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Cyclodiphosphazane cis-{(o-MeOC₆H₄O)P(μ -NtBu)}₂ as a Bridging Bidentate Ligand: Synthesis, Structures of Heterometallic Complexes, and Halogen Exchange Between Rh–Cl and Cu–X (X = Br, I)

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The mononuclear rhodium complexes of cyclodiphosphazane [(cod)RhCl{L- κ P}] (1a) (L = *cis*-{(*o*-MeOC₆H₄O)P(μ -N*t*Bu)}₂) and *trans*-[Rh(CO)Cl{L- κ P}₂] (1b) react in a 1:1 molar ratio with [AuCl(SMe₂)] to form the heteronuclear complexes [(cod)RhCl{ μ -L- κ P, κ P}AuCl] (2) and *trans*-[Rh(CO)-Cl{ μ -L- κ P, κ P}₂(AuCl)₂] (7), respectively, in quantitative yield. The reaction between 1a and CuCl afforded a tetranuclear complex [(cod)RhCl{ μ -L- κ P, κ P}Cu(μ -Cl)]₂ (3). Under similar reaction conditions 1 reacts with 2 equiv. of CuX (X = Br, I) to produce the heteronuclear complexes [(cod)RhBr{ μ -L- κ P, κ P}Cu(μ -Br)]₂ (4) and [((cod)RhI{ μ -L- κ P, κ P})₂Cu(μ -X)₂Cu] (X ≈ 1:1 mixture of Cl and I disordered over both sites) (5), respectively, in which two molecules of 1a are bridged by the rhombic, disordered, mixed halide [Cu(μ -X)₂Cu] (5: X = Br;

Introduction

The cooperativity or synergism present in heterometallic complexes gives remarkable chemical and biological properties compared to homonuclear complexes.^[1] These heteromultinuclear complexes have applications in the formation of new materials with useful physicochemical properties,^[2] and as polyfunctional catalysts for organic transformations.^[3] The ligand design is important for the synthesis of heteronuclear complexes because the dimensionality and topology of the final structures are predominantly controlled by the location of donor sites in the ligand and their coordination preferences towards different metal centers.^[4] Several phosphane ligands have been utilized for the synthesis of heterometallic complexes; however, in many cases formation of homonuclear complexes was observed along with the expected heterometallic complexes, due to the competition between different metal centers for the coordination sites and also due to the symmetric nature of bis(phosphanes). Preparation of heterometallic complexes can be **6**: X = Cl, I) unit. The crystal structures of **4** and **5** confirm the halogen exchange between the Rh–Cl and CuX (X = Br, I) moieties which leads to the formation of Rh–Br and Rh–I bonds. The heterodinuclear Rh^I/Pd^{II} complex [(cod)RhCl{ μ -L- κ P, κ P}PdCl(η^3 -C₃H₅)] (**6**) was synthesized by the reaction of **1a** with [PdCl(η^3 -C₃H₅)]₂ in a 2:1 ratio. Reaction of **1b** with CuI leads to the formation of the tetranuclear complex [Rh(CO)I{ μ -L- κ P, κ P}₂Cu(μ -I)]₂ (**8**) containing two terminal uncoordinated phosphorus(III) centers irrespective of reactant ratio and reaction conditions. Halogen exchange reaction which leads to the formation of the Rh–I bond was also observed during the preparation of complex **8**.

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made easier by choosing robust bidentate ligands which can perform as monodentate ligands under mild reaction conditions to give mononuclear complexes containing one or two free phosphorus(III) sites. These metalloligands containing uncoordinated phosphorus(III) centers can be conveniently treated with appropriate metal centers to form a variety of heterometallic complexes. In this context, cyclodiphosphazanes containing saturated four-membered P_2N_2 rings are interesting since they often exhibit monodentate coordination with several metal reagents under mild reaction conditions as shown in Scheme 1.^[5,6] These mononuclear complexes containing uncoordinated phosphorus centers can be utilized to form heterometallic complexes. Such complexes can be of importance in homogeneous catalysis to promote



Scheme 1.



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more than one type of catalysis and also for exploring the catalytic activity of multimetallic systems.^[7] As a continuation of our work on transition metal chemistry of phosphorus-based ligands and their catalytic applications,^[8] we describe in this article the synthesis and molecular structures of several heterometallic complexes of cyclodiphosphazanes.

Results and Discussion

Synthesis of Heterometallic Complexes

The rhodium(I) complex containing monocoordinated cyclodiphosphazane, $[(cod)RhCl{L-\kappa P}]$ (1a), chosen for the construction of heterometallic complexes was synthesized by treating cis-{(o-MeOC₆H₄O)P(μ -NtBu)}₂ (L) with [Rh(cod)Cl]₂ as described previously.^[6] The reaction of **1a** with 1 equiv. of [AuCl(SMe₂)] in dichloromethane at room temperature affords the heterodimetallic Rh^I/Au^I complex 2 in good yield as shown in Scheme 2. The ³¹P NMR spectrum of 2 consists of two sets of doublets of doublets centered at $\delta = 104.7$ and 94.1 ppm, respectively, for Au-coordinated and Rh-coordinated centers of the cyclodiphosphazane together with a low-intensity singlet at δ = 107.9 ppm attributable to the presence of a small amount of $[ClAu\{(o-MeOC_6H_4O)P(\mu-NtBu)\}_2AuCl].^{[9]}$ The formation of the dinuclear complex may be due to the replacement of the RhCl(cod) moiety present in 2 by [AuCl(SMe₂)] which was used in slight excess quantity for the complete conversion of 1a into 2. In order to confirm this metathesis reaction between Au and Rh centers, we carried out an NMRtube reaction between $[(cod)RhCl{L-\kappa P}]$ (1a) and 2 equiv. of [AuCl(SMe₂)] in CDCl₃. We observed complete conversion of 1a into dinuclear gold complex [ClAu{(o-MeO-C₆H₄O)P(µ-NtBu)}₂AuCl] as indicated by its ³¹P NMR



