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Tetraphosphinitoresorcinarene Complexes: Dynamic Clusters with Silver(I) and Copper(I) Halides

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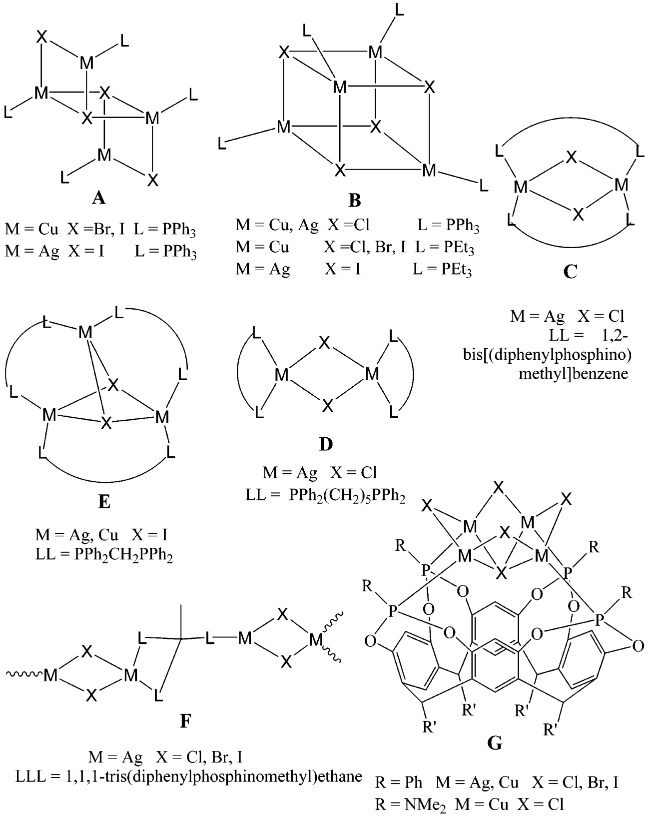
Silver(I) and copper(I) halide derivatives of several tetrakis(diphenylphosphinito)resorcinarene ligands are reported. The complexes [resorcinarene(O_2CR)$_4$($OPPh_2$)$_4$(M_5X_5)], with resorcinarene = ($PhCH_2CH_2CHC_6H_2$)$_4$, R = C_6H_{11}, 4-C_6H_4Me, C_4H_3S, OCH_2CCH, or OCH_2Ph, M = Ag, X = Cl, Br, or I, M = Cu, and X = Cl or I, contain a crownlike [$P_4M_5X_5$] metal halide cluster. These crown clusters were found to be dynamic in solution, as studied by variable-temperature NMR, and easily fragment to give the corresponding complexes containing [$P_4M_4X_5$]$^-$ and [$P_4M_2(\mu$-X)]$^+$ units. Reaction of pentasilver crown clusters with triflic acid gave the corresponding disilver complexes [resorcinarene(O_2CR)$_4$($OPPh_2$)$_4${$Ag_2(\mu$-Cl)}]CF_3SO_3. Thus, these resorcinarene-based ligands act as a platform for the easy and reversible assembly of copper(I) and silver(I) clusters with novel structures.

Introduction

Chart 1. Structural Types Observed for Phosphine Complexes of Silver(I) and Copper(I) Halides



Silver(I) and copper(I) halides form many complexes with phosphine ligands in which the coordination number at the metal center can be two, three, or four. Ladder- and cubane-type cluster structures **A** and **B** (Chart 1) are often obtained,[1] although halide-bridged dimers,[2] trimers,[3] and polymers[4] have also been observed (**C**−**F**, Chart 1). Resorcinarene-based ligands have attracted considerable interest for use in coordination chemistry,[5] and interesting resorcinarene complexes of silver(I) and copper(I) halides have been reported.[6] The unusual crownlike cluster structure **G** (Chart 1) obtained from the resorcinarene ligand **H** (Chart 2) appears to be

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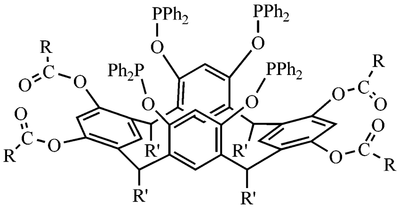
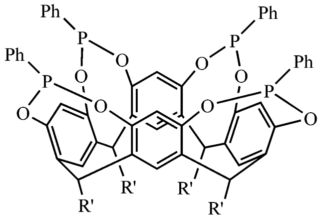
Chart 2



1 R = C_6H_{11} **2** R = 4-$C_6H_4CH_3$ **3** R = C_4H_3S

4 R = OCH_2CCH **5** R = OCH_2Ph



H

R' = CH_2CH_2Ph

unique to resorcinarene-based phosphine ligands.[6] These stable crown clusters were found to occlude an unusual μ_4-bridging halide, resulting in anionic complexes which were then shown to act as cation receptors.[6]

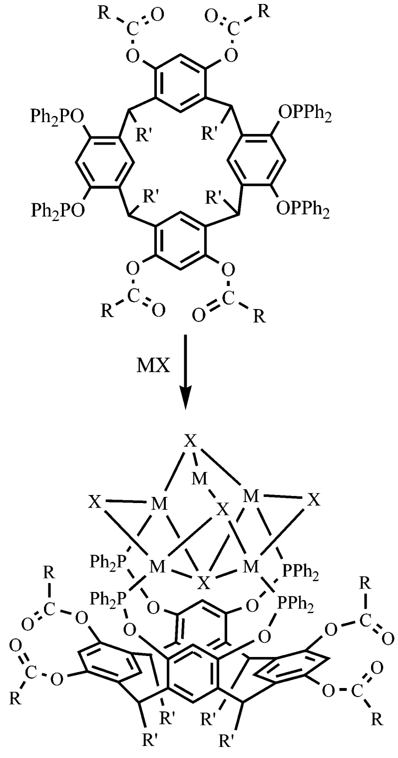
The tetraphosphinite resorcinarene compounds **1**−**5** (Chart 2) are flexible ligands which tend to adopt a boat conformation,[7] in contrast to the tetraphosphonite resorcinarene ligand **H** (Chart 2), which has a rigid cone conformation.[6] Thus, it was of interest to determine if the tetraphosphinite ligands **1**−**5** would form crownlike metal halide clusters similar to **G** or if the more flexible ligands would give new structural types. It was found that crown complexes can be formed but they are susceptible to easy fragmentation to give disilver complexes.

Results and Discussion

Synthesis of the Silver(I) and Copper(I) Resorcinarene Complexes. The reactions of silver(I) and copper(I) halides with the tetraphosphinite ligands **1**−**5** were carried out using several different reagent stoichiometries, but only with excess metal halide were pure compounds formed. The new complexes $[P_4\{MX\}_5]$, **6a**−**c**, **7a,b**, **8**, **9**, **10a**−**c**, **11**, **12a,b**, and **13a,b** (Scheme 1), were obtained, where P_4 represents the appropriate tetraphosphinitoresorcinarene ligand **1**−**5**.

The presence of five metal halide units per resorcinarene molecule was proved in the case of complexes **6c** and **8** by X-ray structure determinations. All combinations of the tetraphosphinitoresorcinarene ligands and metal halides MX, with M = Cu or Ag and X = Cl, Br, or I, were studied, but not all gave analytically pure products, probably as a result of partial decomposition during crystallization. The pure complexes **6a**−**c**, **7a,b**, **8**, **9**, **10a**−**c**, **11**, **12a,b**, and **13a,b** were obtained as white solids that are soluble in chloroform, dichloromethane, and THF, but sparingly soluble in most other common organic solvents. The silver complexes were air stable but light sensitive, while the copper complexes were air sensitive, and were handled under a nitrogen atmosphere at all times.

