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Tetraphosphinitoresorcinarene Complexes: Cationic Silver(I) and Copper(I) Halide Complexes as Mercurate(II) Anion Receptors

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The reactions of mercury(II) halides with the tetraphosphinitoresorcinarene complexes $[P_4M_5X_5]$, where M = Cu or Ag, X = Cl, Br, or I, and $P_4 = (PhCH_2CH_2CHC_6H_2)_4(O_2CR)_4(OPPh_2)_4$ with R = C_6H_{11}, 4-C_6H_4Me, C_4H_3S, OCH_2CCH, or OCH_2Ph, have been studied. The reactions of the complexes with HgX_2 when M = Ag and X = Cl or Br occur with elimination of silver(I) halide and formation of $[P_4Ag_2X(HgX_3)]$, but when M = Ag and X = I, the complexes $[P_4Ag_4I_5(HgI)]$ are formed. When M = Cu and X = I, the products were the remarkable capsule complexes $[(P_4Cu_2I)_2(Hg_2X_6)]$. When M = Ag and X = I, the reaction with both CuI and HgI_2 gave the complexes $[P_4Cu_2I(Hg_2I_5)]$. Many of these complexes are structurally characterized as containing mercurate anions weakly bonded to cationic tetraphosphinitoresorcinarene complexes of copper(I) or silver(I) in an unusual form of host–guest interaction. In contrast, the complex $[P_4Ag_4I_5(HgI)]$ is considered to be derived from an anionic silver cluster with an iodomercury(II) cation. Fluxionality of the complexes in solution is interpreted in terms of easy, reversible making and breaking of secondary bonds between the copper(I) or silver(I) cations and the mercurate anions.

Introduction

There is continuing interest in the design of coordination compounds which can function as cation or anion receptors.[1–4] Anion receptors are of current interest because they have potential applications as sensors[2] and in the recovery of environmental pollutants.[3] The bowl-like calixarenes and resorcinarenes are versatile host molecules, and derivatives have been designed that can accommodate neutral, cationic, or anionic guests.[1–6] In particular, cone-shaped tetraphosphonitoresorcinarene derivatives, such as the ligand **1** (Chart 1, M = Ag, X = I), form complexes of silver(I) and copper(I) halides which can act as receptors for either anions or salts.[6] To develop this chemistry further, the more flexible tetraphosphinitoresorcinarene ligands **2** (Chart 1, abbreviated below as P_4) were prepared. These ligands tend to exist in a boat rather than a cone conformation, and their electronic or steric properties can be varied by changing the substituents R of the four ester groups.[7] The ligands **2** react with mercury(II) halides to give the tetramercury compounds $[P_4(Hg_2X_4)_2]$, **3**, in which the phosphinite groups are in the flattened equatorial position.[7c] However, they react with copper(I) or silver(I) halides to give the pentanuclear complexes $[P_4(Ag_5X_5)]$, **4**, in which the arene groups carrying the phosphinite substituents are upright, as required for cluster formation (Chart 1).[7b] The neutral silver(I) and copper(I) halide cluster complexes **4** exhibit fluxionality that involves loss of one metal ion to give the anionic tetranuclear complexes $[P_4(Ag_4X_5)]^-$, **5**. In addition, when X = Cl or Br (but not I), loss of more metal and halide ions can occur to give the cationic binuclear complexes $[P_4(Ag_2X)]^+$, **6** (Scheme 1).[7]

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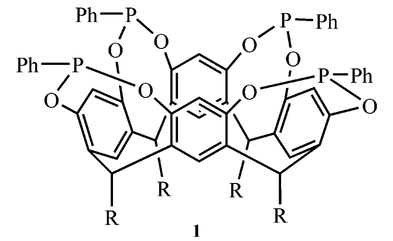
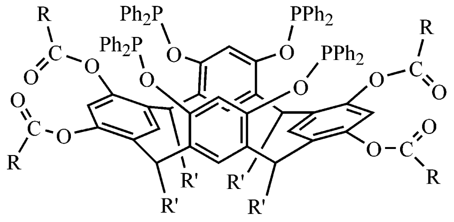
Chart 1. R′ = CH_2CH_2Ph

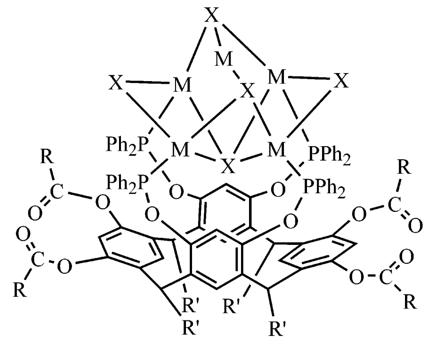


1

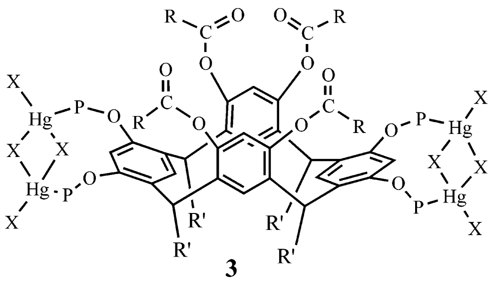


2a R = OCH_2Ph **2b** R = C_4H_3S **2c** R = OCH_2CCH

2d R = C_6H_{11} **2e** R = 4-$C_6H_4CH_3$



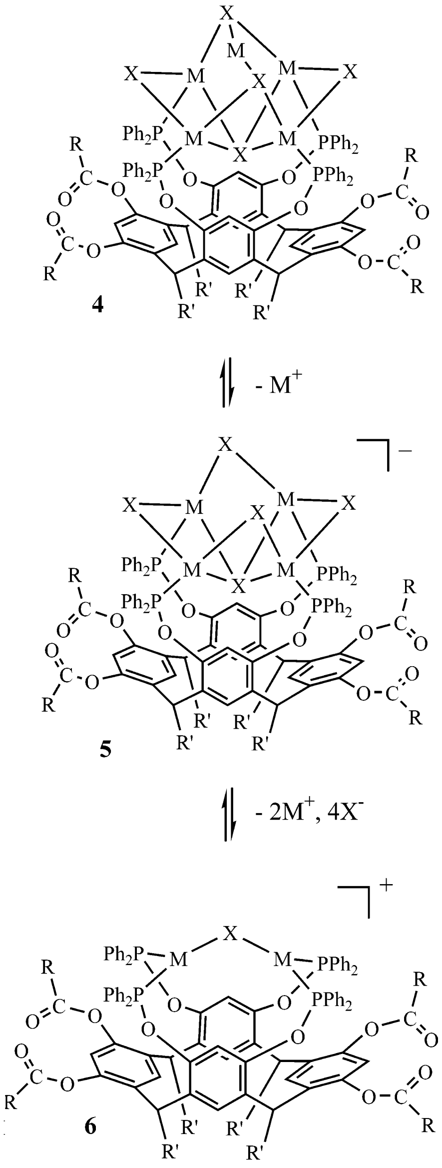
R = OCH_2Ph	**4a** M = Ag X = Cl	**4b** M = Ag X = Br
R = C_4H_3S	**4c** M = Ag X = Cl	**4d** M = Ag X = Br
R = OCH_2CCH	**4e** M = Ag X = Cl	**4f** M = Ag X = Br
R = C_6H_{11}	**4g** M = Ag X = Cl	
R = C_6H_{11}	**4h** M = Ag X = I	
R = 4-$C_6H_4CH_3$	**4i** M = Ag X = I	
R = C_6H_{11}	**4j** M = Cu X = I	
R = 4-$C_6H_4CH_3$	**4k** M = Cu X = I	



3

Since the fifth copper(I) or silver(I) ion (the one that is bound only to halide) in the complexes **4** is particularly labile,[7] it was envisaged that it might be possible to replace this metal ion by a mercury(II) ion that could bridge between two units of the tetranuclear complexes to form a molecular capsule. The reactions of the complexes **4** with mercury(II) halides did lead to a new type of capsule complex, but the system was considerably more complex than envisioned. The results are reported below.

Scheme 1

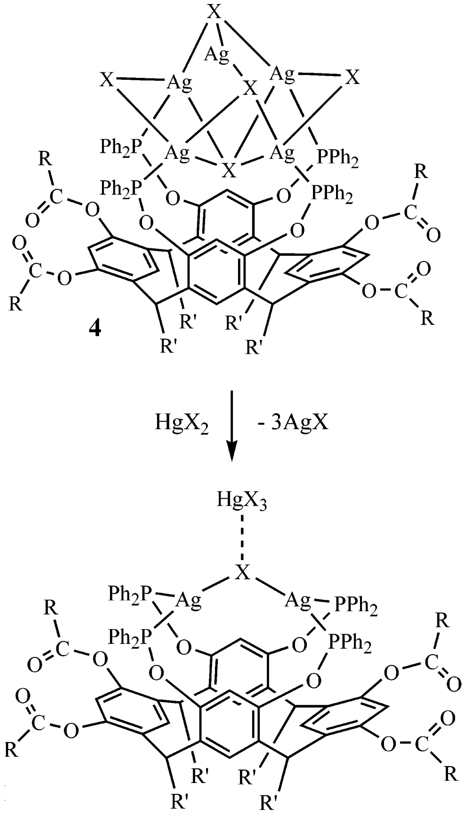


Results and Discussion

Synthesis of the Complexes. The chloro- and bromosilver(I) resorcinarene complexes **4a**−**4g** (Chart 1) each reacted with 1 equiv of the corresponding mercury(II) halide with precipitation of 3 equiv of silver halide and formation of the complexes **7**. These complexes **7** are formulated as $[P_4Ag_2X][HgX_3]$, with secondary bonding between the disilver cation and mercurate anion, as outlined in simplified form in Scheme 2. Addition of excess mercury(II) halide led to a slow reaction involving complete displacement of silver(I) and formation of the corresponding mercury(II) halide complex **3** (Chart 1),[7] but no intermediates in this reaction could be identified.

