Inorg. Chem. **2005**, *44*, 4666–4678

Inorganic Chemistry
Article

Tetraphosphinite Resorcinarene Complexes: Silver(I) Capsule Complexes

Dana J. Eisler and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada, N6A 5B7

Received January 20, 2005

Resorcinarene tetraphosphinite ligands, $\mathbf{P_4}$, react with silver(I) trifluoroacetate or silver(I) triflate, AgX, to give the corresponding $[Ag_4X_4(\mathbf{P_4})]$ complexes. The resorcinarene skeleton in these complexes adopts a boat conformation with the silver(I) phosphinite units on the horizontal, rather than the upright, arene units of the resorcinarene. The $[Ag_4X_4(\mathbf{P_4})]$ complexes react with free $\mathbf{P_4}$ ligand to yield the $[Ag_2X_2(\mathbf{P_4})]$ or $[AgX(\mathbf{P_4})]$ complexes, which are characterized in solution by NMR spectroscopy to have a conformation opposite to that of the $[Ag_4X_4(\mathbf{P_4})]$ complexes; the silver(I) phosphinite groups are on the upright arene rings of the resorcinarene “boat” instead of the horizontal arene units. There is an easy equilibrium between these complexes. When X = triflate, the $[Ag_4X_4(\mathbf{P_4})]$ complexes disproportionate and add aqua ligands during slow crystallization to give “capsule complexes”, which are characterized crystallographically as $[Ag_{10}(O_3SCF_3)_{10}(OH_2)_6(\mathbf{P_4})_2]$, $[Ag_{10}(O_3SCF_3)_6(OH_2)_8(\mathbf{P_4})_2][\,O_3SCF_3]_4$, or $[Ag_{13}(O_3SCF_3)_{13}(OH_2)_7(\mathbf{P_4})_2]$ depending on the resorcinarene tetraphosphinite ligand $\mathbf{P_4}$ used. These unusual capsule complexes are formed by the tail-to-tail self-assembly of pairs of $[Ag_4(\mathbf{P_4})]^{4+}$ units linked by additional silver ions that bind to the phenyl substituents of one resorcinarene through $\{Ag(\eta^2\text{-}C_6H_5)\}^+$ binding and to the bridging triflate ligands, aqua ligands, or both of the other resorcinarene unit.

Introduction

The current interest in the synthesis and design of supramolecular structures through the use of coordination chemistry with polymers, helices, sheet, or network structures, and cage complexes as typical targets is intense.[1−3] Supramolecular structures that are self-assembled from macrocyclic building blocks, for example those derived from molecules possessing a cavity such as calixarenes and resorcinarenes, are particularly interesting because they have potential applications as size and shape selective functional materials. Silver(I) salts are often used in forming supramolecular architectures because silver(I) is a labile coordination center and can easily form complexes with coordination numbers of 2, 3, or 4 as needed to form many different architectures.[5−8] Many silver(I) salts are readily available, and carboxylate or sulfonate salts such as CF_3COOAg and CF_3SO_3Ag have proved to be particularly useful because the anions can act as versatile bridging ligands in forming network structures, as illustrated in Chart 1.[5,6]

---

* To whom correspondence should be addressed. E-mail: pudd@uwo.ca. Fax: (519)661-3022.

(1) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460. (b) Pan, L.; Woodlock, E. B.; Wang, X.; Lam, K.-C.; Rheingold, A. *Chem. Commun.* **2001**, 1762. (c) Ino, I.; Zhong, J. C.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Kitamori, Y. *Inorg. Chem.* **2000**, *39*, 4273.

(2) (a) Mislin, G.; Graf, E.; Hosseini, M. W.; De Cian, A.; Kyritsakas, N.; Fischer, J. *Chem. Commun.* **1998**, 2545. (b) Webb, H. R.; Hardie, M. J.; Raston, C. L.; *Chem.—Eur. J.* **2001**, *7*, 3616.

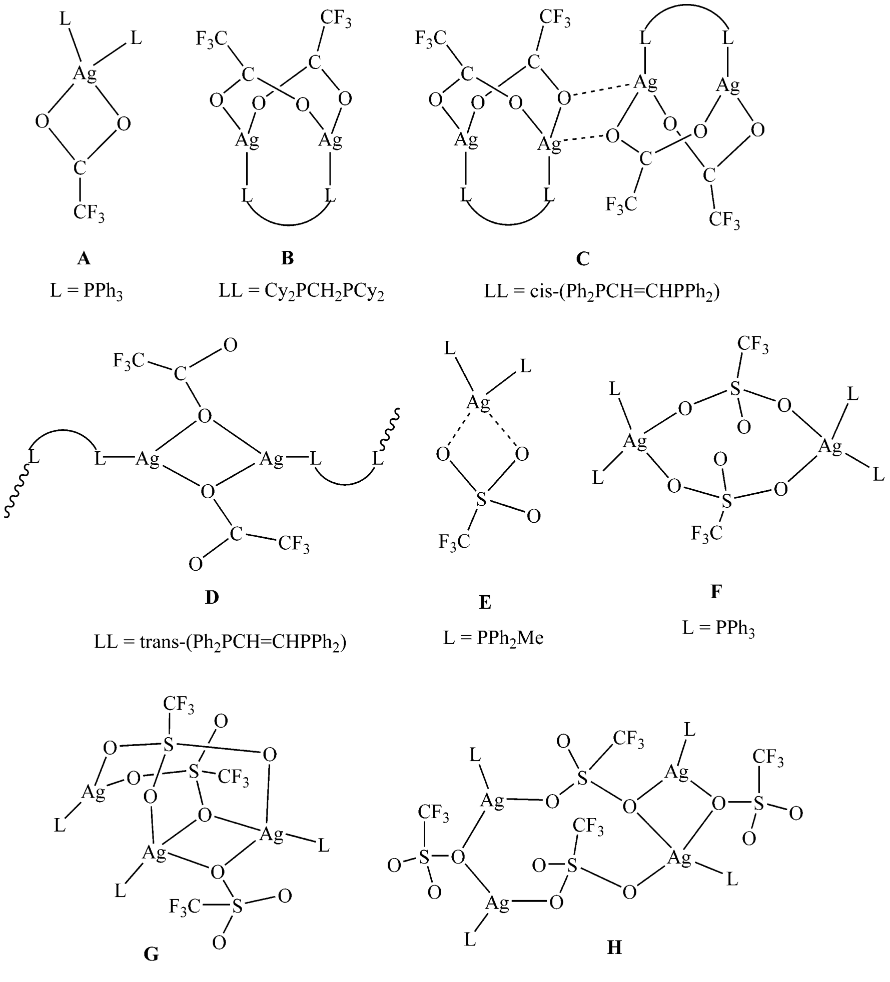
(3) (a) Bibal, B.; Tinant, B.; Declercq, J.-P.; Dutasta, J.-P. *Chem. Commun.* **2002**, 432. (b) Harrison, R. G.; Fox, O. D.; Meng, M. O.; Dalley, N. K.; Barbour, L. J. *Inorg. Chem.* **2002**, *41*, 838. (c) Park, S. J.; Hong, J.-I. *Chem. Commun*. **2001**, 1554. (d) Fox, O. D.; Dalley, N. K.; Harrison, R. G. *Inorg. Chem.* **2000**, *39*, 620. (e) Fox, O. D.; Dalley, N. K.; Harrison, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 7111. (f) Fox, O. D.; Drew, M. G. B.; Wilkinson, E. J. S.; Beer, P. D. *Chem. Commun.* **2000**, 391. (g) Fox, O. D.; Leung, J. F. Y.; Hunter, J. M.; Dalley, N. K.; Harrison, R. G. *Inorg. Chem.* **2000**, *39*, 783. (h) Fox, O. D.; Drew, M. G. B.; Beer, P. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 135. (i) Fox, O. D.; Dalley, N. K.; Harrison, R. G. *Inorg. Chem.* **1999**, *38*, 5860. (j) Jacopozzi, P.; Dalcanale, E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 613.

(4) (a) Xu, W.; Rourke, J. P.; Vittal, J.; Puddephatt, R. J. *Inorg. Chem.* **1995**, *34*, 323. (b) Xu, W.; Vittal, J.; Puddephatt, R. J. *Inorg. Chem.* **1997**, *36*, 86. (c) Xu, W.; Vittal, J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8362. (d) Sakhaii, P.; Neda, I.; Freytag, M.; Thönnessen, H.; Jones, P. G.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1246.

(5) (a) Burchell, T. J.; Eisler, D. J.; Puddephatt, R. J. *Chem. Commun.* **2004**, 944. (b) Che, C.-M.; Tse, M.-C.; Chan, M. C. W.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. *J. Am. Chem. Soc.* **2000**, *122*, 2464. (c) Brandys, M.-C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 3946. (d) Powell, J.; Horvath, M. J.; Lough, A.; Phillips, A.; Brunter, J. *J. Chem. Soc., Dalton Trans.* **1998**, 637.

10.1021/ic050095b CCC: $30.25

Chart 1



A L = PPh$_3$

B LL = Cy$_2$PCH$_2$PCy$_2$

C LL = cis-(Ph$_2$PCH=CHPPh$_2$)

D LL = trans-(Ph$_2$PCH=CHPPh$_2$)

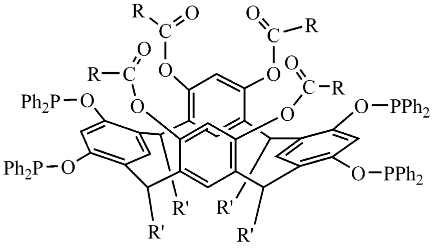
E L = PPh$_2$Me

F L = PPh$_3$

G L = PPh$_3$

H L = PPh$_2$Me

Chart 2 [a]



1 R = 4-C$_6$H$_4$CH$_3$ **2** R = C$_4$H$_3$S

3 R = C$_6$H$_{11}$ **4** R = OCH$_2$Ph

[a] R′ = CH$_2$CH$_2$Ph.

