedral Zn(II) center, **60** and **61** are coordination polymers containing interconnected macrocyclic rings. Remarkably, these coordination polymers contain large 24-membered macrocycles. The metal ions act as the connecting nodes for successive macrocycle repeat motifs (Fig. 14).

Summary

Chlorocyclophosphazenes and carbophosphazenes are excellent precursors for the construction of multi-site coordination platforms. Pyridyloxy cyclophosphazenes and carbophosphazenes constructed from these precursors have been shown to be extremely versatile multi-site coordinating ligands. Another virtue of these ligands is their flexible nature owing to the presence of the spacer oxygen atom that separates the coordinating pyridyloxy arm from the inorganic ring skeleton. The utility of these new coordination ligands for the assembly of novel multi-metallic architectures has been presented. In most of the compounds

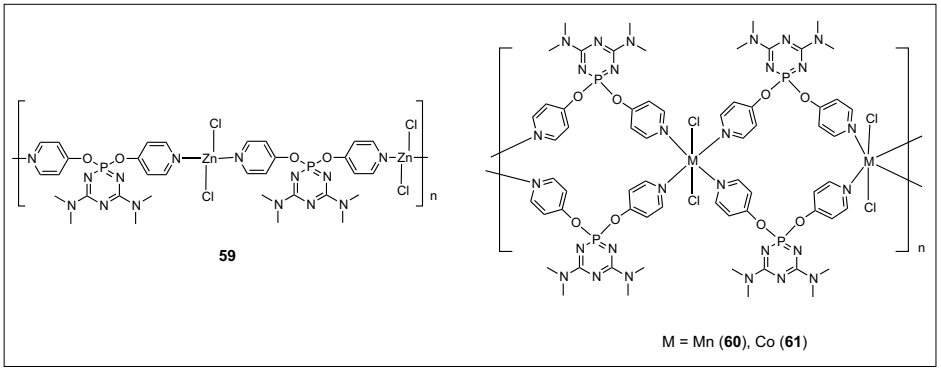


Fig. 14.

that have been prepared and structurally characterized, the cyclophosphazene or the carbophosphazene ring skeleton remains completely unaffected in terms of not suffering any structural distortion. The coordination response of these ligands can be readily modulated by the variation of the pyridyloxy nitrogen atom. Thus, replacing the 2-pyridyloxy substituent with a 4-pyridyloxy group leads to the formation of coordination polymers as exemplified in the coordination behavior of $[NC(NMe_2)]_2[NP(O\text{-}C_5H_4N\text{-}4]_2$. The possibility of utilizing this family of ligands for the construction of molecular materials is quite intriguing and this is an aspect that is bound to receive attention in the coming years.

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