Scheme 1



R = C_6H_{11}	M = Ag	**6a** X = Cl	**6b** X = Br	**6c** X = I
R = C_6H_{11}	M = Cu	**7a** X = Cl	**7b** X = I	
R = 4-C_6H_4Me	M = Ag	**8** X = I		
R = 4-C_6H_4Me	M = Cu	**9** X = I		
R = C_4H_3S	M = Ag	**10a** X = Cl	**10b** X = Br	**10c** X = I
R = C_4H_3S	M = Cu	**11** X = Cl		
R = OCH_2CCH	M = Ag	**12a** X = Cl	**12b** X = Br	
R = OCH_2Ph	M = Ag	**13a** X = Cl	**13b** X = Br	

R ' = CH_2CH_2Ph

The penta[silver(I) chloride] complexes reacted rapidly with triflic acid with precipitation of silver chloride and formation of the cationic disilver resorcinarene complexes **14**−**17**, and these complexes could also be prepared by reaction of the tetrakis(diphenylphosphinito)resorcinarene ligands with silver trifluoromethanesulfonate in the presence of sodium chloride as outlined in Scheme 2. The disilver complexes were obtained as white solids.

Solid-State Structures. The complexes **6c**, **8**, and **16** were characterized by X-ray structure determinations. The structure of the iodosilver(I) complex **6c** is shown in Figure 1, with selected bond distances and angles in Table 1. The resor-

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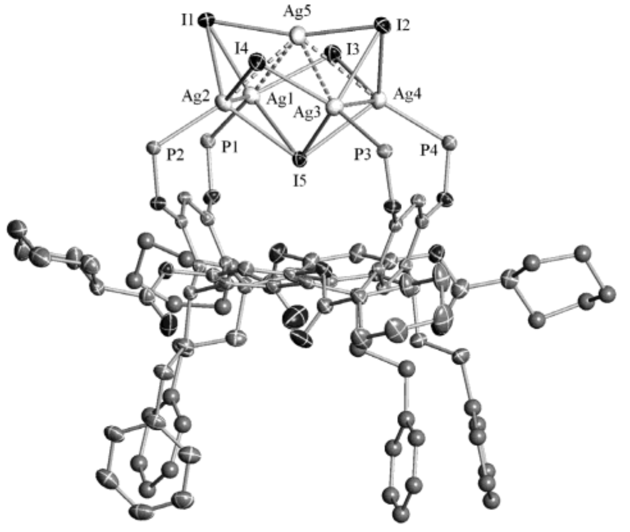

Figure 1. A view of the structure of complex **6c**. The phenyl rings of the diphenylphosphinite groups are removed for clarity.

Scheme 2

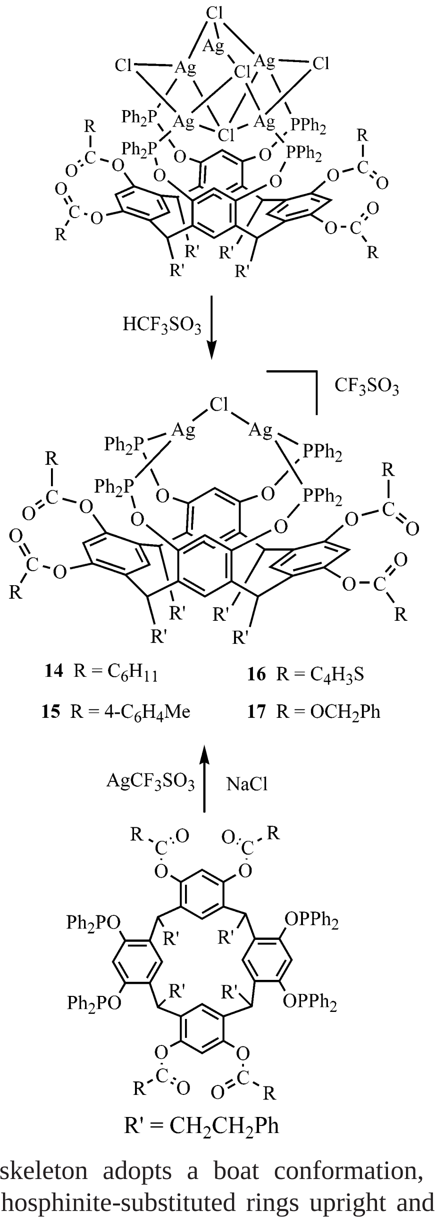

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **6c**

P1−Ag1	2.434(1)	Ag1−Ag2	3.0979(5)
P2−Ag2	2.440(1)	Ag3−Ag4	3.3160(5)
P3−Ag3	2.443(1)	Ag1−Ag5	2.948(2)
P4−Ag4	2.438(1)	Ag2−Ag5	3.090(2)
Ag1−I1	2.8792(5)	Ag3−Ag5	3.215(2)
Ag1−I3	2.8367(5)	Ag4−Ag5	3.103(2)
Ag2−I1	2.9477(5)	P1−Ag1−I1	119.19(3)
Ag2−I4	2.8159(5)	P1−Ag1−I5	109.20(3)
Ag3−I2	2.9685(5)	I3−Ag1−I5	95.95(1)
Ag3−I4	2.8418(5)	P2−Ag2−I5	112.84(3)
Ag4−I2	2.9003(5)	I4−Ag2−I5	106.16(1)
Ag4−I3	2.8486(5)	P3−Ag3−I2	111.76(3)
Ag1−I5	3.0086(5)	P3−Ag3−I5	114.02(3)
Ag2−I5	2.9448(5)	I4−Ag3−I5	106.54(2)
Ag3−I5	2.9059(5)	P4−Ag4−I2	117.94(3)
Ag4−I5	2.9657(7)	P4−Ag4−I5	113.50(3)
Ag5−I1	2.760(2)	I3−Ag4−I5	96.64(1)
Ag5−I2	2.696(2)	I2−Ag5−I1	160.96(7)

Table 2. Fold and Twist Angles (deg) and Ligand Bite Distance (Å) for Complexes **6c**, **8**, and **16**[a]

complex	Θ_1	Θ_2	Φ_1	Φ_2	*d*(PP)
6c	46	153	1	1	7.35, 7.06
8	39	167	0	8	7.46, 6.73
16	5	187	4	6	4.35, 4.26

[a] Θ_1 and Θ_2 are the fold angles between the upright and flattened arene rings, respectively, and Φ_1 and Φ_2 are the corresponding twist (dihedral) angles; *d*(PP) is the closest distance between phosphorus atoms on opposite aryl groups (these are the chelating phosphorus atoms in **16**).

cinarene skeleton adopts a boat conformation, with the diphenylphosphinite-substituted rings upright and the acylated rings flat. In this conformation, the four phosphorus atoms of the resorcinarene ligand can bind to the Ag$_5$I$_5$ cluster as shown in Figure 1. The upright rings of the resorcinarene skeleton are folded outward, as measured by the fold angle between the planes of opposite rings, $\Theta_1 = 46°$ (Table 2), presumably to accommodate the bulky Ag$_5$I$_5$ cluster (Figure 1). The corresponding fold angle between the flattened acylated rings, Θ_2, is 53°. There is virtually no twisting distortion of the resorcinarene skeleton, as seen by the dihedral angles (Φ) between opposing resorcinol rings for either the upright or flattened rings ($\Phi_1 = \Phi_2 = 1°$).