spectrum which shows a single resonance at $\delta = 107.9$ ppm. The gold-bound phosphorus center of **2** shows ${}^{2}J_{\rm PP}$ and ${}^{3}J_{\rm RhP}$ couplings of 30 and 5.5 Hz, respectively. The magnitude of ${}^{3}J_{\rm RhP}$ is comparable with literature values,^[10] while the rhodium-coordinated phosphorus atom shows a ${}^{1}J_{\rm RhP}$ coupling of 247 Hz along with ${}^{2}J_{\rm PP}$ However, compound **1a** did not show any ${}^{2}J_{\rm PP}$ coupling and the ${}^{1}J_{\rm RhP}$ coupling (229 Hz) was smaller than that of **2** (Table 1). The mass spectrum of **2** exhibits a peak at m/z = 893.21 which corresponds to the [M – Cl] ion (Figure 1).

Table 1. ³¹P{¹H} NMR spectroscopic data for complexes 1–7.

Compound	δ (RhP) [ppm]	$^{1}J_{\mathrm{RhP}}$ [Hz]	δ (MP) [ppm] (other J values [Hz])
1a	102.8 (d)	229	131.7 (s) ^[a]
1b	112.5 (d)	187	130.8 (s) ^[a]
2	94.1 (dd)	247	104.7 (dd, ${}^{2}J_{PP} = 30$, ${}^{3}J_{RhP} = 5.58)^{[b]}$
3	93.2 (d)	227	93.8 (br. s) ^[c]
4	93.0 (d)	236	92.3 (br. s) ^[c]
5	91.0 (d)	259	90.2 (br. s) ^[c]
6	94.1 (dd)	240	130.6 (d, ${}^{2}J_{\rm PP} = 37)^{\rm [d]}$
7	104.8 (d)	219	106.8 (s) ^[b]

[a] M = lone pair. [b] M = Au. [c] M = Cu. [d] M = Pd.

The equimolar reaction of **1a** with CuCl in CH₃CN/ CH₂Cl₂ produces the tetranuclear, dimetallic complex **3**. The ³¹P NMR spectrum of **3** exhibits a doublet at δ = 93.2 ppm for the rhodium-coordinated phosphorus atom of the cyclodiphosphazane, while the signal due to the coppercoordinated phosphorus atom appears as a broad singlet at δ = 93.8 ppm. Reaction of 2 equiv. of CuX (X = Br, I) with **1a** leads to the formation of heterotetranuclear derivatives [(cod)RhBr(μ -L- κ P, κ P)Cu(μ -Br)]₂ (**4**) and [{(cod)RhI(μ -L- κ P, κ P)}₂Cu(μ -X)₂Cu] (**5**), respectively. The rhombic [Cu(μ -X)₂Cu] unit in complex **5** contains a ca. 1:1 mixture of Cl and I disordered over both sites as indicated by X-ray dif-



Scheme 2.

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Figure 1. ³¹P{¹H} NMR (161 MHz) spectrum of 1a and 2 in CDCl₃.

fraction studies. Complexes 3-5 show a slight increase in their ${}^{1}J_{\rm RhP}$ values as the halide varies from chloride to iodide (3: 227; 4: 236; 5: 259 Hz). Similar variations in ${}^{1}J_{\rm RhP}$ have been seen in complexes containing the [RhXP₃] unit depending on the nature of the anionic ligand X situated *cis* to the phosphorus atom in question^[11] although the range is smaller than observed here. However, the remaining ligand set on Rh here is two C=C moieties which are weaker σ -donors than the two P atoms in the other examples and since the magnitude of ${}^{1}J_{\rm MP}$ is sensitive to the sorbital character in the M-P bond,^[12] there should be more s-orbital character to share between Rh and X in the present case. Thus, a larger variation in the s-orbital character of the Rh-P bond with the nature of the halide ligand might be expected. The X-ray crystal structure of 5 reveals the presence of an Rh-I bond instead of the Rh-Cl bond present in the starting complex as well as the presence of a rhombic [Cu(μ -X)₂Cu] unit which clearly contains a mixture of chloride and iodide but because the unit sits on a crystallographic center of symmetry, the two halides are disordered over the two bridging sites. This result was unexpected since CuI was used in the reaction and suggests that the halogen exchange reaction occurs between the Rh-Cl bond present in 1a and CuI to form the Rh-I derivative with concomitant formation of CuCl, which later coordinates to the uncoordinated phosphorus center of cyclodiphosphazane to produce a tetranuclear complex 5. This indicates that the halogen exchange 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 the HSAB principle.^[13]

The reaction of **1a** with $[PdCl(\eta^3-C_3H_5)]_2$ in dichloromethane in a 2:1 ratio produces the heterodinuclear complex $[(cod)RhCl(\mu-L-\kappa P,\kappa P)PdCl(\eta^3-C_3H_5)]$ (**6**) in good yield. The ³¹P NMR spectrum of **6** exhibits a doublet centered at $\delta = 130.6$ ppm with ${}^2J_{PP} = 37$ Hz for the palladiumcoordinated phosphorus atom, whereas the signal corresponding to the rhodium-coordinated phosphorus atom appears as a doublet of doublets centered at $\delta = 94.1$ ppm $({}^1J_{RhP} = 240$ Hz, ${}^2J_{PP} = 37$ Hz). Compounds **2–6** are stable solids and soluble in CH₂Cl₂, CHCl₃, and THF.

The complex *trans*-[Rh(CO)Cl(L- κ P)₂] (**1b**)^[6] containing two uncoordinated phosphorus centers from two *trans*-disposed cyclodiphosphazanes, when treated with 2 equiv. of [AuCl(SMe₂)] in dichloromethane, afforded trinuclear complex 7 in quantitative yield (Scheme 3). The ³¹P NMR spectrum of 7 consists of a singlet at $\delta = 106.8$ ppm, which is assigned to the gold-coordinated phosphorus centers. The doublet appearing at $\delta = 104.8$ ppm (¹J_{PRh} = 218 Hz) is due to the rhodium-coordinated phosphorus centers. The IR spectrum of 7 shows v_{CO} at 2019 cm⁻¹.

