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Review

Cyclodiphosphazanes with functionalities: Synthesis, reactivity and transition metal chemistry

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ABSTRACT

The saturated, four-membered rings of the type $[XP(\mu\text{-}NR)]_2$ containing alternating phosphorus(III) and nitrogen atoms are known as cyclodiphosphazanes or diazadiphosphetidines. The current interest in these well-known heterocycles is due to their catalytic and biological applications besides their excellent synthetic utility as scaffolds to design interesting macrocycles with or without involving main group or transition metals. Although the rigid and nearly-planar neutral P_2N_2 rings resemble $[Cu(\mu\text{-}X)]_2$ (X = Cl, Br or I) rhombic units ($[Cu(\mu\text{-}X)]_2$ are known for giving a variety of structures with suitable ligands), their utility in designing the high-nuclearity clusters, cages or coordination polymers is scarce. In this context, we fine tuned the coordinating ability of these ligands by incorporating pendant hemi-labile functionalities on phosphorus centers which resulted in the isolation of several interesting molecules. The details are described.

Contents

1. Introduction

The ever-growing interest in the chemistry of cyclodiphosphazanes or diazadiphosphetidines is due to the application of the planar saturated P_2N_2 framework as building blocks to design a variety of cages, clusters and macrocycles with main group [1–3] or transition metal spacers [4–6] as well as their interesting coordination behavior both as neutral and anionic ligands [7–10]. Many of these complexes find application in homogeneous catalysis [11], polymerization of olefins [12], and in biological studies [13]. Cyclodiphosphazanes have also been used to probe organic reaction mechanisms [12b]. Recently, we have reported on the synthesis, reactivity and transition metal chemistry of several cyclodiphosphazanes with a variety of donor functionalities [14–20]. Slight variations in the donor atoms and their electronic, and steric attributes resulted in a remarkable variation in their coordination behavior [10] and as a result several interesting metallomacrocycles, homo- and hetero-polynuclear complexes including 1D, 2D and 3D coordination polymers were isolated and structurally characterized. The details are summarized in this account.

2. Synthesis of cyclodiphosphazanes containing donor functionalities

The reactions of *cis*-$[^tBuNPCl]_2$ (**1**) with two equivalents of phenol derivatives or 2-substituted ethanols in the presence of

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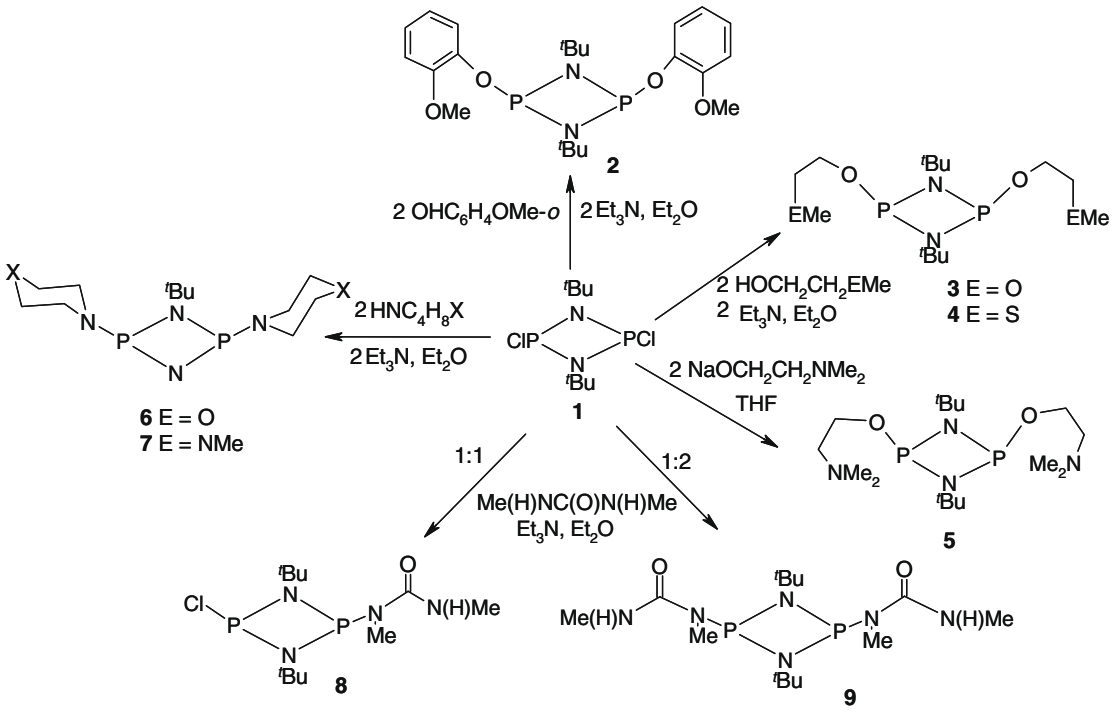
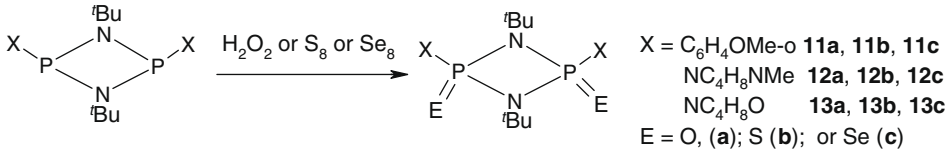


Scheme 1.



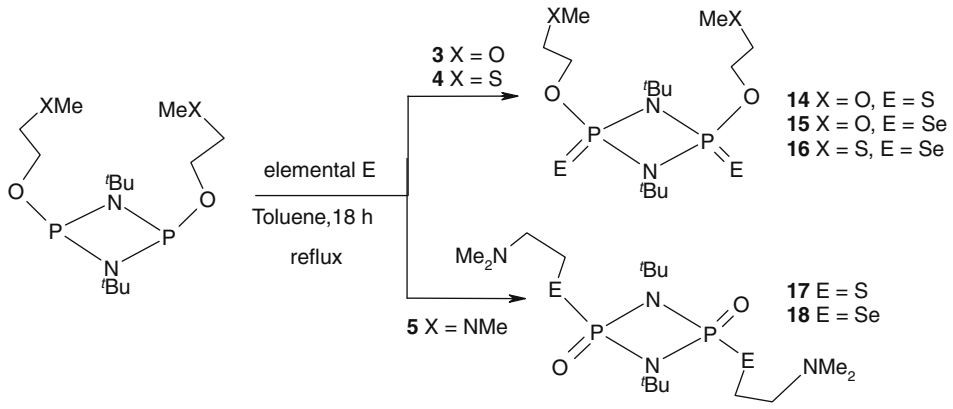
Scheme 2.

triethylamine or their sodium salts afforded the corresponding cyclodiphosphazanes **2**–**5** as shown in Scheme 1 [14,15]. Treatment of *cis*-[^{t}BuNPCl]$_2$ with N-methyl piperazine or morpholine gave the corresponding derivatives, *cis*-[^{t}BuNPNC$_4$H$_8$X]$_2$ (X = NMe, **6**; X = O, **7**) in good yield [13,7]. The reaction between *cis*-[^{t}BuNPCl]$_2$ and *N,N′*-dimethylurea in equimolar ratio in the presence of triethylamine at −78 °C afforded the mono-substituted derivative [ClP(μ-N^{t}Bu)$_2$P(NMeCON(H)Me)] (**8**) in 55% yield along with a small quantity of the disubstituted derivative [^{t}BuNP(NMeCON(H)Me)$_2$] (**9**) (10%). A similar reaction of *cis*-[^{t}BuNPCl]$_2$ with two equivalents of *N,N′*-dimethylurea in THF at 0 °C resulted in the exclusive formation of **9** in moderate yield [21]. The reaction of ethylene glycol with two equivalents of monochloro derivative, [ClP(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] in diethylether at 0 °C gave the acyclic dimer of the cyclodiphosphazane [–CH$_2$OP(μ-N^{t}Bu)PN(H)^{t}Bu]$_2$ (**10**) in quantitative yield (Eq. (1)) [19]. Interestingly, all these compounds exist in the *cis*-conformation as indicated by phosphorus-31 NMR chemical shifts [23,5].