The lability of silver(I) phosphine complexes is well established and it is known that up to four phosphorus donors can coordinate to a single silver(I) center.[5−8] The tetraphosphinite resorcinarene compounds **1**−**4** (Chart 2) have the potential to form many types of silver(I) complexes because there are multiple coordination sites available on the macrocyclic skeleton. Some silver cluster complexes and self-assembled polymers have been reported earlier.[7] The present work is concerned with the formation of capsule complexes derived from these resorcinarenes by coordination to silver(I) salts. We note that there are earlier reports of the formation of elegant cage and capsule complexes from resorcinarenes with nitrogen or sulfur donor groups incorporated. These capsules are formed by the coupling of two bowl-shaped molecules through the formation of coordination compounds with metals bridging between the bowls.[3]

Results and Discussion

Synthesis of the Complexes. The reaction of the tetraphosphinite resorcinarene compounds **1**−**4** with 4 equiv of the silver salts AgX (X = CF$_3$COO, CF$_3$SO$_3$) resulted in the formation of complexes **5a**−**8b**, as outlined in Scheme 1 in which the X groups are drawn as terminal ligands for simplicity. Silver complexes **5a**−**8b** were isolated as analyti-

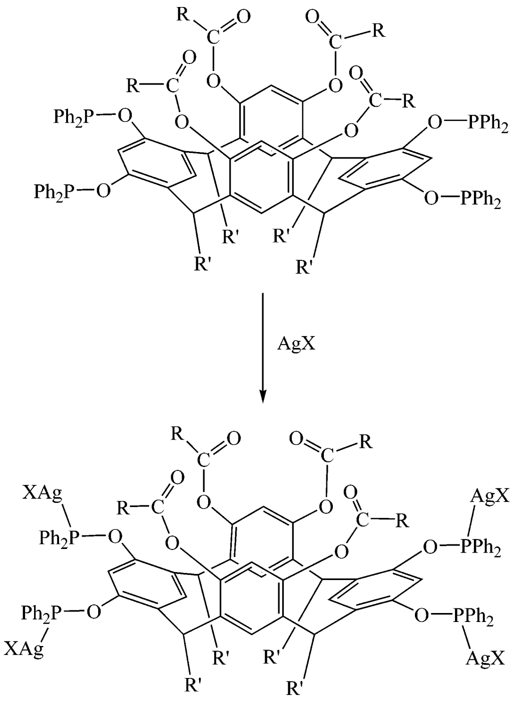
---

(6) (a) Buchholz, H. A.; Prakash, G. K. S.; Vaughan, J. F. S.; Bau, R.; Olah, G. A. *Inorg. Chem.* **1996**, *35*, 4076. (b) Laguna, M.; Villacampa, M. D. *Inorg. Chem.* **1998**, *37*, 133. (c) Kuang, S.-M.; Zhang, Z.-Z.; Wang, Q.-G.; Mak, T. C. W. *Inorg. Chem.* **1998**, *37*, 6090. (d) Lozano, E.; Nieuwenhuyzen, M.; James, S. L. *Chem.*—*Eur. J.* **2001**, *7*, 2644. (e) James, S. L.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2323. (f) Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2000**, *122*, 7608.

(7) Eisler, D. J.; Puddephatt, R. J. *Cryst. Growth Des.* **2005**, *5*, 57.

(8) (a) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W. S.; Schröder, M. *Chem. Commun.* **1997**, 1675. (b) Hannon, M. J.; Painting, C. L.; Errington, W. *Chem. Commun.* **1997**, 1805. (c) Blake, A. J.; Champness, N. R.; Cooke, P. A.; Nicolson, J. E. B.; Wilson, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3811. (d) Jeunesse, C.; Dieleman, C.; Steyer, S.; Matt, D. *J. Chem. Soc., Dalton Trans.* **2001**, 881.

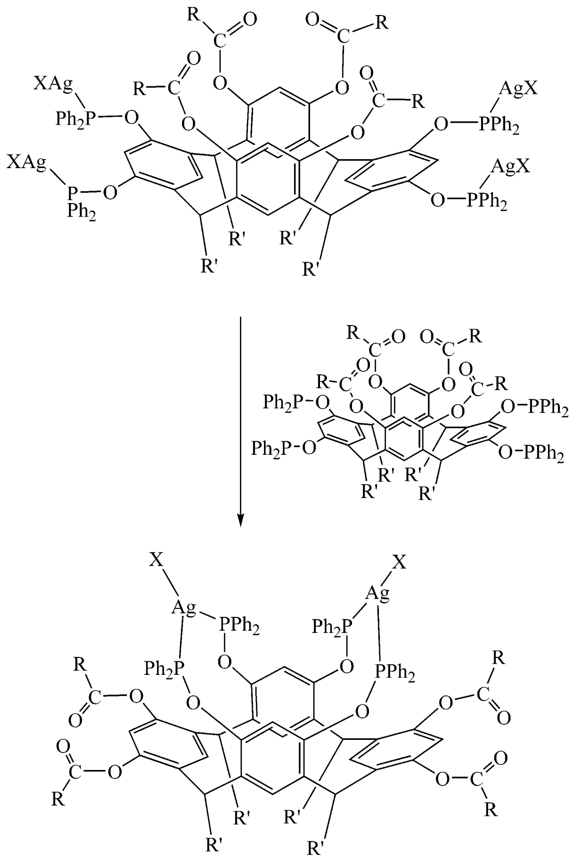
Scheme 1[a]



R = 4-$C_6H_4CH_3$	**5a** X = CF_3COO	**5b** X = CF_3SO_3
R = C_4H_3S	**6a** X = CF_3COO	**6b** X = CF_3SO_3
R = C_6H_{11}	**7a** X = CF_3COO	**7b** X = CF_3SO_3
R = OCH_2Ph	**8a** X = CF_3COO	**8b** X = CF_3SO_3

[a] R′ = CH_2CH_2Ph.

Scheme 2[a]



R = 4-$C_6H_4CH_3$	**9a** X = CF_3COO	**9b** X = CF_3SO_3
R = C_4H_3S	**10a** X = CF_3COO	**10b** X = CF_3SO_3
R = C_6H_{11}	**11a** X = CF_3COO	**11b** X = CF_3SO_3
R = OCH_2Ph		**12b** X = CF_3SO_3

[a] R′ = CH_2CH_2Ph.

cally pure white solids, [$\mathbf{P_4}$(AgX)$_4$] (where $\mathbf{P_4}$ = a resorcinarene ligand **1**−**4**), which were characterized by ^{1}H and ^{31}P NMR spectroscopy. The trifluoroacetate derivative, **5a**, was also characterized by X-ray structure determination and confirmed the stoichiometry [$\mathbf{P_4}$(AgX)$_4$]. However, the triflate complexes, **5b**, **6b**, and **7b**, decomposed during slow crystallization and produced the capsule complexes, containing additional silver triflate units bridging between pairs of [$\mathbf{P_4}$(AgX)$_4$] units, which are described below.

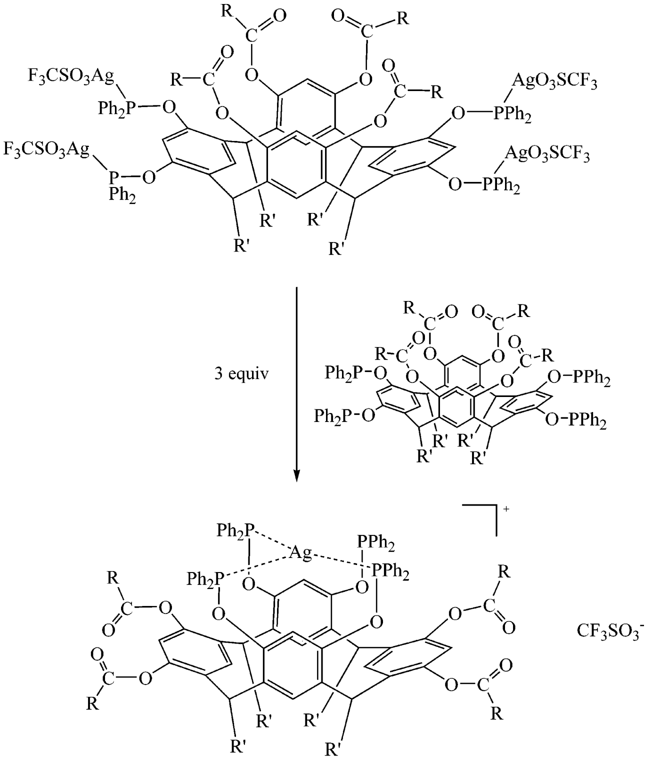
The reaction of the tetrasilver(I) resorcinarene complexes with 1 equiv of the appropriate tetraphosphinite ligand produced the disilver complexes **9a**−**12b** as outlined in Scheme 2. Microanalyses were consistent with the formulation of the complexes as [$\mathbf{P_4}$(AgX)$_2$] (X = CF_3COO^-, $CF_3SO_3^-$). The disilver complexes, **9a**−**12b**, which are all white solids, were also characterized by ^{1}H and ^{31}P NMR spectroscopy.

Complexes **13**−**15** were prepared by the addition of the appropriate tetraphosphinite ligand to CD_2Cl_2 solutions of complexes **5b**, **7b**, and **8b** until a stoichiometry of one silver per four phosphorus atoms was reached (Scheme 3). Complexes **13**−**15** were not isolated but were characterized by ^{1}H and ^{31}P NMR spectroscopy. The complexes are unstable in solution and decompose within several hours. Attempts to prepare similar 1:4 (Ag/P) complexes from the silver trifluoroacetate complexes resulted in the formation of complex mixtures of products which were not identified.

Structural Characterization of the Complexes. Tetrasilver(I) Trifluoroacetate Complex [$\mathbf{Ag_4(\mu\text{-}O_2CCF_3)_4(P_4)}$] (5a) ($\mathbf{P_4}$ = 1). The structure of complex **5a** is shown in Figure 1. Selected bond distances are listed in Table 1, and some conformational parameters for the resorcinarene skeleton are given in Table 2. The resorcinarene skeleton adopts a boat conformation in which the aryl rings with phosphinite substituents are flattened with the angle between the planes of the rings, the fold angle, Θ2 = 154° (Table 2). The aryl rings with carboxylate substituents are upright and near parallel with fold angle Θ1 = 5°. There is little twisting distortion of the resorcinarene skeleton, as can be seen from the dihedral angles between opposite aryl rings (Φ1 = 1°, Φ2 = 10°; Φ1 and Φ2 are defined as the dihedral angles between the pairs of upright and flattened aryl rings, respectively).

There are two well-separated pairs of silver atoms (Ag1 and Ag2, Ag3 and Ag4) at each end of the resorcinarene macrocyclic skeleton, with each pair bridged by two trifluoroacetate groups. This type of bidentate coordination by the trifluoroacetate groups has been observed in other diphosphine complexes of silver trifluoroacetate (**B**, Chart

Scheme 3[a]



13 R = 4-$C_6H_4CH_3$ **14** R = C_6H_{11} **15** R = OCH_2Ph

[a] R′ = CH_2CH_2Ph.

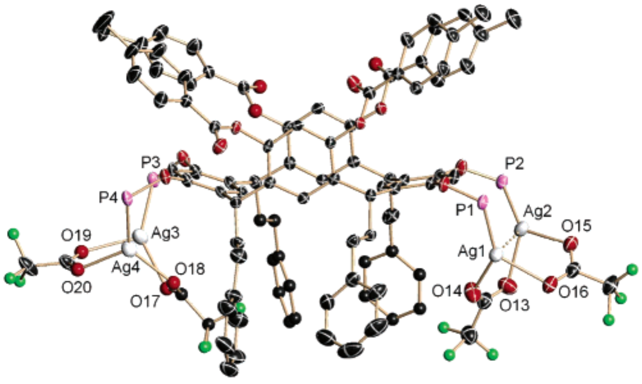


Figure 1. Thermal ellipsoid diagram of complex **5a**. Phenyl rings of the diphenylphosphinite groups have been removed for clarity. Fluorine atoms are shown in green.