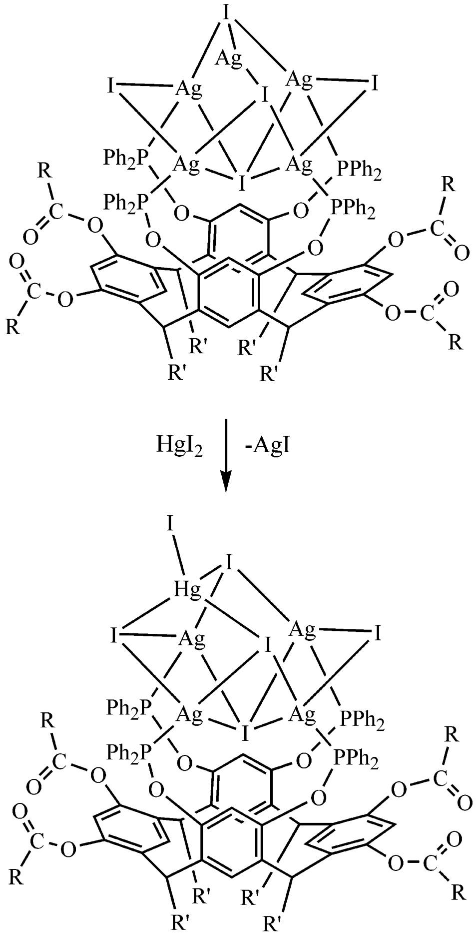
The iodosilver(I) complexes **4h** and **4i** (Chart 1) reacted with 1 equiv of mercury(II) iodide to give silver(I) iodide and the complexes $[P_4Ag_4HgI_6]$, **8a** and **8b**, respectively, as outlined in Scheme 3. The addition of the mercury(II) iodide resulted in slow precipitation of yellow silver(I) iodide. The reaction with excess mercury(II) iodide occurred over a

Scheme 2. R′ = CH_2CH_2Ph



R = OCH_2Ph	**7a** X = Cl	**7b** X = Br
R = C_4H_3S	**7c** X = Cl	**7d** X = Br
R = OCH_2CCH	**7e** X = Cl	**7f** X = Br
R = C_6H_{11}	**7g** X = Cl	

Scheme 3. R′ = CH_2CH_2Ph



8a R = C_6H_{11}

8b R = 4-$C_6H_4CH_3$

period of several days with displacement of all silver(I) and formation of the corresponding iodomercury(II) derivative $[P_4Hg_4I_8]$, **3** (Chart 1).[7c]

Reaction of the iodocopper(I) complexes **4j** and **4k** with 1 equiv of mercury(II) iodide occurred with loss of copper(I) iodide to give the copper−mercury complexes **9a** and **9b**, respectively, as outlined in Scheme 4. The complexes **9** can be formulated as $[P_4Cu_2I]_2[Hg_2I_6]$, in which two $[P_4Cu_2I]^+$ ions are bridged by an $[Hg_2I_6]^{2-}$ anion to form an unusual molecular capsule.

Another interesting type of copper−mercury complex was prepared by reaction of excess copper(I) iodide and mercury(II) iodide with the iodosilver(I) complexes **4h** and **4i**. All of the silver(I) units were displaced with formation of complexes **10a** and **10b**, respectively (Scheme 5). These complexes have the composition $[P_4Cu_2Hg_2I_6]$, and can be considered as $[P_4Cu_2I]^+$ cations associated with $[Hg_2I_5]^-$ anions. Although the complexes **9** (Scheme 4) and **10** (Scheme 5) are related, it was not possible to interconvert them, and the complexes **10** could only be prepared by reaction with the silver complexes **4**.

Structures of the Crystalline Complexes. The structure of the chlorosilver(I) complex **7a** is shown in Figure 1, with bond parameters in Table 1. There are two molecules in the asymmetric unit, but since they differ mainly in the arrangement of the flexible phenethyl and benzyl carbonate substituents, only one will be discussed. Each molecule can be viewed as a resorcinarene cation of the form $[P_4Ag_2(\mu\text{-}Cl)]^+$ which is weakly bound to an $[HgCl_3]^-$ anion.

The conformation of the resorcinarene skeleton in complex **7a** is intermediate between the boat and saddle conformations, as defined in Chart 2. The diphenylphosphinite derivatized arene rings are upright, and tilted slightly outward, with the angle between opposite rings, defined as the fold angle, $\Theta 1 = 5°$ (Table 2). The acylated arene rings are flattened, but are angled downward with the fold angle $\Theta 2 = 198°$, past the ideal 180° angle for a boat conformation and toward the saddle conformation (Chart 2).[8] The saddle conformation is unusual in resorcinarene compounds and, while it has been established in solution by NMR studies,[9] this appears to be the first structural characterization.[8,9]

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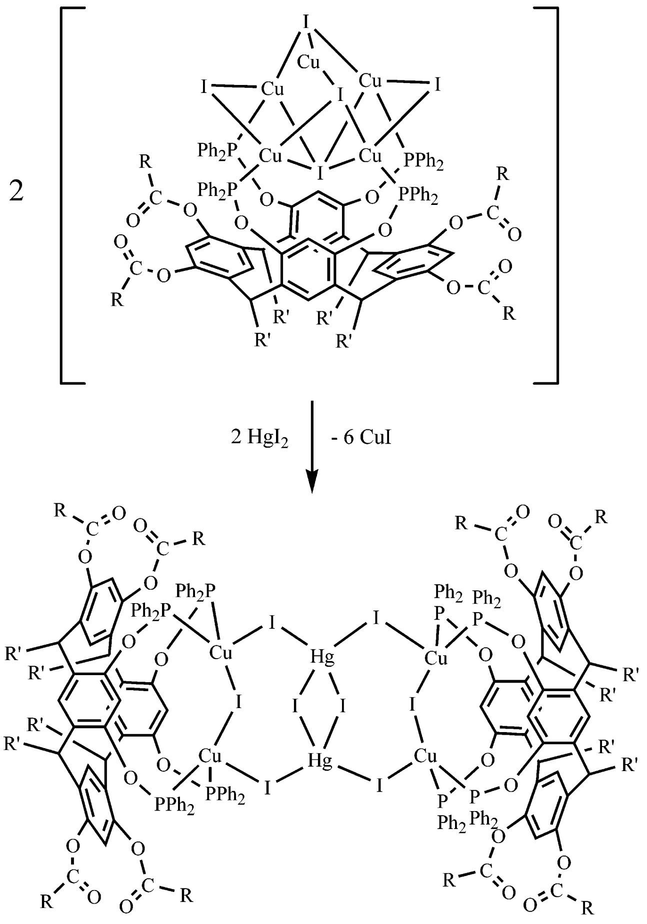
Scheme 4. R′ = CH_2CH_2Ph



9a R = C_6H_{11}

9b R = 4-$C_6H_4CH_3$

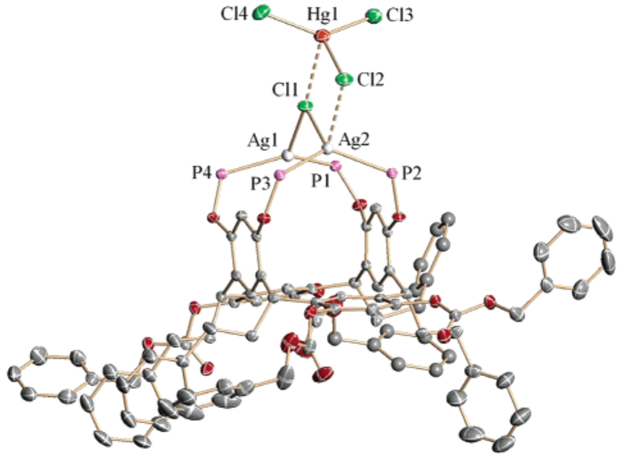
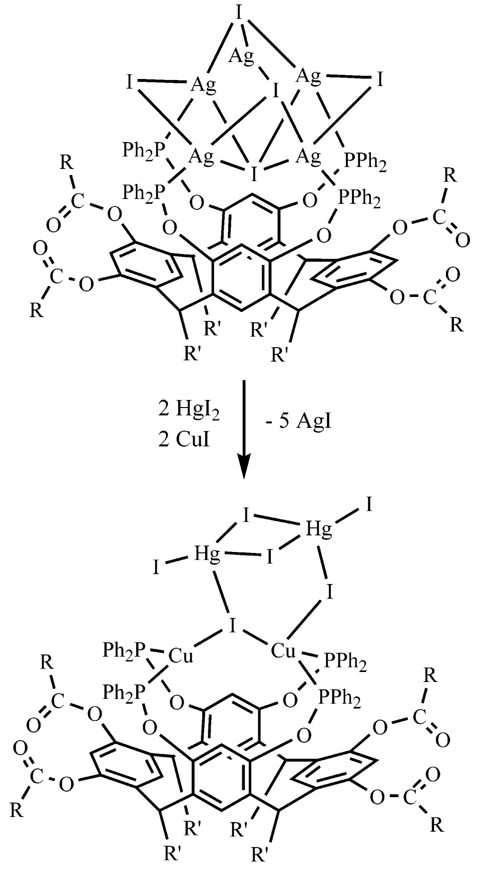


Figure 1. Thermal ellipsoid diagram of complex **7a**, molecule 1. Phenyl rings of the diphenylphosphinite groups have been removed for clarity. Oxygen atoms are shown in red.