The slow addition of 2 equiv. of copper(I) iodide dissolved in acetonitrile to a dichloromethane solution of 1baffords complex 8 containing two Rh^I and two Cu^I centers



Scheme 3.

along with two uncoordinated P^{III} ends. Complex 8 crystallizes from the mother liquor at room temperature and the X-ray quality yellow crystals obtained are insoluble in most organic solvents, thus preventing solution spectroscopic characterization. The IR spectrum of 8 shows a strong v_{CO} band at 2021 cm⁻¹ which is slightly lower than that of the parent compound 1b.^[6] The analytical data for 8 indicate the formation of a 1:1 complex between 1b and CuI, and also the presence of an Rh-I bond. The structure of 8 was confirmed by low-temperature X-ray diffraction studies. Surprisingly, only one of the two dangling phosphorus(III) centers of complex 1b coordinates to CuI with the resulting dimetallic Rh/Cu complex dimerizing through the formation of a rhombic $[Cu(\mu-I)_2Cu]$ unit, leaving the other phosphorus(III) center uncoordinated. Since phosphorus prefers the softer CuI for coordination over the CuCl which is generated from the halogen exchange reaction, we carried out the reaction between 1b and CuI in a 1:3 ratio to force coordination of CuI to the heretofore uncoordinated phosphorus atom in anticipation of the formation of a heteronuclear metallopolymer containing rhodium(I) and $[Cu(\mu-I)_2Cu]$ units bridged by the cyclodiphosphazane. However, we observed exclusive formation of complex 8 in this reaction as well as under various other conditions.

Molecular Structures of 2, 4, 5, 7, and 8

Molecular structures of complexes 2, 4, 5, 7, and 8 with atom numbering schemes are shown in Figures 2, 3, 4, 5, and 6, respectively. Crystallographic information and the details of the structure determination are summarized in Table 6. The pertinent bond lengths and bond angles are listed in Tables 2, 3, and 4. A compilation of Cremer–Pople puckering parameters^[14] for the cyclodiphosphazane rings in 2, 4, 5, 7, and 8 appears in Table 5.

X-ray quality crystals of **2** were grown from a 1:1 solution of CH₂Cl₂/Et₂O at -30 °C. In complex **2**, the cyclodiphosphazane bridges the rhodium(I) and gold(I) moieties in a *cis* fashion through P-coordination. As noted in the previous section, the crystal used for the structure determination proved to contain about 3.8% of cocrystallized



Figure 2. Molecular structure of **2**. Ellipsoids are drawn at the 50% probability level and H atoms and solvent molecules are omitted for clarity.

 $[ClAu\{(o-MeOC_6H_4O)P(\mu-NtBu)\}_2AuCl]$, but this impurity appears to have no effect on the derived structural parameters for 2. Previously, Krishnamurthy and co-workers have reported^[15] the crystal structure of a heterodimetallic Mo⁰/ W^0 complex containing μ -cyclodiphosphazane, *cis*-[(*p*-Me- C_6H_4O $P(\mu$ -NPh)]₂, which is the only structurally characterized heterometallic complex of cyclodiphosphazanes to date. The geometry around the gold center in complex 2 is linear with a P2-Au-Cl2 angle of 178.36(3)°, whereas the rhodium center is in a distorted square-planar environment. The P1-Rh bond length is 2.2269(8) Å, which is considerably shorter than that in the parent compound 1 [2.2439(9) Å]. The Rh–Cl and Rh–C bond lengths are almost equal in both the complexes [Rh-Cl 2.3605(5) Å for 1b, 2.3612(9) Å for 2]. The presence of a shorter Rh–P bond in 2 is also reflected in its ³¹P NMR spectrum, which shows a large ${}^{1}J_{\rm RhP}$ coupling of 247 Hz, whereas that in complex 1 is 229 Hz. The Au–P2 bond length in 2 is 2.2084(8) Å, which is comparable to that found in the mononuclear gold complex $[ClAu\{(o-MeOC_6H_4O)P(\mu-NtBu)\}_2]$ [2.210(1) Å].^[9] Assessment of these bond parameters suggests a stronger metal-ligand interaction in the heterodimetallic complex 2 as compared to the homodimetallic complex. The exocyclic phenyl substituents on the phosphorus centers are arranged in an *exo*, endo manner. The P_2N_2 ring present in 2 is unevenly puckered (see Table 5) with the sum of the angles around N1 and N2 being 359.00(18)° and 355.46(12)°, respectively. The crystal structure of 2 contains a molecule of dichloromethane in the lattice which forms a weak C-H…Cl hydrogen bond with the chlorido ligand on the rhodium atom (C21-H31A···Cl1 153°; H31A···Cl1 2.56 Å which is significantly less than the 2.88 Å average normalized distance determined previously for this type of interaction^[16]). The other hydrogen atom on this solvent molecule (H31B) makes a contact of less than the sum of the van der Waals radii with the chlorido ligand on the gold atom (Cl2), but the C-H···Cl angle is too small for this to be considered a hydrogen bond.



Figure 3. Molecular structure of 4. Ellipsoids are drawn at the 50% probability level and H atoms and substituents on N (except α -C) are omitted for clarity.



Figure 4. Molecular structure of 5. Ellipsoids are drawn at the 50% probability level and H atoms and substituents on N (except α -C) are omitted for clarity.



Figure 5. Molecular structure of 7. Ellipsoids are drawn at the 50% probability level and H atoms and substituents on N (except α -C) are omitted for clarity.



Figure 6. Molecular structure of 8. Ellipsoids are drawn at the 50% probability level and H atoms and substituents on N (except α -C) are omitted for clarity.

