Functionalized cyclodiphosphazanes *cis*-[^{t}BuNP(OR)]$_2$ (R=C$_6$H$_4$OMe-*o*, CH$_2$CH$_2$OMe, CH$_2$CH$_2$SMe, CH$_2$CH$_2$NMe$_2$) as neutral 2e, 4e or 8e donor ligands

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Abstract

Cyclodiphosphazanes having donor functionalities such as *cis*-[^{t}BuNP(OR)]$_2$ (R = C$_6$H$_4$OMe-*o* (**2**); R = CH$_2$CH$_2$OMe (**3**); R = CH$_2$CH$_2$SMe (**4**); R = CH$_2$CH$_2$NMe$_2$ (**5**)) were obtained in good yield by reacting *cis*-[^{t}BuNPCl]$_2$ (**1**) with corresponding nucleophiles. The reactions of **2**–**5** with [RuCl$_2$(η^6-cymene)]$_2$, [MCl(COD)]$_2$ (M = Rh, Ir), [PdCl$_2$(PEt$_3$)]$_2$ and [MCl$_2$(COD)] (M=Pd, Pt) result in the formation of exclusively monocoordinated mononuclear complexes of the type *cis*-[{^{t}BuNP(OR)}$_2$ML$_n$-κP] irrespective of the reaction stoichiometry and the reaction conditions. In contrast, **2**–**5** react with [RhCl(CO)$_2$]$_2$, [PdCl(η^3-C$_3$H$_5$)]$_2$, CuX (X=Cl, Br, I) to give homobinuclear complexes. Interestingly, CuX produces both mono and binuclear complexes depending on the stoichiometry of the reactants and the reaction conditions. The mononuclear complexes on treatment with appropriate metal reagents furnish heterometallic complexes.
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Keywords: Cyclodiphosphazanes; Transition metals; Monodentate; Bidentate; Heterometallic complexes; Coordination polymers

1. Introduction

The main group and transition metal chemistry of dianionic bis(amido)cyclodiphophazanes, *cis*-[^{t}BuNP(^{t}BuN$^-$)]$_2$ and their chalcogen derivatives, *cis*-[^{t}BuNP(E)(^{t}BuN$^-$)]$_2$ (E = S or Se) has been extensively studied by Chivers [1] and Stahl [2]. Several other groups have explored the reactivity of chloro derivative *cis*-[^{t}BuNPCl]$_2$ (**1**) which resulted not only in the isolation of dimeric to pentameric macrocycles but also in understanding the thermodynamics and mechanistic aspects involved in these reactions [3]. Surprisingly, the coordination chemistry of neutral cyclodiphosphazanes is scant in spite of their ability to show monodentate and bridged bidentate modes of coordination. Krishnmurthy and coworkers [4] have reported some homo- and heterobi-

nuclear complexes of group 6 and 8 metals with cyclodiphosphazanes showing both mono- and bridged bidentate modes of coordination. Recently, we have reported [5–8] on the synthesis, reactivity and transition metal chemistry of several functionalized cyclodiphosphazanes of the type *cis*-[ROP(μ-N^{t}Bu)]$_2$(R=C$_6$H$_4$OMe-*o* (**2**), CH$_2$CH$_2$OMe (**3**), CH$_2$CH$_2$SMe (**4**), CH$_2$CH$_2$NMe$_2$ (**5**)) and the details are summarized in this account.

2. Synthesis of functionalized cyclodiphosphazanes

Cyclodiphosphazanes of the type [ROP(μ-N^{t}Bu)]$_2$ (R = C$_6$H$_4$OMe-*o* (**2**), CH$_2$CH$_2$OMe (**3**), CH$_2$CH$_2$SMe (**4**), CH$_2$CH$_2$NMe$_2$ (**5**)) containing donor functionalities have been prepared by reacting [ClP(μ-N^{t}Bu)]$_2$ (**1**) with two equivalents of 2-(methoxy)phenol or 2-substituted ethanols, HOCH$_2$CH$_2$E (E = OMe, SMe, NMe$_2$) as shown in Scheme 1. The reactions were carried out either in presence of Et$_3$N or by using the sodium salts of