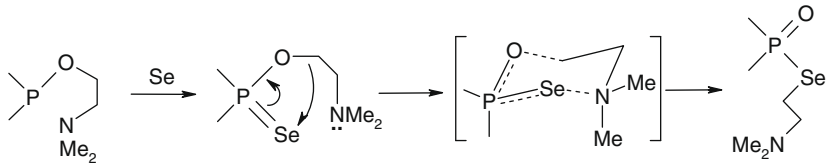
3. Chalcogen derivatives

Most of these compounds on treatment with aqueous H_2O_2 (30% w/v) at 0 °C give the corresponding oxide (**11**) derivatives [24]. Similar oxidation reactions with elemental sulfur or grey selenium in toluene under refluxing conditions produce the corresponding sulfides or selenides (**12**–**16**) in quantitative yields (Scheme 2) [25]. Interestingly, the reactions of sulfur or selenium with 2-dimethylaminoethoxy derivative **5** did not give the expected dichalcogenides, instead thio-, and selenophosphates, *trans*-[{(^{t}BuN-μ)P(O)SCH$_2$CH$_2$NMe$_2$}$_2$] (**17**) and *trans*-[{(^{t}BuN-μ)P(O)SeCH$_2$CH$_2$NMe$_2$}$_2$] (**18**) are formed *via* [1,3]-sigma tropic rearrangement as shown in Scheme 3. Several amine-functionalized phosphites such as P(OCH$_2$CH$_2$X)$_3$ (X = OMe, SMe, NMe$_2$) were prepared and their interactions with sulfur and selenium were studied in order to get more insight into the [1,3]-sigma tropic rearrangement of amine-functionalized cyclodiphosphazanes. After monitoring all these reactions it was observed that only the aminophosphite or phosphites containing amine-arm(s) produces the rearranged product indicating the intramolecular mechanism involving a cyclic intermediate through N···Se interactions with the lone pair of electrons on nitrogen playing an important role as shown in Scheme 4. These kinds of N···Se interactions are well documented in the literature [26] compared to O···Se or S···Se interactions [27] and could be the reason for the formation of rearranged products.

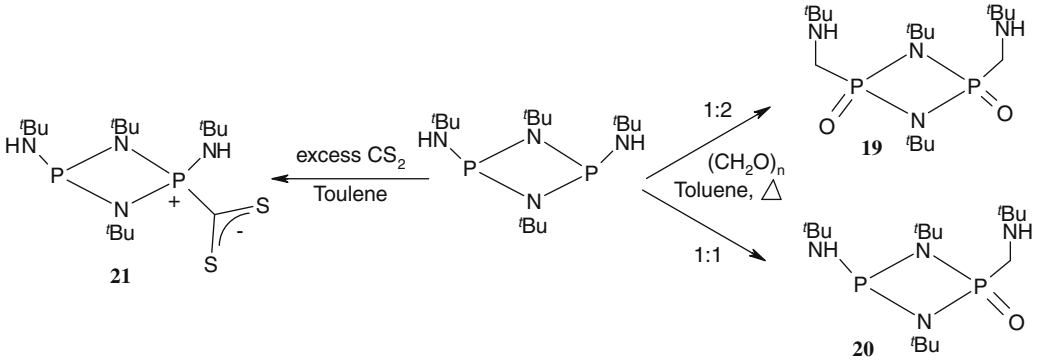
The reaction of **2** with two equivalents of paraformaldehyde in toluene under reflux conditions gave methylene-inserted product [^{t}BuN(H)CH$_2$P(O)(μ-N^{t}Bu)]$_2$ (**19**), whereas the 1:1 reaction leads to the mono inserted product [^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(O)CH$_2$N(H)^{t}Bu] (**20**) as shown in Scheme 5 [22]. Previously, we suggested a mechanism for the methylene insertion into the P–N bonds in aminophosphines involving a Staudinger-Wittig pathway, in which



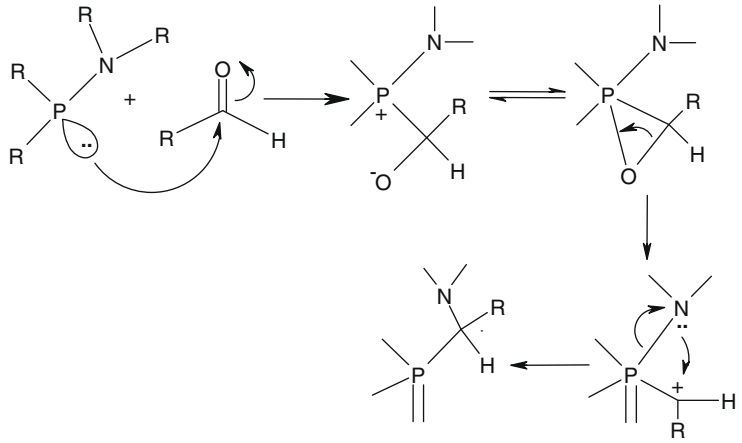
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6. Plausible mechanism for the insertion of carbon fragments into the P—N bonds.

proton transfer occurs from nitrogen to the phosphorus center to give $R_2P(O)H$ as an intermediate [28]. However, this mechanism fails to explain the insertion observed in non-proton containing aminophosphines such as $RN(PPh_2)_2$ and $Ph_2PN(C_2H_4)_2PPh_2$, hence it was concluded that the presence of the NH group is not a requirement [29,30].

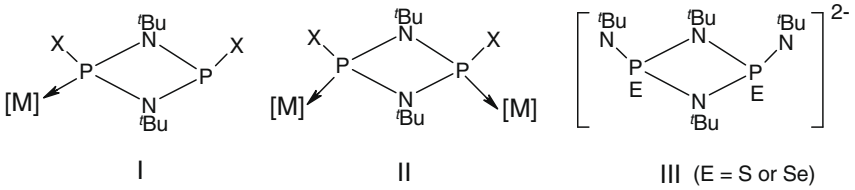


Chart 1. Possible coordination modes for cyclodiphosphazanes.

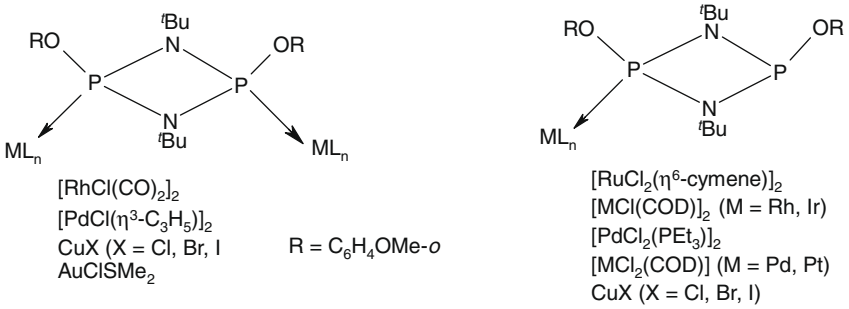


Chart 2. Preferred coordination modes for various transition metals.

The reactivity of *cis*-[{P(μ-N^{t}Bu)N(H)^{t}Bu}$_2$] towards paraformaldehyde indicates that the preferential exocyclic P–N bond insertion is essentially due to the relatively more basic nature of the amide nitrogens compared to the ring nitrogen atoms. The four-membered ring does not favor ring expansion *via* an insertion reaction. Generally, the tertiary amines (R_3N) or phosphines (PR_3) react with CO_2, COS or CS_2 to produce derivatives of the type R_3N–CE_2 and R_3P–CE_2, respectively [31]. In contrast, similar reactions with aminophosphines lead to the insertion of CE_2 into the P–N bonds to form carbamate or thiocarbamates of the type R_2P–C(E)–E–NR_2; interestingly, P(V) compounds also show similar reactivity [32]. In bis(amido)cyclodiphosphazanes, competition exists between the phosphorus and the nitrogen lone pair for nucleophilic attack by CE_2. The reaction of *cis*-[{P(μ-N^{t}Bu)N(H)^{t}Bu}$_2$] with CS_2 gives selectively the phosphonium salt [^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(CS_2)N(H)^{t}Bu] (**21**) as proved by single crystal X-ray analysis [33]. These observations suggest that the paraformaldehyde would interact first with the phosphorus center to form a betaine intermediate similar to CS_2 involving a phosphaoxirane intermediate as shown in Scheme 6. The existence of three-membered POC rings has been proved structurally [34].