Table 1. Selected Bond Lengths (Å) for Complexes **5a**, **17**, and **18**

5a		17		18	
Ag1–P1	2.354(2)	Ag1–P1	2.357(2)	Ag1–P1	2.338(2)
Ag2–P2	2.357(2)	Ag2–P2	2.335(2)	Ag2–P2	2.337(2)
Ag3–P3	2.356(2)	Ag3–P3	2.332(2)	Ag3–P3	2.337(2)
Ag4–P4	2.352(2)	Ag4–P4	2.330(2)	Ag4–P4	2.345(2)
Ag1–O14	2.248(6)	Ag5–C5T	2.485(5)	Ag5–C3T	2.345(6)
Ag1–O16	2.319(5)	Ag5–C6T	2.675(4)	Ag5–C4T	2.554(7)
Ag2–O13	2.290(6)	Ag1–O14	2.439(5)	Ag6–C4Q	2.613(8)
Ag2–O15	2.246(6)	Ag1–O16	2.424(4)	Ag6–C5Q	2.528(7)
Ag3–O17	2.24(2)	Ag1–O28	2.379(4)	Ag6–C3R	2.541(7)
Ag3–O19	2.34(1)	Ag2–O13	2.204(6)	Ag6–C4R	2.492(7)
Ag4–O18	2.19(1)	Ag2–O17	2.397(5)	Ag1–O14	2.379(8)
Ag4–O20	2.34(1)	Ag3–O23	2.389(4)	Ag1–O16	2.392(6)
Ag1···Ag2	3.0541(8)	Ag3–O29	2.472(4)	Ag1–O39	2.409(6)
		Ag3–O30	2.349(4)	Ag2–O17	2.430(6)
		Ag4–O22	2.421(4)	Ag2–O38	2.408(6)
		Ag4–O29	2.233(4)	Ag2–O39	2.411(6)
		Ag5–O24A	2.467(5)	Ag3–O29	2.551(6)
		Ag5–O30A	2.535(4)	Ag3–O34	2.561(9)
		Ag5–O31	2.586(4)	Ag3–O40	2.251(7)
				Ag4–O30	2.370(6)
				Ag4–O32	2.398(8)
				Ag4–O35	2.418(7)
				Ag5–O17	2.464(6)
				Ag5–O31	2.362(6)
				Ag5–O38	2.431(6)
				Ag6–O24	2.46(1)

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

	Θ1	Θ2	Φ1	Φ2
5a	5	154	1	10
16	-5^{b}	166	11	14
17	-11^{b}	163	13	17
18	2	168	11	12

[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.

1).[5b] The coordination geometry around each silver atom is distorted trigonal planar, $AgPO_2$, with the angles around each silver center ranging from O–Ag–O = 89.6(2) to 108.2(5)° and P–Ag–O = 118.8(3) to 141.1(2)°. Although there is much distortion from the ideal 120° bond angles, the sum of the angles around the silver centers is close to the ideal 360° in each case (Ag1, 360°; Ag2, 352°; Ag3, 360°; Ag4, 360°). There is a single short silver–silver contact between Ag1 and Ag2 (3.0541(8) Å) which indicates a weak secondary bonding interaction.[9] The conformation of the $[Ag_4(\mathbf{P_4})]^{4+}$ unit is similar in all of the complexes studied (Table 2), but a more complex association of the units occurs with the more weakly bonded silver triflate derivatives, as described below.

Capsule Complex Derived from Complex 5b. Recrystallization of complex **5b** led to partial decomposition and the formation of the neutral capsule complex $[Ag_{10}(O_3SCF_3)_4(\mu\text{-}O_3SCF_3)_2(\mu_3\text{-}O_3SCF_3)_4(OH_2)_4(\mu\text{-}OH_2)_2(\mathbf{P_4})_2]$ **(16)** whose structure is shown in Figure 2.

The capsule shown in Figure 2 can be considered to be formed by the combination of two units of $[Ag_4(\mathbf{P_4})]^{4+}$ with two extra silver(I) ions bridging between them. These extra bridging Ag^+ ions are bound to one of the phenethyl groups of $\mathbf{P_4}$ ligand **1** and by triflate and aqua ligands. The decomposition during crystallization involves some disproportionation of **5b** (silver triflate is released from some molecules, perhaps with formation of **9b**, and added to others). There is also the addition of water molecules that act as ligands for some of the silver(I) ions.

In the structure of **16**, each silver(I) center has different coordination. Both Ag1 and Ag2 have terminal triflate ligands, and a third triflate ion acts as a μ_3-κ^3-OO′O″ ligand bridging Ag1, Ag2, and the extra silver ion, Ag5. There is an aqua ligand bonded to Ag1; therefore, Ag1 and Ag2 have PO_3 and PO_2 coordinations, respectively. In contrast, Ag3 and Ag4 are bridged by two triflate ligands, one of which is μ_2-κ^2-OO′ and the other μ_3-κ^2-OO′ (the O3S atom bridges Ag3 and Ag5). The Ag4 atom has a terminal aqua ligand,

---

(9) (a) Brandys, M.-C.; Puddephatt, R. J. *Chem. Commun.* **2001**, 1508. (b) Deivaraj, T. C.; Vittal, J. J. *J. Chem. Soc., Dalton Trans.* **2001**, 329.

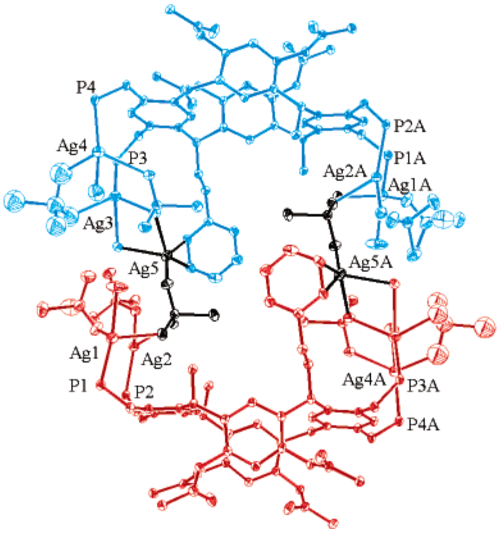


Figure 2. View of the structure of the capsule complex **16**. The two resorcinarene units, $[Ag_4(O_3SCF_3)_4(OH_2)_3(\mathbf{P_4})_2]$, are shown in red and blue, while the bridging AgO_3SCF_3 units are shown in black. All of the phenylphosphorus units and aryl groups of the carboxylate units are omitted, and only the phenethyl groups that are involved in binding to silver(I) are shown. The capsule contains a center of symmetry and is formed by tail-to-tail association. Selected distances: Ag1−P1 2.343(2), Ag2−P2 2.352(2), Ag3−P3 2.345(2), Ag4−P4 2.338(2) Å.

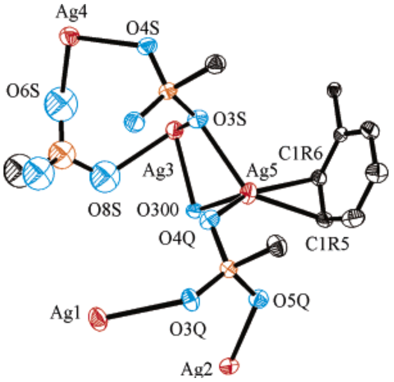


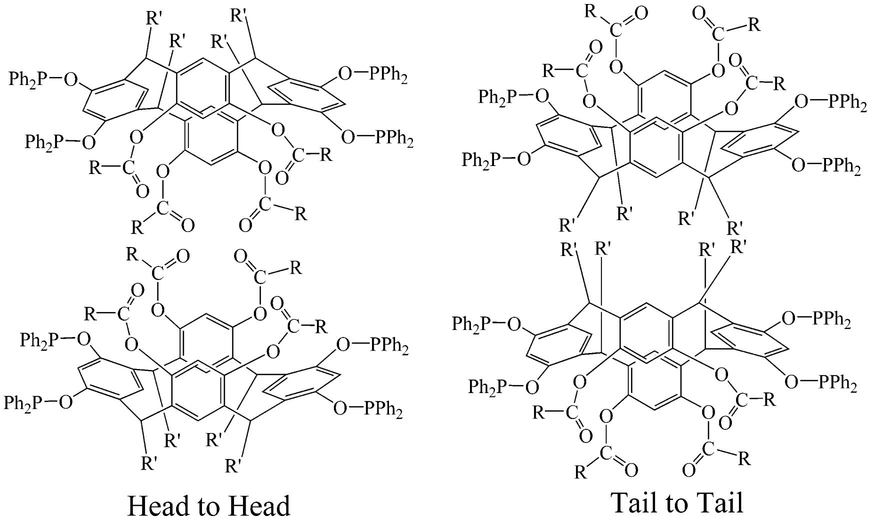
Figure 3. Coordination of the Ag5 atom, and its links to atoms Ag3 and Ag4 of one bowl and to atoms Ag1 and Ag2 of the other bowl. Selected distances: Ag1−O3Q 2.446(5), Ag2−O5Q 2.371(4), Ag3−O300 2.442(5), Ag3−O3S 2.467(5), Ag3−O8S 2.437(2), Ag4−O4S 2.518(6), Ag4−O6S 2.48(2), Ag5−C1R5 2.369(5), Ag5−C1R6 2.594(5), Ag5−O300 2.440(5), Ag5−O4Q 2.352(5) Å.

while Ag3 has an aqua ligand that also bridges to Ag5. Hence, both Ag3 and Ag4 have PO_3 coordination. There is no silver···silver bonding because the shortest distance, Ag3···Ag5, is 3.71 Å.

The manner in which the extra silver triflate units link pairs of resorcinarene units to create the capsule molecule is shown in Figure 3. The Ag5 atom is coordinated asymmetrically to an ortho, meta pair of carbon atoms from a phenyl group which is from a phenethyl unit of one unit. It is linked to the Ag3 atom of the same unit through bridging aqua and triflate ligands and to the Ag1 and Ag2 atoms of the other unit through the μ_3-κ^3-OO′O″ triflate ligand. The center of symmetry relates Ag5 and Ag5A so that there is a double link between the two resorcinarene units, as shown in Figure 2. The molecular capsule architecture depicted in Figure 2 is different from the known examples because it is formed by a tail-to-tail association rather than the more common head-to-head association (Chart 3).[3] The space between the two resorcinarene units of capsule complex **16** is occupied by eight dangling phenethyl substituents and by the silver and triflate ions, as shown in Figure 2. In terms of the capsule description, the linking silver triflate units can also be considered to occupy part of the capsule cavity, and there is insufficient space for the incorporation of organic solvent molecules.

Capsule Complex Derived from Complex 6b. The recrystallization of complex **6b** led to partial decomposition and the formation of the tetracationic capsule complex $[Ag_{10}(\mu\text{-}O_3SCF_3)_2(\mu_3\text{-}O_3SCF_3)_4(OH_2)_4(\mu\text{-}OH_2)_4(\mathbf{P_4})_2][CF_3SO_3]_4$ (**17**) whose structure is depicted in Figure 4 with selected bond distances in Table 1. As in complex **16**, the overall structure of **17** can be considered to be formed by the combination of two units of $[Ag_4\mathbf{P_4}]^{4+}$ with two extra Ag^+ ions bridging them, with the bridging Ag^+ ions bound to one of the phenethyl groups of $\mathbf{P_4}$ ligand **2** and by triflate and aqua ligands. However, the extent of hydrolysis is greater in formation of **17** from **6b** than in the formation of **16** from **5b**; therefore, there are differences between the structures

Chart 3. Depiction of the Head-to-Head and Tail-to-Tail Orientations of the Resorcinarene Macrocycle



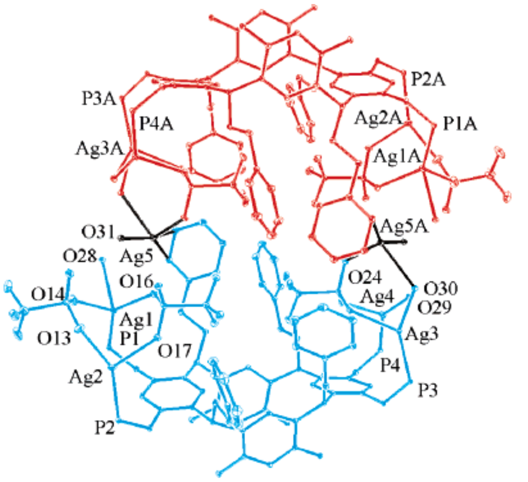


Figure 4. Structure of complex **17**. The two resorcinarene units are shown in blue and red with the extra bridging silver ion (and its terminal aqua ligand) in black. The acyl groups, SC_4H_3CO, and the phenyl substituents on phosphorus are omitted for clarity.