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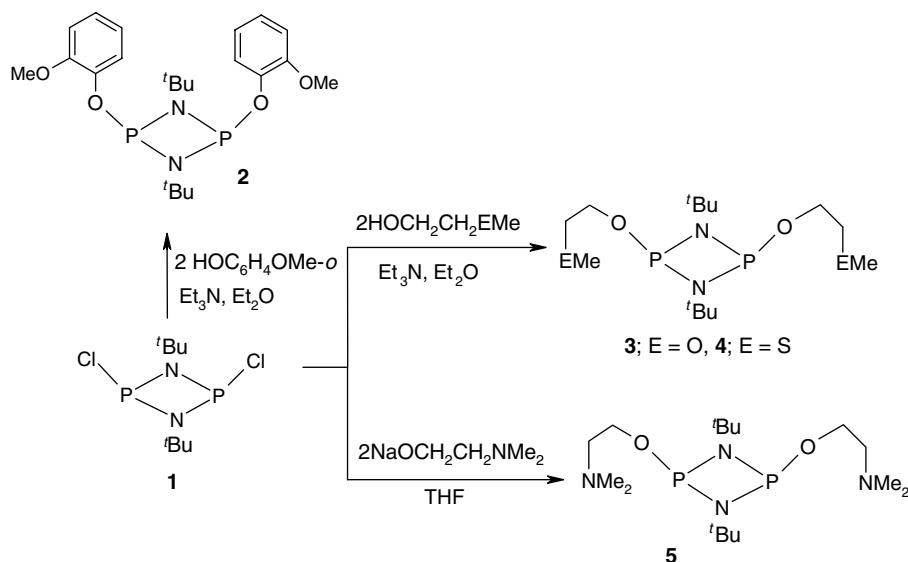
Scheme 1.

respective alkoxide derivatives. The phenol derivative **2** is a crystalline solid whereas the others are oily liquids which are purified by vacuum distillation [5,6]. All these compounds exist as cis isomers as confirmed by their ^{31}P NMR spectral data (^{31}P NMR data (δ_P in ppm): **2**, 145.6; **3**, 133.8; **4**, 134.1; **5**, 133.7). The phosphorus-31 chemical shifts due to cis-isomers are more shielded relative to that of *trans*-isomers.

3. Transition metal chemistry of cyclodiphosphazanes

The cyclodiphosphazanes **2**–**5** containing a donor arm on each phosphorus(III) center can act as 2e, 4e, 6e or 8e donor ligands depending on the nature of the metal derivatives employed, stoichiometry and the reaction conditions (Chart 2). Compounds **2** and **3** have shown only the bidentate mode and the side arms did not coordinate to the transition metals whereas the compounds **4** and **5** perform as bischelating ligands with platinum metals (see Chart 1).