4. Transition metal complexes

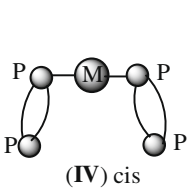
The interest in the coordination chemistry of cyclodiphosphazanes is two fold; the first one involves the utility of phosphorus(III) centers and its donor arms as neutral ligands (**I** and **II**) with cyclodiphosphazanes acting as $2e^-$ to $8e^-$ donors towards various transition metal fragments. The second is the utility of diamidocyclodiphosphazanes as dianionic ligands (**III**) towards both main group and transition elements (Chart 1). We have been exploring the transition metal chemistry of cyclodiphosphazanes with various donor functionalities. The ability of these rigid four-membered P_2N_2 rings to act as multidentate ligands resulted in the formation of species ranging from simple mononuclear complexes to multinuclear clusters, 1D, 2D and 3D coordination polymers. After treating cyclodiphosphazanes with several transition metal precursors we observed the *cis*-[(*o*-MeC_6H_4O)P(μ-N^{t}Bu)]$_2$ selectively forming mononuclear complexes with metal reagents such as [$RuCl_2$(η^6-cymene)]$_2$, [M(COD)Cl]$_2$ (M = Rh, Ir), [$PdCl_2(PEt_3)$]$_2$ and AgCN irrespective of the stoichiometry of the reactants and the reaction conditions.

4.1. Group 8–10 derivatives

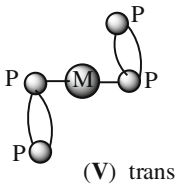
In contrast, reactions with [$Rh(CO)_2Cl$]$_2$, [PdCl(η^3-C_3H_5)]$_2$, CuX (X = Cl, Br, I), AgOTf and AuCl(SMe_2) afforded complexes with ligand exhibiting both monodentate and bridged bidentate coordination modes (Chart 2). Further, the metal complexes containing two of these monodentate ligands showed two conformations with respect to the uncoordinated phosphorus atoms: one containing both the uncoordinated phosphorus atoms in a mutually *cis*-disposition (face-to-face) (**IV**) and the other one in a mutually *trans*-disposition (**V**) as shown in Chart 3.

These two types of metalloligands are found to retain the conformations in solution state and on further treatment with appropriate metal precursors form homo- and hetero-binuclear to polynuclear complexes, metallamacrocycles (**VI**) or coordination polymers (**VII**). Since the dangling phosphorus centers are flexible with respect to the pivotal angle at metal centre, the size of the metallamacrocycle can vary in the 'coiling process', which also depends on the transition metal fragments and the other ancillary ligands coordinated to the metal centers. The mononuclear Rh^I (**22**) and Pd^{II} (**23**) complexes are typical examples of **IV** and **V** which show versatile reactivity towards various transition metals. A few representative mononuclear complexes are shown in Chart 4. This section also includes heteronuclear complexes containing both the group 8–10 and the group 11 metals.

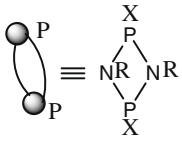
The reaction of *cis*-[(*o*-MeC_6H_4O)P(μ-N^{t}Bu)]$_2$ with [$RhCl(CO)_2$]$_2$ in a 4:1 ratio affords a mononuclear complex, *trans*-[RhCl(CO){{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$}] (**22**) containing two monodentate cyclodiphosphazanes with uncoordinated phosphorus centers *cis* to each other indicating its ability to form macrocycles [14,15]. As expected, by altering the stoichiometry and the reaction conditions, two different types of tetrameric complexes **26** and **27** were obtained which can also be prepared starting from the mononuclear complex **22** as shown in Scheme 7. Most of these complexes are structurally characterized. The attempts to grow the single crystals of **27** have been unsuccessful; however, the structure and the molecular composition of **27** were established by ana-



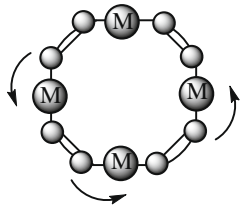
(**IV**) cis



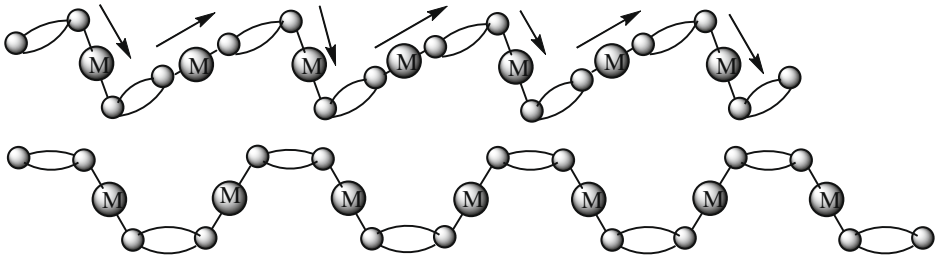
(**V**) trans



[M = Rh or Rh_2X_2; Cu or Cu_2X_2, Ag, Au] [M = Pd, Ag, Cu_2X_2 ; X = Cl, Br or I]

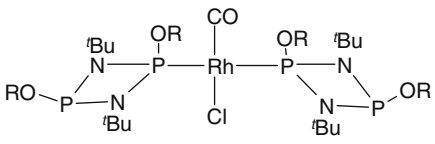


(**VI**) metallamacrocycles (Rh^I, Cu^I, Ag^I, Au^I)



(**VII**) linear, zigzag or spiral coordination polymers (Cu^I, Ag^I)

Chart 3.



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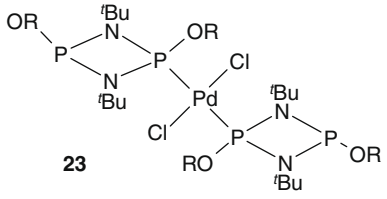

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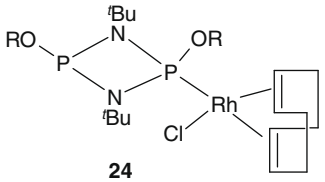

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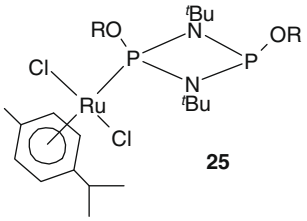


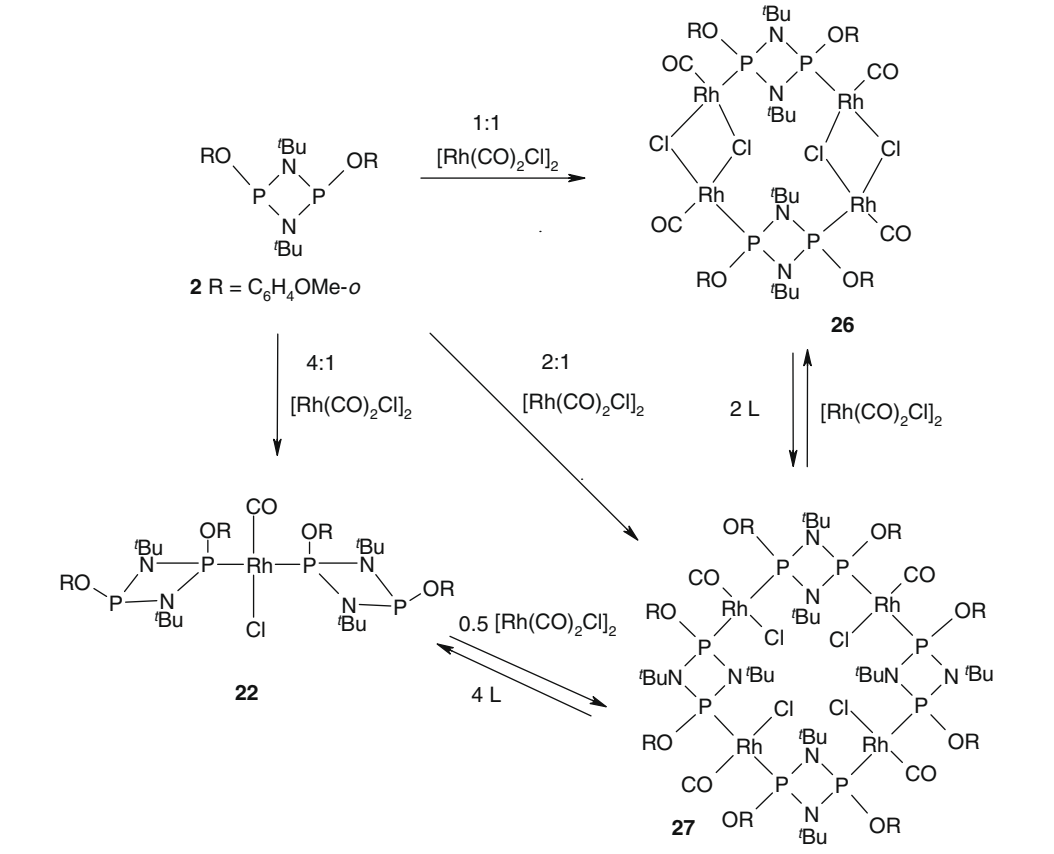
25

Chart 4.