The Ag$_5$I$_5$ cluster contains a P$_4$Ag$_4$(μ-I)$_4$ group in which the Ag$_4$(μ-I)$_4$ unit has a crownlike appearance and in which each silver atom is bound to a phosphorus atom and two bridging iodide ligands. There is a fifth iodide at the center that bridges to all of these four silver atoms, which are almost coplanar (the mean deviation of silver atoms from the best plane of the Ag$_4$ unit is 0.004 Å). This Ag$_4$I$_5$ unit is similar to that in the known phosphonite complexes **G** (Chart 1), but the presence of a fifth silver atom is unprecedented.[1,6] This fifth silver atom is bonded to two opposite, more upright iodide atoms of the Ag$_4$(μ-I)$_4$ unit, and so has roughly linear stereochemistry. These iodide atoms are therefore triply bridging overall, while the other two doubly bridging iodides of the Ag$_4$(μ-I)$_4$ unit are distorted away from the fifth silver atom. Overall, the coordination environment of the four coplanar silver atoms is distorted tetrahedral, with each silver having AgP(μ_2-I)(μ_3-I)(μ_4-I) coordination, with bond angles ranging from 95.95(1)° to 119.53(3)° (Table 1). The Ag−μ_2-I bond distances are roughly equal, ranging from 2.8159(5) to 2.8486(5) Å. In comparison, the Ag−μ_3-I and Ag−μ_4-I bond distances for the four silver atoms of the

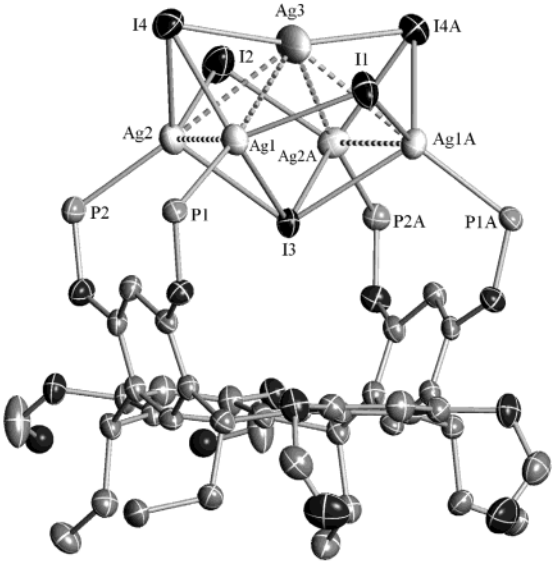

Figure 2. A view of the structure of complex **8**. The phenyl rings of the diphenylphosphinite and phenethyl groups and the tolyl groups are removed for clarity.

crown are longer and show more variation with distances ranging from 2.8792(5) to 2.9685(5) Å and from 2.9059(5) to 3.0086(5) Å, respectively. The occluded fifth silver atom, which is two-coordinate, is distorted from linearity, with the angle I1−Ag5−I2 = 160.96(7)°, and the Ag−μ_3-I bond distances are considerably shorter than the other Ag−I bond distances in the cluster, with values of 2.696(2) and 2.760(2) Å.

There are several close silver−silver contacts in the cluster, with distances between the silver atoms bonded to the diphenylphosphinite groups on the same aryl ring of 3.0979(5) and 3.3160(5) Å (the van der Waals diameter of silver is 3.4 Å).[8] The occluded fifth silver atom has close contacts with all of the other four silver atoms, with distances Ag···Ag ranging from 2.948(2) to 3.215(2) Å. The close silver−silver contacts are likely indicative of weak argentophilic interactions,[8] and may account for the distortion from linearity observed for the occluded fifth silver atom. It can be seen in the structure of **6c** (Figure 1) that the occluded fifth silver atom is bent inward toward the four other silver atoms, further suggesting the presence of weak silver−silver interactions.

The structure of the iodosilver(I) complex **8** (Figure 2) is similar to that of complex **6c**, as can be seen by comparison of the conformational features (Table 2) and the bond distances and angles of the silver iodide cluster (Tables 1 and 3). However, complex **8** has crystallographically imposed C_s symmetry, while complex **6c** has no crystallographically imposed symmetry.

The structure of the disilver complex **16** is shown in Figure 3 with selected bond distances and angles listed in Table 4. The silver atoms are each chelated by two phosphorus atoms belonging to diphenylphosphinite groups on opposing upright resorcinol arene rings, and are bridged by a single chlorine atom. The coordination geometries of the silver(I) centers are near trigonal planar, and although there is distortion from the ideal bond angles (Table 4), the sums of the angles around the metal centers are near 360° (Ag1, 359°; Ag2, 359°). The silver atoms are slightly out of the plane made by the two phosphorus atoms and the bridging chloride (Cl1), with Ag1 0.108 Å below the P1−P4−Cl1 plane, and Ag2 0.160 Å above the P2−P3−Cl1 plane.

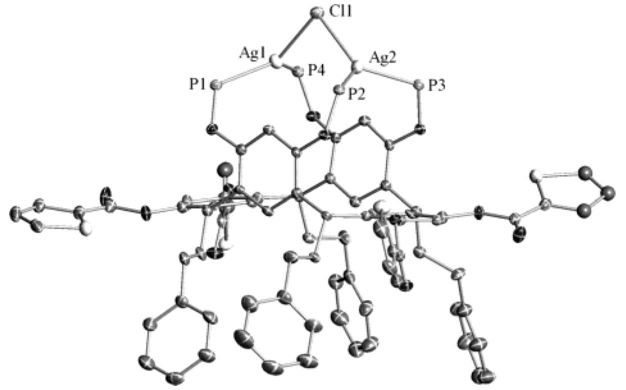

Figure 3. A view of the structure of complex **16**. The phenyl rings of the diphenylphosphinite groups are removed for clarity.

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

Ag1−P1	2.438(2)	Ag1−Ag2	3.208(1)
Ag2−P2	2.453(3)	Ag1−Ag3	3.148(2)
Ag1−I1	2.860(1)	Ag2−Ag3	3.147(2)
Ag1−I4	2.887(1)	P1−Ag1−I4	119.36(6)
Ag2−I2	2.859(1)	P1−Ag1−I3	109.81(6)
Ag2−I4	2.940(1)	I1−Ag1−I3	93.25(3)
Ag1−I3	3.002(1)	P2−Ag2−I4	121.21(7)
Ag2−I3	2.931(1)	P2−Ag2−I3	109.51(6)
Ag3−I4	2.756(1)	I2−Ag2−I4	95.77(4)
		I4−Ag3−I4A	164.8(1)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **16**

P1−Ag1	2.421(3)	P1−Ag1−P4	127.78(8)
P2−Ag2	2.430(3)	P1−Ag1−Cl1	118.11(8)
P3−Ag2	2.424(2)	P4−Ag1−Cl1	113.53(8)
P4−Ag1	2.423(3)	P3−Ag2−P2	122.79(8)
Ag1−Cl1	2.528(2)	P2−Ag2−Cl1	116.44(8)
Ag2−Cl1	2.489(2)	P3−Ag2−Cl1	116.44(8)
		Ag1−Cl1−Ag2	90.37(8)

The resorcinarene skeleton in **16** again adopts a boat conformation with the arene rings bearing the diphenylphosphinite groups in the upright position, but in this case, the resorcinarene skeleton adopts a near ideal boat conformation as seen by the fold angles $\Theta_1 = 5°$ and $\Theta_2 = 187°$ (Table 2). Thus, the conformation of the resorcinarene can adapt to bind the disilver unit. For example, the nonbonding phosphorus−phosphorus distances are much shorter for the disilver complex **16** compared to the pentasilver complexes (Table 2). Clearly, the ligand bite distance can be altered significantly by variation of the fold angle Θ_1, thus giving the tetraphosphinitoresorcinarene ligands a versatile coordination chemistry.