4. Rhodium(I) and ruthenium(II) derivatives

The reactions of cyclodiphosphazane derivatives with [Rh(CO)$_2$Cl]$_2$ afford a variety of products, depending upon the stoichiometry of the reactants, reaction conditions and also on the nature of the donor functionalities present in the pendant groups as shown in Schemes 2 and 3 [5,6]. The tetranuclear complexes **6** and **7** containing two [Rh(μ-Cl)]$_2$ units and two bridging cyclodiphosphazanes are obtained when the [Rh(CO)$_2$Cl]$_2$ and **2** or **3** were used in 1:1 molar ratios. Treatment of [Rh(CO)$_2$Cl]$_2$ with four equivalents of **2** afforded *trans*-[Rh(CO)Cl{(RO)P(μ-N^{t}Bu)$_2$P(OR)}$_2$] (**10**) in quantitative yield [5]. Interestingly, the reaction of **4** and **5** with one equivalent of [Rh(CO)$_2$Cl]$_2$ in acetonitrile under reflux conditions afforded the dinuclear bischelated Rh(I) complexes **8** and **9**, respectively, as shown in Scheme 2. These are the first examples of cyclodiphosphazanes acting as 8e$^-$ bischelating ligands. The ^{31}P NMR spectra of complexes **6**–**9** show multiplets with chemical shifts in the range of 115–124 ppm. The
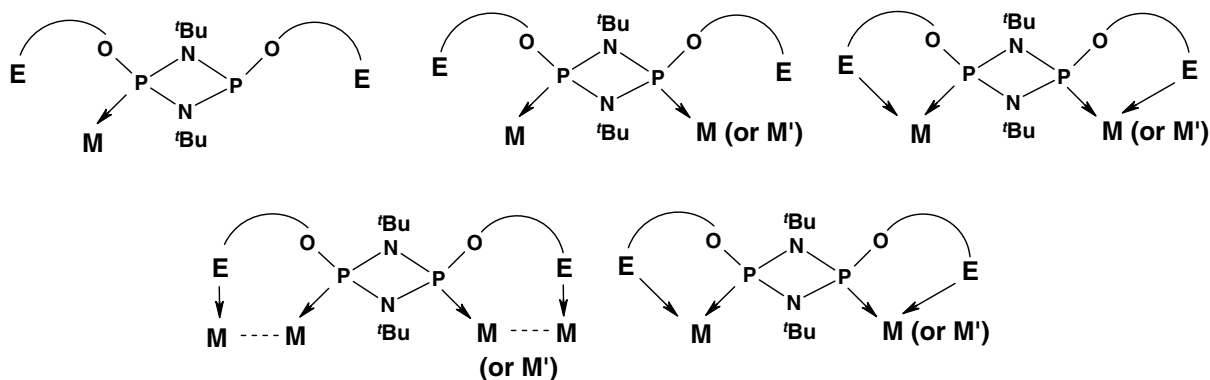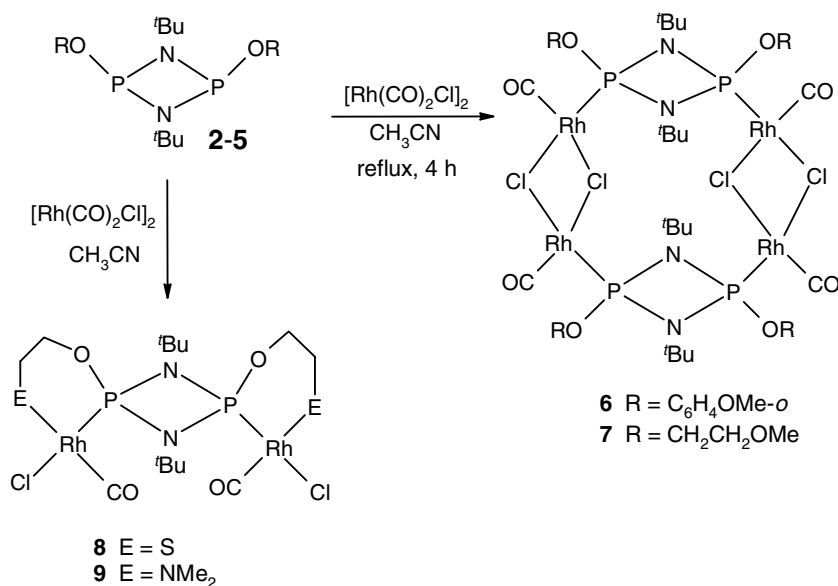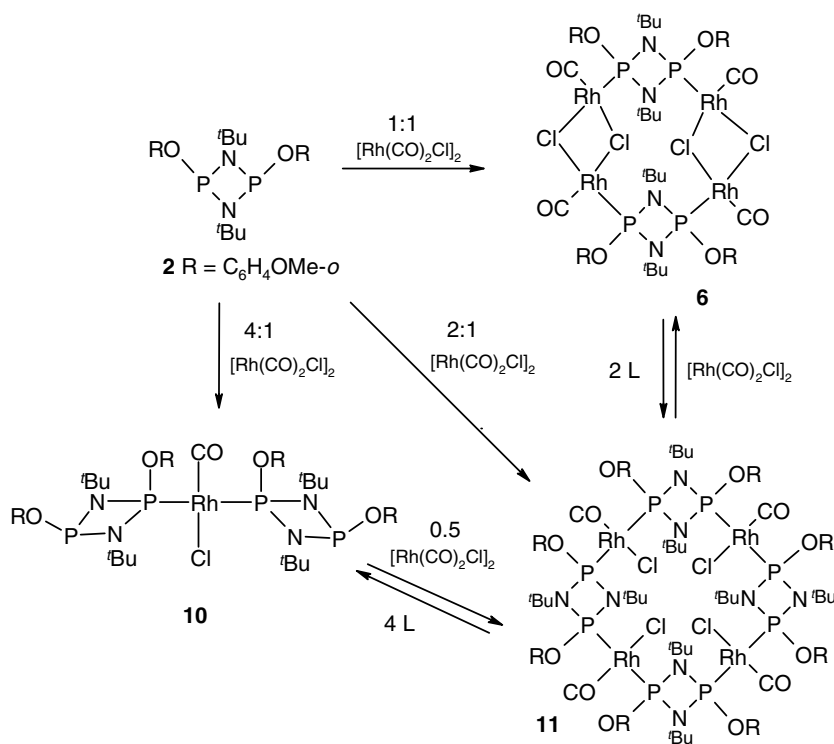