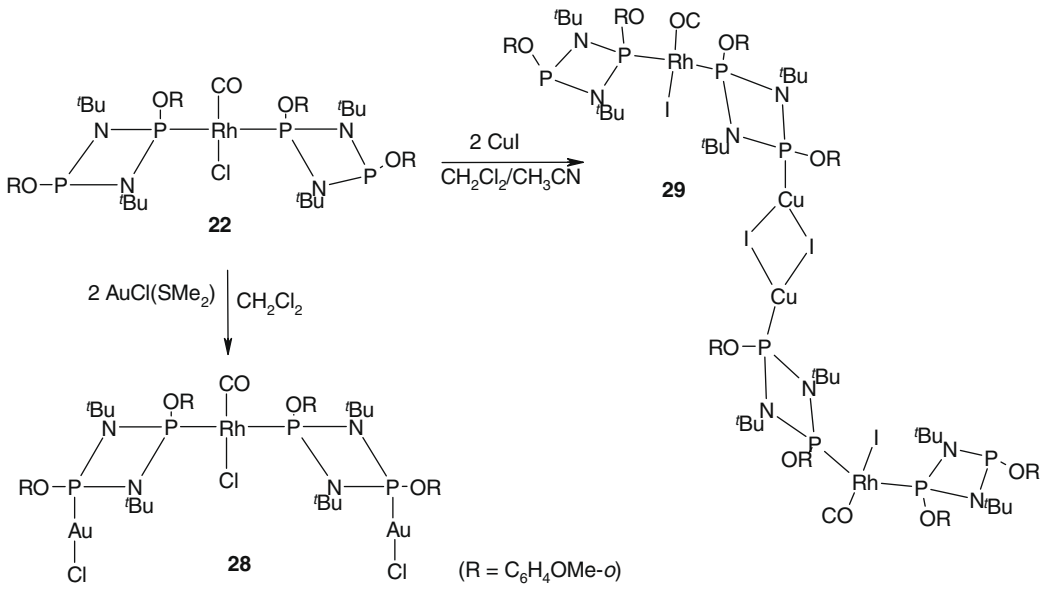
lytical and spectroscopic data. Further, the treatment of **27** with four equivalents of ligand **2** and two equivalents of $[RhCl(CO)_2]_2$ showed quantitative conversion to complexes **22** and **26**, respectively.

Treatment of **22** with two equivalents of $AuCl(SMe_2)$ resulted in the formation of trinuclear complex *trans*-[RhCl(CO){{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$AuCl}$_2$] (**28**) in quantitative yield. The slow addition of CuI dissolved in acetonitrile to a dichloromethane solution of **22** affords complex **29** containing two Rh^I and two Cu^I centers along with two uncoordinated ends (Scheme 8). Surprisingly, only one of the two dangling phosphorus centers of complex **22** coordinates to CuI with the resulting dimetallic Rh^I/Cu^I complex dimerizing through the formation of a rhombic $[Cu(\mu\text{-}I)_2Cu]$ unit, leaving the other phosphorus center uncoordinated. Since the phosphorus prefers the softer CuI for coordination over CuCl which is generated from the halogen exchange reaction, the reaction between **22** and an excess of CuI was carried out to force the coordination of end phosphorus atoms to form coordination polymer containing alternate [RhCl(CO)] and $[Cu(\mu\text{-}I)_2Cu]$ units. However, exclusive formation of only the complex **29** was observed [35].

The reaction of [(COD)RhCl{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$] (**24**) with one equivalent of $[AuCl(SMe_2)]$ affords the Rh^I/Au^I complex [(COD)RhCl{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$AuCl] (**30**) in good yield [35]. Similar reaction of **24** with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in dichloromethane in a 2:1 ratio produces a heteronuclear complex, [(COD)RhCl{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$PdCl(η^3-C_3H_5)] (**31**) in good yield [36].

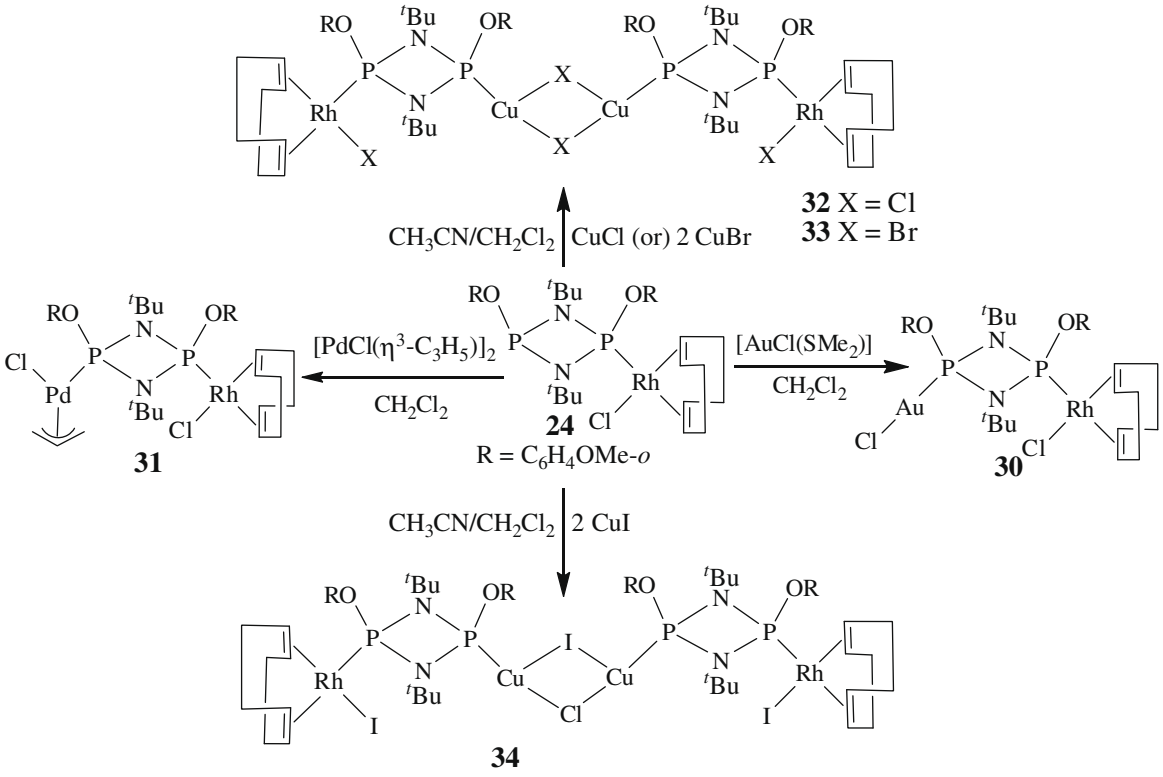


Scheme 7.