The closest approach of silver(I) to the triflate anion (which is disordered at 50% occupancy over two positions in the structure of complex **16**) is 2.9 Å (to Ag1), but this trigonal-planar silver(I) atom is actually distorted away from the

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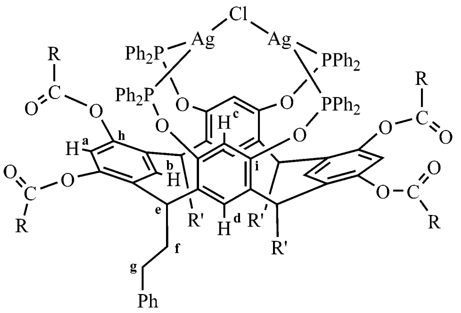
Table 5. ^{31}P NMR Data for Complexes **6a**, **8**, and **14**−**17**

complex	T (°C)	δ (ppm)	$^1J_{^{109}AgP}$	$^1J_{^{107}AgP}$
6aI	−40	107.7	733	635
6aJ	−40	106.1	719	627
6aK	−40	112.4	502	439
6aL	−40	104.1	497	433
8I	−40	99.6	563	491
8J	−40	101.1	558	480
14	20	106.9	530	459
15	20	106.3	528	457
16	20	105.8	527	457
17	20	105.9	527	457

Chart 3. NMR Labeling Scheme



triflate so no bonding interaction appears to be present. Thus, the overall structure of complex **16** is best viewed as a cation of the form $[P_4Ag_2(\mu\text{-Cl})]^+$ with a triflate anion.

Solution NMR Studies of the Complexes. The ^{1}H and ^{31}P NMR spectra for the disilver complexes **14**−**17** were well resolved at room temperature and indicated that the compounds have effective C_{2v} symmetry. For example, complex **16** gave only a single resonance for the methine protons of the resorcinarene in the ^{1}H NMR, and only a single phosphorus resonance, with coupling due to $^1J_{AgP}$, in the ^{31}P NMR. The magnitude of the coupling constant $^1J_{^{109}AgP} = 527$ Hz (Table 5) is consistent with the presence of AgP_2Cl coordination,[10] in accordance with the solid-state structure. Variable-temperature NMR experiments were performed on the complexes **14**−**17**, and in each case the NMR spectra remained virtually unchanged down to −80 °C.

It has been established that the conformation of the resorcinarene skeleton can be assigned in solution by comparison of the chemical shift for the arene resonances CH^b and CH^d (Chart 3), since CH^b in the flattened ring is more shielded.[7] The assignment of the resonances for CH^b and CH^d requires the ^{1}H−^{13}C gHSQC and gHMBC correlated NMR spectra.[7a] However, a simplified procedure for the unambiguous assignment of the resonances CH^b and CH^d from the ^{1}H−^{13}C gHMBC and ^{1}H−^{31}P gHMBC correlated NMR spectra was developed during the course of the work reported here, and the data obtained for complex **14** will serve as an example. The bridging methine carbon C^e couples to H^b and H^d in the ^{1}H−^{13}C gHMBC experiment, thus allowing assignment of these two protons (Figure 4a). The assignment of H^d can be readily made from the ^{1}H−^{31}P gHMBC experiment, as the phosphorus atoms couple to both H^d and H^c as seen in Figure 4b. For complex **14**, the resonance for H^b is more shielded ($\delta = 6.43$ ppm) than the resonance for H^d ($\delta = 7.79$ ppm), indicating that the conformation adopted in solution by the resorcinarene skeleton is that in which the acylated arene rings are flattened, and the phosphinite-derivatized arene rings are upright, as expected.

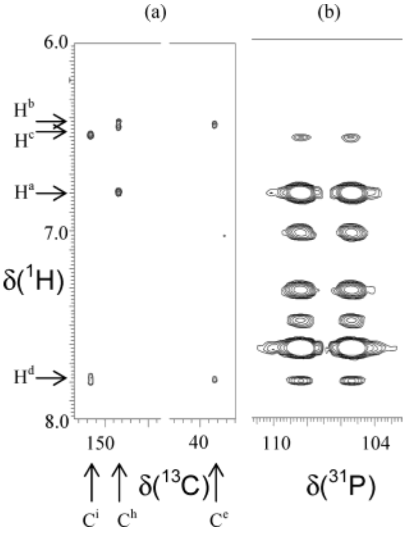


Figure 4. Relevant portions of the 2D NMR spectra of complex **14**: (a) ^{1}H−^{13}C gHMBC NMR spectrum and (b) ^{1}H−^{31}P gHMBC NMR spectrum.

The ^{1}H and ^{31}P NMR data for complexes **6a**−**c**, **7a,b**, **8**, **9**, **10a**−**c**, **11**, **12a,b**, and **13a,b** indicated that the complexes are fluxional in solution, as indicated by broad resonances at room temperature, so variable-temperature NMR experiments were performed. The NMR spectra showed that the resorcinarene skeleton retained the boat conformation with the phosphinite groups in the upright position throughout, and that the fluxionality involves the metal halide cluster.

The simplest form of fluxionality was observed for the silver iodide complexes **6c**, **8**, and **10c**, and the spectra of **8** will be discussed as a representative example. At room temperature, a single broad resonance was observed for the bridging methine protons of the resorcinarene in the ^{1}H NMR and a single broad doublet resonance was observed for the phosphinite groups in the ^{31}P NMR, indicating that the complex has effective C_{2v} symmetry (**8I**, Figure 5; only an average coupling for $^1J_{AgP}$ is resolved at 293 K). The ^{31}P NMR resonance narrowed at lower temperatures, to give the expected pattern of two doublets, arising from coupling of the phosphorus nuclei with the two spin-active isotopes of silver (^{107}Ag and ^{109}Ag, relative abundance 51.82% and 48.18%, respectively).[9] At −40 °C, a second set of doublets appeared (**8J**, Figure 5), which increase in intensity as the temperature is decreased. The magnitudes of the coupling constants $^1J_{AgP}$ for **8I** and **8J** are very similar (Table 5), indicating that the complexes have similar phosphine coordination. The magnitude of the coupling constants is

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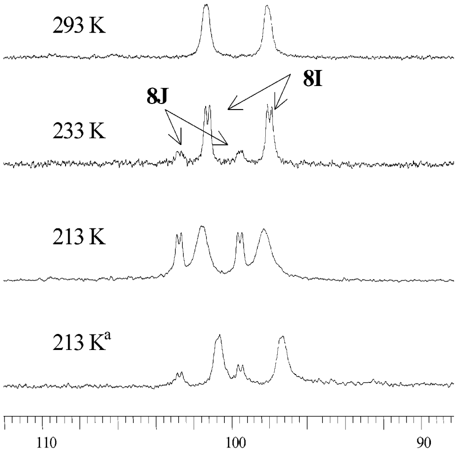


Figure 5. Variable-temperature ^{31}P NMR spectra of complex **8**. The bottom spectrum labeled with a superscript “a” is of a more dilute solution.

consistent with there being a single phosphorus atom coordinated to each silver(I), as found for the solid-state structure of **8**, but clearly there are two different complexes present at low temperature in the solution phase.[1,6] Variable-temperature ^{31}P NMR spectra were recorded for several concentrations of complex **8**, and it was found that the equilibrium between **8I** and **8J** was concentration dependent, and that the resonances for **8J** increase in intensity at higher concentrations (Figure 5).

Since the $^{1}H-^{13}C$ gHMBC and $^{1}H-^{31}P$ gHMBC correlated 2D NMR show that both **8I** and **8J** are present in the same resorcinarene conformation (phosphinite-derivatized arene rings upright), the fluxionality observed in the variable-temperature NMR data of complex **8** is likely to be associated with changes in the $P_4Ag_5I_5$ cluster unit. One possibility is that it involves the dissociation and association of the occluded fifth silver atom as depicted in Scheme 3, and this equilibrium would be concentration dependent. This is in agreement with the ^{31}P NMR data obtained for complex **8**, where it was observed that the resonances for **8J** decreased in intensity with increasing dilution. The resonances observed at room temperature then probably correspond to the dissociated species **8I**, while the associated complex **8J** is only observed at low temperature (Figure 5).