Chart 1. Possible coordination modes of cyclodiphosphazanes with donor functionalities.

Scheme 2.

Scheme 3.

$^2J_{PP}$ and $^2J_{RhP}$ couplings are in the range 42–47 Hz and 230–250 Hz, respectively. The IR spectra of complexes 6–10 show two absorptions in the range 1993–2034 cm^{-1} which is clearly consistent with the cis related CO/phosphine structures proposed for these complexes [10]. The structures of compounds 6, 7 and 9 were further confirmed by low temperature single-crystal X-ray diffraction studies [5,6].

The NMR tube reaction of complexes 6 and 10, respectively, with 6 equivalents of ligand and 1.5 equivalents of [RhCl(CO)$_2$]$_2$ showed quantitative conversion into each other with complex [RhCl(CO){ROP(μ-N^{t}Bu)}$_2$]$_4$ (11) as an intermediate as revealed by the ^{31}P NMR spectroscopic data [10]. Both mono- and tetranuclear complexes have been structurally characterized. In a separate reaction, treatment of [Rh(CO)$_2$Cl]$_2$ with {ROP(μ-N^{t}Bu)}$_2$ in 1:1

ratio afforded the complex **11** in quantitative yield which shows a doublet at 105 ppm in its ^{31}P NMR spectrum with $^{1}J_{RhP} = 246$ Hz. Attempts to grow suitable crystals of **11** for X-rays studies have been unsuccessful.

The reaction between [MCl(COD)]$_2$ and **2** gave exclusively the monocoordinated complexes, [(COD)MCl-{ROP(μ-N^{t}Bu)}$_2$] (**12** M = Rh, $\delta_{PA} = 102.8$ ppm ($^{1}J_{RhP} = 229$ Hz), $\delta_{PX} = 131.7$ ppm; **13** M = Ir, $\delta_{PA} = 88.5$ ppm; $\delta_{PX} = 133$ ppm;) irrespective of the stoichiometry of the reactants and the reaction conditions. The rhodium(I) complex **12** containing a free phosphorus(III) center is used as a metalloligand to generate a series of heterometallic complexes and the details are summarized later in Scheme 6.

The mononuclear Ru(II) complex **14** was prepared [6] by reacting two equivalents of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**) with [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ in dichloromethane. Even, with an excess of metal reagent, only the mononuclear product was obtained. In the ^{31}P NMR spectrum of **14**, the uncoordinated phosphorus appears as a doublet centered at 133.5 ppm whereas the chemical shift due to the coordinated phosphorus appears at 109.6 ppm. The $^{2}J_{PP}$ coupling is 8.7 Hz.

R = C$_6$H$_4$OMe-*o*

12, M = Rh
13, M = Ir

14
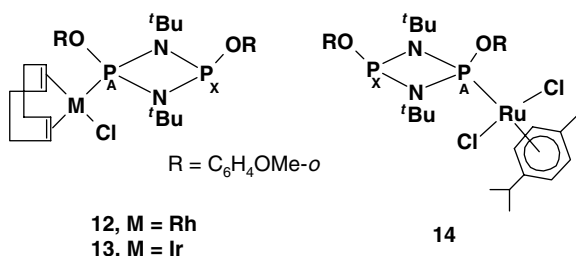
5. Palladium and platinum derivatives