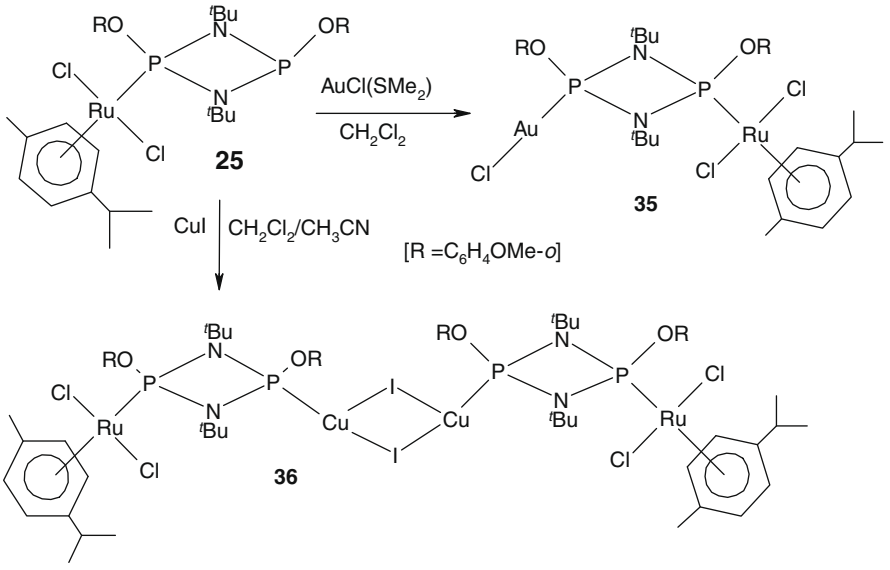


Scheme 8.

The reaction between **24** and CuCl or two equivalents of CuX (X = Br, I) in acetonitrile/dichloromethane produce tetranuclear complexes **32**–**34** (Scheme 9). The X-ray structure of [(COD)Rh-Cl{(*o*-MeC$_6$H$_4$O)P(μ-N^{t}Bu)}$_2${CuX}$_2$] (**34**) revealed the presence of [Cu(μ-X)$_2$Cu] containing both Cl and I and also a Rh–I bond instead of a Rh–Cl bond present in the starting complex. The result was unexpected since CuI was used in the reaction, and this suggests that the halogen exchange reaction occurs between the Rh–Cl bond present in **24** and CuI to form the Rh–I derivative with concomitant formation of CuCl, which later coordinated to the uncoordinated phosphorus center of cyclodiphosphazanes to produce a tetranuclear complex **34** [36]. This indicates that the halogen exchange



Scheme 9.



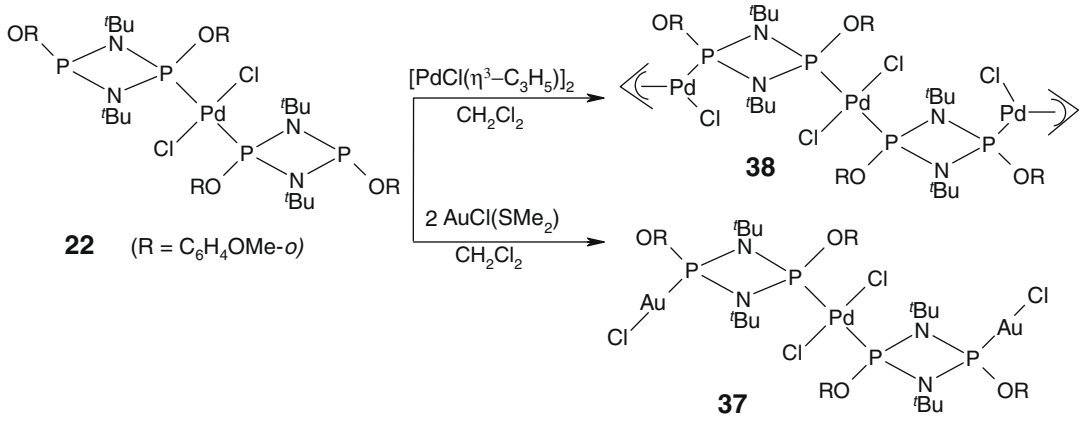
Scheme 10.

reaction occurs prior to the formation of Cu–P bonds. The formation of Rh–X (X = Br, I) through the halogen exchange between Rh–Cl and CuX (X = Br, I) as well as the preference for CuI over CuCl in coordination with phosphorus can be explained on the basis of HSAB principle [37]. Similar reactions of the ruthenium(II) complex, [(Cymene)$RuCl_2${(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$] (**25**) produce Ru/Au (**35**) and Ru_2/Cu_2 (**36**) complexes as shown in Scheme 10.

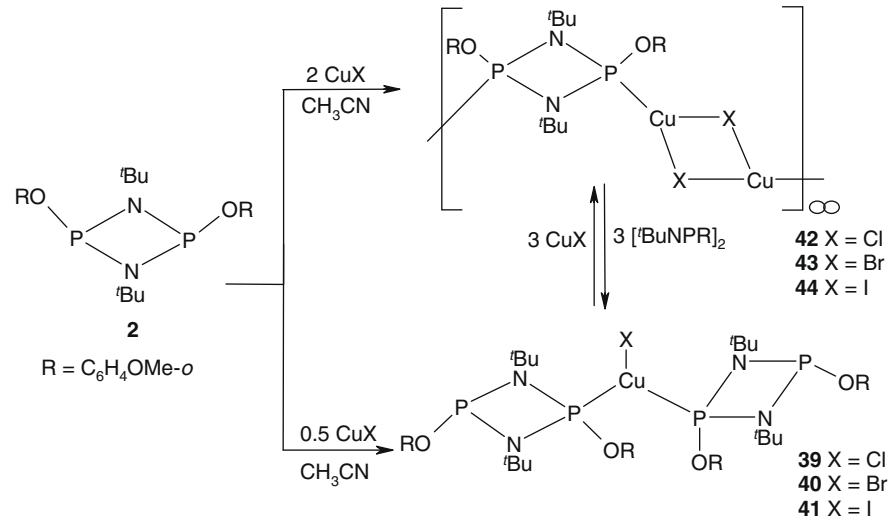
The 1:2 reaction between *trans*-[$PdCl_2${{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$}$_2$] (**23**) and [$AuCl(SMe_2)$] in dichloromethane affords a $Pd^{II}/2Au^{I}$ heteronuclear complex **37**. Another interesting tripalladium complex **38** was isolated in the reaction of **22** with [$PdCl(\eta^3$-$C_3H_5)]_2$ as shown in Scheme 11 [36].

4.2. Group 11 metal complexes

The interaction of *cis*-[(*o*-MeC_6H_4O)P(μ-N^{t}Bu)]$_2$ (**2**) with CuX in a 2:1 ratio in acetonitrile leads to the formation of highly soluble, tricoordinated Cu^{I} complexes **39**–**41**, with the cyclodiphosphazane showing a monodentate mode of coordination. Treatment of **2** with two equivalents of CuX leads to the formation of Cu^{I} coordination



Scheme 11.



Scheme 12.

polymers **42**–**44**, whereas a 1:1 reaction produces a mixture of both polymeric and tricoordinated complexes as shown in Scheme 12. Single-crystal X-ray structure determinations established the structures of all these complexes. The interesting feature of these coordination polymers is that they undergo depolymerization (reversible coordination) in the presence of added ligands to give simple tricoordinated Cu^{I} complexes, a process that is not facile with covalently bonded polymers. Similarly, the mononuclear complexes on addition of three equivalents of CuX afforded the corresponding polymers [16].