Variable-temperature ^{1}H and ^{31}P NMR studies on complex **10c** showed solution behavior similar to that described for complex **8**, indicating a similar fluxional process, but many of the complexes exhibited more complex fluxionality. Of these cases, the ^{31}P NMR spectra of the silver chloride cluster complex **6a** were the best resolved and will be discussed in detail. At room temperature, the ^{31}P NMR spectrum of **6a** contained only a very broad resonance, which split at −40 °C to give four separate resonances with different intensities, each showing the characteristic $^{1}J_{AgP}$ couplings. These are labeled as **6aI**−**L** in Figure 6. At −60 °C, the intensity of the resonances for **6aL** increased, while those for the other three species decreased. At −80 °C, the resonance for **6aL** remained sharp, while the resonance for **6aI** was broad and those for **6aJ** and **6aK** were no longer detected. Thus, Figure 6 shows that complex **6a** is present in solution as a rapidly equilibrating mixture of four different species.

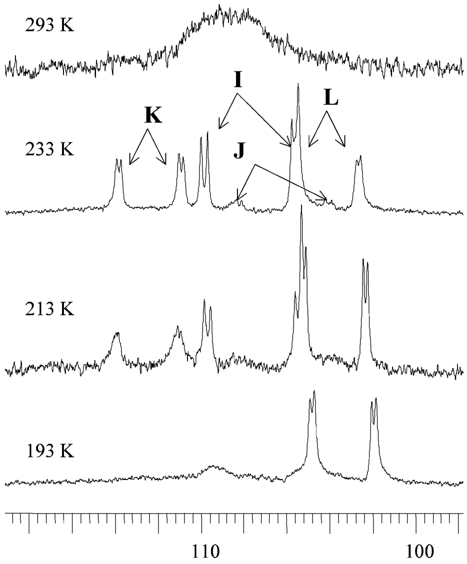
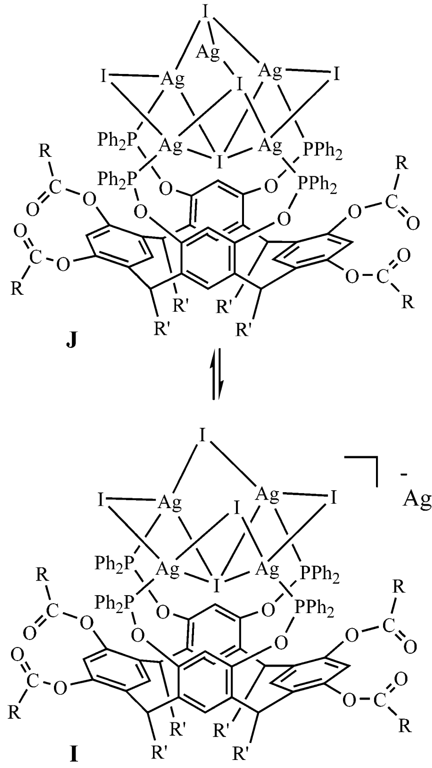


Figure 6. Variable-temperature ^{31}P NMR spectra of complex **6a**.

Scheme 3



The problem is to identify the four different complexes present, and although there is not a definitive solution, some insight can be obtained from the ^{31}P NMR spectra at varying temperature and concentration. The coupling constants $^{1}J_{AgP}$ vary according to the number of phosphorus atoms coordinated to silver and the nature of the halide ligand(s) present. For chloride complexes, couplings $^{1}J_{^{109}AgP}$ in the regions around 700 and 500 Hz are characteristic for AgP and AgP_2 coordination, respectively.[1,6] Thus, from the parameters in Table 5, the compounds **6aI** and **6aJ** are assigned as having AgP coordination, while **6aK** and **6aL** are assigned as having AgP_2 coordination. At lower concentration, the resonances for **6aJ** decreased in intensity compared to those for **6aI**, so by analogy with complex **8**, it is suggested that **6aI** is the dissociated complex $Ag^+[P_4(Ag_4Cl_5)]^-$ and that **6aJ** is the parent complex $[P_4(Ag_5Cl_5)]$ (Scheme 3). The relative intensities of the ^{31}P resonances for complexes **6aI**, **6aK**, and **6aL** were essentially independent of concentration, indicating that each is formed by dissociation of **6aJ** into two fragments. The complexes **6aK** and **6aL** are characterized by having coupling constants $^1J_{AgP}$ that are slightly smaller than for the well-defined disilver complexes **14**–**17**, suggesting that they may have AgP_2Cl or AgP_2Cl_2 coordination (Table 5).[10] One possibility is that complexes **6aK** and **6aL** have a cationic core structure $[P_4(Ag_2(\mu\text{-}Cl)]^+$ similar to that observed in the solid state for complex **16** (Figure 3), with each silver atom bound to two phosphorus atoms and a bridging chloride, with further weak association with the "$Ag_3Cl_4^-$" unit required by stoichiometry for formation from **6aJ**. The easy conversion of the pentasilver(I) complex **6a** to the disilver(I) complex **14** by reaction with triflic acid lends credibility to this hypothesis. While silver halide anions, such as $[Ag_2Cl_4]^{2-}$, are known, there are few structurally characterized examples.[11,12] Another possibility is that each silver(I) center has a terminal chloride, giving AgP_2Cl coordination. Hence, the complete structures of the complexes **6aK** and **6aL**, and how they differ, are not defined. However, it is clear that they both have AgP_2 coordination, so the remarkably easy, reversible extrusion of silver chloride units from **6a** to give complexes similar to **14** is established.

The low-temperature ^{31}P NMR spectra of the copper(I) clusters, with either chloride or iodide ligands, resembled those of the silver(I) chloride derivatives, but because there is no additional information from metal–phosphorus coupling in this case, a detailed interpretation is not attempted.

Conclusions

The tetraphosphinite ligands are shown to have an interesting and complex coordination chemistry with silver(I) and copper(I). In all cases studied, the arene rings with the diphenylphosphinite substituents are upright, which allows the ligands to bind binuclear or cluster metal units. When the ligands form four MP bonds, crownlike silver(I) and copper(I) halide cluster complexes are formed based on $P_4M_4(\mu\text{-}X)_4$ units, and these incorporate a fifth halide ion at the center and a fifth copper(I) or silver(I) ion at the top to give the final $P_4M_5X_5$ units. This is a new type of cluster unit, though it can be considered to be related to the known clusters $P_4M_4X_5^-$, supported on a resorcinarene tetraphosphonite framework,[6] by addition of the fifth M^+ ion.

In solution, it is shown that the cluster complexes undergo easy and reversible fragmentation. In every case, reversible dissociation of the fifth M^+ ion occurs to form the $P_4M_4X_5^-$ unit. This reaction leaves the parent crown structure with four MP units intact, and for the iodide derivatives, this is the only form of fluxionality observed. However, the silver chloride and bromide derivatives take part in more extensive fluxionality, with reversible extrusion of silver halide and formation of chelate AgP_2X or AgP_2X_2 units. The disilver chloride complexes $[P_4Ag_2(\mu\text{-}Cl)]^+$ could be prepared independently in pure form and isolated as the triflate salts, but attempts to prepare the corresponding iodide complexes were unsuccessful. In the structurally characterized complex $[P_4Ag_2(\mu\text{-}Cl)]^+$, the resorcinarene was in a more ideal boat conformation than in the pentasilver complexes, and it is clear that the flexibility of the resorcinarene skeleton is important in allowing this easy transformation between pentasilver and disilver units. The halide dependence of the equilibrium is presumably related to size effects. For example, it has been noted previously that the $Ag_4(\mu_4\text{-}X)$ unit present in the cluster complexes is more easily formed by the larger iodide than by the smaller chloride ligand.[6] The dynamic behavior of the pentasilver(I) and pentacopper(I) halide complexes appears to be unprecedented.