Table 2. Selected bond lengths [Å] and bond angles [°] for 2.

Bond lengths		Bond angles			
Rh–P1	2.2269(8)	P1-Rh-Cl1	88.91(3)		
Au-P2	2.2084(8)	P2-Au-Cl2	178.36(3)		
Rh-Cl1	2.3612(9)	P1-Rh-C23	164.7(1)		
Au-Cl2	2.2868(8)	P1-Rh-C24	159.9(1)		
Rh-C23	2.245(3)	P1-Rh-C27	91.52(9)		
Rh–C24	2.254(3)	P1-Rh-C28	95.79(9)		
Rh–C27	2.123(3)	C23-Rh-C28	81.6(1)		
Rh–C28	2.128(3)	C23-Rh-C24	35.4(1)		
P1-N1	1.693(2)	P1-N1-P2	96.2(1)		
P1-N2	1.704(3)	P1-N2-P2	95.6(1)		
P2-N1	1.667(2)	N1-P1-N2	82.8(1)		
P2-N2	1.673(3)	N1-P2-N2	84.5(1)		
P1O1	1.607(2)	P1-O1-C9	127.7(2)		
P2-O3	1.607(2)	P2-O3-C16	125.7(2)		
N1-C1	1.494(4)	P1-N1-C1	131.32(20)		
N2-C5	1.496(4)	P2-N1-C1	131.48(20)		

Crystals of 4 and 5 suitable for X-ray structure determination were obtained by slow evaporation of dichloromethane from respective 1:1 CH₃CN/CH₂Cl₂ solutions at room temperature. The core structures of 4 and 5 consist of a rhombic [Cu(μ -X)₂Cu] [X = Br (4) and X = apparent equimolar mixture of Cl and I (5)] unit bridging the two [(cod)-RhX] (X = Br, I) moieties through two cyclodiphosphazanes as shown in Figures 3 and 4, respectively. Because the [Cu(μ -X)₂Cu] unit in 5 sits on a crystallographic center of symmetry, the bridging chlorido and iodido ligands are necessarily disordered, so it is not possible to say whether each molecule actually has a discrete [Cu(μ -Cl)(μ -I)Cu] unit at its center or if a more random distribution of Cl and I is present. The best model for refinement proved to be one in which Cl and I were given the same atomic coordinates and

Table 3. Selected bond lengths [Å] and bond angles [°] for 4 and 5.

Bond lengths		Bond angles			
Complex 4					
Rh–P1	2.243(2)	Br1-Rh-P1	89.72(4)		
Rh–Br1	2.484(2)	Br1-Rh-C26	91.45(18)		
Rh–P1	2.243(2)	Br1-Rh-P1	89.72(4)		
Rh–Br1	2.484(2)	Br1-Rh-C26	91.45(18)		
Rh-C23	2.153(6)	Br1-Rh-C27	90.19(19)		
Rh-C26	2.234(6)	P1-Rh-C23	93.11(16)		
Rh-C27	2.261(6)	P1-Rh-C30	94.30(18)		
Rh-C30	2.112(6)	C23-Rh-C26	81.0(2)		
Cu–P2	2.154(2)	Br2–Cu–P2	136.71(6)		
Br2–Cu	2.370(2)	Cu-Br2-Cu ⁱ	80.50(4)		
P1O1	1.630(4)	Br2-Cu-Br2i	99.50(4)		
P2-O3	1.625(4)	P2-Cu···O4	79.87(12)		
P1-N1	1.685(5)	Cu-P2-O3	110.99(17)		
P1-N2	1.690(5)	P1O1C9	128.1(4)		
P2-N1	1.706(5)	P2-O3-C16	125.2(3)		
P2-N2	1.692(5)	P1-N1-P2	96.5(3)		
Cu···O4	2.691(4)	P1-N2-P2	96.8(3)		
CuCu ⁱ	3.082	N1-P1-N2	83.6(2)		
		N1-P2-N2	82.9(2)		
Complex 5					
Rh–P1	2.2318(9)	P1-Rh-I2	88.30(2)		
Cu–P2	2.166(1)	P1-Rh-C23	157.5(1)		
Rh–I2	2.6779(4)	P1-Rh-C24	167.4(1)		
Rh-C23	2.256(3)	P1-Rh-C27	93.9(1)		
Rh-C24	2.279(3)	P1-Rh-C28	94.8(1)		
Rh-C27	2.122(3)	C23-Rh-C28	80.5(1)		
Rh-C28	2.154(3)	C23-Rh-C24	35.1(1)		
Cu- (Cl,I1)	2.4894(7)	P2Cu(Cl,I1)	130.59(4)		
$Cu-(Cl^i,I1^i)$	2.4647(7)	$P2-Cu-(Cl^i,I1^i)$	123.40(3)		
P1-N1	1.691(3)	$(Cl,I1)$ – Cu – $(Cl^i,I1^i)$	103.79(2)		
P1-N2	1.681(3)	Cu-(Cl,I1)-Cu ⁱ	76.21(2)		
P2-N1	1.694(3)	P1-N1-P2	96.2(2)		
P2-N2	1.686(3)	P1-N2-P2	96.9(2)		
CuCu ⁱ	3.033	N1-P1-N2	82.9(1)		
		N1-P2-N2	82.6(1)		

displacement parameters after which refinement of occupancy factors converged at ca. 0.5 for each atom type. Copper complexes containing mixed halide bridges are rare but in a copper(I) complex containing a mixed halide [Cu₄Br₂Cl₂] unit of distorted cubane geometry a 50:50 occupancy of all bridging halide sites was used as the model for refinement of the structure as we have done here. A similar disorder model was used in refining the structures of a series of $[Cu_2Cl_{6-x}Br_x]^{2-}$ (x = 0.70–4.78) salts.^[17] Copper centers adopt a distorted trigonal-planar geometry in both the molecules 4 and 5. The bromo derivative 4 shows larger P2–Cu–Br [136.71(6)°] and short Br–Cu–Brⁱ angles [99.50(4)°] compared with 5 [P2–Cu–Xⁱ 130.59(4)°, X–Cu– X^{i} 103.79(2)°]. In structure 4, the OMe groups present on exocyclic phosphorus substituents show strong interaction with the copper center [Cu···O4 2.691(4) Å], and this interaction leads to the formation of a boat-shaped six-membered ring around each copper center. However, complex 5 does not show such Cu-O interactions. The rhodium centers in 4 and 5 are located in the center of a distorted square-planar environment with the corners being occupied by iodido, phosphorus, and 1,5-cyclooctadiene ligands. The Rh–P1 bond lengths in 4 and 5 are 2.243(1) and 2.232(1) Å,