Interestingly, the reaction between morpholine (**6**) or N-methyl piperizine (**7**) derivatives and two equivalents of CuX (X = Cl, Br or I) in a mixture of dichloromethane and acetonitrile afforded the novel, octanuclear complexes $[Cu_8(\mu\text{-}I)_8(NCCH_3)_4\{(^tBuNPNC_4H_8X)_2\}_4]$ (**45**, X = O; **46**, X = NMe) in quantitative yield. The compounds **45** and **46** are 24-membered metallamacrocycles containing P_2N_2 rings and rhombic $[Cu_2(\mu\text{-}I)_2]$ units in an alternating fashion. These are rare examples of copper(I) macrocycles containing phosphorus based ligands; the only other known phosphorus containing CuI complex is a hexanuclear complex $[Cu_6Cl_6(^tBu_2PCH_2C_6H_4CH_2P^tBu_2)_6]$ containing six tricoordinated Cu^{I} ions linked *via* a bisphosphine, as shown in Chart 5 [38]. Interaction of octanuclear complexes **45** or **46** with 4,4′-bipyridine in 1:2 molar ratio gave hexanuclear 2D grid-like polymers $[\{[(4,4'\text{-bpy})_2Cu_2(\mu\text{-}I)\{\mu\text{-}(^tBuNPNC_4H_8X)_2][Cu_2(\mu\text{-}I)\{\mu\text{-}(^tBuNPNC_4H_8X)_2\}(I)_2]\}_\infty]$ (**47**, X = O; **48**, X = NMe) as yellow crystalline complexes (Scheme 13). The molecular structure consists of interesting cationic 2-dimensional grid-like coordination polymers $[\{[(4,4'\text{-bpy})_2Cu_2(\mu\text{-}I)\{\mu\text{-}(^tBuNPNC_4H_8X)_2\}\}_\infty]^+$ containing $[Cu_2(\mu\text{-}I)\{\mu\text{-}(^tBuNPNC_4H_8X)_2\}(I)_2]\}_\infty]^-$ anions trapped inside the hexanuclear metallamacrocyclic units as shown in Chart 6 [7]. The mechanism of this transformation is not known at present although it is clear that a considerable amount of rearrangement must occur since four Cu–I bonds have to be cleaved in addition to the loss of

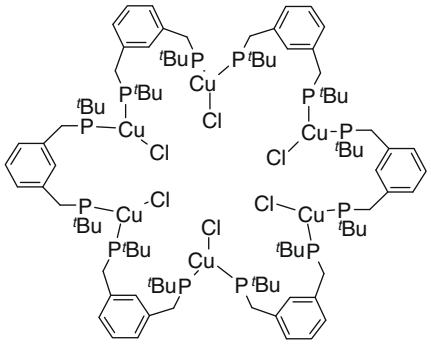
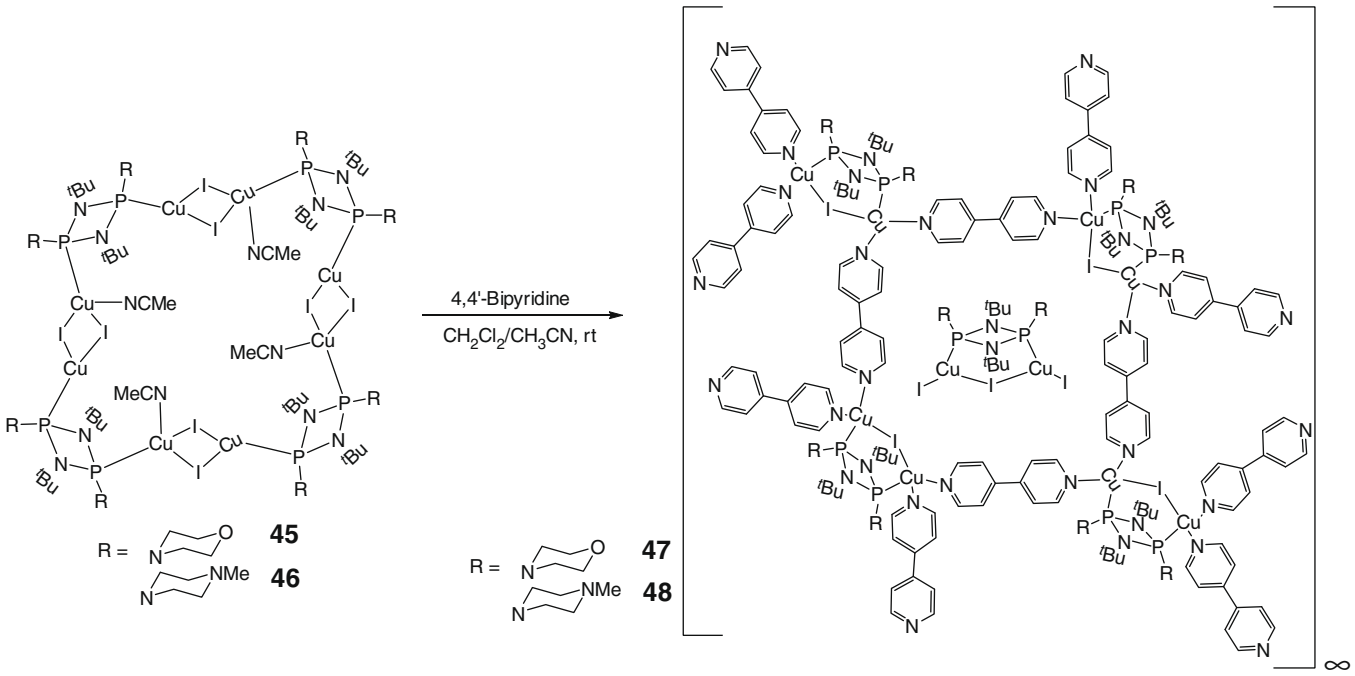


Chart 5.



Scheme 13.

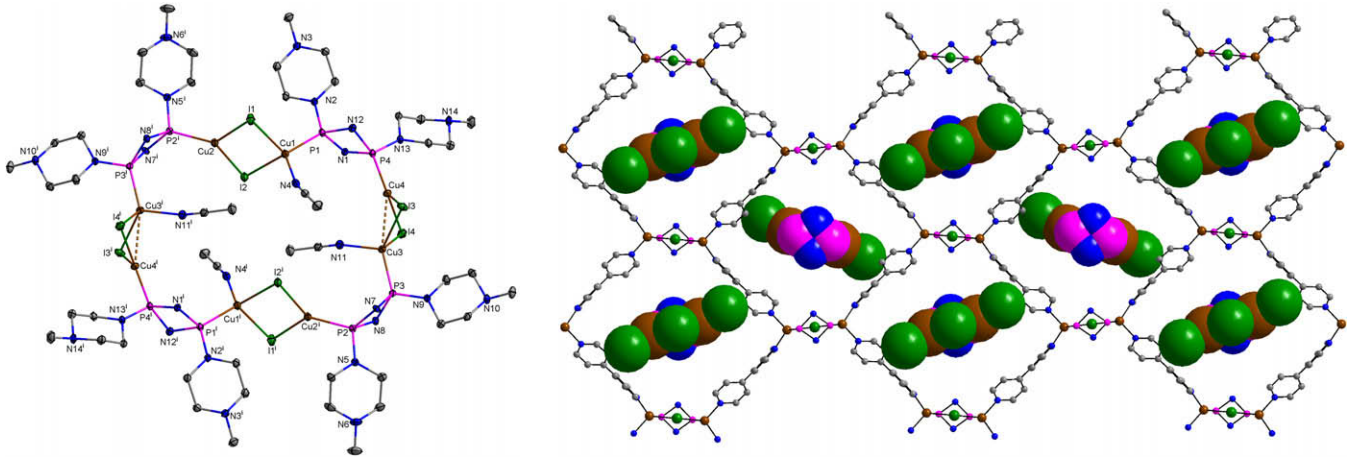
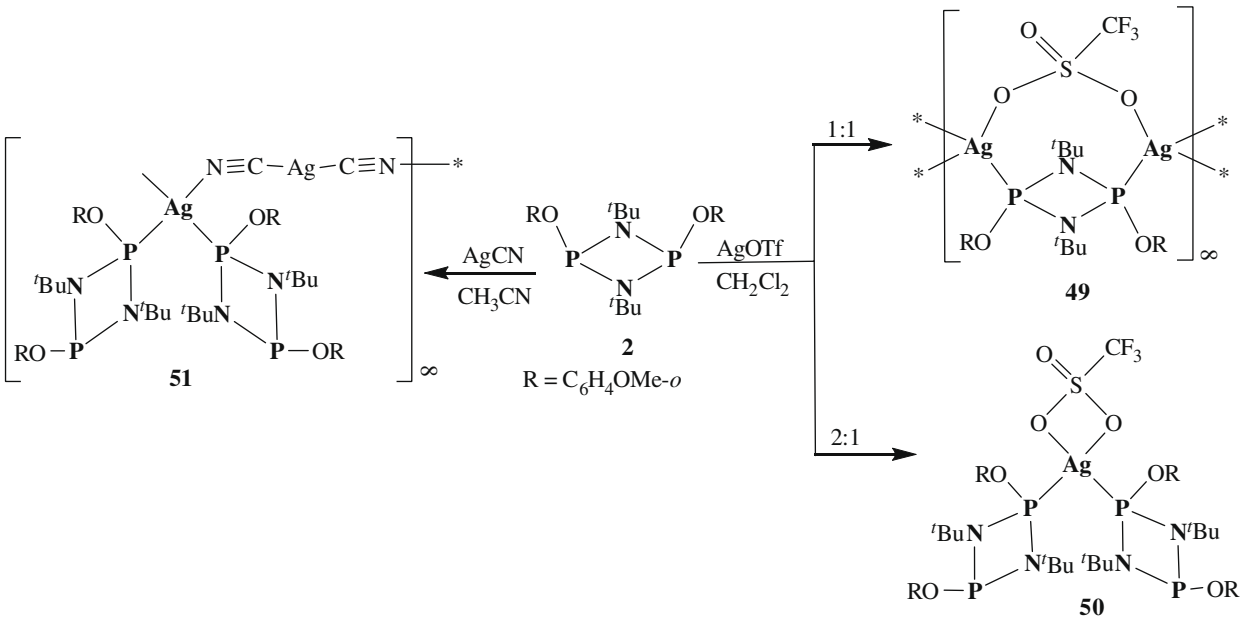