Scheme 5. R′ = CH_2CH_2Ph



10a R = C_6H_{11}

10b R = 4-$C_6H_4CH_3$

The resorcinarene conformation allows each of the two silver atoms to be chelated by a phosphorus donor from each of the opposing upright resorcinol arene rings, and a bridging chloride completes the trigonal AgP_2Cl coordination of each silver ion (Figure 1) of the $[P_4Ag_2(\mu\text{-}Cl)]^+$ cation. The mercury(II) center of the $[HgCl_3]^-$ anion also has approximately trigonal planar stereochemistry, and this anion is coordinated to the cation through two weak bonding interactions (Figure 1). There is a secondary bonding interaction between the mercury(II) center and the chlorine atom which bridges the two silver atoms, and the distance Hg(1)···Cl(1) = 2.849(2) Å (Table 1) is at the lower end of the range of 2.80−3.20 Å that is considered typical for such interactions (the sum of the van der Waals radii for Hg and Cl is 3.30 Å).[10,11] The second weak bonding interaction occurs between a chloride of the $[HgCl_3]^-$ anion and one of the silver atoms of the cation. The distance Ag(2)···Cl(2) = 2.760(2) Å is longer than typical Ag−Cl bridging bond distances (2.50−2.64 Å),[12] and in particular, it is longer than the Ag−Cl distances within the $Ag_2(\mu\text{-}Cl)$ unit of **7a** [Ag(1)−Cl(1) = 2.518(2) Å; Ag(2)−Cl(1) = 2.587(2) Å]. Similar long Ag···Cl distances have been observed previously and assigned to secondary bonding interactions (the sum of the van der Waals radii for Ag and Cl is 3.47 Å).[6,10,13] In support, it is noted that the distance Hg(1)−Cl(2) = 2.536(2) Å is significantly lengthened compared to the other Hg−Cl distances in the $[HgCl_3]^-$ anion [Hg(1)−Cl(3) = 2.360(2) Å; Hg(1)−Cl(4) = 2.369(2) Å], presumably as a result of the secondary bonding to

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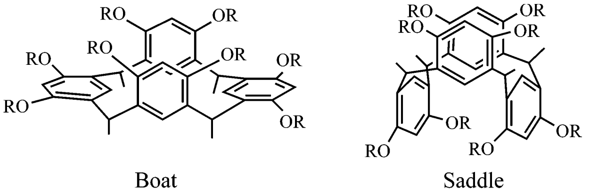
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **7a** (Molecule 1), **7c**, and **7d**

	7a (mol 1, X = Cl)	**7c** (X = Cl)	**7d** (X = Br)
P1−Ag1	2.411(2)	2.440(2)	2.445(2)
P4−Ag1	2.412(2)	2.429(2)	2.435(2)
P2−Ag2	2.439(2)	2.402(3)	2.409(3)
P3−Ag2	2.437(2)	2.410(2)	2.412(2)
Ag1−X1	2.518(2)	2.557(2)	2.646(1)
Ag2−X1	2.587(2)	2.526(2)	2.610(1)
Hg1−X2	2.536(2)	2.397(4)	2.528(9)
Hg1−X3	2.360(2)	2.390(3)	2.504(1)
Hg1−X4	2.369(2)	2.455(3)	2.557(1)
Hg1−X1	2.849(2)	2.820(2)	2.968(1)
P1−Ag1−X1	113.95(6)	112.40(9)	113.09(6)
P4−Ag1−X1	114.21(6)	118.32(8)	118.43(6)
P1−Ag1−P4	130.53(5)	128.58(8)	128.05(8)
P2−Ag2−X1	117.58(5)	119.20(8)	119.25(7)
P3−Ag2−X1	118.67(5)	112.78(9)	112.22(6)
P2−Ag2−P3	121.74(5)	127.04(8)	127.15(8)
X2−Hg1−X3	110.72(7)	120.6(1)	118.4(3)
X2−Hg1−X4	108.43(7)	118.3(1)	119.7(3)
X3−Hg1−X4	136.92(7)	118.7(1)	121.26(5)
Ag2···X2	2.760(2)		
Ag1−X1−Ag2	101.56(5)	97.93(8)	92.99(4)

Chart 2



Boat

Saddle

Table 2. Fold and Twist Angles (deg) and Ligand Bite Distances (Å)[a]

complex	Θ1	Θ2	Φ1	Φ2	d(PP)
7a, molecule 1	5	198	4	4	4.26, 4.38
7a, molecule 2	2	187	2	4	4.29, 4.33
7c	4	188	4	9	4.31, 4.39
7d	3	187	4	9	4.32, 4.39
8a	42	154	2	3	7.22, 7.17
9b	−**17**[b]	199	2	4	3.88, 3.90
10a	−**13**[b]	199	0	2	3.91, 3.91

[a] Θ1 and Θ2 are the fold angles between the upright and flattened arene rings, respectively, and Φ1 and Φ2 are the corresponding twist (dihedral) angles. [b] Negative sign indicates an inward tilt.

silver. The coordination geometries of the silver(I) and mercury(II) centers are near trigonal planar in each case (sums of the angles around the metal centers are Ag(1), 358°; Ag(2), 358°; Hg(1), 356°), so the secondary Ag···Cl and Hg···Cl bonding does not lead to a significant tetrahedral distortion. It is likely that the secondary bonding stabilizes the $[HgCl_3]^-$ ion since discrete $HgCl_3^-$ anions are uncommon,[8,14] and usually undergo self-association to form dimers, oligomers, or polymers.[8] Hence, the structure of complex **7a** is best described as a $[P_4Ag_2(\mu\text{-}Cl)]^+$ cation which has captured an $[HgCl_3]^-$ anion through formation of complementary Ag···Cl and Hg···Cl secondary bonds.

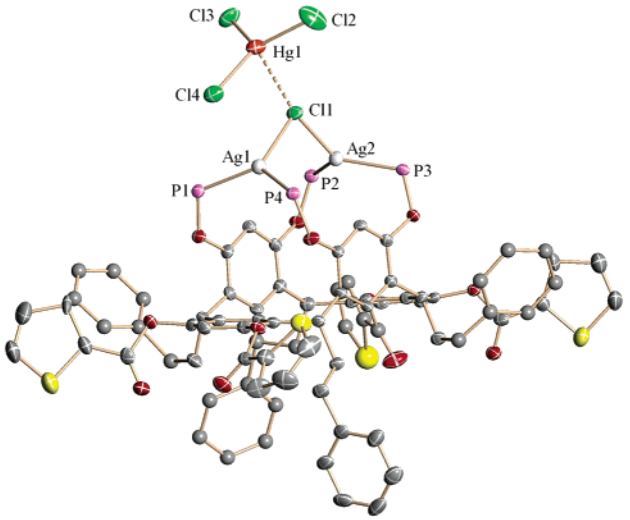


Figure 2. Thermal ellipsoid diagram of complex **7c**. Phenyl rings of the diphenylphosphinite groups have been removed for clarity. Oxygen atoms are shown in red; sulfur atoms are shown in yellow.