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Table 4. Selected bond lengths [Å] and bond angles [°] for 7 and 8.

Bond lengths		Bond angles			
Complex 7					
Rh–P1	2.2687(7)	P1-Rh-Cl1	88.80(2)		
Rh-Cl1	2.341(1)	P1-Rh-C1	91.12(2)		
Rh–C1	1.841(4)	P1–Rh–P1 ⁱ	176.33(4)		
Au–P2	2.1968(7)	Cl1-Rh-Cl	176.6(1)		
Au-Cl2	2.2720(7)	Au-P2-O4	113.61(8)		
C101	1.133(5)	P2-Au-Cl2	179.70(3)		
P1-N1	1.699(2)	P1-N1-P2	95.8(1)		
P1-N2	1.689(2)	P1-N2-P2	96.1(1)		
P2-N1	1.671(2)	N1-P1-N2	82.9(1)		
P2-N2	1.674(2)	N1-P2-N2	84.2(1)		
P1O2	1.608(2)	P1-O2-C10	126.9(2)		
P2O4	1.606(2)	P2O4C17	125.4(2)		
Complex 8					
P2–Rh	2.288(2)	P2-Rh-C45	91.0(2)		
P3–Rh	2.302(2)	P3-Rh-C45	87.8(2)		
P1–Cu	2.173(2)	P2-Rh-I2	88.19(4)		
Rh–I2	2.6799(7)	P3–Rh–I2	93.00(4)		
Rh–C45	1.832(7)	P2-Rh-P3	178.25(6)		
Cu–I1	2.505(1)	I2-Rh-C45	179.1(2)		
Cu ⁱ –I1	2.564(1)	P1-Cu-I1	128.95(6)		
P1-N1	1.701(5)	P1-Cu-I ⁱ	122.46(6)		
P1-N2	1.701(5)	I1–Cu–I ⁱ	105.01(3)		
P2-N1	1.683(5)	Cu–I1–Cu ⁱ	74.99(3)		
P2-N2	1.686(5)	P1-N1-P2	95.9(3)		
P3-N3	1.671(5)	P1-N2-P2	95.7(3)		
P3-N4	1.685(5)	N1-P1-N2	82.6(3)		
P4–N3	1.716(5)	N1-P2-N2	83.6(3)		
P4-N4	1.725(6)	P3-N3-P4	97.7(7)		
CuCu ⁱ	3.085	P3-N4-P4	96.8(3)		
Cu···I2	3.262	N3-P3-N4	83.1(3)		
		N3-P4-N4	80.6(2)		

Table 5. Cremer–Pople puckering parameters for the cyclodiphosphazane in 2, 5, 7, and 8.

Complex	Q_2 [Å]	Dihedral angle [°] P1–N1–N2 vs. N1–P2–N2	Dihedral angle [°] P1–N1–P2 vs. P1–P2–N2
2	0.106	170.3	169.2
5	-0.131	168.2	166.7
7	-0.111	169.8	168.7
8	0.167	164.8	163.0
	0.155 ^[a]	166.2 ^[b]	164.2 ^[c]

[a] For the P3–N3–P4–N4 ring. [b] Dihedral angle P3–N3–N4 vs. P3–N4–P4. [c] Dihedral angle P3–N3–P4 vs. P3–P4–N4.

respectively, which is slightly shorter than that in the parent complex **1a**. The Cu···Cuⁱ separation of 3.082(1) and 3.057(1) Å, respectively, in complexes **4** and **5**, indicate the absence of cuprophilicity.^[18] The two rhodium moieties present in **4** and **5** are arranged in a *trans* disposition with respect to the [Cu(μ -X)₂Cu] plane; however, the molecules maintain the *cis* disposition of substituents on the phosphorus atom with respect to the P₂N₂ plane as was found in the molecular structure of **1a**.

Single crystals of 7 were grown by slow diffusion of hexane into a dichloromethane solution of the complex at room temperature. Complex 7 contains two gold centers bridged by rhodium-bound cyclodiphosphazanes to form a trinuclear complex with a conformation very similar to that of the parent complex 1b. The geometry around the rhodium center is slightly distorted square-planar with cis angles varying from 88.80(2) (P1-Rh-Cl1) to 91.12(2)° (P1-Rh-C1). The gold centers are dicoordinated and have a linear geometry with a P2-Au-Cl2 angle of 179.70(3)° which is more linear than that in the monometallic complex of the same ligand [176.83(2)°] but comparable with that in Ph₃PAuCl [179.63(2)°].^[19] The Rh-P1 distance in 7 is 2.2687(7) Å, which is shorter than those in the parent compound [1b: 2.2784(6), 2.2863(6) Å] – a situation comparable to that in the Rh^I/Au^I complex 2. The Au–P2 bond length is 2.1968(7) Å which is slightly shorter than that in 3 but much shorter than that in the mononuclear gold complex of the same ligand, $[AuCl({(o-MeOC_6H_4O)P(\mu-NtBu)}_2 \kappa$ P)].^[11] The phenyl substituents on the phosphorus centers are arranged in an exo, endo manner.