Chart 6. Molecular structures of **46** and **48**.

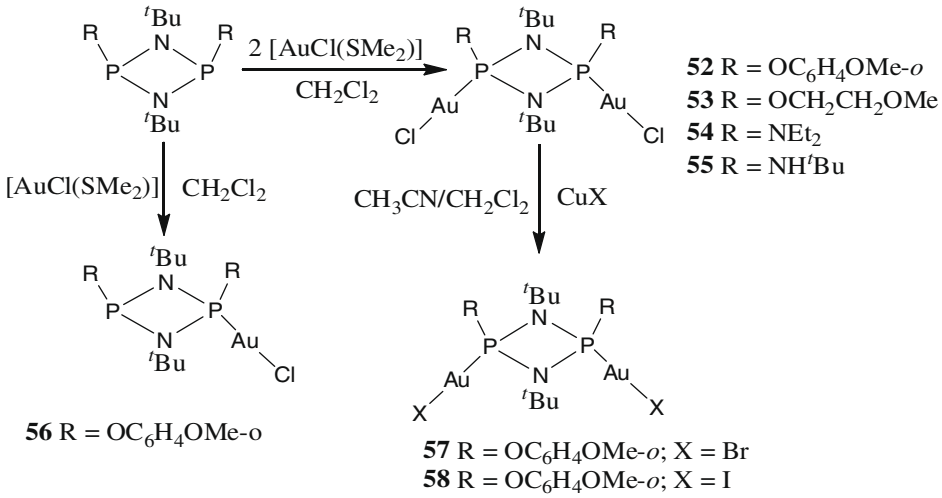
acetonitrile ligands. It is tempting to suggest that the initial attack of the 4,4′-bipyridine occurs at one of the 3-coordinate metals in **45** or **46**.

Although Ag^{I} coordination polymers containing rigid sulfur and nitrogen donor ligands are known, analogous compounds containing phosphorus donors are less extensive. Cyclodiphosphazanes react with various silver reagents to form different types of complexes as shown in Scheme 14. Reaction of *cis*-[(*o*-MeC_6H_4O)P(μ-N^{t}Bu)]$_2$ (**2**) with AgOTf in a 1:1 stoichiometry in dichloromethane at 25 °C affords the Ag^{I} coordination polymer [{Ag(μ-OTf)}$_2${(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$]$_\infty$ (**49**) in good yield. Under similar reaction conditions 2:1 reaction between **2** and AgOTf produces mononuclear complex [{Ag(μ-OTf)}{{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$}$_2$] (**50**). Treatment of **2** with AgCN in acetonitrile leads to the formation of a strain-free zigzag polymer [{AgCN}$_2${{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$}$_2$]$_\infty$ (**51**), irrespective of the stoichiometry of the reactants and the reaction conditions. In complex [{Ag(μ-OTf)}{{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$}$_2$] (**49**) the cyclodiphosphazane **2** exhibits a bridging coordination mode, whereas the monodentate mode of coordination was observed in complexes **50** and **51**. The molecular structures of **49** and **51** were confirmed by single crystal X-ray diffraction studies, whereas the proposed structure of **50** is based on NMR spectroscopy, elemental analysis and mass spectrometry [17].

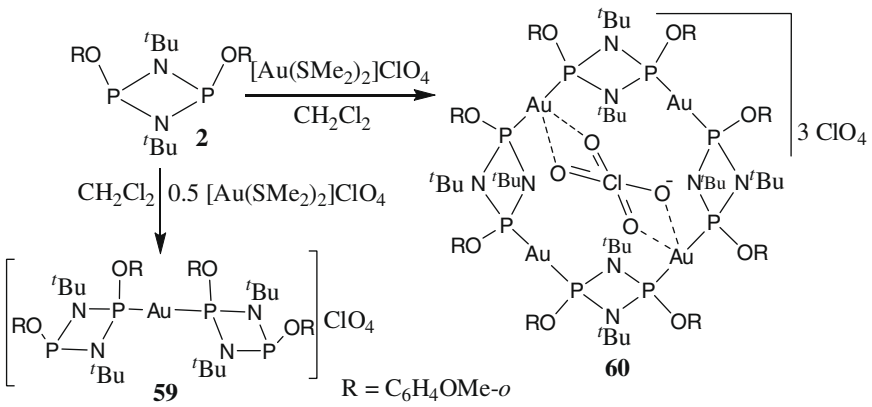
Cyclodiphosphazanes readily react with AuCl(SMe_2) to form both mono and binuclear complexes. Mononuclear complexes readily form heteronuclear complexes with other transition metal derivatives. Addition of two equivalents of [AuCl(SMe_2)] to a dichloromethane solution of the cyclodiphosphazanes at 25 °C leads to the formation of dinuclear complexes **52**–**55**. The mononuclear complex **56** was isolated from a similar 1:1 reaction between **2** and [AuCl(SMe_2)] as shown in Scheme 15. Complexes **52**–**56** are stable white solids but are found to be light-sensitive as they turned from white to pink color after a week when exposed to light. Although tricoordinated T-shaped Au^{I} complexes of the type [AuX(PR_3)$_2$] are well documented, attempts to prepare similar



Scheme 14. Synthesis of Silver(I) complexes of cyclodiphosphazane.



Scheme 15.



Scheme 16.

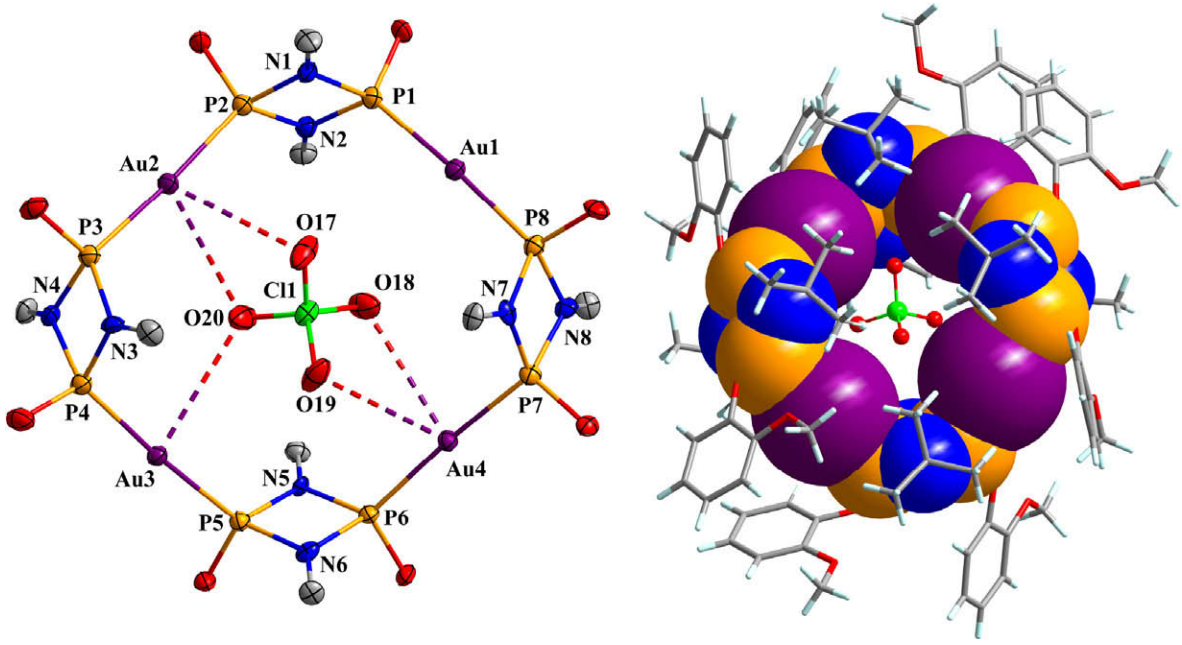


Chart 7. Core Structure of tetranuclear complex **60**.