The structures of the chloro and bromo complexes **7c** and **7d**, having thiophenecarboxylate ester groups, are isomorphous and exhibit very similar features (Tables 1 and 2), so only the structure of **7c** is shown (Figure 2). The overall structure and the conformation of the resorcinarene skeleton are similar to those discussed for complex **7a** (Tables 1 and 2), but with one significant difference with respect to the interaction between the $[P_4Ag_2(\mu\text{-}X)]^+$ cation and the $[HgX_3]^-$ anion (X = Cl or Br). In complexes **7c** and **7d** there is still a secondary Hg(1)···X(1) bonding interaction, and the distance Hg(1)···Cl(1) = 2.820(2) Å in **7c** is slightly shorter than the corresponding distance in complex **7a** of 2.849(2) Å. The shortest Ag···Cl distance between the $[P_4Ag_2(\mu\text{-}Cl)]^+$ cation and the $[HgCl_3]^-$ anion in **7c** [Ag(1)···Cl(4) = 3.06-(1) Å] is considerably longer than that observed in **7a** [2.760-(2) Å]. Since this interaction is weak in **7c**, the Hg−X bond distances within the $[HgCl_3]^-$ anions lie in a closer range than for **7a** (Table 1) and the stereochemistry at silver(I) and mercury(II) is roughly trigonal planar. For complex **7d**,

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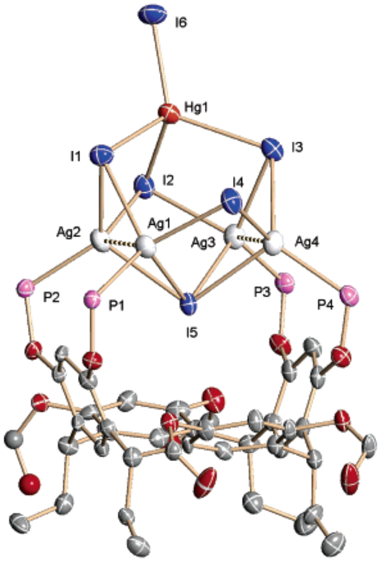

Figure 3. Thermal ellipsoid diagram of complex **8a**. Phenyl rings of the diphenylphosphinite and phenethyl groups, and cyclohexyl moieties have been removed for clarity. Oxygen atoms are shown in red.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **8a**

Ag1−P1	2.453(3)	P1−Ag1−I1	118.31(9)
Ag2−P2	2.434(3)	P1−Ag1−I5	111.93(7)
Ag3−P3	2.438(3)	I1−Ag1−I4	98.63(4)
Ag4−P4	2.450(3)	P2−Ag2−I2	124.48(8)
Ag1−I1	2.908(1)	P2−Ag2−I5	114.04(8)
Ag1−I4	2.840(1)	I1−Ag2−I2	95.56(4)
Ag4−I3	2.910(1)	P3−Ag3−I3	123.38(9)
Ag4−I4	2.880(1)	P3−Ag3−I5	112.16(8)
Ag3−I5	2.920(1)	I2−Ag3−I3	95.46(4)
Ag4−I5	2.951(1)	P4−Ag4−I3	123.44(9)
Ag1−Ag2	3.157(2)	P4−Ag4−I5	110.72(8)
Ag3−Ag4	3.190(2)	I3−Ag4−I4	97.33(4)
Hg1−I1	2.913(1)	I1−Hg1−I2	95.40(4)
Hg1−I2	2.848(1)	I1−Hg1−I3	110.07(4)
Hg1−I6	2.660(2)	I2−Hg1−I6	123.55(6)

the shortest Ag···BrHg distance Ag(1)···Br(4) = 3.29(1) Å, and the stereochemistry is very close to that of **7c** (Table 1).

The structure of complex **8a** is disordered, and the major (60%) component is depicted in Figure 3, with selected bond distances and angles listed in Table 3. There are two minor components (20%, 20%) that are less well-defined, and they are not shown. The structure can be considered to arise by bonding of a $[P_4Ag_4I_5]^-$ anion to an $[HgI]^+$ cation through three bridging iodide ligands. Alternatively, the structure can be considered to be derived from the parent complex $[P_4Ag_5I_5]$, **4h**, by replacement of the fifth Ag^+ ion by the $[HgI]^+$ ion. The $Ag_4I_5^-$ unit in **8a** is similar to that in **4h**, but there are some differences arising from the replacement of the linearly coordinated Ag(I) in **4h** by the tetrahedrally coordinated Hg(II) center in **8a**, as can be seen by comparison of the data in Table 4.

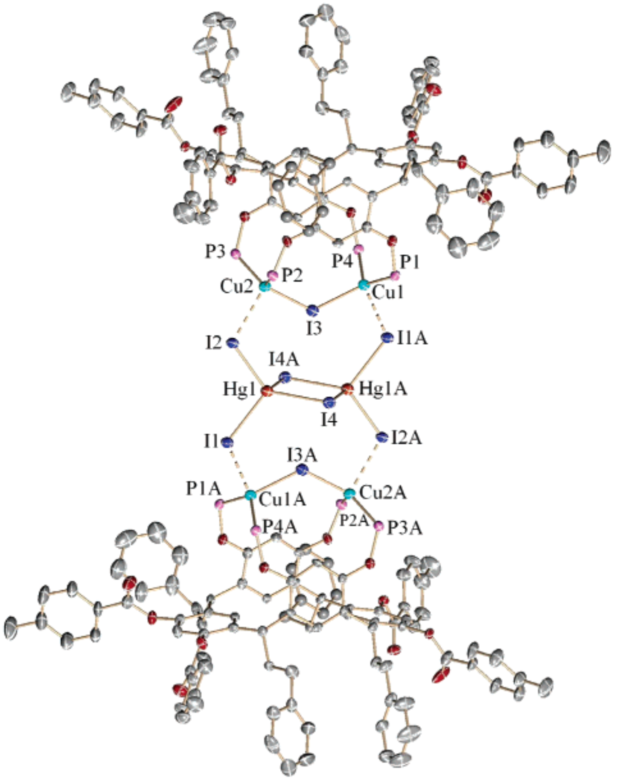

Figure 4. Thermal ellipsoid diagram of complex **9b**. Phenyl rings of the diphenylphosphinite groups have been removed for clarity. Oxygen atoms are shown in red.

Table 4. Comparison of Ag_5I_5 Cluster to Ag_4I_5HgI Cluster, Bond Lengths (Å) and Angles (deg)

	4h	8a
Ag−μ_2I	2.8159(5)−2.8486(5)	2.840(1)−2.880(1)
Ag−μ_2I−Ag	74.72(1)−85.26(1)	77.39(4)
Ag−μ_3I	2.8792(5)−2.9685(5)	2.844(1)−2.910(1)
Ag−μ_3I−Ag	62.99(3)−68.78(1)	66.57(4)−80.45(4)
Ag−μ_4I	2.9059(5)−3.0086(5)	2.920(1)−2.951(1)
Ag−μ_4I−Ag	62.70(1)−80.24(1)	65.29(3)−79.81(4)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex **9b**

P1−Cu1	2.229(3)	P1−Cu1−P4	121.6(1)
P4−Cu1	2.237(3)	P1−Cu1−I3	112.2(1)
P2−Cu2	2.243(3)	P4−Cu1−I3	113.24(9)
P3−Cu3	2.235(3)	I1A−Cu1−I3	95.06(5)
Cu1−I3	2.529(2)	P2−Cu2−P3	120.3(1)
Cu2−I3	2.539(2)	P2−Cu2−I3	114.0(1)
Cu1−I1A	2.812(2)	P2−Cu2−I2	103.19(9)
Cu2−I2	2.772(2)	I2−Cu2−I3	92.94(5)
Hg1−I1	2.775(1)	I1−Hg1−I2	102.77(3)
Hg1−I2	2.772(1)	I1−Hg1−I4	113.67(3)
Hg1−I4	2.832(1)	I2−Hg1−I4	118.94(3)
Hg1−I4A	2.907(1)	I4−Hg1−I4A	95.14(3)

The remarkable structure of complex **9b** is shown in Figure 4, with selected bond distances and angles listed in Table 5. It can be considered to comprise two $[P_4Cu_2(\mu\text{-}I)]^+$ cations connected by a bridging $[Hg_2I_6]^{2-}$ anion. There is a crystallographically imposed center of symmetry, so the two $[P_4Cu_2(\mu\text{-}I)]^+$ cations are identical. The resorcinarene skeleton adopts the unusual conformation between the boat and saddle, with the phosphinite derivatized arene rings upright and tilted considerably inward (fold angle $\Theta1 = -17°$) and the acylated rings flattened and directed downward (fold angle $\Theta2 = 199°$). The phosphorus−phosphorus distances are shorter in complex **9b** than in any of the silver complexes, as a result of the chelation to the smaller copper(I) centers, and this also accounts for the large inward tilt of the upright arene rings. There are four weak Cu···I bonding interactions involving the four terminal iodides of the $[Hg_2I_6]^{2-}$ anion and the four copper(I) centers of the two $[P_4Cu_2(\mu\text{-}I)]^+$

cations. These distances Cu···I = 2.772(2) and 2.812(2) Å are significantly longer than the $Cu_2(\mu\text{-I})$ distances of the resorcinarene cation [Cu−I = 2.529(2) and 2.539(2) Å], and in the range found for other Cu···I secondary bonds (the sum of the van der Waals radii for Cu and I is 3.38 Å).[10,15,16] There are no interactions between the mercury centers and the halide ligand of the $[P_4Cu_2(\mu\text{-I})]^+$ cations, in contrast to the structures of the silver−mercury complexes discussed above. The coordination geometry of the copper centers is intermediate between trigonal planar and tetrahedral, with larger distortions from planarity than was observed in the silver complexes **7a**, **7c**, and **7d**, suggesting a stronger interaction between the $[P_4Cu_2(\mu\text{-I})]^+$ cations and the halomercurate(II) anion. The copper centers are considerably out of the plane made up of the chelating phosphorus atoms and the bridging iodide (Cu1, 0.437 Å; Cu2, 0.488 Å) toward the terminal iodides of the $[Hg_2I_6]^{-2}$ anion, as expected if there is a stronger secondary Cu···I interaction. The bond angles around the copper(I) centers range from 92.94(5)° to 120.3(1)° (Table 5). The bond angles at the mercury(II) centers are unremarkable,[17] but the terminal Hg−I bond distances [2.775(1) and 2.772(1) Å] are longer than those observed previously for discrete $[Hg_2I_6]^{2-}$ anions (2.68−2.72 Å),[18] likely due to the secondary interactions between the terminal iodides and the copper(I) centers. Thus, the overall the structure of complex **9b** can be viewed as arising from two $[P_4Cu_2(\mu\text{-I})]^+$ cations which have captured an $[Hg_2I_6]^{2-}$ anion.