Crystals of 8 suitable for X-ray diffraction studies were obtained from a CH2Cl2/CH3CN solution at room temperature. The core structure of 8 consists of two trans- $Rh(P_2N_2)_2$ moieties that are bridged by a $[Cu(\mu-I)_2Cu]$ unit to form a heterometallic complex containing two Rh^I and two Cu^I centers along with an uncoordinated P^{III} site at each end. These two trans-Rh(P2N2)2 moieties are oriented in a *trans* manner with respect to the plane of the rhombic $[Cu(\mu-I)_2Cu]$ unit and gives the molecule an overall S-shape. The rhodium centers are in distorted square-planar geometries, whereas the copper centers are in trigonal-planar environments. The Rh–P2 bond [2.288(2) Å] is shorter than the Rh–P3 distance [2.302(2) Å] while the distance between the two copper atoms (Cu···Cuⁱ) is 3.085 Å at 100 K, which indicates the absence of metal-metal interactions in complex 8. This stands in contrast to the low-temperature structure of (Cy₃P)Cu(µ-I)₂Cu(PCy₃) in which the Cu···Cu separation is 2.893(2) Å.^[20] Interestingly, the molecular structure of 8 shows a weak interaction between the copper and iodine atoms to form two six-membered rings based on the observation that the Cu-I2 distance is 3.262 Å, which is distinctly shorter than the sum of the van der Waals radii for the two atoms (3.38 Å).^[21] There are no unusually short intermolecular contacts apparent that would flex the molecule so as to cause I2 to approach Cu more closely than a van der Waals contact, but since the distance is much longer than normal bonding distances [2.525(4)-2.640(2) Å], ^[22] it is a weak attractive interaction at best. There also appears to be a distinct C-H···I hydrogen bond between the aromatic hydrogen atom H27 and I1 (H27...I1 2.993 Å; C27-H27...I1 156.05°) as the H27...I1 distance is less than the 3.15 Å mean H…I1 distance considered indicative of a C-H····I hydrogen bond.^[16]

Conclusions

Several heterodi-, -tri-, and -tetrametallic complexes [Cu^I/Rh^I (3d/4d), Pd^{II}/Rh^I (4d/4d), and Au^I/Rh^I (5d/4d)] containing cyclodiphosphazanes are described. The selective mono- and bidentate coordination modes exhibited by cyclodiphosphazane with a range of metal precursors gives

a facile synthetic approach for construction of heterometallic systems. The halogen exchange reaction was observed for the first time between Rh–Cl and Cu–X (X = Br, I) during the synthesis of Cu^I/Rh^I derivatives. Formation of rhombic [Cu(μ -X)₂Cu] units increases the nuclearity and can be utilized for the synthesis of a series of heterometallic coordination polymers. The work in this direction is currently underway in our laboratory.

Experimental Section

General: All manipulations were performed under rigorously anaerobic conditions using high-vacuum manifolds and Schlenk techniques. All the solvents were purified by conventional procedures and freshly distilled and degassed prior to use.^[23] Compounds *cis*-{(*o*-MeOC₆H₄O)P(μ -N*t*Bu)}₂ (L), [(cod)RhCl{L- κ P}] (1a), *trans*-[Rh(CO)Cl{L- κ P}₂] (1b),^[6] [AuCl(SMe₂)],^[24] CuX (X = Cl, Br)^[25], and [PdCl(η -C₃H₅)]₂^[26] were prepared according to published procedures. CuI was purchased from commercial sources and used as received.

Instrumentation: ¹H and ³¹P{¹H} NMR (δ in ppm) spectra were recorded with a Varian Mercury Plus spectrometer operating at the appropriate frequencies using TMS and 85% H₃PO₄ as internal and external references, respectively. IR spectra of KBr disks were recorded with a Nicolet Impact 400 FT-IR instrument. Microanalyses were performed with a Carlo Erba Model 1112 elemental analyzer. Mass spectrometry experiments were carried out with a Waters Q-Tof micro-YA-105 instrument. Melting points were recorded in capillary tubes and are uncorrected.

Synthesis of [(cod)RhCl{μ-L-κP,κP}AuCl] (2): A dichloromethane solution (5 mL) of [AuCl(SMe₂)] (22.2 mg, 0.075 mmol) was added dropwise to a well-stirred dichloromethane solution (7 mL) of [(cod)RhCl{L-κP}] (1a) (52.5 mg, 0.075 mmol) at room temperature. The resulting yellow reaction mixture was stirred for 4 h. The solution was concentrated to 5 mL under reduced pressure, diluted with 5 mL of Et₂O and stored at –30 °C for 1 d to give the product as yellow crystals (62.4 mg, 89%). M.p. 222–224 °C (dec). $C_{30}H_{44}AuCl_2N_2O_4P_2Rh$ (929.4): calcd. C 38.76, H 4.77, N 3.01; found C 38.50, H 4.74, N 3.22. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.78–6.79 (m, 8 H, Ph), 5.77, 4.33 (br. s, 4 H, CH), 3.85 (s, 3 H, OMe), 3.82 (s, 3 H, OMe), 2.49–2.24 (m, 8 H, CH₂), 1.66 (s, 18 H, *t*Bu) ppm. ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 25 °C): δ = 104.7 (dd, ²J_{PP} = 30 Hz, ³J_{RhP} = 5.58 Hz, 1 P, PAu), 94.1 (dd, ¹J_{PRh} = 247 Hz, 1 P, PRh) ppm. MS (EI): *m*/*z* = 893.21 [M – CI].