The reactions of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**) with [M(COD)Cl$_2$] (M = Pd or Pt), are independent of stoichiometry and the reaction conditions, and afford exclusively *cis* complexes, **15** and **16** with the ligand exhibiting monodentate coordination. In contrast, the reaction of two equivalents of **2** with [Pd(NCPh)$_2$Cl$_2$] in dichloromethane affords a mononuclear *trans* palladium(II) derivative **17** as shown in Scheme 4. The ^{31}P NMR spectra of complexes **15** and **16** show two doublets with a $^{2}J_{PP}$ coupling of 53 Hz and 7.3 Hz, respectively. The platinum complex shows a large $^{1}J_{PtP}$ coupling of 4861 Hz, which is consistent with the proposed *cis* geometry **16** [9]. The *trans*-palladium(II) complex **17** exhibits two single resonances at 128.3 and 84.6 ppm, respectively, for uncoordinated and coordinated phosphorus centers and no $^{2}J_{PP}$ coupling was observed. Treatment of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**) with palladium(II) dimer, [Pd(PEt$_3$)Cl$_2$]$_2$ in an equimolar ratio also affords a mononuclear complex **18** containing monodentate cyclodiphosphazane and PEt$_3$ ligands in mutually *cis* orientations. The ^{31}P NMR spectrum of complex **18** consists of three resonances; uncoordinated phosphorus of cyclodiphosphazane and PEt$_3$ appear as doublets at 127.2 ($^{2}J_{PP} = 3.9$ Hz) and 35.8 ppm ($^{2}J_{PP} = 16.8$ Hz) respectively and are coupled to the coordinated phosphorus, which appears as a doublet of doublets centered at 85.7 ppm. Further structural evidence come from ^{1}H NMR and mass spectral data, elemental analysis and single crystal X-ray diffraction studies in case of complexes **17** and **18** [6]. The 1:1 reaction between **2** and [PdCl(η^3-C$_3$H$_5$)]$_2$ in dichloromethane affords dinuclear palladium(II) complex, [(PdCl(η^3-C$_3$H$_5$))$_2$-
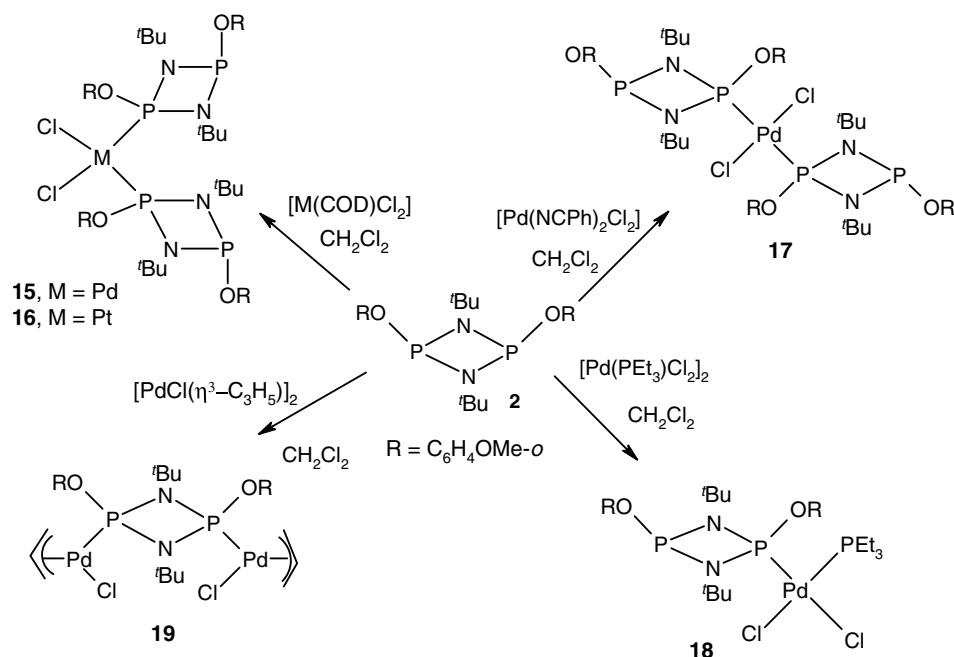
Scheme 4.