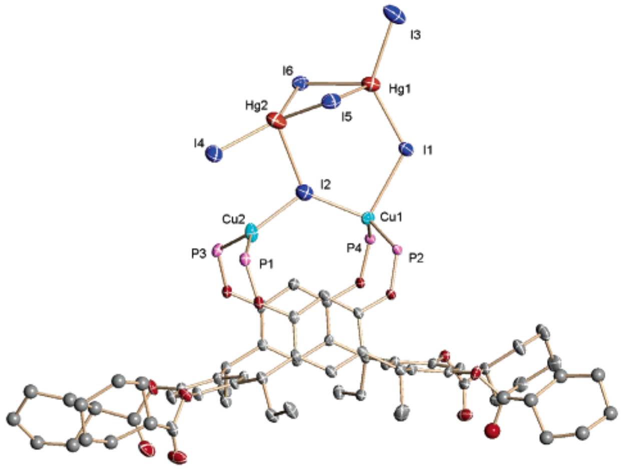

Figure 5. Thermal ellipsoid diagram of complex **10a**. Phenyl rings of the diphenylphosphinite and phenethyl groups have been removed for clarity. Oxygen atoms are shown in red.

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex **10a**

P2−Cu1	2.255(2)	P2−Cu1−P4	120.40(1)
P4−Cu1	2.254(3)	P2−Cu1−I2	115.71(8)
P1−Cu2	2.223(2)	P4−Cu1−I2	111.96(7)
P3−Cu2	2.238(3)	I1−Cu1−I2	96.09(5)
Cu1−I2	2.524(2)	P1−Cu2−P3	122.3(1)
Cu2−I2	2.422(2)	P1−Cu2−I2	120.87(8)
Cu1−I1	2.830(1)	P3−Cu2−I2	115.57(8)
Hg1−I1	2.714(1)	I1−Hg1−I3	133.8(1)
Hg1−I3	2.659(6)	I1−Hg1−I5	102.81(3)
Hg1−I5	3.043(1)	I3−Hg1−I5	102.4(1)
Hg1−I6	2.957(1)	I5−Hg1−I6	93.36(3)
Hg2−I2	2.901(1)	I2−Hg2−I4	85.75(6)
Hg2−I4	2.559(2)	I2−Hg2−I5	100.37(4)
Hg2−I5	2.731(1)	I4−Hg2−I5	130.76(7)
Hg2−I6	2.874(1)	I5−Hg2−I6	102.28(3)

The structure of complex **10a** is shown in Figure 5 with selected bond distances and angles listed in Table 6. The structure can be considered to arise from a $[P_4Cu_2(\mu\text{-I})]^+$ cation, in which the conformation of the resorcinarene skeleton is similar to that in **9b** (Table 2), with a coordinated $[Hg_2I_5]^-$ anion. This coordination has two components. There is coordination by a terminal iodide of the $[Hg_2I_5]^-$ anion and one of the copper atoms, with Cu(1)···I(1) = 2.812(2) Å, and the coordination geometry of Cu(1) is intermediate between trigonal planar and tetrahedral [Cu(1) is 0.470 Å out of the P(2)P(4)I(2) plane] while that of Cu(2), which does not have a secondary bond to the anion, is much closer to trigonal [Cu(2) is 0.147 Å out of the P(1)P(3)I(2) plane]. The second cation−anion interaction occurs between the iodide of the $Cu_2(\mu\text{-I})$ unit and a mercury atom with Hg(2)···I(2) = 2.901(1) Å. This is a typical $Hg(\mu\text{-I})$ bond distance,[17] and the coordination geometry of Hg(2) is best regarded as distorted tetrahedral with bond angles ranging from 85.75(6)° to 130.76(7)° and with the Hg(2) center lying 0.455 Å out of the I(4)I(5)I(6) plane. The other bridging Hg−I bond distances in the $[Hg_2I_5]^-$ anion range from 2.731(1) to 3.043(1) Å, so it is somewhat arbitrary to assign I(2) to the cation rather than the anion in this case. The $[Hg_2I_5]^-$ anion has not been observed as discrete species, but only as part of a polymeric anion with overall stoichiometry of $Hg_2I_5^-$.[19]

NMR Studies of Solution Structures. The NMR spectra of complexes **7a**−**7g** were similar, and complex **7a** will be considered as an example. At room temperature, there was a single resonance in the ^{1}H NMR spectrum for the methine protons of the resorcinarene skeleton and a broad doublet resonance in the ^{31}P NMR spectrum for the phosphorus atoms, indicating that the complex has effective C_{2v} symmetry. At −20 °C, the ^{31}P resonance was sharper and resolved to give two doublets arising from the couplings $^1J(^{109}AgP)$ and $^1J(^{107}AgP)$,[20] but no further significant change occurred on cooling to −80 °C. The magnitudes of these

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Table 7. ^{31}P NMR Data for Complexes **7** at −20 °C

complex	δ (ppm)	$^{1}J(^{109}AgP)$ (Hz)	$^{1}J(^{107}AgP)$ (Hz)
7a	103.96	538	465
7b	102.86	525	454
7c	103.99	539	467
7d	102.91	528	457
7e	104.26	531	465
7f	103.49	516	452
7g	104.89	528	469

coupling constants (Table 7) indicate that each silver center is coordinated to two phosphorus atoms,[21] as expected from the solid-state structure. However, in the solid-state structure of complex **7a** the two silver atoms have different coordination environments, so two resonances would be expected in the ^{31}P NMR spectrum. If the structure in solution is the same as in the solid state, the complex must be fluxional, with a more symmetrical intermediate similar to the solid-state structures of **7c** (Scheme 6) or perhaps by reversible dissociation of the $[HgCl_3]^-$ anion. In either case, the easy fluxionality is expected since it involves only the making and breaking of weak secondary bonds. It will be seen that similar easy fluxionality is characteristic of several of the mixed metal complexes, but since in many cases it cannot be frozen out, it is not possible to determine and compare activation energies or to determine the mechanisms of fluxionality definitively.

The NMR spectra of complexes **8a** and **8b** were similar, and those of **8a** will be discussed as an example. At room temperature, the ^{31}P NMR spectrum was broad and appeared to contain two poorly resolved, overlapping doublet resonances (Figure 6). At −40 °C, the ^{31}P spectrum of complex **8a** resolved to show a sharp major resonance [$\delta = 102.4$, $^{1}J(^{109}AgP) = 590$ Hz, $^{1}J(^{107}AgP) = 512$ Hz] and a minor broader resonance [$\delta = 100.2$, $^{1}J_{av}(AgP) = 550$ Hz], indicating the presence of two species, each having effective C_{2v} symmetry. Addition of excess HgI_2 to the solution of complex **8a** in CD_2Cl_2 resulted in greater resolution of the ^{31}P spectrum at room temperature, and the minor resonance was no longer present (Figure 6). It should be noted that the structure of complex **8a** in the solid state has approximate C_s symmetry and so should give two equal intensity resonances in the ^{31}P NMR spectrum. We suggest that the major complex present in solution is **8a** and that the complex is fluxional by very easy migration of the HgI unit between the bridging iodide units as shown in Scheme 7. The minor complex is suggested to be formed by loss of HgI^+ from the cluster, and the concentration of the dissociated anionic complex $[P_4Ag_4I_5]^-$, **5** (Scheme 1, M = Ag, X = I), is reduced in the presence of excess HgI_2. This dissociation is similar to the reversible loss of Ag^+ from **4** to give **5** (Scheme 1, M = Ag, X = I).[7]