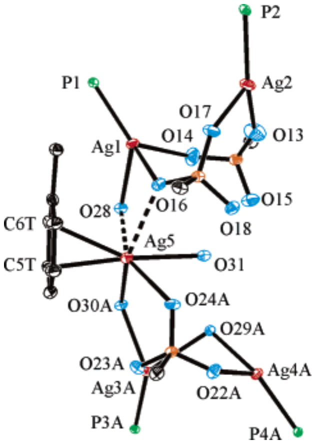


Figure 5. Coordination of bridging atom Ag5 in complex **17**.

of **16** and **17**. The structure of complex **17** is again somewhat simplified by the presence of a crystallographically imposed center of symmetry.

There is great variation in the coordination environments of the silver centers as shown in Figure 4. Of the silver atoms contained within each $[Ag_4(\mathbf{P_4})]^{4+}$ unit, the silver atoms Ag1 and Ag2 are each bound to one phosphorus atom and they are bridged by a pair of triflate anions; Ag1 also has a terminal aqua ligand. Thus, Ag1 and Ag2 have PO_3 and PO_2 coordination, respectively. The Ag3 and Ag4 pair of atoms are each bonded to a phosphorus atom, and they are bridged by an aqua ligand (O29) and by a triflate group, which also bridges the extra silver ion, Ag5, and so is triply bridged overall. There is another aqua ligand that bridges Ag3 and Ag5. Overall, Ag3 and Ag4 have PO_3 and PO_2 coordination, respectively. The bridging silver ion, Ag5, binds to one resorcinarene unit by forming an $Ag(\eta^2\text{-}C_6H_5)$ group to an ortho, meta pair of carbon atoms from a phenethyl group and to the other by linking to Ag3 and Ag4 through the bridging triflate and aqua ligands described above. There is also a terminal aqua ligand bound to Ag5, so overall the bridging silver ion has $(C_2)O_3$ coordination (Figure 5). The Ag−O bonds to Ag5 are all weak (Table 1). The shortest distance is Ag5−O24A = 2.467(5) Å, the distance to the bridging triflate group, while the bonds to the aqua ligands are longer at Ag5−O30A = 2.535(4) Å and Ag5−O31 = 2.586(4) Å. There are also long contacts to the triflate and aqua ligand oxygen atoms bound to the Ag1 and Ag2 units with Ag5···O16 = 2.63(1) Å and Ag5···O28 = 2.66(1) Å, respectively, that are probably too long to be considered as bonds. Several silver(I)−π-arene complexes of calixarenes and resorcinarenes have been reported, and the η^2-coordination mode of the arene ring in **16** and **17** is unremarkable.[11] However, the silver ion is usually coordinated to the arene rings that make up the macrocyclic skeleton, whereas in complexes **16** and **17**, the silver is coordinated to a pendant arene substituent.

The Capsule Complex Derived from Complex 7b. The recrystallization of complex **7b** led to more extensive disproportionation than that found with either **5b** or **6b** and produced the $[Ag_{13}(OH_2)_3(\mu\text{-}OH_2)_4(O_3SCF_3)_6(\mu\text{-}O_3SCF_3)_3(\mu_3\text{-}O_3SCF_3)_4(\mathbf{P_4})_2]$ complex, with $\mathbf{P_4}$ = ligand **3** or **18**, whose structure is shown in Figure 6, with selected bond distances in Table 1. The structure of **18**, again, contains an inversion center; therefore, the presence of an odd number of silver atoms in the formula requires an explanation. The formula can be understood by considering **18** to be made up of the $[\{Ag_6(OH_2)(\mu\text{-}OH_2)_2(O_3SCF_3)_3(\mu\text{-}O_3SCF_3)(\mu_3\text{-}O_3SCF_3)_2(\mathbf{P_4})\}_2\text{-}\{Ag(OH_2)(\mu\text{-}O_3SCF_3)\}]$ units. The last unit, $\{Ag(OH_2)(\mu\text{-}O_3SCF_3)\}$, is necessarily present at 50% occupancy compared to the resorcinarene units, and because the associated triflate group is disordered, it is less well defined than the rest of the structure. This disordered unit, containing silver atom Ag7, lies on the outside of the resorcinarene unit and is connected to Ag6 through the disordered triflate ion; it is not included in Figure 6. Of the four phosphinite-bound silver atoms, Ag1 and Ag2 are bridged by an aqua and a triflate ligand, which also bridges to Ag5 as a $\mu_3\text{-}\kappa^2$-OO′ ligand; Ag1 also bears a terminal triflate ligand, and Ag2 has another aqua ligand that bridges to Ag5. Ag3 and Ag4 are bridged by two triflate ligands, one of which also bridges to Ag5; Ag3 also carries a terminal aqua ligand, and Ag4 has a terminal triflate ligand. In this case, Ag1−Ag4 all have PO_3 coordination.

The connecting silver atom is Ag5. It is bound to a phenyl substituent of a phenethyl group and is connected to Ag2 of the same resorcinarene unit through bridging aqua and triflate ligands. It is alos connected to Ag3 and Ag4 of the other resorcinarene unit through the $\mu_3\text{-}\kappa_3$-OO′O″ triflate ligand, as shown in Figure 7a. The sixth silver atom is fully enclosed

---

(10) Pirondini, L.; Bonifazi, D.; Menozzi, E.; Wegelius, E.; Rissanen, K.; Massera, C.; Dalcanale, E. *Eur. J. Chem.* **2001**, 2311.

(11) (a) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K.; Ino, I. *J. Chem. Soc., Dalton Trans.* **1999**, 373. (b) Xu, W.; Puddephatt, R. J.; Muir, K. W.; Torabi, A. A. *Organometallics* **1994**, *13*, 3054. (c) Budka, J.; Lhoták, P.; Stibor, I.; Michlová, V.; Sykora, J.; Cisarová, I. *Tetrahedron Lett.* **2002**, *43*, 2657. (d) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8610. (e) Kimura, K.; Yajima, S.; Tatsumi, K.; Yokoyama, M.; Oue, M. *Anal. Chem.* **2000**, *72*, 5290. (f) Ikeda, A.; Tsuzuki, H.; Shinkai, S. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 2073. (g) Thomaier, J.; Boulmaâz, S.; Schönberg, H.; Rüegger, H.; Currao, A.; Grützmacher, H.; Hillebrecht, H.; Pritzkow, H. *New. J. Chem.* **1998**, 947.

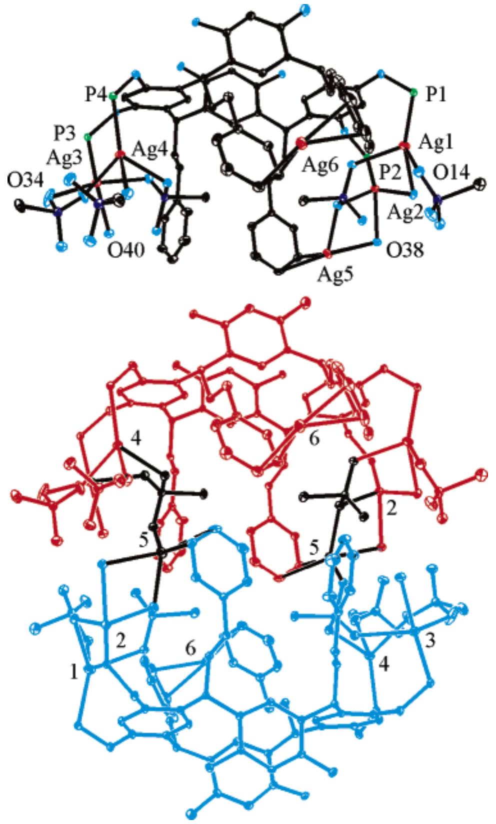


Figure 6. Structure of complex **18** (bottom). A single resorcinarene unit showing the positions of the extra silver ions, Ag5 and Ag6 (top). The phenyl rings from the diphenylphosphinite groups, the $C_6H_{11}CO$ groups, the fluorine atoms, the triflate group connected to Ag6, and the partial occupation $Ag7O_3SCF_3$ group have been removed for clarity.

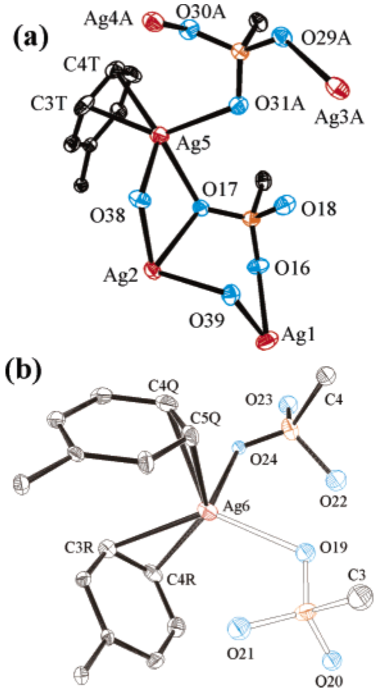


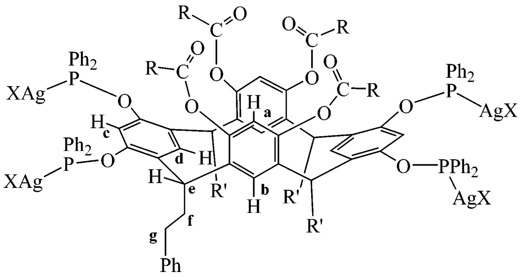
Figure 7. (a) Coordination of the bridging atom Ag5 and (b) of the encapsulated atom Ag6.

Table 3. ^{31}P NMR Data for the Complexes **5a**−**15**

	δ^a	$^1J(^{109}AgP)^b$		δ^a	$^1J(^{109}AgP)^b$
5a	122.0	850	**9b**	106.4	609
5b	119.9	911	**10b**	105.4	608
6a	120.3	848	**11a**	407.6	580
6b	119.3	912	**11b**	106.9	609
7a	121.5	847	**12a**	107.1	576
7b	119.9	910	**12b**	105.3	604
8a	118.3	854	**13**	114.5	308
8b	116.5	914	**14**	114.2	310
9a	107.6	582	**15**	113.1	309

[a] δ are reported in ppm. [b] All $^1J_{AgP}$ are reported in Hz.