{(^{t}BuNP(OC$_6$H$_4$OMe-o))$_2$-κP}](19) with cyclodiphosphaz-
ane acting as a bridging ligand. The ^{31}P NMR spectrum of
19 shows a sharp singlet at 121.1 ppm indicating the sym-
metrical coordination of cyclodiphosphazane.

6. Copper(I) derivatives

Cyclodiphosphazanes containing two P(III) centers in a
mutually *cis*-orientations can interact with CuX, which
prefers either trigonal planar or tetrahedral geometries, to
give a variety of products as shown in Chart 2. In these
reactions, the choice of the product formation depends
on the stoichiometry of the reactants and the reaction con-
ditions which is also guided by both the kinetic and the
thermodynamic aspects. So far, the stoichiometry con-
trolled reactions have yielded products of the type I–III
[8] and attempts are being made to synthesize the products
of the type IV and V.

The reactions of cyclodiphosphazane, *cis*-[^{t}BuNP(O-
C$_6$H$_4$OMe-o)]$_2$ (1) with two equivalents of CuX in acetoni-
trile afforded one dimensional copper(I) coordination

polymers [Cu$_2$X$_2${^{t}BuNP(OC$_6$H$_4$OMe-o)}$_2$]$_n$ (20; X = Cl,
21; X = Br, 22; X = I). The crystal structures of 20 and
22 reveal a zig-zag arrangement of [P(μ-N)$_2$P] and [Cu(μ-
X)$_2$Cu] units in an alternating manner to form one dimen-
sional copper(I) coordination polymers. The reaction
between *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-o)]$_2$ (1) and CuX in a
2:1 ratio afforded mononuclear tricoordinated copper(I)
complexes of the type [CuX{(^{t}BuNP(OC$_6$H$_4$OMe-o))$_2$}$_2$]
(23; X = Cl, 24; X = Br, 25; X = I). The single crystal X-
ray structures were established for the mononuclear cop-
per(I) complexes 23 and 24. When the reactant ratios are
1:1, the formation of a mixture of polymeric and mononu-
clear products was observed. The Cu(I) polymers (20–22)
were converted into the mononuclear complexes (23–25)
by reacting with three equivalents of *cis*-[^{t}BuNP(O-
C$_6$H$_4$OMe-o)]$_2$ (1) in DMSO. Similarly, the mononuclear
complexes (23–25) were converted into the corresponding
polymeric complexes (20–22) with three equivalents of cop-
per(I) halide under mild reaction conditions. The com-
plexes are the first examples coordination polymers
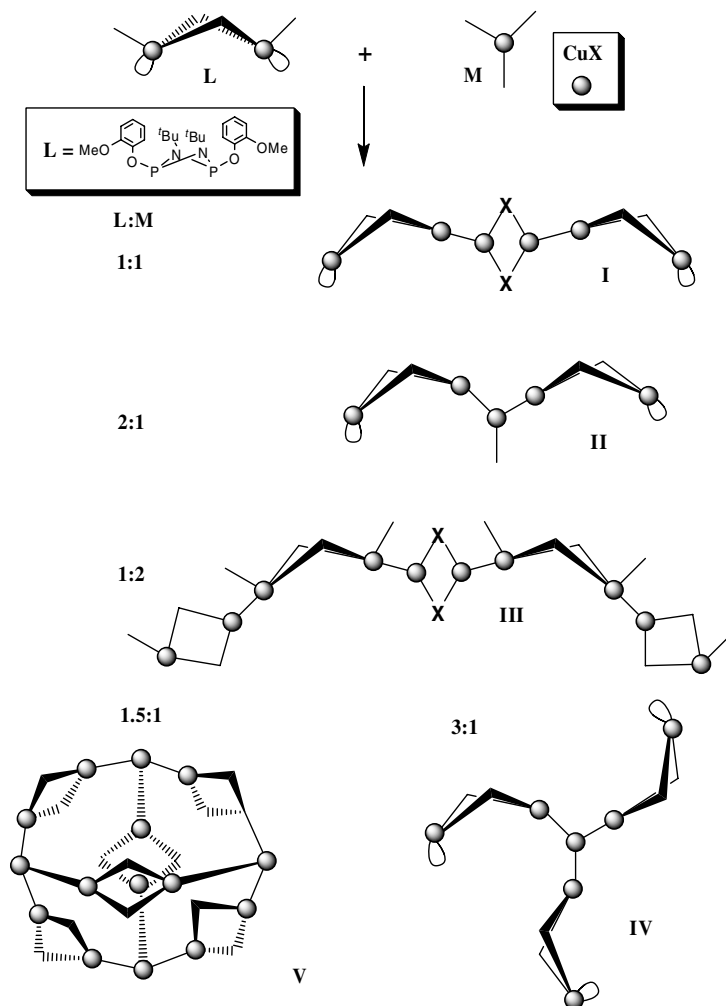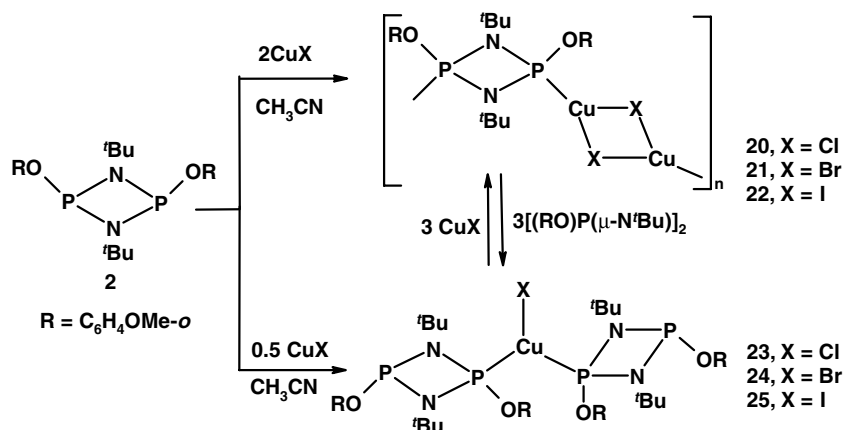containing cyclodiophosphazanes [8] (see Scheme 5).