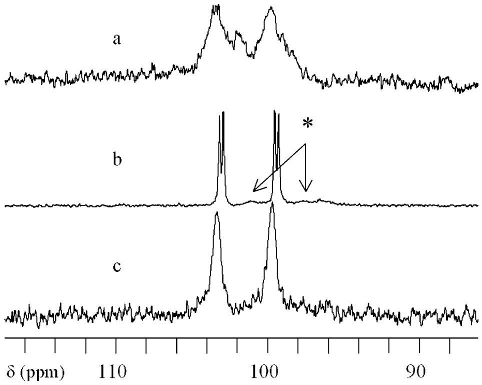
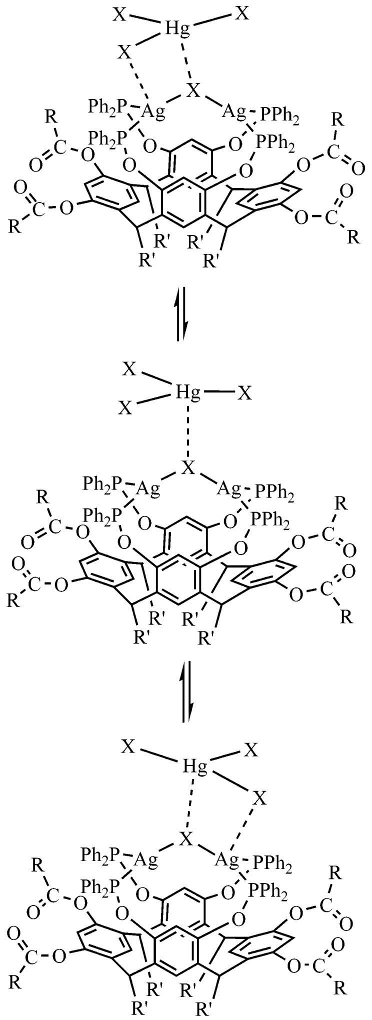


Figure 6. ^{31}P NMR spectra of complex **8a** in CD_2Cl_2: (a) broad spectrum obtained at room temperature; (b) spectrum at −20 °C, showing major and minor (denoted by the ∗) components; (c) spectrum at room temperature in the presence of free HgI_2.

Scheme 6. Proposed Fluxional Process Occurring in Solution for Complexes **7**



The copper(I) complexes **9a**, **9b** and **10a**, **10b** each gave only a single resonance in the ^{1}H NMR spectra for the bridging methine protons of the resorcinarene, and a single

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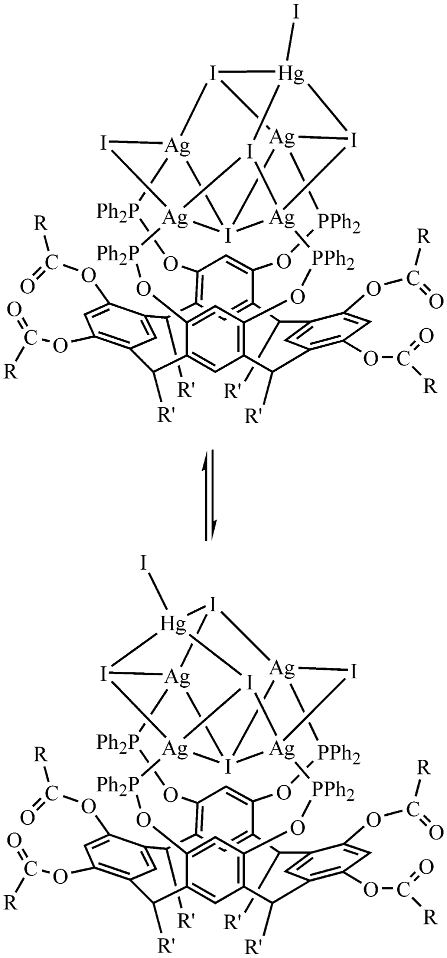
Scheme 7. Proposed Fluxionality for Complexes **8**

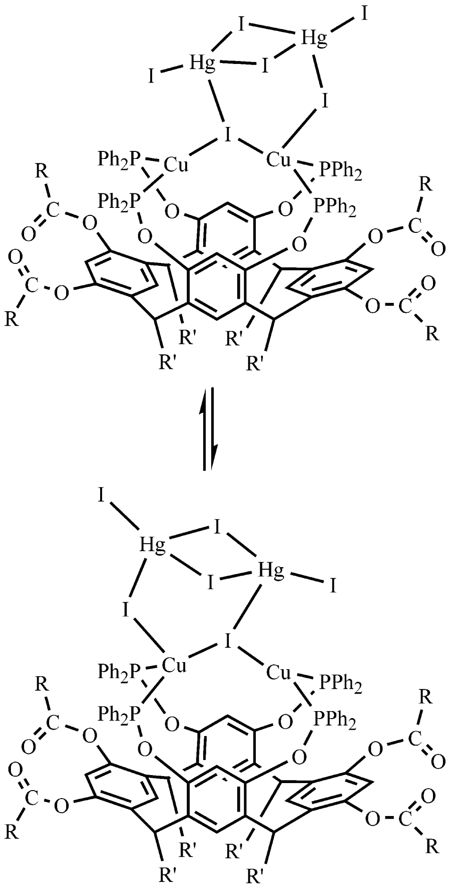


resonance in the ^{31}P phosphorus spectrum, and the spectra did not change greatly at low temperature. Hence each has effective C_{2v} symmetry. This pattern is expected for complexes **9** (Scheme 4) since the $[Hg_2I_6]^{2-}$ anion bridges symmetrically to give a structure with approximate C_{2v} symmetry, but it is not expected for the solid-state structures of **10a**, **10b** in which the two copper atoms are nonequivalent. These complexes are therefore fluxional. This fluxionality is likely to involve rotation of the $[Hg_2I_5]^-$ anion about the central $Cu_2I{-}Hg$ bond as shown in Scheme 8. Reversible dissociation of the anion to give free $[P_4Cu_2(\mu\text{-}I)]^+$ units is considered unlikely, because of the strength of the I$-$Hg bridge and because each complex has distinctive NMR spectra. For example, if complete dissociation of the mercurate anions occurred, it would be expected that **9a** and **10a** might have identical spectra, but this is not the case.

Conclusions

The silver(I) and copper(I) halide tetraphosphinitoresorcinarene complexes $[P_4M_5X_5]$, **4**, react with mercury(II) halides in several different ways. In most cases, the reactions lead to the loss of 3 equiv of MX and one halide anion to give the corresponding cationic complexes $[P_4M_2(\mu\text{-}X)]^+$. The halide ion combines with mercury(II) halide to give the anions $[HgX_3]^-$, $[Hg_2X_6]^{2-}$, or $[Hg_2X_5]^-$ that are captured by the cations in a number of different ways, which can be considered as an unusual form of host$-$guest chemistry. When M = Ag and X = Cl or Br, the anion was always $[HgX_3]^-$, but it could be bound to the cation by one (as in complexes **7c** and **7d**, as in Figure 2) or two (as in **7a**, Figure 1) secondary bonding interactions. The stronger interaction is probably the $Ag_2X{\cdots}Hg$ bond since it is present in all of the structurally characterized complexes. When M = Cu and X = I, the anions were $[Hg_2I_6]^{2-}$ or $[Hg_2I_5]^-$ and they were captured to give the complexes $[P_4Cu_2(\mu\text{-}I)]_2[Hg_2I_6]$, **9** (Scheme 4), or $[P_4Cu_2(\mu\text{-}I)][Hg_2I_5]$, **10** (Scheme 5). Many of these complexes were fluxional in solution, and it is proposed that this involves the making and breaking of secondary X$\cdots$M bonds that allows easy rotation of the mercurate anions with respect to the $[P_4M_2(\mu\text{-}X)]^+$ cation, as illustrated in Schemes 5, 7, and 8.

Scheme 8



The most robust complexes $[P_4M_5X_5]$, **4**, were found when M = Ag and X = I. These reacted with mercury(II) iodide with loss of just one silver ion and with formation of the complexes $[P_4Ag_4I_5(HgI)]$, **8** (Scheme 3). These complexes undergo easy migration of the HgI unit about the cluster and also partial dissociation of the HgI^+ unit. Thus, it can be considered that the $[P_4Ag_4I_5]^-$ anion is a receptor for the HgI^+ cation. The high stability of the $[P_4Ag_4I_5]^-$ anion probably arises from the favorable geometry of both the peripheral $Ag_4(\mu\text{-}I)_4$ cluster and the central $Ag_4(\mu_4\text{-}I)$ unit, for which iodide is large enough to bridge to all four silver atoms.

Clearly, the chemistry of the tetraphosphinitoresorcinarene complexes $[P_4M_5X_5]$, **4**, with mercury(II) halides leads to formation of very unusual mixed M, Hg cluster complexes. The chemistry appears to be largely independent of the nature of the ester groups RCO_2 of the resorcinarene (Chart 1) but strongly dependent on the nature of M and X. Formally, complexes have been obtained that can act as receptors for either mercury halide cations or anions and the resulting mixed-metal clusters exhibit unusual structures and dynamics.