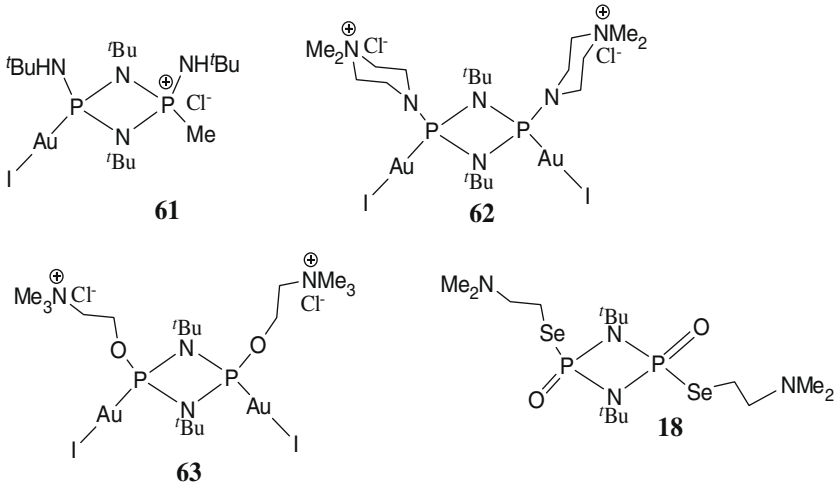


Chart 8.

complexes of cyclodiphosphazanes have been unsuccessful. However, cyclodiphosphazanes readily form tricoordinated Cu^{I} complexes. Recently we observed CuBr and CuI to function as excellent halogen exchange reagents for the preparation of bromo- and iodo-derivatives of Rh^{I} complexes from the chloro analogs containing cyclodiphosphazanes [35]. Similar reactions between **53** and CuX (X = Br, I) in 1:2 molar ratios afforded the bromo- (**57**) and iodo- (**58**) derivatives, respectively. The proposed structures were confirmed by ^{1}H NMR, analytical data, mass spectrometry and by single crystal X-ray diffraction studies in case of compounds **54**, **57** and **58** [18].

The cationic Au^{I} complex, $[Au(SMe_2)_2]ClO_4$ prepared from the equimolar reaction between $[AuCl(SMe_2)]$ and $AgClO_4$ in dichloromethane in the presence of an excess of SMe_2, on treatment with **2** in 1:2 ratio afforded a mononuclear complex $[Au\{\{(o\text{-}MeC_6H_4O)P(\mu\text{-}N^tBu)\}_2\}_2]ClO_4$ (**59**), whereas a 1:1 reaction resulted in the tetranuclear complex $[\{Au\{(o\text{-}MeC_6H_4O)P(\mu\text{-}N^tBu)\}_2\}_4][ClO_4]_4$ (**60**) in good yield (Scheme 16). The ^{31}P NMR chemical shift due to the coordinated phosphorus of **60** appears at 131.6 ppm, whereas the uncoordinated phosphorus resonates at 126.6 ppm. The ^{31}P NMR spectrum of **60** consists of a single resonance at 127.8 ppm. The molecular structure of **60** consists of four cyclodiphosphazanes connected *via* four dicoordinated gold centers to form a tetranuclear macrocycle with a cavity of 7.932 Å (Au1···Au3) × 7.311 Å (Au2···Au4). Gold centers are in distorted linear geometry with P–Au–P angles of 175.69(7)°. Interestingly, one of the perchlorate anions is present inside the macrocyclic cavity while the other three are on the periphery of the macrocycle as shown in Chart 7. The perchlorate ion present inside the cavity is one of the rare examples of host–guest systems with gold macrocycles and is held through a combination of weak O···Au and C–H···Au interactions [18].

5. Catalytic and biological applications

Cyclodiphosphazanes are effectively used as building blocks by Wright and coworkers to make inorganic versions of crown ethers and cryptands which may find application in host–guest chemistry to trap both anions and cations. The titanium metal complexes containing diamidocyclodiphosphazanes promote polymerization of olefins with moderate turnover numbers. Cyclodiphosphazanes have also been used by Kumaraswamy and coworkers to probe organic reaction mechanisms. Recently we have examined the palladium complexes containing cyclodiphosphazanes in Suzuki-Miyaura and Mizoraki-Heck cross coupling reactions with quantitative conversions under mild reaction conditions. The rhodium complex [(COD)RhCl{(*o*-MeC_6H_4O)P(μ-N^{t}Bu)}$_2$] (**24**) catalyses the olefin hydrogenation reactions under mild conditions [39].

The gold complexes *cis*-[^{t}BuN(H)(AuI)P(μ-N^{t}Bu)$_2${P(CH_3)N(H)^{t}Bu}Cl] (**61**), *cis*-[(MeNC_4H_8N)(AuI)P(μ-N^{t}Bu)$_2${P(CH_3)NC_4H_8NMe$_2$}(Cl)$_2$] (**62**), [{(^{t}BuN-μ) P(AuI)OCH_2CH_2NMe_3}$_2$](Cl)$_2$ (**63**) and *trans*-[{(^{t}BuN-μ)P(O)SeCH_2CH_2NMe_2}$_2$] (**18**) (Chart 8) were tested for their anticancer activity on a human cervical cancer cell line (HeLa). The gold mononuclear complex, **61** and the selenophosphate, **18** showed strong antiproliferative activity against HeLa cells. The complex **61** exhibited about 38 ± 4 and 83 ± 6% inhibition of proliferation with 5 and 20 μM, respectively, while **18** exhibited about 53 ± 8 and 93 ± 7% inhibition of proliferation with 5 and 20 μM, respectively [13]. Under similar experimental conditions, the benchmark anticancer drug cisplatin was found to inhibit HeLa cell proliferation with half-maximal inhibitory concentration of 8 ± 1 μM; therefore the antiproliferative activities of compounds **61** and **18** in HeLa cells are found to be superior to that of cisplatin. Further work in this direction is under active investigation in our laboratory.

6. Summary

Cyclodiphosphazanes with donor arms exhibit versatile coordination properties. The preferential coordination behavior shown towards transition metals and their preferred conformations is thoughtfully utilized in our laboratory to isolate several metal based macrocycles, homo- or heteropolynuclear complexes, and coordination polymers. In the reactions of cyclodiphosphazanes with cuprous halides, slight variations in the phosphorus substituents, resulted in the formation of either Cu^I coordination polymers or rare octanuclear complexes both containing rhombic [Cu(μ-X)$_2$Cu] units. Interestingly, the octanuclear complexes on further treatment with 4,4′-bipyridine afford novel 2D-hexanuclear complexes containing hexanuclear cationic macrocycles linked on four sides by 4,4′-bipyridines and encapsulating anionic [Cu(I)(μ-I)(μ-L)Cu(I)] (L = **6** or **7**) moieties in a typical host–guest fashion. Many of these complexes, especially Ru^{II}, Rh^I Pd^{II} derivatives can be potential catalysts for various organic transformations and Cu^I, Ag^I and Au^I complexes can function as antitumor reagents and the work in this direction is in progress.

Acknowledgments

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