Chart 4. The NMR Labeling Scheme



within a single resorcinarene and is bound to two η^2-phenyl substituents of phenethyl units and to a terminal triflate ligand, as shown in Figure 7b. Clearly, it is a guest ion in the overall capsule. There is also a link to the partial occupation triflate of Ag7 (shown as an open-bonded unit in Figure 7b). An interesting feature is that the Ag(η^2-phenyl) interactions all involve meta, para pairs of carbon atoms (Figures 7a and 7b), whereas the analogous links in **16** and **17** all involve ortho, meta pairs of carbon atoms.

Solution NMR Studies of Complexes 5a−8b. The ^1H NMR spectra of complexes **5a**−**8b** at room temperature were consistent with the presence of a single complex with effective C_{2v} symmetry. For example, the NMR spectra indicated that all of the bridging methine protons and all of the phosphorus atoms were equivalent. The phosphorus resonances appeared as pairs of doublets resulting from the coupling of the ^{31}P nuclei with ^{107}Ag and ^{109}Ag (relative abundance 52% and 48%, respectively).[12] The magnitudes of the $^1J_{AgP}$ coupling constants (Table 3) are consistent with the coordination of a single phosphorus donor to each silver center, on the basis of many precedents.[13]

It has been established that the conformation of the resorcinarene skeleton can be assigned in solution by comparison of the chemical shift for arene resonances CH^b and CH^d (Chart 4) because CH^d in the flattened ring is more shielded.[14] A large chemical shift separation for the resonances associated with CH^b and CH^d is indicative of a boat conformation in solution.[14] The resonances for CH^b and CH^d can be readily assigned from the ^1H, ^{13}C gHMBC and ^1H, ^{31}P gHMBC correlated NMR spectra as reported elsewhere.[14a,b] For complexes **5a** and **7b**, the boat conformation, in solution,

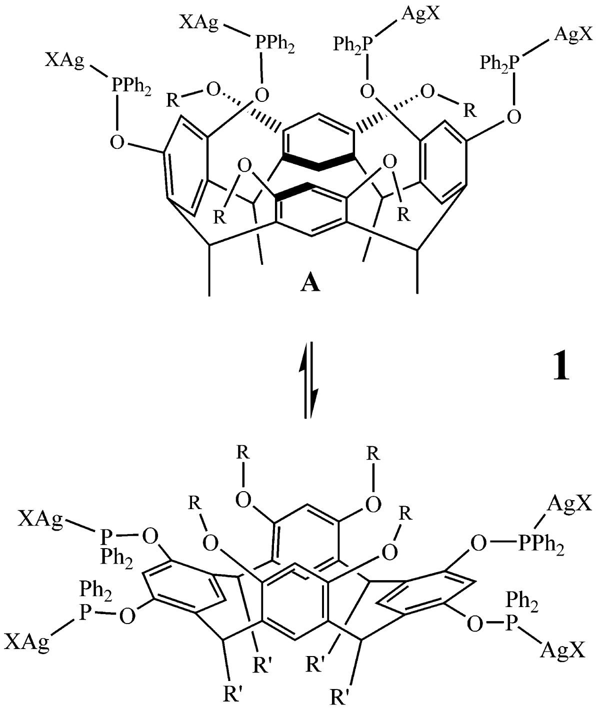
---

(12) Affandi, D.; Berners-Price, S. J.; Effendy; Harvey, P. J.; Healy, P. C.; Ruch, B. E.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1411.

(13) (a) Baker, L.-J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Steiglemann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656. (b) Alyea, E. C.; Malito, J.; Nelson, J. H. *Inorg. Chem.* **1987**, *26*, 4294.

(14) (a) Eisler, D. J.; Puddephatt, R. J. *Can. J. Chem.* **2004**, *82*, 185. (b) Eisler, D. J.; Kirby, C. W.; Puddephatt, R. J. *Inorg. Chem.* **2003**, *42*, 7626. (c) Eisler, D. J.; Puddephatt, R. J. *Inorg. Chem.* **2003**, *42*, 8192. (d) Shivanyuk, A.; Paulus, E. F.; Rissanen, K.; Kolehmainen, E.; Böhmer, V. *Chem.—Eur. J.* **2001**, *7*, 1944.

was unambiguously assigned from the NMR data and was found to be the conformation in which the acylated rings are upright and the phosphinite derivatized rings are flattened (**B**, eq 1). This is in accordance with the solid-state structure obtained for complex **5a**. Variable-temperature NMR studies were undertaken for several of the complexes, **5a**−**8b**, and in each case, the ^{1}H and ^{31}P NMR spectra remained virtually unchanged down to −80 °C, the lowest temperature at which data were recorded. Thus, it appears that, in solution, complexes **5a**−**8b** are most stable in conformation **B** (equation 1).



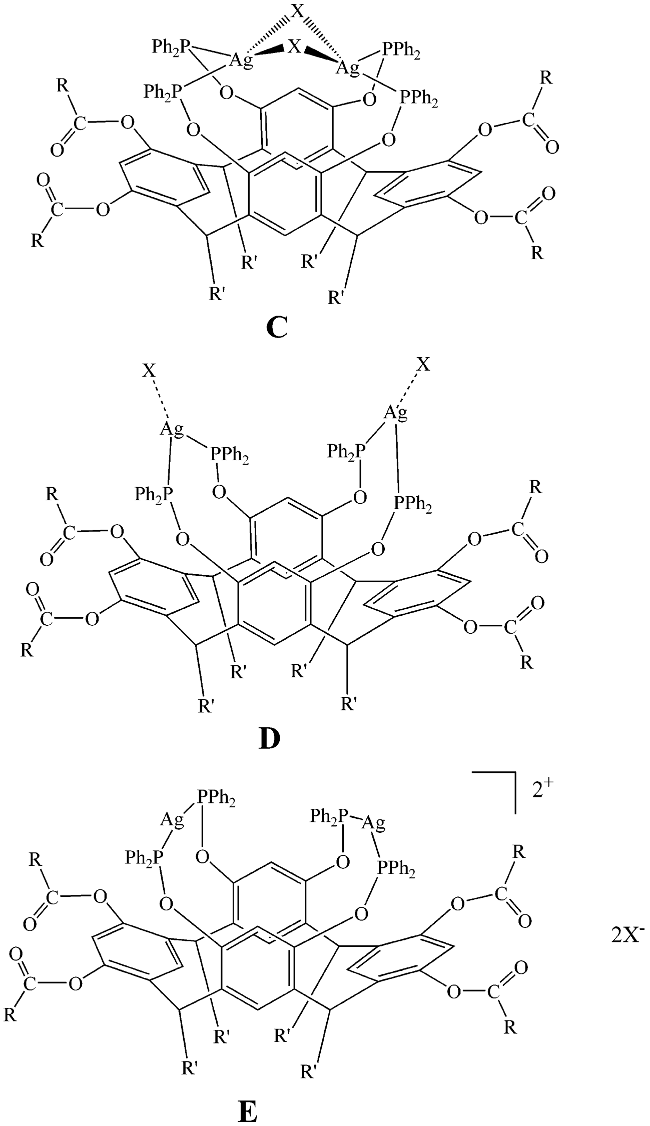
1

The results of the NMR studies suggest that the solution-state structure of complexes **5a**−**8b** is similar to the solid-state structure observed for complex **5a**. The lack of boat−boat transitions for complexes **5a**−**8b** suggests that the pairs of silver centers are bridged by the anionic ligands in solution, thus adding rigidity to the structure and inhibiting fluxionality, according to eq 1.

Disilver and Monosilver Complexes. As outlined in Scheme 2, disilver complexes were synthesized by the addition of an equimolar amount of the free tetraphosphinite ligand to the tetrasilver resorcinarene complexes **5a**−**8b**. The magnitude of the couplings constants, $^1J_{AgP}$, obtained from the ^{31}P NMR spectra, are considerably smaller for the disilver complexes than those for the parent tetrasilver complexes (Table 3), suggesting the presence of AgP_2 coordination. It has been well established that the magnitude of the $^1J_{AgP}$ coupling constant is influenced by the number of phosphorus atoms coordinated to silver; an increase in the phosphorus coordination leads to a decrease in the magnitude of the coupling constant, $^1J_{AgP}$.[15]

From the ^{1}H, ^{13}C gHMBC and ^{1}H, ^{31}P gHMBC correlated NMR spectra of complexes **11b** and **12b**, it was unambiguously established that, in both cases, the disilver complexes are present in solution in conformation **A** (eq 1). Variable-temperature NMR studies were performed on several of the complexes, **9a**−**12b**, and in each case, the spectra remained essentially unchanged down to −80 °C, the lowest temperature at which data were recorded. Thus, there is no evidence that the boat−boat transitions depicted in eq 1 are occurring in solution, suggesting a rigid solution-state structure for complexes **9a**−**12b**.

Chart 5 [a]



[a] $X^- = CF_3COO^-, CF_3SO_3^-$.

From the magnitude of the coupling constants, $^1J_{AgP}$, which indicate two phosphorus atoms are coordinated to each silver center, and the rigid structure suggested by the lack of boat−boat transitions in solution, it is reasonable to propose a chelate structure for complexes **9a**−**12b** (Chart 5). The chelate binding mode depicted in Chart 5 has been structur-

---

(15) (a) Bowmaker, G. A.; Hanna, J. V.; Rickard, C. E. F.; Lipton, A. S. *J. Chem. Soc., Dalton Trans.* **2001**, 20. (b) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Rodríguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Chem.*—*Eur. J.* **2000**, *6*, 636. (c) Cooke, P. A.; Perera, S. D.; Shaw, B. L.; Thornton-Pett, M.; Vessey, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 435.