Experimental Section

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled, dried, and degassed prior to use. NMR spectra were recorded using a Varian Inova 400 spectrometer. In the formulas below, the resorcinarene skeleton $(C_6H_2CH\{CH_2CH_2Ph\})_4$ is represented as "resorcinarene". The silver(I) and copper(I) halide complexes **4** were prepared by the reported method.[7b]

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2$)$_4${Ag$_2$(μ-Cl)}{HgCl$_3$}], 7a. To a solution of **4a** (0.100 g, 0.035 mmol) in CH_2Cl_2 (5 mL) was added $HgCl_2$ (0.010 g, 0.037 mmol), causing an immediate precipitation of AgCl. The solution was stirred for 15 min in a darkened flask and then filtered through Celite, and the white solid product was precipitated with pentane, dried, and recrystallized from $CHCl_3$/hexane. Yield 0.052 g, 54%. NMR (CD_2Cl_2, −20 °C): $\delta(^1H)$ 1.96, 2.35 [m, 8H, $CHC\mathit{H}_2CH_2Ph$]; 2.51, 2.71 [m, 8H, $CHCH_2C\mathit{H}_2Ph$]; 4.69 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 5.25 [m, 8H, $OC\mathit{H}_2Ph$]; 6.23 [s, 4H, Ar-*H*]; 6.85−7.68 [m, 84H, Ar-*H*, *Ph*]. Anal. Calcd for $C_{140}H_{116}Ag_2Cl_4HgO_{16}P_4$: C, 61.45%; H, 4.27%. Found: C, 61.09%; H, 4.24%.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2$)$_4${Ag$_2$(μ-Br)}{HgBr$_3$}], 7b. This was prepared similarly from **4b** (0.100 g, 0.032 mmol) and $HgBr_2$ (0.012 g, 0.033 mmol). Yield 0.072 g, 77%. NMR (CD_2Cl_2, −20 °C): $\delta(^1H)$ 2.02, 2.37 [m, 8H, $CHC\mathit{H}_2CH_2Ph$]; 2.55, 2.74 [m, 8H, $CHCH_2C\mathit{H}_2Ph$]; 4.70 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 5.27 [m, 8H, $OC\mathit{H}_2Ph$]; 6.23, 6.25 [s, 4H, Ar-*H*]; 6.82−7.70 [m, 84H, Ar-*H*, *Ph*]. Anal. Calcd for $C_{140}H_{116}Ag_2Br_4HgO_{16}P_4$: C, 57.70%; H, 4.01%. Found: C, 57.74%; H, 4.01%.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2$)$_4${Ag$_2$(μ-Cl)}{HgCl$_3$}], 7c. This was prepared similarly from **4c** (0.100 g, 0.036 mmol) and $HgCl_2$ (0.010 g, 0.037 mmol). Yield 0.059 g, 62%. NMR (CD_2Cl_2, −20 °C): $\delta(^1H)$ 2.08 [m, 4H, $CHC\mathit{H}_2CH_2Ph$]; 2.52 [m, 8H, $CHC\mathit{H}_2C\mathit{H}_2Ph$]; 2.74 [m, 4H, $CHCH_2C\mathit{H}_2Ph$]; 4.89 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 6.48 [s, 4H, Ar-*H*]; 6.73−7.78 [m, 76H, Ar-*H*, *Ph*, $C_4\mathit{H}_3S$]. This complex occluded solvent (the X-ray sample contained 2.25 $C_2H_4Cl_2$ and 1 H_2O molecule) that was incompletely removed under vacuum, and reproducible analytical data were not obtained.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2$)$_4${Ag$_2$(μ-Br)}{HgBr$_3$}], 7d. This was prepared similarly from **4d** (0.100 g, 0.033 mmol) and $HgBr_2$ (0.012 g, 0.033 mmol). Yield 0.070 g, 75%. NMR (CD_2Cl_2, −20 °C): $\delta(^1H)$ 2.00 [m, 4H, $CHC\mathit{H}_2CH_2Ph$]; 2.52 [m, 8H, $CHC\mathit{H}_2C\mathit{H}_2Ph$]; 2.75 [m, 4H, $CHCH_2C\mathit{H}_2Ph$]; 4.83 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 6.39, 6.41 [s, 4H, Ar-*H*]; 6.70−7.86 [m, 76H, Ar-*H*, *Ph*, $C_4\mathit{H}_3S$]. Anal. Calcd for $C_{128}H_{100}Ag_2Br_4HgO_{12}P_4S_4$: C, 54.55%; H, 3.58%. Found: C, 55.05%; H, 3.93%.

[Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OPPh$_2$)$_4${Ag$_2$(μ-Cl)}{HgCl$_3$}], 7e. This was prepared similarly from **4e** (0.100 g, 0.037 mmol) and $HgCl_2$ (0.010 g, 0.037 mmol). Yield 0.055 g, 59%. NMR (CD_2Cl_2, −20 °C): $\delta(^1H)$ 1.96, 2.41 [m, 8H, $CHC\mathit{H}_2CH_2Ph$]; 2.57, 2.78 [m, 8H, $CHC\mathit{H}_2CH_2Ph$]; 2.64 [s, br, 4H, $OCH_2C{\equiv}C\mathit{H}$]; 4.70 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 4.81 [s, 8H, $OC\mathit{H}_2C{\equiv}CH$]; 6.26, 6.27 [s, 4H, Ar-*H*]; 6.88−7.92 [m, 64H, Ar-*H*, *Ph*]. Anal. Calcd for $C_{124}H_{100}Ag_2Cl_4HgO_{16}P_4$: C, 58.91%; H, 3.99%. Found: C, 59.25%; H, 3.81%.

[Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OPPh$_2$)$_4${Ag$_2$(μ-Br)}{HgBr$_3$}], 7f. This was prepared similarly from **4f** (0.100 g, 0.034 mmol) and $HgBr_2$ (0.013 g, 0.036 mmol). Yield 0.077 g, 84%. NMR (CD_2Cl_2, −20 °C): $\delta(^1H)$ 2.02, 2.42 [m, 8H, $CHC\mathit{H}_2CH_2Ph$]; 2.61, 2.82 [m, 8H, $CHC\mathit{H}_2CH_2Ph$]; 2.63 [t, 4H, $^3J_{HH} = 2$ Hz, $OCH_2C{\equiv}C\mathit{H}$]; 4.69 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 4.81 [s, 8H, $OC\mathit{H}_2C{\equiv}CH$]; 6.29, 6.31 [s, 4H, Ar-*H*]; 6.81−7.80 [m, 64H, Ar-*H*, *Ph*]. Anal. Calcd for $C_{124}H_{100}Ag_2Br_4HgO_{16}P_4$: C, 55.04%; H, 3.72%. Found: C, 54.83%; H, 3.52%.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2$)$_4${Ag$_2$(μ-Cl)}{HgCl$_3$}], 7g. This was prepared similarly from **4g** (0.100 g, 0.036 mmol) and $HgCl_2$ (0.010 g, 0.037 mmol). Yield 0.042 g, 44%. NMR (CD_2Cl_2, −20 °C): $\delta(^1H)$ 1.14−2.10 [m, 44H, $C_6\mathit{H}_{11}$]; 1.98, 2.41 [m, 8H, $CHC\mathit{H}_2CH_2Ph$]; 2.55, 2.78 [m, 8H, $CHCH_2C\mathit{H}_2Ph$]; 4.72 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 6.37, 6.43 [s, 4H, Ar-*H*]; 6.78−7.74 [m, 64H, Ar-*H*, *Ph*]. Anal. Calcd for **7g**·0.5CHCl$_3$, $C_{136.5}H_{132.5}Ag_2Cl_{5.5}HgO_{12}P_4$: C, 60.77%; H, 4.95%. Found: C, 60.55%; H, 4.83%.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2$)$_4${Ag$_4$I$_5$}{HgI}], 8a. To a solution of **4h** (0.100 g, 0.031 mmol) in CH_2Cl_2 (5 mL) was added HgI_2 (0.014 g, 0.031 mmol), causing a slow precipitation of yellow AgI. The solution was stirred for 30 min in a darkened flask and then filtered through Celite, and the pale yellow solid product was precipitated with pentane, dried, and recrystallized from CH_2ClCH_2Cl/hexane. Yield 0.073 g, 68%. NMR (CD_2Cl_2, −40 °C): $\delta(^1H)$ 0.65−1.65 [m, 44H, $C_6\mathit{H}_{11}$]; 1.93 [m, 4H, $CHC\mathit{H}_2CH_2Ph$]; 2.31 [m, 8H, $CHC\mathit{H}_2C\mathit{H}_2Ph$]; 2.52 [m, 4H, $CHCH_2C\mathit{H}_2Ph$]; 4.60 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 6.42, 6.81 [s, 4H, Ar-*H*]; 6.86−7.76 [m, 64H, Ar-*H*, *Ph*]. $\delta(^{31}P)$ 102.38 [m, $^1J(^{109}AgP) = 590$ Hz, $^1J(^{107}AgP) = 512$ Hz]. Anal. Calcd for **8a**·(CH_2ClCH_2Cl), $C_{138}H_{136}Ag_4Cl_2HgI_6O_{12}P_4$: C, 46.37%; H, 3.83%. Found: C, 45.98%; H, 3.87%.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OPPh$_2$)$_4${Ag$_4$I$_5$}{HgI}], 8b. This was prepared similarly from **11** (0.100 g, 0.030 mmol) and HgI_2 (0.014 g, 0.031 mmol) and isolated as a pale yellow solid. Yield 0.074 g, 70.3%. NMR (CD_2Cl_2, −40 °C): $\delta(^1H)$ 2.05 [m, 4H, $CHC\mathit{H}_2CH_2Ph$]; 2.36, 2.50 [m, 12H, $CHC\mathit{H}_2C\mathit{H}_2Ph$]; 2.40 [s, 12H, $C_6H_4C\mathit{H}_3$]; 4.94 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 6.59, 7.91 [s, 4H, Ar-*H*]. 6.69−7.64 [m, 80H, Ar-*H*, *Ph*, $C_6\mathit{H}_4CH_3$]. $\delta(^{31}P)$ 102.80 [m, $^1J(^{109}AgP) = 596$ Hz, $^1J(^{107}AgP) = 522$ Hz]. Anal. Calcd for $C_{140}H_{116}Ag_4HgI_6O_{12}P_4$: C, 47.94%; H, 3.33%. Found: C, 48.47%; H, 3.52%.