Synthesis of [(cod)RhCl{μ-L-κP,κP}Cu(μ-Cl)]₂ (3): Copper(I) chloride (4.5 mg, 0.045 mmol), dissolved in acetonitrile (5 mL), was added dropwise to a well-stirred CH₂Cl₂ solution (10 mL) of [(cod)RhCl{L-κP}] (1a) (31.1 mg, 0.045 mmol) at room temperature. The resulting yellow reaction mixture was stirred for 6 h. The solution was concentrated to 5 mL under reduced pressure, diluted with Et₂O (5 mL) and stored at -30 °C for 1 d to afford yellow crystals of the product (33.9 mg, 61%). M.p. 228–230 °C (dec). C₆₀H₈₈Cl₄Cu₂N₄O₈P₄Rh₂ (1519.9): calcd. C 45.26, H 5.57, N 3.51; found C 45.53, H 5.39, N 3.44. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.89–6.84 (m, 16 H, Ph), 5.72, 4.32 (s, 8 H, CH), 3.93 (s, 6 H, OMe), 3.81 (s, 6 H, OMe), 2.48–2.22 (m, 16 H, CH₂), 1.57 (s, 36 H, *t*Bu) ppm. ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 25 °C): δ = 93.8 (br. s, 2 P, CuP), 93.2 (d, ¹J_{PRh} = 227 Hz, 2 P, RhP) ppm.

Synthesis of $[(cod)RhBr{\mu-L-\kappa P,\kappa P}Cu(\mu-Br)]_2$ (4): The synthesis was the same as that for 3, using copper(I) bromide (18.4 mg,

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0.128 mmol) and [(cod)RhCl{L- κ P}] (1a) (44.9 mg, 0.064 mmol). Yield: 74% (42.07 mg). M.p. 236–238 °C (dec). C₆₀H₈₈Br₄Cu₂N₄-O₈P₄Rh₂ (1769.7): calcd. C 40.71, H 5.01, N 3.16; found C 40.94, H 5.17, N 3.24. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.94–6.84 (m, 16 H, Ph), 5.78, 4.44 (m, 8 H, CH), 3.93 (s, 6 H, OMe), 3.82 (s, 6 H, OMe), 2.41–2.19 (m, 16 H, CH₂), 1.55 (s, 36 H, *t*Bu) ppm. ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 25 °C): δ = 93.0 (d, ¹J_{PRh} = 236 Hz, 2 P, RhP), 92.3 (br. s, 2 P, CuP) ppm.

Synthesis of [((cod)RhBr{μ-L-κP,κP})₂Cu(μ-Cl,I)Cu] (5): The synthesis was the same as that for **3**, using copper(I) iodide (27.5 mg, 0.144 mmol) and [(cod)RhCl{L-κP]] (**1a**) (50.3 mg, 0.072 mmol). Yield: 85% (57.10 mg). M.p. 224–226 °C (dec). $C_{60}H_{88}ClCu_2I_3N_4-O_8P_4Rh_2$ (1866.3): calcd. C 38.61, H 4.75, N 3.00; found C 38.83, H 4.81, N 3.07. ¹H NMR (400 MHz, CDCI₃, 25 °C): δ = 7.98–6.87 (m, 16 H, Ph), 5.87, 4.67 (br. s, 8 H, CH), 3.82 (s, 6 H, OMe), 3.81 (s, 6 H, OMe), 2.47–2.01 (m, 16 H, CH₂), 1.53 (s, 36 H, *t*Bu) ppm. ³¹P{¹H} NMR (161.9 MHz, CDCI₃, 25 °C): δ = 91.0 (d, ¹J_{PRh} = 259 Hz, 2 P, RhP), 90.2 (br. s, 2 P, CuP) ppm.

Synthesis of [(cod)RhCl{µ-L-κP,κP}PdCl(η³-C₃H₅)] (6): A dichloromethane solution (5 mL) of $[PdCl(\eta^3-C_3H_5)]_2$ (16.9 mg, 0.046 mmol) was added dropwise to a well-stirred dichloromethane (10 mL) solution of $[(cod)RhCl{L-\kappa P}]$ (1a) (64.6 mg, 0.093 mmol) at room temperature. The reaction mixture was stirred for 6 h, concentrated to 5 mL under reduced pressure, diluted with diethyl ether (5 mL) and stored at -30 °C for 1 d to give a yellow crystalline solid (61.3 mg, 75%). M.p. 160-162 °C (dec). C33H49Cl2N2O4P2PdRh (879.9): calcd. C 45.04, H 5.61, N 3.18; found C 45.31, H 5.82, N 3.37. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.79–6.76 (m, 8 H, Ph), 5.60 (br. s, 1 H, allyl CH), 5.73, 4.32 (s, 4 H, cod CH), 4.66, 3.65 (m, 4 H, allyl CH₂), 3.84 (s, 3 H, OMe), 3.82 (s, 3 H, OMe), 2.46-2.25 (m, 8 H, CH₂), 1.57 (s, 18 H, *t*Bu) ppm. ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 25 °C): δ = 130.6 $(d, {}^{2}J_{PP} = 37 \text{ Hz}, 1 \text{ P}, \text{PPd}), 94.1 (dd, {}^{1}J_{PRh} = 240 \text{ Hz}, 1 \text{ P}, \text{PRh})$ ppm.

Synthesis of trans-[Rh(CO)Cl{µ-L-KP,KP}2(AuCl)2] (7): To a suspension of trans-[Rh(CO)Cl{L- κ P}₂] (1b) (100 mg, 0.093 mmol) in acetonitrile (5 mL), a dichloromethane solution (10 mL) of [AuCl-(SMe₂)] (55.1 mg, 0.187 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 4 h, concentrated to 10 mL under reduced pressure, and diluted with hexane (5 mL). Storing the resulting clear yellow solution overnight afforded a crystalline product (132 mg, 93%). M.p. 236–238 °C. C45H64Au2Cl3N4O9P4Rh (1532.1): calcd. C 35.27, H 4.21, N 3.65; found C 35.02, H 4.10, N 3.88. IR (KBr disk): ṽ = 2019 [v(C≡O)] cm⁻¹. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.31–6.91 (m, 16 H, Ph), 3.93 (s, 6 H, OMe), 3.91 (s, 6 H, OMe), 1.73 (s, 36 H, tBu) ppm. ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 25 °C): δ = 106.8 (s, 2 P, PAu), 104.8 (d, ${}^{1}J_{PRh}$ = 218.5 Hz, 2 P, PRh) ppm.