Chart 2. Structural possibilities in the reactions of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-o)]$_2$ with CuX (X=Cl, Br, I).

Scheme 5.

7. Heterometallic complexes of cyclodiphosphazanes

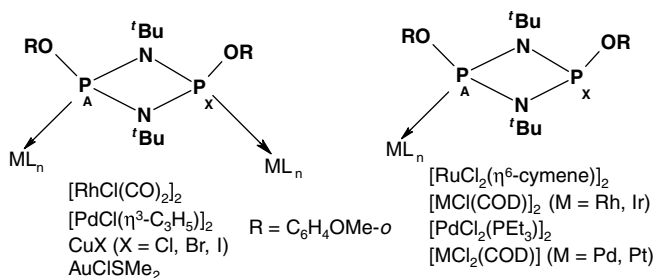Previously Krishnamurthy and coworkers have reported [4b,4c] molybdenum(0) based homo- and hetero-

Chart 3. Preferred coordination modes for various transition metals.

bimetallic complexes bridged by the cyclodiphosphazane, cis-[$^tBuNP(OC_6H_4Me$-$p)]_2$. Apart from this, there are no reports on any other heterometallic complexes of cyclodiphosphazanes. Our recent studies on transition metal chemistry of cyclodiphosphazane have shown the following preferential coordination modes (Chart 3) depending upon the type of metal derivatives employed in the complexation reactions. From the chart it is clear that some of the rhodium(I), palladium(II) and ruthenium(II) derivatives preferably form monocoordinated complexes leaving the other phosphorus(III) center uncoordinated. Interestingly, these isolated complexes containing a free phosphorus(III) end react further with various metal derivatives to give a series of heterometallic complexes [10,11] as shown in Scheme 6.