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 NMR spectrometer. The tetraphosphinite resorcinarene ligands were prepared as reported elsewhere.[7a] In the formulas below the resorcinarene skeleton is $(C_6H_2CH\{CH_2CH_2Ph\})_4$. The proton and carbon resonances of the resorcinarene skeleton are identified according to the labeling scheme shown in Chart 3.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2$\{AgCl\})$_4$\{AgCl\}], 6a. A mixture of **1** (0.150 g, 0.072 mmol) and AgCl (0.057 g, 0.398 mmol) in CH_2Cl_2 (10 mL) in a darkened flask was stirred for 16 h. The solution was filtered through Celite, and a white solid was precipitated by addition of pentane (10 mL). The solid was collected, washed with ether (10 mL), and recrystallized from $CHCl_3$/hexane. Yield: 0.138 g, 69%. NMR (CD_2Cl_2, 20 °C): $\delta(^1H)$ 1.10–2.10 [m, 48H, H^f, C_6H_{11}]; 2.24 [m, 4H, H^f]; 2.42, 2.62 [m, 8H, H^g]; 4.63 [m, 4H, H^e]; 6.22–7.79 [m, 68H, Ar-H, Ph]; $\delta(^{31}P)$ 109.1 [br]. Anal. Calcd for **6a**·0.5(hexane), $C_{139}H_{139}Ag_5Cl_5O_{12}P_4$: C, 58.74; H, 4.93. Found: C, 58.99; H, 5.35.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2$\{AgBr\})$_4$\{AgBr\}], 6b. This was prepared similarly from **1** (0.150 g, 0.072 mmol) and AgBr (0.074 g, 0.394 mmol). Yield: 0.168 g, 77%. NMR (CD_2Cl_2, 20 °C): $\delta(^1H)$ 1.04–1.90 [m, 44H, C_6H_{11}]; 1.97, 2.29 [m, 8H, H^f]; 2.41, 2.59 [m, 8H, H^g]; 4.64 [m, 4H, H^e]; 6.64 [s, 2H, Ar-H]; 6.90–7.75 [m, 66H, Ar-H, Ph]; $\delta(^{31}P)$ 106.0 [m, $^1J_{AgP} = 614$ Hz]. Anal. Calcd for $C_{136}H_{132}Ag_5Br_5O_{12}P_4$: C, 54.07; H, 4.40. Found: C, 53.78; H, 4.78.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2$\{AgI\})$_4$\{AgI\}], 6c. This was prepared similarly from **1** (0.200 g, 0.096 mmol) and AgI (0.124 g, 0.528 mmol). Yield: 0.224 g, 72%. NMR (CD_2Cl_2, 0 °C): $\delta(^1H)$ 0.93–1.80 [m, 44H, C_6H_{11}]; 1.94 [m, 4H, H^f]; 2.31 [m, 8H, H^f, H^g]; 2.50 [m, 4H, H^g]; 4.59 [m, 4H, H^e]; 6.51, 6.81, 7.72 [s, 6H, Ar-H]; 6.87–7.57 [m, 62H, Ar-H, Ph]; $\delta(^{31}P)$ 98.5 [m, $^1J_{^{109}AgP} = 563$ Hz, $^1J_{^{107}AgP} = 491$ Hz]. Anal. Calcd for $C_{136}H_{132}Ag_5I_5O_{12}P_4$: C, 50.16; H, 4.09. Found: C, 50.53; H, 4.55.

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[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2${CuCl})$_4${CuCl}], 7a. This was prepared similarly from **1** (0.075 g, 0.036 mmol) and CuCl (0.020 g, 0.202 mmol). Yield: 0.052 g, 56%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 1.04−2.16 [m, 48H, H^f, C$_6$$H_{11}$]; 2.36 [m, 4H, H^f]; 2.46, 2.64 [m, 8H, H^g]; 4.63 [m, 4H, H^e]; 6.54, 6.82 [s, 4H, Ar-*H*]; 6.91−8.02 [m, 64H, Ar-*H, Ph*]; δ(^{31}P) 91.7 [s, br]. Anal. Calcd for C$_{136}$H$_{132}$Cl$_5$Cu$_5$O$_{12}$P$_4$: C, 63.38; H, 5.16. Found: C, 63.04; H, 5.36.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2${CuI})$_4${CuI}], 7b. This was prepared similarly from **1** (0.150 g, 0.072 mmol) and CuI (0.075 g, 0.394 mmol). Yield: 0.116 g, 53%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 0.94−2.14 [m, 48H, H^f, C$_6$$H_{11}$]; 2.38 [m, 8H, H^f, H^g]; 2.59 [m, 4H, H^g]; 4.67 [m, 4H, H^e]; 6.22−7.96 [m, 68H, Ar-*H, Ph*]; δ(^{31}P) 84.0 [s, br]. Anal. Calcd for C$_{136}$H$_{132}$Cu$_5$I$_5$O$_{12}$P$_4$: C, 53.83; H, 4.38. Found: C, 54.01; H, 4.52.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OPPh$_2${AgI})$_4${AgI}], 8. This was prepared similarly from **2** (0.150 g, 0.071 mmol) and AgI (0.92 g, 0.392 mmol). Yield: 0.153 g, 66%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 1.99 [m, 4H, H^f]; 2.31 [m, 8H, H^f, H^g]; 2.38 [s, 12H, C$_6$H$_4$CH_3]; 2.52 [m, 4H, H^g]; 4.86 [m, 4H, H^e]; 6.62 [s, 2H, H^c]; 7.22, [s, 2H, H^b]; 6.66−7.66 [m, 78H, H^a, *Ph*, C$_6$$H_4CH_3$]; 7.84 [s, 2H, H^d]; δ(^{31}P) 99.7 [m, $^1J_{\mathrm{AgP}}$ = 508 Hz]. Anal. Calcd for C$_{140}$H$_{116}$Ag$_5$I$_5$O$_{12}$P$_4$: C, 51.14; H, 3.56. Found: C, 50.60; H, 3.82.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OPPh$_2${CuI})$_4${CuI}], 9. This was prepared similarly from **2** (0.160 g, 0.076 mmol) and CuI (0.079 g, 0.415 mmol). Yield: 0.166 g, 71%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 2.04 [m, 4H, H^f]; 2.28 [m, 8H, H^f, H^g]; 2.36 [s, 12H, C$_6$H$_4$CH_3]; 2.56 [m, 4H, H^g]; 4.82 [m, 4H, H^e]; 6.53 [s, br, 2H, Ar-*H*]. 6.62−7.69 [m, 82H, Ar-*H, Ph*, C$_6$$H_4CH_3$]; δ(^{31}P) 85.1 [s, br]. Anal. Calcd for C$_{140}$H$_{116}$Cu$_5$I$_5$O$_{12}$P$_4$: C, 54.83; H, 3.81. Found: C, 55.08; H, 3.65.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2${AgCl})$_4${AgCl}], 10a. This was prepared similarly from **3** (0.100 g, 0.048 mmol) and AgCl (0.038 g, 0.265 mmol). Yield: 0.090 g, 67%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 2.02, 2.32 [m, 8H, H^f]; 2.41, 2.59 [m, 8H, H^g]; 4.81 [m, 4H, H^e]; 6.59 [s, br, 2H, Ar-*H*]; 6.71−7.78 [m, 78H, Ar-*H, Ph*, C$_4$$H_3$S]; δ(^{31}P) 109.2 [br]. Anal. Calcd for C$_{128}$H$_{100}$Ag$_5$Cl$_5$O$_{12}$P$_4$S$_4$: C, 54.93; H, 3.60. Found: C, 54.53; H, 3.66.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2${AgBr})$_4${AgBr}], 10b. This was prepared similarly from **3** (0.100 g, 0.048 mmol) and AgBr (0.050 g, 0.266 mmol). Yield: 0.117 g, 81%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 1.97 [m, 4H, H^f]; 2.36 [m, 8H, H^f, H^g]; 2.57 [m, 4H, H^g]; 4.84 [m, 4H, H^e]; 6.41−7.82 [m, 80H, Ar-*H, Ph*, C$_4$$H_3$S]; δ(^{31}P) 106.0 [m, $^1J_{\mathrm{AgP}}$ = 594 Hz]. Anal. Calcd for C$_{128}$H$_{100}$Ag$_5$Br$_5$O$_{12}$P$_4$S$_4$: C, 50.89; H, 3.37. Found: C, 51.23; H, 3.57.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2${AgI})$_4${AgI}], 10c. This was prepared similarly from **3** (0.150 g, 0.072 mmol) and AgI (0.093 g, 0.396 mmol). Yield: 0.182 g, 78%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 1.96 [m, 4H, H^f]; 2.37 [m, 8H, H^f, H^g]; 2.54 [m, 4H, H^g]; 4.93 [m, 4H, H^e]; 6.62 [s, 2H, Ar-*H*]; 6.70−7.93 [m, 78H, Ar-*H, Ph*, C$_4$$H_3$S]; δ(^{31}P) 99.4 [m, $^1J_{\mathrm{AgP}}$ = 518 Hz]. Anal. Calcd for C$_{128}$H$_{100}$Ag$_5$I$_5$O$_{12}$P$_4$S$_4$: C, 47.21; H, 3.10. Found: C, 46.80; H, 3.18.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2${CuCl})$_4${CuCl}], 11. This was prepared similarly from **3** (0.100 g, 0.048 mmol) and CuCl (0.026 g, 0.263 mmol). Yield: 0.088 g, 71%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 1.99 [m, 4H, H^f]; 2.45 [m, 8H, H^f, H^g]; 2.65 [m, 4H, H^g]; 4.88 [m, 4H, H^e]; 6.67−7.78 [m, 80H, Ar-*H, Ph*, C$_4$$H_3$S]; δ(^{31}P) 86.2 [s, br]. C$_{128}$H$_{100}$Cl$_5$Cu$_5$O$_{12}$P$_4$S$_4$: C, 59.65; H, 3.91. Found: C, 59.52; H, 3.91.

[Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OPPh$_2${AgCl})$_4${AgCl}], 12a. This was prepared similarly from **4** (0.100 g, 0.051 mmol) and AgCl (0.040 g, 0.279 mmol). Yield: 0.091 g, 66%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 2.00, 2.38 [m, 8H, H^f]; 2.57, 2.78 [m, 8H, H^g]; 2.63 [s, 4H, OCH$_2$C≡C*H*]; 4.61 [m, br, 4H, H^e]; 4.75 [m, br, 8H, OCH_2C≡CH]; 6.37 [s, br, 2H, Ar-*H*]; 6.80−7.96 [m, 66H, Ar-*H, Ph*]; δ(^{31}P) 110.2 [s, br]. Anal. Calcd for C$_{124}$H$_{100}$Ag$_5$Cl$_5$O$_{16}$P$_4$: C, 55.44; H, 3.75. Found: C, 55.50; H, 3.90.

[Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OPPh$_2${AgBr})$_4${AgBr}], 12b. This was prepared similarly from **4** (0.100 g, 0.051 mmol) and AgBr (0.052 g, 0.277 mmol). Yield: 0.092 g, 62%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 2.02, 2.17 [m, 8H, H^f]; 2.32, 2.54 [m, 8H, H^g]; 2.53 [s, br, 4H, OCH$_2$C≡C*H*]; 4.46 [m, br, 8H, $^2J_{\mathrm{HH}}$ = 16 Hz, OCH_2C≡CH]; 4.48 [br, 4H, H^e]; 6.13 [s, br, 2H, Ar-*H*]; 6.70−7.88 [m, 66H, Ar-*H, Ph*]; δ(^{31}P) 110.5 [m, $^1J_{\mathrm{AgP}}$ = 611 Hz]. Anal. Calcd for C$_{124}$H$_{100}$Ag$_5$Br$_5$O$_{16}$P$_4$: C, 51.20; H, 3.47. Found: C, 50.97; H, 3.70.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2${AgCl})$_4${AgCl}], 13a. This was prepared similarly from **5** (0.100 g, 0.046 mmol) and AgCl (0.036 g, 0.251 mmol). Yield: 0.078 g, 59%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 1.98, 2.25 [m, 8H, H^f]; 2.45, 2.62 [m, 8H, H^g]; 4.65 [m, 4H, H^e]; 5.20 [m, 8H, $^2J_{\mathrm{HH}}$ = 12 Hz, OCH_2Ph]; 6.43−7.63 [m, 88H, Ar-*H, Ph*]; δ(^{31}P) 106.4 [br]. Anal. Calcd for C$_{140}$H$_{116}$Ag$_5$Cl$_5$O$_{16}$P$_4$: C 58.09; H 4.04. Found: C, 57.82; H, 3.91.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2${AgBr})$_4${AgBr}], 13b. This was prepared similarly from **5** (0.100 g, 0.046 mmol) and AgBr (0.047 g, 0.250 mmol). Yield: 0.080 g, 56%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 1.94, 2.17 [m, 8H, H^f]; 2.32, 2.54 [m, 8H, H^g]; 4.54 [br, 4H, H^e]; 4.85 [m, br, 8H, OCH_2Ph]; 6.27 [s, br, 2H, Ar-*H*]; 6.69−7.88 [m, 86H, Ar-*H, Ph*]; δ(^{31}P) 110.6 [m, $^1J_{\mathrm{AgP}}$ = 613 Hz]. Anal. Calcd for C$_{140}$H$_{116}$Ag$_5$Br$_5$O$_{16}$P$_4$: C 53.94; H 3.75. Found: C, 53.76; H, 3.93.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2$)$_4${Ag$_2$-μ-Cl}]CF$_3$SO$_3$, 14. Method 1. To a solution of **6a** (0.100 g, 0.36 mmol) in CD$_2$Cl$_2$ (1 mL) was added triflic acid (3.2 μL, 0.36 mmol), which resulted in the precipitation of silver chloride within 1 min. The solution was filtered through Celite, and a white solid was precipitated with hexane. The solid was washed with ether (10 mL), recrystallized from dichloroethane/hexane, and dried under reduced pressure. Yield: 0.072 g, 81%.

Method 2. 1 (0.100 g, 0.048 mmol), AgCF$_3$SO$_3$ (0.025 g, 0.097 mmol), and NaCl (0.010 g, 0.171 mmol) in a darkened flask were dissolved/suspended in CH$_2$Cl$_2$ (10 mL) and stirred for 16 h. The solution was filtered through Celite and concentrated, and a white solid was precipitated with hexane. The solid was collected, washed with methanol (10 mL) and ether (10 mL), and dried under reduced pressure. Yield: 0.078 g, 65%. NMR (CD$_2$Cl$_2$, 0 °C): δ(^{1}H) 1.14−1.90 [m, 44H, C$_6$$H_{11}$]; 2.10, 2.44 [m, 8H, H^f]; 2.53, 2.77 [m, 8H, H^g]; 4.72 [m, 4H, H^e]; 6.43 [s, 2H, H^b]; 6.49 [s, 2H, H^c]; 6.77 [s, 2H, H^a]; 7.79 [s, 2H, H^d]; 6.79−7.62 [m, 60H, *Ph*]. Anal. Calcd for **14**·ClCH$_2$CH$_2$Cl, C$_{139}$H$_{136}$Ag$_2$Cl$_3$F$_3$O$_{15}$P$_4$S: C, 64.67; H, 5.35. Found: C, 64.24; H, 5.44.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OPPh$_2$)$_4${Ag$_2$-μ-Cl}]CF$_3$SO$_3$, 15. This was prepared similarly (method 2) from **2** (0.120 g, 0.057 mmol), AgCF$_3$SO$_3$ (0.030 g, 0.117 mmol), and NaCl (0.010 g, 0.171 mmol). Yield: 0.105 g, 73%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 2.12 [m, 4H, H^f]; 2.48 [m, 8H, H^f, H^g]; 2.47 [s, 12H, C$_6$H$_4$CH_3]; 2.72 [m, 4H, H^g]; 4.85 [m, 4H, H^e]; 6.52 [s, 2H, H^b]; 6.53 [s, 2H, H^c]; 7.85 [s, 2H, H^d]; 6.70−7.75 [m, 78H, H^a, *Ph*, C$_6$$H_4CH_3$]. Anal. Calcd for C$_{141}H_{116}Ag_2ClF_3O_{15}P_4$S: C, 67.35; H, 4.65. Found: C, 66.99; H, 4.67.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2$)$_4${Ag$_2$-μ-Cl}]CF$_3$SO$_3$, 16. This was prepared similarly (method 2) from **3** (0.100 g, 0.048 mmol), AgCF$_3$SO$_3$ (0.025 g, 0.097 mmol), and NaCl (0.010 g, 0.171 mmol). Yield: 0.87 g, 73%. NMR (CD$_2$Cl$_2$, 20 °C): δ(^{1}H) 2.10 [m, 4H, H^f]; 2.51 [m, 8H, H^f, H^g]; 2.73 [m, 4H, H^g];