Synthesis of [Rh(CO)I{ μ -L- κ P, κ P}₂Cu(μ -I)]₂ (8): Copper(I) iodide (0.019 g, 0.101 mmol) in CH₃CN (5 mL) was added dropwise to a well-stirred dichloromethane solution (10 mL) of *trans*-[Rh(CO)-Cl{L- κ P}₂] (1b) (0.054 g, 0.051 mmol) at room temperature. The reaction mixture was stirred for 6 h. Upon standing at room temperature for 3 d, the yellow solution afforded compound 8 as dark yellow crystals (47.5 mg, 69%). M.p. 248–250 °C (dec). C₉₀H₁₂₈-Cu₂I₄N₈O₁₈P₈Rh₂ (2698.3): calcd. 40.06, H 4.78, N 4.15; found C 40.38, H 4.42, N 4.27. IR (KBr disk): $\tilde{\nu} = 2021$ [ν (C=O)] cm⁻¹.

X-ray Crystallography: Crystals of **2**, **4**, **5**, **7**, and **8** were mounted in a CryoLoop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer (Table 6). For each, a full sphere of data was collected using a protocol of 400 scans in ω (0.5° per scan) at ϕ =

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Table 6.	Crystallograph	ic parameters and	d refinement	details for	complexes 2,	4, 5, 7, and 8.
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	$2 \cdot CH_2Cl_2$	4	5	7	8
Empirical formula	C ₃₁ H ₄₆ AuCl ₄ N ₂ O ₄ P ₂ Rh	C ₆₀ H ₈₈ Br ₄ Cu ₂ N ₄ O ₈ P ₄ Rh ₂	C ₆₀ H ₈₈ ClCu ₂ I ₃ N ₄ O ₈ P ₄ Rh ₂	C45H64Au2Cl3N4O9P4Rh	C ₉₀ H ₁₂₈ Cu ₂ I ₄ N ₈ O ₁₈ P ₈ Rh ₂
Formula mass	1023.61	1769.76	1866.27	1532.08	2698.29
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$	PĪ	$P2_1/c$	Pnma	PĪ
a [Å]	11.161(1)	9.863(1)	10.7191(8)	13.642(1)	12.119(1)
b [Å]	17.253(2)	10.319(1)	18.665(1)	29.323(3)	15.336(2)
c [Å]	19.776(2)	18.877(2)	17.017(1)	15.236(1)	16.499(2)
a [°]	90	91.670(1)	90	90	106.365(1)
β [°]	100.281(1)	98.434(1)	91.675(1)	90	103.718(1)
γ [°]	90	114.655(1)	90	90	104.491(1)
V [Å ³]	3746.9(6)	1718.3(3)	3403.1(4)	6094.6(9)	2687.8(5)
Ζ	4	1	4	4	1
$\rho_{\rm calcd.} [\rm g cm^{-3}]$	1.815	1.710	1.812	1.670	1.667
μ (Mo- K_a) [mm ⁻¹]	4.758	3.554	2.641	5.355	2.024
F(000)	2015	888	1834	2992	2696
Crystal size [mm]	$0.10 \times 0.15 \times 0.18$	$0.05 \times 0.15 \times 0.19$	$0.15 \times 0.17 \times 0.20$	$0.09 \times 0.17 \times 0.17$	$0.17 \times 0.13 \times 0.06$
T [K]	100	100	100	100	100
θ range [°]	2.1-28.3	2.2-28.2	2.2–28.3	1.4-28.3	1.4-28.3
Total no. reflns.	65502	29820	59384	52609	23883
No. of indep. reflns.	9318 ($R_{int} = 0.041$)	8357 ($R_{int} = 0.051$)	8484 ($R_{\rm int} = 0.035$)	7582 ($R_{int} = 0.037$)	12230 ($R_{int} = 0.025$)
$R_1^{[a]}$	0.0269	0.0558	0.0381	0.0255	0.0635
$wR_2^{[b]}$	0.0636	0.1602	0.1056	0.0615	0.1926
Goodness-of-fit on F^2	1.05	1.03	0.97	1.04	1.04

[a] $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$. [b] $wR_2 = \{ [\Sigma w (F_0^2 - F_c^2) / \Sigma w (F_0^2)^2] \}^{1/2}$.

0, 90, and 180° plus 800 scans in ϕ (0.45° per scan at $\omega = -30$ and 210° for 2, 4, and 5) and one of 606 scans in ω (0.3° per scan) at $\phi = 0$, 120, and 240° for 7 and 8 using the SMART software package.^[27] The raw data were reduced to F^2 values using the SAINT+ software^[28] and global refinements of unit cell parameters employing 8555-9267 reflections chosen from the full data set were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS^[29]). The structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package.^[30] Hydrogen atoms were placed in calculated positions [C-H 0.95 Å (aromatic rings) or 0.98 Å (methyl groups)] and included as riding contributions with isotropic displacement parameters 1.2 (aromatic rings) or 1.5 (methyl groups) times those of the attached non-hydrogen atoms. Near the end of the refinement of the structure of 2, two significant peaks were observed in a difference map near the rhodium atom which formed a linear unit with P1. These were treated as the second Au and Cl atoms of the [ClAu{(o-MeOC₆H₄O)P(µ-NtBu)}₂AuCl] impurity which had been identified by NMR spectroscopy in the original sample and which presumably had cocrystallized with 2. Addition of these to the model significantly improved the refinement and resulted in a refined occupancy of the digold complex impurity of 0.038. CCDC-642038 (2), -642039 (4), -642040 (5), -642041 (7), and -642042 (8) contain the supplementary crystallographic data for this paper. This can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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