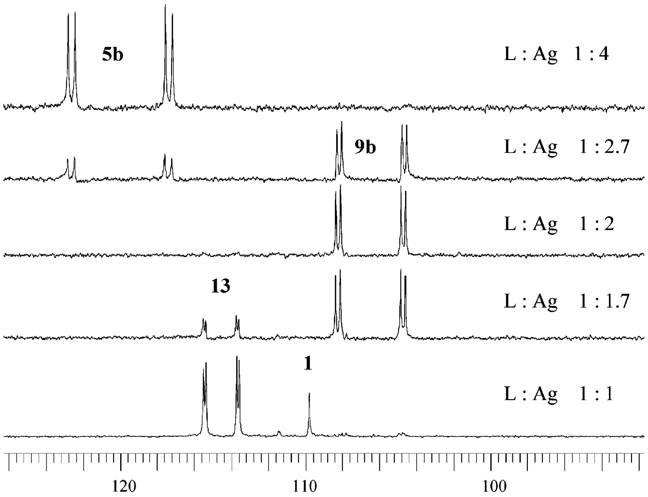


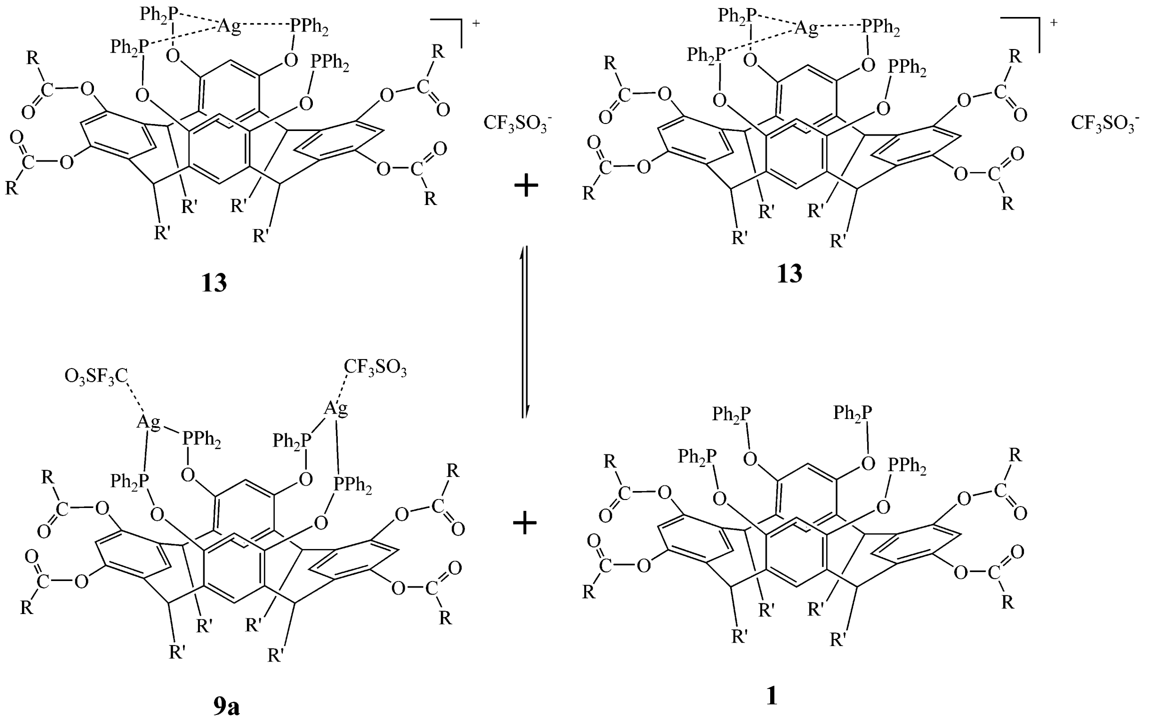
Figure 8. ^{31}P NMR spectra showing the results of the sequential addition of **1** to a solution of complex **5b**. L:Ag = ratio of tetraphosphinite ligand **1** to $AgCF_3SO_3$.

ally characterized for silver halide complexes of resorcinarene ligands **1**−**4**.[14b,c] There are several possible chelate structures that can be proposed for complexes **9a**−**12b**. The anion could be coordinated in a bidentate (**C**, Chart 5) or monodentate (**D**, Chart 5) fashion or not coordinated at all (**E**, Chart 5). The bidentate coordination mode seems unlikely because of steric interactions that would arise, between the phenyl rings of the diphenylphosphinite groups and the anions, to allow the correct geometry of two bridging ligands to be adopted. The ^{1}H and ^{31}P NMR spectra for the silver salts, with a given resorcinarene ligand but different anions (trifluoroacetate or triflate), are very similar indicating either weak association of the anion or no association at all. Thus, structures **D** or **E** are more probable than structure **C** (Chart 5). Unfortunately, all attempts to grow suitable crystals for X-ray diffraction studies of complexes **9a**−**12b** were unsuccessful.

Sequential additions of ligand **1** to a solution of **5b** in CD_2Cl_2 were followed by ^{1}H and ^{31}P NMR experiments; the ^{31}P spectra are shown in Figure 8. The addition of less than 1 equiv of **1** to tetrasilver complex **5b** results in the immediate formation of a mixture the tetrasilver and disilver complexes, **5b** and **9b**. The lability of Ag−P bonds in solution is well established; therefore, the solution behavior of complex **5b** is not surprising.[8] Further addition of **1** to the solution leads to increased formation of the disilver complex, **9b**, with a concomitant reduction in the intensity of the resonances associated with the tetrasilver complex, **5b**. When a ratio of 1 equiv of ligand **1** per two silver atoms is reached, only the disilver complex, **9b**, is present in solution (Figure 8).

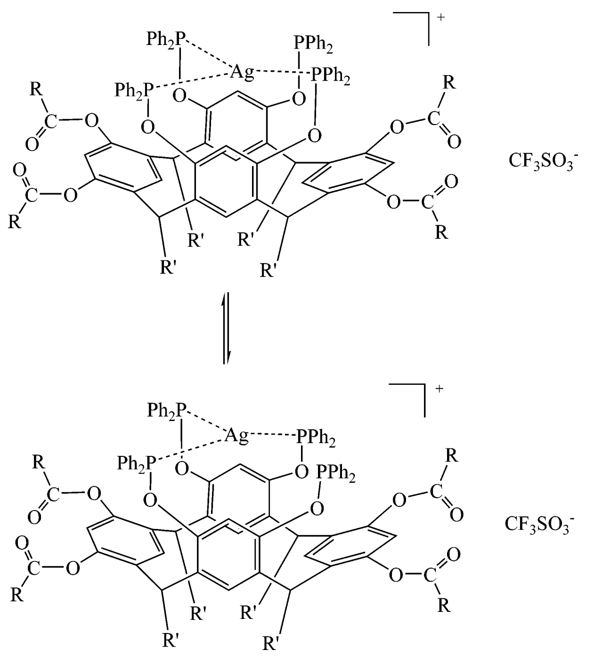
Interestingly, further addition of ligand **1** to the solution results in the appearance of resonances for a third complex, **13** (Figure 8). The intensity of the resonances for complex **13** increases with the continued addition of **1** at the expense of the disilver complex, **9b**. When a ligand-to-silver ratio of 1:1 is reached, the major species present in solution is complex **13**, although trace amounts of **9b** are still visible; the resonance associated with the free ligand **1** is also present in solution (Figure 8). Thus, the NMR data suggest that an equilibrium among complexes **13**, **9b**, and the free ligand (**1**) exists in solution (Scheme 4). Similar intermolecular migration has been suggested to occur in gold complexes with a calixarene-based tetraphosphine ligand.[16] Variable-temperature NMR studies provided further evidence for such an equilibrium. It was found that the resonances for **13** decreased in intensity with decreasing temperature, while

Scheme 4[a]



[a] R = 4-$C_6H_4CH_3$, R′ = CH_2CH_2Ph.

Scheme 5



those for the free ligand and the disilver complex increased. An increase in the concentration of complex **9b** would, necessarily, result in an increase in the concentration of free ligand **1** (Figure 8).

All attempts to isolate pure samples of complexes **13**−**15** were unsuccessful. The magnitude of the coupling constants, $^1J_{\mathrm{AgP}}$, for complexes **13**−**15** (Table 3) are much smaller than those observed for the disilver complexes, suggesting higher phosphorus coordination. Similar $^1J_{\mathrm{AgP}}$ coupling constants have been observed for silver phosphine complexes of the form $[\mathrm{AgP_4}]^+$, in which there are four phosphorus atoms coordinated to a single silver center.[17] However, it seems unlikely that all four phosphorus donors of a single resorcinarene macrocycle would be coordinated at one time to a single silver center because of the geometric constraints of the ligand. It is also unlikely that two tetraphosphinite ligands coordinate to a single silver center, each via two phosphorus donors because of the steric bulk of the compounds. It is more likely that the silver center rapidly migrates between the phosphorus atoms around the macrocyclic skeleton resulting in effective four coordination around the silver center (Scheme 5). This would lead to the equivalence of all four phosphorus donors, which is borne out by the presence of a single silver-coupled phosphorus resonance in the ^{31}P NMR spectra of complexes **13**−**15**. Furthermore, from the ^{1}H, ^{13}C gHMBC and ^{1}H, ^{31}P gHMBC correlated NMR spectra of complex **14**, it was established that the complex is present in solution in conformation **A** (eq 1), which is consistent with the structure proposed in Scheme 5. Variable-temperature NMR studies were performed on complexes **13**−**15**, but no splitting was observed down to −80 °C. The structure of complexes **13**−**15** is tentatively assigned as depicted in Scheme 5, but it has not been proven by the limited data available.

Conclusions

The tetraphosphinite resorcinarene ligands, **1**−**4**, were shown to be excellent platforms for the formation of silver(I) complexes with interesting supramolecular architectures. The unusual architecture offered by the resorcinarene ligands, with two well-separated diphosphine ends, resulted in the formation of a coordination polymer in the solid state for silver trifluoroacetate complex **8a** and silver triflate complex **8b**, as reported previously.[7] The silver triflate complexes, **5b**, **6b**, and **7b**, were shown to form molecular capsule complexes in the solid state through the unexpected inclusion of additional silver centers coordinated to the dangling phenethyl substituents via cation−π-arene interactions. The presence of these additional silver atoms suggests the possibility that other interesting structures can be obtained through judicious choice of the dangling substituents and demonstrates the versatility offered by the resorcinarene ligands. In addition, the tail-to-tail capsule architecture adopted by these complexes is unprecedented in resorcinarene coordination complexes.[3] Although the capsules are formed through adventitious disproportionation and hydrolysis during crystallization, the syntheses are reproducible for a given precursor complex and solvent system. Thus, several independent syntheses, in each case, produced single crystals with identical cell parameters.

The versatility of the tetraphosphinite resorcinarene ligands was further demonstrated by the formation of both disilver and monosilver complexes. The coupling constants, $^1J_{\mathrm{AgP}}$, for the monosilver complexes are consistent with effective $\mathrm{AgP_4}^+$ coordination, which is presumed to be the result of the rapid migration of the silver center around the planar platform of four phosphorus atoms. It is not possible to determine the number of phosphorus donors which are coordinated at any given point in time to the silver center, although the rigidity of the structure suggests the coordination of two or three. In summary, a series of tetra-, di-, and monosilver(I) complexes have been synthesized and characterized, and a new type of coordination capsule architecture is reported.

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.[14a] In the formulas below, the resorcinarene skeleton $(\mathrm{C_6H_2CH\{CH_2CH_2Ph\}})_4$ is represented as resorcinarene. The proton and carbon resonances of the resorcinarene skeleton are identified according to the labeling scheme shown in Chart 4. Note that monosilver complexes **13**−**15** were characterized only by their NMR spectra because they could not be isolated in pure form (see text).

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OPPh$_2$\{AgCF$_3$COO\})$_4$] (5a). A mixture of **1** (0.100 g, 0.047 mmol) and AgCF$_3$COO (0.042 g,

---

(16) Dieleman, C. B.; Matt, D.; Neda, I.; Schmutzler, R.; Thönnessem, H.; Jones, P. G.; Harriman, A. *J. Chem. Soc., Dalton Trans.* **1998**, 2115.

(17) (a) Price, S. J. B.; Brevard, C.; Pagelot, A.; Sadler, P. J. *Inorg. Chem.* **1985**, *24*, 4278. (b) Berners-Price, S. J.; Bowen, R. J.; Harvey, P. J.; Healy, P. C.; Koutsantonis, G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 1743.