The complex **12** reacts with AuCl(SMe$_2$) to give heterobinuclear complex **26** in quantitative yield. Treatment of **12**
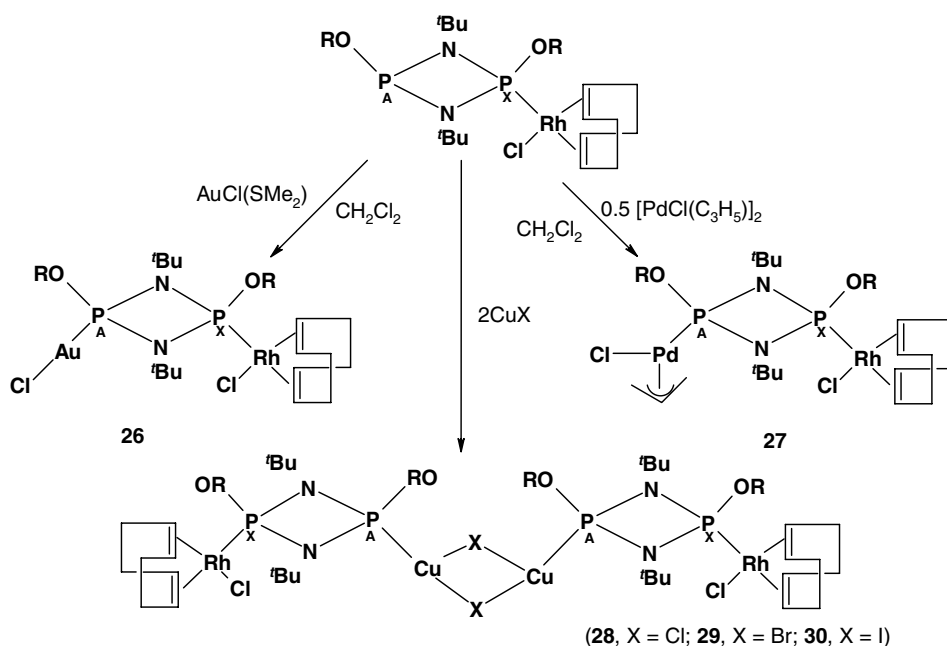
Scheme 6.

with 0.5 equivalent of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ produces Pd/Rh complex **27**, whereas the reaction between **12** and CuX (X = Cl, Br, I) produces tetranuclear ($2Rh^I/2Cu^I$) complexes (**28–30**) containing rhombic $[Cu(\mu\text{-}X)_2Cu]$ units as shown in Scheme 6. The ^{31}P NMR spectrum of **26** consists of two sets of doublet of doublets centered at 104.7 and 94.1 ppm assigned to gold- and rhodium-coordinated phosphorus centers respectively. The gold bound phosphorus center shows $^3J_{RhP}$ of 5.5 Hz along with a $^2J_{PP}$ of 30 Hz. The rhodium bound phosphorus center shows $^1J_{RhP}$ coupling of 247 Hz. The Pd/Rh complex **27** shows a doublet at 130.6 ppm ($^2J_{PP} = 37$ Hz) for palladium coordinated phosphorus center and a doublet of doublets centered at 94.1 ppm ($^1J_{RhP} = 240$ Hz) is assigned to rhodium bound phosphorus center. The complexes **28–30** show broad singlets in the range 90–93 ppm for copper coordinated phosphorus centers and the rhodium bound phosphorus centers appear as doublets in the region 91–93 ppm with an average $^1J_{RhP}$ of 235 Hz. The structures of complexes **26** and **28** have been confirmed by single crystal X-ray studies [10–12].

8. Summary

The cyclodiophosphazanes containing donor functionalities exhibit versatile coordination properties. The exclusive formation of either cis or trans palladium(II) complexes was achieved by using appropriate metal reagents. The reactions with Rh^I, Ir^I, Pd^{II} and Ru^{II} metal dimers selectively afforded the corresponding mononuclear complexes which are effectively used as metalloligands to generate a series of heterometallic complexes. Cyclodiphosphzanes containing ether functionalities were found to preferably form tetranuclear rhodium(I) complexes, whereas those with thioether and amine functionalities gave the corresponding bischelated complexes. The latter complexes are the first examples of cyclodiphosphazanes performing as eight-electron donor tetradenate ligands. The Cu^I coordination polymers of cyclodiphosphazanes undergo rare reversible transformations into the corresponding mononuclear complexes. Although, cis conformers are not kinetically suited for extending the linear propagation to give the coordination polymers, the formation of rhombic $[Cu(\mu\text{-}X)]_2$ units during the reaction and their flexible orientations and variable coordination numbers of Cu^I centers facilitated the formation of coordination polymers. Further preparation of polynuclear complexes and high nuclearity clusters of platinum metals is in progress.

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