Table 6. Crystallographic Data for Complexes **6c**, **8**, and **16**

	6c	**8**	**16**
empirical formula	$C_{145.2}H_{151.2}Ag_5I_5O_{14.3}P_4$	$C_{143}H_{118}Ag_5Cl_9I_5O_{13.50}P_4$	$C_{134.5}H_{111}Ag_2Cl_{6.5}F_3O_{15.25}P_4S_5$
fw	3422.79	3669.15	2758.58
space group	$P2(1)/c$	$P2(1)/m$	$P\bar{1}$
a (Å)	15.9824(1)	19.3247(2)	18.426(4)
b (Å)	25.2649(1)	22.8616(4)	19.698(4)
c (Å)	35.4313(1)	19.7339(3)	21.242(4)
α (deg)			79.25(3)
β (deg)	101.705(1)	117.315(1)	73.09(3)
γ (deg)			63.73(3)
vol (Å^3)	14009.4(1)	7746.2(2)	6600(2)
Z	4	2	2
D_{calcd} (Mg/m^3)	1.623	1.573	1.388
μ (mm^{-1})	1.894	1.868	0.621
R1, wR2 [$I > 2\sigma(I)$]	0.0413, 0.1112	0.0880, 0.2720	0.0913, 0.2436
R indices (all data)	0.0808, 0.1248	0.1312, 0.3103	0.1484, 0.2822

4.87 [m, 4H, H^e]; 6.48 [s, 2H, H^b]; 6.52 [s, 2H, H^c]; 7.39 [s, 2H, H^a]; 7.82 [s, 2H, H^d]; 6.73−7.69 [m, 72H, *Ph*, C_4H_3S]. Anal. Calcd for $C_{129}H_{100}Ag_2ClF_3O_{15}P_4S_5$: C, 62.41; H, 4.06. Found: C, 62.23; H, 4.23.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2$)$_4${Ag$_2$-μ-Cl}]-CF$_3$SO$_3$, 17. This was prepared similarly from **5** (0.100 g, 0.046 mmol), $AgCF_3SO_3$ (0.024 g, 0.093 mmol), and NaCl (0.010 g, 0.171 mmol). Yield: 0.85 g, 72%. NMR (CD_2Cl_2, 20 °C): $\delta(^1H)$ 2.04, 2.36 [m, 8H, H^f]; 2.51, 2.70 [m, 8H, H^g]; 4.72 [m, 4H, H^e]; 5.26 [s, 8H, OCH_2Ph]; 6.30 [s, 2H, H^b]; 6.35 [s, 2H, H^c]; 7.70 [s, 2H, H^d]; 6.94−7.58 [m, 82H, H^a, *Ph*]. Anal. Calcd for $C_{141}H_{116}Ag_2ClF_3O_{19}P_4S$: C, 65.68; H, 4.53. Found: C, 65.45; H, 4.57.

X-ray Structure Determinations. A crystal suitable for X-ray analysis was mounted on a glass fiber. Data were collected using a Nonius-Kappa CCD diffractometer using COLLECT (Nonius, B.V., 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 (Nonius, B.V., 1998). The SHELX-TL V5.1 and SHELX-TL V6.1 (Sheldrick, G. M.) program packages were used to solve and refine the structures. The structures of complexes **6c** and **16** were solved by direct methods, while complex **8** was solved by the automated Patterson routine of the SHELX-TL software package. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. Except as mentioned, all non-hydrogen atoms were refined with anisotropic thermal parameters. Crystal data are summarized in Table 6. All thermal ellipsoid diagrams are shown at 30% probability.

[Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OPPh$_2${AgI})$_4${AgI}], 6c. Crystals of $[C_{136}H_{132}O_{12}P_4Ag_5I_5]\cdot1.9(THF)\cdot0.4(ether)$ were grown from diffusion of ether into a THF solution. The occluded fifth silver atom was disordered over two positions and was modeled as a 65:35 anisotropic mixture. One of the dangling phenethyl groups was modeled as a 70:30 isotropic mixture with geometric restraints. A phenyl ring of one of the dangling phenethyl groups was modeled as a 50:50 isotropic mixture with geometric restraints. Two of the phenyl rings of the diphenylphosphinite groups were disordered, one of which was modeled as a 70:30 isotropic mixture while the other was modeled as a 55:45 isotropic mixture, and in both cases geometric restraints were applied. Two of the cyclohexyl substituents were disordered. One was modeled as a 50:50 isotropic mixture and the other a 55:45 isotropic mixture, and each was modeled with geometric restraints. The full-occupancy THF molecule was modeled as a 60:40 mixture, while the half-occupancy THF was modeled as a 25:25 mixture. The final solvent was modeled as a 40:40 mixture of a THF molecule and an ether molecule. All solvent molecules were refined with isotropic thermal parameters and with geometric restraints. The largest residual electron density peak (1.242 e/Å^3) was associated with one of the disordered solvent molecules.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OPPh$_2${AgI})$_4${AgI}], 8. Crystals of $[C_{140}H_{116}O_{12}P_4Ag_5I_5]\cdot3(CHCl_3)\cdot1.5(H_2O)$ were grown from diffusion of hexane into a chloroform solution. One of the phenyl rings bonded to a phosphorus atom was modeled as an isotropic mixture of two half-occupancy groups. Both of the tolyl substituents were also modeled as an isotropic mixture of two half-occupancy groups. One of the carbonyl oxygens was modeled as a 50:50 isotropic mixture. There is significant thermal motion of the occluded fifth silver atom, suggesting the atom is disordered, but no suitable disorder model could be refined. The carbon−chlorine bond lengths and the chlorine−chlorine distances of the solvents were fixed at 1.75 and 2.75 Å, respectively. One of the chloroform molecules was disordered across a symmetry element and was modeled as an isotropic mixture of two half-occupancy groups without the hydrogen atom. The molecules of adventitious water were modeled as single isotropic oxygen atoms. The center of the molecule is situated on a crystallographic mirror plane. The largest residual electron density peak (2.957 e/Å^3) was associated with one of the iodine atoms (I4).

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OPPh$_2$)$_4${Ag$_2$-μ-Cl}]-CF$_3$SO$_3$, 16. Crystals of $[C_{128}H_{100}Ag_2ClO_{12}P_4S_4][CF_3SO_3]\cdot2.75(ClCH_2CH_2Cl)\cdot0.25(H_2O)$ were grown from slow diffusion of hexane into a dichloroethane solution. Two of the thiophene rings were modeled as 75:25 disorder with geometric restraints,[13] and only the sulfur atoms were refined with anisotropic thermal parameters. The triflate anion was disordered equally over two positions, and only the sulfur atom was refined with anisotropic thermal parameters. The solvents of crystallization were poorly ordered and were refined with geometrical constraints and with isotropic thermal parameters for carbon atoms. The partial-occupancy molecule of water was modeled as a single isotropic oxygen atom. The largest residual electron density peak (2.093 e/Å^3) was associated with one of the solvent molecules.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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