0.190 mmol) in THF (10 mL) in a darkened flask was stirred for 1 h. The solution was filtered through Celite, and a white solid was precipitated with pentane. Yield: 0.107 g, 76%. ^{1}H NMR (CD_2Cl_2): δ 2.04, 2.18 (m, 8H, H^f), 2.29, 2.48 (m, 8H, H^g), 2.46 (s, 12H, $C_6H_4CH_3$), 4.60 (m, 4H, H^e), 6.01 (s, 2H, H^c), 6.47 (s, 2H, H^d), 6.89 (s, 2H, H^a), 7.71 (s, 2H, H^b), 6.79−7.82 (m, 76H, *Ph*, $C_6H_4CH_3$). ^{31}P NMR (CD_2Cl_2): δ 122.01 (m, $^1J_{^{109}AgP} = 850$ Hz, $^1J_{^{107}AgP} = 737$ Hz). Anal. Calcd for $C_{148}H_{116}Ag_4F_{12}O_{20}P_4$: C, 59.30; H, 3.90. Found: C, 59.83; H, 3.91.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2${AgCF_3SO_3})$_4$] (5b). This was prepared in a manner similar to that described above from **1** (0.100 g, 0.047 mmol) and $AgCF_3SO_3$ (0.049 g, 0.190 mmol). Yield: 0.120 g, 81%. ^{1}H NMR (CD_2Cl_2): δ 1.92−2.60 (m, 16H, H^f, H^g), 2.47 (s, 12H, $C_6H_4CH_3$), 4.57 (m, 4H, H^e), 5.87, 6.52 (s, 4H, Ar-*H*), 6.75−7.83 (m, 80H, Ar-*H*, *Ph*, $C_6H_4CH_3$). Anal. Calcd for $C_{144}H_{116}Ag_4F_{12}O_{24}P_4S_4$: C, 55.05; H, 3.72. Found: C, 54.68; H, 3.68.

[Resorcinarene(OC(O)C_4H_3S)$_4$(OPPh$_2${AgCF_3COO})$_4$] (6a). This was prepared in a manner similar to that described above from **2** (0.100 g, 0.048 mmol) and $AgCF_3COO$ (0.042 g, 0.190 mmol). Yield: 0.090 g, 63%. ^{1}H NMR (CD_2Cl_2): δ 2.03, 2.19 (m, 8H, H^f), 2.28, 2.47 (m, 8H, H^g), 4.61 (m, 4H, H^e), 6.17, 6.41 (s, 4H, Ar-*H*), 6.77−7.81 (m, 76H, Ar-*H*, *Ph*, C_4H_3S). Anal. Calcd for $C_{136}H_{100}Ag_4F_{12}O_{20}P_4S_4$: C, 55.08; H, 3.40. Found: C, 55.04; H, 3.52.

[Resorcinarene(OC(O)C_4H_3S)$_4$(OPPh$_2${AgCF_3SO_3})$_4$] (6b). This was prepared in a manner similar to that described above from **2** (0.100 g, 0.048 mmol) and $AgCF_3SO_3$ (0.049 g, 0.191 mmol). Yield: 0.112 g, 75%. ^{1}H NMR (CD_2Cl_2): δ 1.94−2.56 (m, 16H, H^f, H^g), 4.56 (m, 4H, H^e), 5.95, 6.45 (s, 4H, Ar−H), 6.74−7.76 (m, 76H, Ar−H, Ph, C_4H_3S). Anal. Calcd for $C_{132}H_{100}Ag_4F_{12}O_{24}P_4S_8$: C, 50.98; H, 3.24. Found: C, 51.42; H, 3.52.

[Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2${AgCF_3COO})$_4$] (7a). This was prepared in a manner similar to that described above from **3** (0.100 g, 0.048 mmol) and $AgCF_3COO$ (0.042 g, 0.190 mmol). Yield: 0.088 g, 62%. ^{1}H NMR (CD_2Cl_2): δ 1.02−1.89, 2.08 (m, 44H, C_6H_{11}), 2.02, 2.24 (m, 8H, H^f), 2.31, 2.43 (m, 8H, H^g), 4.40 (m, 4H, H^e), 6.28, 6.40, 6.60 (s, 6H, Ar-*H*), 6.73−7.68 (m, 62H, Ar-*H*, *Ph*). Anal. Calcd for $C_{144}H_{132}Ag_4F_{12}O_{20}P_4$: C, 58.31; H, 4.49. Found: C, 58.88; H, 4.64.

[Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2${AgCF_3SO_3})$_4$] (7b). This was prepared in a manner similar to that described above from **3** (0.100 g, 0.048 mmol) and $AgCF_3SO_3$ (0.049 g, 0.191 mmol). Yield: 0.110 g, 74%. ^{1}H NMR (CD_2Cl_2): δ 1.06−2.51 (m, 60H, H^f, H^g, C_6H_{11}), 4.38 (m, 4H, H^e), 6.21 (s, 2H, H^c), 6.33 (s, 2H, H^d), 6.67 (s, 2H, H^a), 7.61 (s, 2H, H^b), 6.76−7.68 (m, 62H, Ar-*H*, *Ph*). Anal. Calcd for $C_{140}H_{132}Ag_4F_{12}O_{24}P_4S_4 \cdot 0.5THF$: C, 54.21; H, 4.36. Found: C, 54.72; H, 4.54.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2${AgCF_3COO})$_4$] (8a). This was prepared in a manner similar to that described above from **4** (0.100 g, 0.046 mmol) and $AgCF_3COO$ (0.041 g, 0.186 mmol). Yield: 0.115 g, 82%. ^{1}H NMR (CD_2Cl_2): δ 2.13 (m, 4H, H^f), 2.32 (m, 8H, H^f, H^g), 2.45 (m, 4H, H^g), 4.63 (m, 4H, H^e), 4.68 (m, 8H, $^2J_{HH} = 12$ Hz, OCH_2Ph), 6.36, 6.40, 6.76 (s, 6H, Ar-*H*), 6.93−7.68 (m, 82H, Ar-*H*, *Ph*). Anal. Calcd for $C_{148}H_{116}Ag_4F_{12}O_{24}P_4$: C, 58.06; H, 3.82. Found: C, 58.14; H, 3.59.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2${AgCF_3SO_3})$_4$] (8b). This was prepared in a manner similar to that described above from **4** (0.100 g, 0.046 mmol) and $AgCF_3SO_3$ (0.047 g, 0.183 mmol). Yield: 0.120 g, 82%. ^{1}H NMR (CD_2Cl_2): δ 2.16 (m, 4H, H^f), 2.31 (m, 8H, H^f, H^g), 2.47 (m, 4H, H^g), 4.57 (t, 4H, $^3J_{HH} = 8$ Hz, H^e), 4.69 (m, 8H, $^2J_{HH} = 12$ Hz, OCH_2Ph), 6.17, 6.40 (s, 4H, Ar-*H*), 6.82−7.63 (m, 84H, Ar-*H*, *Ph*). Anal. Calcd for $C_{148}H_{116}Ag_4F_{12}O_{24}P_4$: C, 53.95; H, 3.65. Found: C, 54.35; H, 3.86.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$({OPPh$_2$}$_2${AgCF_3COO})$_2$] (9a). A mixture of **5a** (0.037 g, 0.012 mmol) and **1** (0.026 g, 0.012 mmol) in THF (5 mL) in a darkened flask was stirred for 15 min. The solution was filtered through Celite, and a white solid was precipitated with pentane. Yield: 0.052 g, 83%. ^{1}H NMR (CD_2Cl_2): δ 2.13 (m, 4H, H^f), 2.47 (m, 20H, H^f, H^g, $C_6H_4CH_3$), 2.74 (m, 4H, H^g), 4.85 (m, 4H, H^e), 6.42, 6.51 (s, 4H, Ar-*H*), 6.73−7.88 (m, 80H, Ar-*H*, *Ph*, $C_6H_4CH_3$). Anal. Calcd for $C_{144}H_{116}Ag_2F_6O_{16}P_4$: C, 67.66; H, 4.57. Found: C, 67.63; H, 4.72.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$({OPPh$_2$}$_2${AgCF_3SO_3})$_2$] (9b). This was prepared in a manner similar to that described above from **5b** (0.032 g, 0.010 mmol) and **1** (0.021 g, 0.010 mmol). Yield: 0.042 g, 78%. ^{1}H NMR (CD_2Cl_2): δ 2.20 (m, 4H, H^f), 2.50 (m, 20H, H^f, H^g, $C_6H_4CH_3$), 2.75 (m, 4H, H^g), 4.82 (m, 4H, H^e), 6.43, 6.51 (s, 4H, Ar-*H*), 6.73−7.90 (m, 80H, Ar-*H*, *Ph*, $C_6H_4CH_3$). Anal. Calcd for $C_{142}H_{116}Ag_2F_6O_{18}P_4S_2$: C, 64.89; H, 4.45. Found: C, 64.23; H, 4.16.

[Resorcinarene(OC(O)C_4H_3S)$_4$({OPPh$_2$}$_2${AgCF_3SO_3})$_2$] (10b). This was prepared in a manner similar to that described above from **6b** (0.025 g, 0.008 mmol) and **2** (0.017 g, 0.008 mmol). Yield: 0.024 g, 59%. ^{1}H NMR (CD_2Cl_2): δ 2.10 (m, 4H, H^f), 2.56 (m, 8H, H^f, H^g), 2.78 (m, 4H, H^g), 4.86 (m, 4H, H^e), 6.44, 6.46, 7.89 (s, 6H, Ar-*H*), 6.76−7.72 (m, 74H, Ar-*H*, *Ph*, C_4H_3S). Anal. Calcd for $C_{130}H_{100}Ag_2F_6O_{18}P_4S_6$: C, 60.14; H, 3.88. Found: C, 60.18; H, 4.08%.

[Resorcinarene(OC(O)C_6H_{11})$_4$({OPPh$_2$}$_2${AgCF_3COO})$_2$] (11a). This was prepared in a manner similar to that described above from **7a** (0.026 g, 0.009 mmol) and **3** (0.019 g, 0.009 mmol). Yield: 0.035 g, 80%. ^{1}H NMR (CD_2Cl_2): δ 1.10−1.90, 2.11 (m, 44H, C_6H_{11}), 1.98, 2.27 (m, 8H, H^f), 2.52, 2.78 (m, 8H, H^g), 4.67 (m, 4H, H^e), 6.34, 6.63, 7.77 (s, 8H, Ar-*H*), 6.82−7.70 (m, 60H, *Ph*). Anal. Calcd for $C_{140}H_{132}Ag_2F_6O_{16}P_4$: C, 66.62; H, 5.27. Found: C, 67.12; H, 5.27.