[(Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2$)$_4${Cu$_2$(μ-I)})$_2${Hg$_2$I$_6$}], 9a. To a solution of **4j** (0.100 g, 0.033 mmol) in CH_2Cl_2 (5 mL) was added HgI_2 (0.015 g, 0.033 mmol), causing an immediate precipitation of CuI. The solution was stirred for 15 min and then filtered through Celite, and the yellow solid product was precipitated with pentane, collected, and dried. Yield 0.066 g, 68%. NMR (CD_2Cl_2, 20 °C): $\delta(^1H)$ 0.98−1.81 [m, 48H, $CHC\mathit{H}_2CH_2Ph$, $C_6\mathit{H}_{11}$]; 2.00 [m, 4H, $CHC\mathit{H}_2CH_2Ph$]; 2.42 [m, 8H, $CHC\mathit{H}_2C\mathit{H}_2Ph$]; 2.63 [m, 4H, $CHCH_2C\mathit{H}_2Ph$]; 4.77 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 6.84, 7.81 [s, 4H, Ar-*H*]; 6.93−7.60 [m, 64H, Ar-*H*, *Ph*]. $\delta(^{31}P)$ 86.30[s]. Anal. Calcd for $C_{272}H_{264}Cu_4Hg_2I_8O_{24}P_8$: C, 55.99%; H, 4.56%. Found: C, 56.05%; H, 4.17%.

[(Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OPPh$_2$)$_4${Cu$_2$(μ-I)})$_2${Hg$_2$I$_6$}], 9b. This was prepared similarly from **4k** (0.100 g, 0.033 mmol) and HgI_2 (0.015 g, 0.033 mmol). Yield 0.059 g, 61%. NMR (CD_2Cl_2, 20 °C): $\delta(^1H)$ 2.04 [m, 4H, $CHC\mathit{H}_2CH_2Ph$]; 2.39, 2.55 [m, 12H, $CHC\mathit{H}_2C\mathit{H}_2Ph$]; 2.38 [s, 12H, $C_6H_4C\mathit{H}_3$]; 4.91 [m, 4H, $C\mathit{H}CH_2CH_2Ph$]; 6.27 [s, 2H, Ar-*H*]. 6.66−7.98 [m, 82H, Ar-*H*,

Table 8. Crystallographic Data for Complexes **7a**, **7c**, and **7d**

	7a	**7c**	**7d**
formula	$C_{286}H_{244}Ag_4Cl_{20}Hg_2O_{33.5}P_8$	$C_{132.5}H_{109}Ag_2Cl_{8.5}HgO_{13}P_4S_4$	$C_{130.6}H_{105.2}Ag_2Br_4Cl_{5.2}HgO_{12}P_4S_4$
fw	6006.23	2878.97	3038.98
space Group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	23.1700(1)	16.5490(2)	16.3074(2)
b (Å)	23.9968(1)	19.3490(3)	19.5444(2)
c (Å)	26.2223(2)	23.5899(4)	23.4087(3)
α (deg)	99.520(1)	98.176(1)	97.440(1)
β (deg)	90.650(1)	103.417(1)	103.327(1)
γ (deg)	106.628(1)	92.471(1)	91.871(1)
volume (Å^3)	13751.1(1)	7250.0(2)	7183.6(2)
Z	2	2	2
D_{calcd} (mg/m^3)	1.451	1.319	1.405
μ (mm^{-1})	1.699	1.635	2.700
R1, wR2 [$I > 2\sigma(I)$]	0.0612, 0.1767	0.0828, 0.2440	0.0776, 0.2301
R indices (all data)	0.1003, 0.2011	0.1260, 0.2779	0.1115, 0.2562

Table 9. Crystallographic Data for Complexes **8a**, **9b**, and **10a**

	8a	**9b**	**10a**
formula	$C_{140}H_{140}Ag_4Cl_4HgI_6O_{12}P_4$	$C_{285}H_{242}Cl_8Cu_4Hg_2I_8O_{24}P_8$	$C_{138}H_{136}Cl_4Cu_2Hg_2I_6O_{12}P_4$
fw	3673.67	6052.69	3541.81
space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$
a (Å)	30.7483(2)	26.4290(2)	16.1754(1)
b (Å)	22.1450(2)	18.6148(2)	17.8785(1)
c (Å)	25.0229(3)	32.9030(3)	25.1879(3)
α (deg)			104.636(1)
β (deg)	105.070(1)	109.243(1)	90.822(1)
γ (deg)			107.361(1)
volume (Å^3)	16452.6(3)	15282.9(2)	6694.9 (1)
Z	4	2	2
D_{calcd} (mg/m^3)	1.483	1.359	1.757
μ (mm^{-1})	2.676	2.249	4.169
R1, wR2 [$I > 2\sigma(I)$]	0.1012, 0.3153	0.0803, 0.2356	0.0769, 0.2154
R indices (all data)	0.1809, 0.3650	0.1324, 0.2634	0.1026, 0.2347

Ph, $C_6H_4CH_3$]. $\delta(^{31}P)$ 87.06 [s]. Anal. Calcd for $C_{280}H_{232}Cu_4Hg_2I_8O_{24}P_8$: C, 57.01%; H, 3.96%. Found: C, 57.08%; H, 4.02%.

[Resorcinarene(OC(O)$C_6H_{11})_4(OPPh_2)_4$\{$Cu_2(\mu$-I)\}\{Hg_2I_5\}], 10a. To a solution of **4h** (0.090 g, 0.028 mmol) in CH_2Cl_2 was added HgI_2 (0.038 g, 0.084 mmol), causing the slow precipitation of yellow silver iodide. The solution was stirred for 30 min and CuI (0.016 g, 0.084 mmol) was added, causing the immediate precipitation of silver iodide. The solution was stirred for 5 min and filtered through Celite; the yellow solid product was precipitated with pentane and recrystallized from CH_2Cl_2/hexane. Yield 0.056 g, 59%. NMR (CD_2Cl_2, 20 °C): $\delta(^1H)$ 0.88−2.14 [m, 44H, C_6H_{11}]; 2.05, 2.47 [m, 8H, $CHCH_2CH_2Ph$]; 2.62, 2.84 [m, 8H, $CHCH_2CH_2Ph$]; 4.68 [m, 4H, $CHCH_2CH_2Ph$]; 6.30, 7.73 [s, 4H, Ar-*H*]; 6.57−7.68 [m, 64H, Ar-*H*, *Ph*]. $\delta(^{31}P)$ 85.90[s]. Anal. Calcd for $C_{136}H_{132}Cu_2Hg_2I_6O_{12}P_4\cdot H_2O$: C, 48.18%; H, 3.98%. Found: C, 48.22%; H, 4.37%.

[Resorcinarene(OC(O)$C_6H_4CH_3)_4(OPPh_2)_4$\{$Cu_2(\mu$-I)\}\{Hg_2I_5\}], 10b. This was prepared similarly from **4i** (0.080 g, 0.024 mmol), HgI_2 (0.033 g, 0.073 mmol), and CuI (0.014 g, 0.074 mmol). Yield 0.033 g, 40%. NMR (CD_2Cl_2, 20 °C): 2.19 [m, 4H, $CHCH_2CH_2Ph$]; 2.44 [s, 12H, $C_6H_4CH_3$]; 2.57 [m, 8H, $CHCH_2CH_2Ph$]; 2.80 [m, 4H, $CHCH_2CH_2Ph$]; 4.79 [m, 4H, $CHCH_2CH_2Ph$]; 6.44, 7.80 [s, 4H, Ar-*H*]. 6.70−7.77 [m, 80H, Ar-*H*, *Ph*, $C_6H_4CH_3$]. $\delta(^{31}P)$ 86.26[s]. Anal. Calcd for **10b**·0.5hexane, $C_{143}H_{123}Cu_2Hg_2I_6O_{12}P_4$: C, 49.83%; H, 3.60%. Found: C, 49.81%; H, 3.83%.

X-ray Structure Determinations. A suitable crystal was mounted on a glass fiber. Data were collected using a Nonius-Kappa CCD diffractometer using COLLECT (B. V. Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (B. V. Nonius, 1998). The SHELX-TL V5.1 and V6.1 (G. M. Sheldrick) program packages were used to solve and refine the structures. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. Crystal data are summarized in Tables 8 and 9. All thermal ellipsoid diagrams are shown at 30% probability. Details of the individual structure determinations are given as Supporting Information.

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Supporting Information Available: Full details of the X-ray structure solutions and crystallographic tables in CIF format for complexes **7a**, **7c**, **7d**, **8a**, **9b**, and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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