[Resorcinarene(OC(O)C_6H_{11})$_4$({OPPh$_2$}$_2${AgCF_3SO_3})$_2$] (11b). This was prepared in a manner similar to that described above from **7b** (0.030 g, 0.010 mmol) and **3** (0.021 g, 0.010 mmol). Yield: 0.040 g, 80.2%. ^{1}H NMR (CD_2Cl_2): δ 1.12−2.10 (m, 44H, C_6H_{11}), 2.11, 2.44 (m, 8H, H^f), 2.57, 2.80 (m, 8H, H^g), 4.67 (m, 4H, H^e), 6.38 (s, 2H, H^c), 6.40 (s, 2H, H^b), 6.77 (s, 2H, H^a), 7.82 (s, 2H, H^d), 6.84−7.57 (m, 60H, *Ph*). Anal. Calcd for $C_{138}H_{132}Ag_2F_6O_{18}P_4S_2$: C, 63.84; H, 5.12. Found: C, 63.22; H, 4.83.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$({OPPh$_2$}$_2${AgCF_3COO})$_2$] (12a). This was prepared in a manner similar to that described above from **8a** (0.044 g, 0.014 mmol) and **4** (0.031 g, 0.014 mmol). Yield: 0.055 g, 63%. ^{1}H NMR (CD_2Cl_2): δ 2.06, 2.36 (m, 8H, H^f), 2.52, 2.73 (m, 8H, H^g), 4.73 (m, 4H, H^e), 5.28 (s, 8H, OCH_2Ph), 6.23, 6.29, 7.70 (s, 6H, Ar-*H*), 6.88−7.50 (m, 82H, Ar-*H*, *Ph*). Anal. Calcd for $C_{144}H_{116}Ag_2F_6O_{20}P_4$: C, 66.01; H, 4.46. Found: C, 66.10; H, 4.42.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$({OPPh$_2$}$_2${AgCF_3SO_3})$_2$] (12b). This was prepared in a manner similar to that described above from **8b** (0.049 g, 0.015 mmol) and **4** (0.033 g, 0.015 mmol). Yield: 0.058 g, 70%. ^{1}H NMR (CD_2Cl_2): δ 2.09, 2.39 (m, 8H, H^f), 2.55, 2.77 (m, 8H, H^g), 4.71 (m, 4H, H^e), 5.28 (s, 8H, OCH_2Ph), 6.28 (s, 2H, H^c), 6.26 (s, 2H, H^b), 7.16 (s, 2H, H^a), 7.76 (s, 2H, H^d), 6.82−7.51 (m, 82H, Ar-*H*, *Ph*). Anal. Calcd for $C_{142}H_{116}Ag_2F_6O_{22}P_4S_2$: C, 63.35; H, 4.34. Found: C, 62.97; H, 4.10.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2$)$_4${AgCF_3SO_3}] (13). This was prepared in situ from **5b** and 3 equiv of **1**. ^{1}H NMR (CD_2Cl_2): δ 2.29, 2.44 (m, 28H, H^f, H^g, $C_6H_4CH_3$), 4.76 (m, 4H, H^e), 6.38 (s, 2H, Ar-*H*), 6.79−7.75 (m, 82H, Ar-*H*, *Ph*, $C_6H_4CH_3$).

Table 4. Crystallographic Data for Complexes **5a**, **16**, **17**, and **18**

	5a $4.7C_2H_4Cl_2$	**16** $2.2CH_2Cl_2$	**17** $12C_2H_4Cl_2$	**18** $5C_2H_4Cl_2 \cdot H_2O$
formula	$C_{157.4}H_{134.8}Ag_4Cl_{9.4}F_{12}O_{20}P_4$	$C_{292.2}H_{232}Ag_{10}Cl_{4.4}F_{30}O_{60}P_8S_{10}$	$C_{290}H_{248}Ag_{10}Cl_{24}F_{30}O_{62}P_8S_{18}$	$C_{295}H_{284}Ag_{13}Cl_{10}F_{39}O_{71}P_8S_{13}$
fw	3462.84	7076.22	8049.22	8217.57
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	24.2430(2)	21.4642(1)	20.469(4)	24.3660(2)
b (Å)	19.2287(1)	21.7091(2)	22.714(5)	23.5690(2)
c (Å)	34.7743(3)	23.3969(2)	23.171(5)	30.1051(2)
α (deg)		103.815(1)	110.62(3)	
β (deg)	92.938(1)	109.389(1)	101.14(3)	101.929(3)
γ (deg)		112.277(1)	111.42(3)	
vol (Å^3)	16189.1(2)	8646.2(2)	8723(3)	16915.5(2)
Z	4	1	1	2
D_{calc} (mg/m^3)	1.421	1.359	1.532	1.596
μ (mm^{-1})	0.747	0.765	0.960	1.026
R1, wR2 [$I > 2\sigma(I)$]	0.0783, 0.2242	0.0830, 0.2585	0.0685, 0.1935	0.0874, 0.2547
R indices (all data)	0.1127, 0.2537	0.1042, 0.2863	0.1104, 0.2228	0.1336, 0.2913

[Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2$)$_4${AgCF_3SO_3}] (14). This was prepared in a similar manner from **7b** and **3**. ^{1}H NMR (CD_2Cl_2): δ 1.16−2.25 (m, 52H, C_6H_{11}, H^f), 2.39, 2.56 (m, 8H, H^g), 4.61 (m, 4H, H^e), 6.34, 6.52, 7.67 (s, 6H, Ar-H), 6.95−7.60 (m, 62H, Ph).

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OPPh$_2$)$_4${AgCF_3SO_3}] (15). This was prepared in a similar manner from **8b** and **4**. ^{1}H NMR (CD_2Cl_2): δ 2.07, 2.25 (m, 8H, H^f), 2.35, 2.56 (m, 8H, H^g), 4.69 (m, 4H, H^e), 5.08 (s, 8H, OCH_2Ph), 6.36 (s, 2H, H^c), 6.78 (s, 2H, H^b), 7.16 (s, 2H, H^a), 7.60 (s, 2H, H^d), 6.77−7.60 (m, 80H, Ar-H, Ph).

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. After data reduction, the data were scaled on the basis of equivalent reflections 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 were solved by direct methods unless otherwise noted. Except as noted, all atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. Crystal data are summarized in Table 4.

[Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2${AgCF_3COO})$_4$] (5a). Crystals of [$C_{148}H_{116}Ag_4F_{12}O_{20}P_4$]$\cdot$4.7($CH_2ClCH_2Cl$) were grown by diffusion of hexane into a dichloroethane solution. The structure was solved using the automated Patterson routine of the SHELX-TL software package. Two of the carbonyl groups were modeled as a 60:40 isotropic mixture. One of the dangling phenyl rings was modeled as a 50:50 isotropic mixture. A second dangling phenyl ring was poorly ordered, and no suitable disorder model could be refined. Thus, this group was refined isotropically. The fluorine atoms of two of the trifluoroacetate groups were disordered, while both the oxygen and fluorine atoms of the remaining two trifluoroacetate groups were disordered; in each case, the disorder was modeled as a 50:50 isotropic mixture with geometric restraints. The chlorine atoms of the full occupancy solvent molecules were refined anisotropically; however, the carbon atoms were left isotropic. The partial occupancy solvent molecules were severely disordered and were refined isotropically. All solvent molecules were refined with geometric restraints. The largest residual electron density peak (1.288 e/Å^3) was associated with one of solvent molecules.

[{Resorcinarene(OC(O)$C_6H_4CH_3$)$_4$(OPPh$_2$)$_4$}$_2$Ag$_{10}$(O_3SCF_3)$_4$(μ-O_3SCF_3)$_2$(μ_3-O_3SCF_3)$_4$(OH$_2$)$_4$(μ-OH$_2$)$_2$] (16). Crystals of [$C_{290}H_{232}Ag_{10}F_{30}O_{60}P_8S_{10}$]$\cdot$2.2$CH_2Cl_2$ were grown by diffusion of hexane into a dichloromethane solution. One of the monodentate $CF_3SO_3^-$ groups was poorly ordered, although no suitable disorder model could be refined. Thus, this group was refined isotropically with geometric restraints applied. The partial occupancy solvent molecules were refined isotropically without hydrogen atoms and with geometric restraints applied. The adventitious water molecules were refined as single anisotropic oxygen atoms. Except as mentioned above, all non-hydrogen atoms were refined with anisotropic thermal parameters. The center of the molecule is situated on an inversion center. The largest residual electron density peak (3.365 e/Å^3) was associated with the poorly ordered $CF_3SO_3^-$ anion.

[{Resorcinarene(OC(O)C_4H_3S)$_4$(OPPh$_2$)$_4$}$_2$Ag$_{10}$(μ-O_3SCF_3)$_2$(μ_3-O_3SCF_3)$_4$(OH$_2$)$_4$(μ-OH$_2$)$_4$][CF_3SO_3]$_4$ (17). Crystals of [$C_{266}H_{200}Ag_{10}F_{30}O_{62}P_8S_{18}$]$\cdot$12($ClCH_2CH_2Cl$) were grown by diffusion of hexane into a dichloroethane solution. There was disorder of two of the thiophene substituents. One of the thiophene groups was modeled as a 65:35 mixture, while the other was modeled as a 50:50 mixture; in each case, ideal geometric restraints were applied. Only the sulfur atoms of these two thiophene groups were refined with anisotropic thermal parameters. The full occupancy solvent molecules were refined with anisotropic thermal parameters for the chlorine atoms only. All of the solvent molecules were refined with geometric restraints, and the poorly ordered partial occupancy solvent molecules were refined isotropically. The center of the molecule is situated on an inversion center. The largest residual electron density peak (3.038 e/Å^3) was associated with one of the solvent molecules.

[{Resorcinarene(OC(O)C_6H_{11})$_4$(OPPh$_2$)$_4$}$_2$Ag$_{13}$(OH$_2$)$_3$(μ-OH$_2$)$_4$(O_3SCF_3)$_6$(μ-O_3SCF_3)$_3$(μ_3- O_3SCF_3)$_4$] (18). Crystals of [$C_{285}H_{264}Ag_{13}F_{39}O_{70}P_8S_{13}$]$\cdot$5($ClCH_2CH_2Cl$)$\cdot$$H_2O$ were grown by diffusion of hexane into a dichloroethane solution. The structure was solved using the automated Patterson routine of the SHELX-TL software package. There was disorder in the compound. Two of the cyclohexyl groups were poorly ordered; one was modeled as an isotropic 50:50 mixture, while for the second group, no suitable disorder model could be refined. This latter group was refined at full occupancy with isotropic thermal parameters and geometric restraints. One of the phenyl rings of a diphenylphosphinite group was modeled as a 50:50 isotropic mixture. The fluorines of one of the $CF_3SO_3^-$ groups were modeled as a 50:50 isotropic mixture. The fluorines of another of the $CF_3SO_3^-$ groups were modeled as a 60:40 isotropic mixture. A third $CF_3SO_3^-$ group was modeled with the oxygen and fluorine atoms as a 50:50 isotropic mixture; only the sulfur atom of this group was refined anisotropically. The carbon−fluorine distances in the three disordered $CF_3SO_3^-$ groups were fixed to reasonable distances; the disordered oxygen atoms were treated similarly. One of the silver atoms present in the structure has a site occupancy of 50%. There is a poorly ordered $CF_3SO_3^-$ group bound to this silver atom, which, except for the sulfur atom, was refined with isotropic thermal parameters. In addition, there is a molecule of adventitious water bound to this silver atom, which was refined as an isotropic oxygen atom. The remaining molecules of adventitious water were refined as single anisotropic oxygen atoms. The solvents were poorly ordered. The one full occupancy solvent was refined with isotropic thermal parameters for the carbon atoms; the chlorine atoms were refined anisotropically. One solvent molecule was refined as a 60:40 isotropic mixture of one of the CH_2-Cl portions; the remaining CH_2-Cl portion was refined at full occupancy. Another solvent molecule was modeled with a 60:40 site disorder for the two carbon atoms. The two half-occupancy solvent molecules were refined with isotropic thermal parameters. The carbon−carbon and carbon−chlorine distances for all of the solvent molecules were fixed to reasonable distances, and the disordered solvents were all refined with isotropic thermal parameters. The center of the molecule is situated on an inversion center. The largest residual electron density peak (3.063 e/Å^3) was associated with one of the sulfur atoms.

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

IC050095B