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Structure and Dynamics of Tetrakis(thiophosphinato)resorcinarene Complexes of Silver(I), Gold(I), and Palladium(II)

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The coordination chemistry of the tetrakis(thiophosphinato)resorcinarene sulfur-donor ligands [$(C_6H_2CH\{CH_2CH_2Ph\})_4\{OC(O)R\}_4\{OP(=S)Ph_2\}_4$] (L), where R = OCH_2Ph, 4-$C_6H_4CH_3$, C_6H_{11}, C_4H_3S, or OCH_2CCH, is reported. Both silver(I) and gold(I) form cationic complexes of the type $[LM_2]^{2+}$, in which the ligand acts as a bis(chelate) in forming complexes with linear S–M–S (M = Ag or Au) stereochemistry. Gold(I) also forms the unusual complex $[L(AuCl)_2][LAu_2]^{2+}$, which forms a supramolecular polymer through intermolecular aurophilic attractions. Palladium(II) forms the complex $[LPd_2Cl_2(\mu\text{-}Cl)_2]$, in which the dipalladium(II) unit extends the natural bowl structure of the resorcinarene. The solid-state and solution conformations of the complexes, as determined by X-ray structure determination and NMR spectroscopy, respectively, are similar, but several complexes were found to exhibit dynamic behavior in solution, involving either conformational mobility of the resorcinarene unit or intermolecular ligand exchange.

Introduction

There has been intense interest in the synthesis and applications of derivatives of calixarenes and resorcinarenes containing metal atoms, which can be attached directly to the oxygen atoms of the upper rim or to other donor groups appended to the upper rim.[1−5] Furthermore, the ability to vary the substituents on the upper rim of resorcinarene provides an excellent opportunity to generate a wide variety of ligands. For example, the steric and electronic properties of the tetraphosphinite resorcinarene derivatives **1**−**5** (Scheme 1) can be varied by changing the substituents R of the four ester groups.[6]

The ligands **1**−**5** have been shown to have a rich coordination chemistry, arising from the unusual bite distance between neighboring phosphorus donors coupled with the conformational mobility of the resorcinarene skeleton.[6] Some of the known complexes are illustrated in Chart 1. These ligands can bind four silver(I) or gold(I) units (**I**−**III**, Chart 1). For example, silver halides gave the complexes **I** (X = Cl, Br, I), containing a silver halide crown cluster, which is unique to resorcinarene ligands.[4c,6c] The cluster unit holds the resorcinarene ligand in a rigid cone conformation. In contrast, the gold halide derivatives of type **II** contain four

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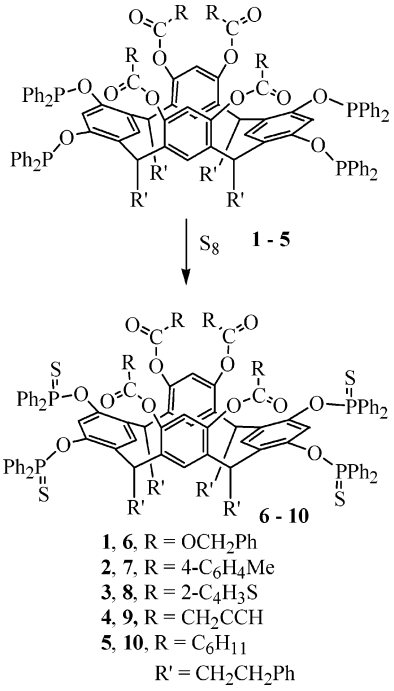
Scheme 1



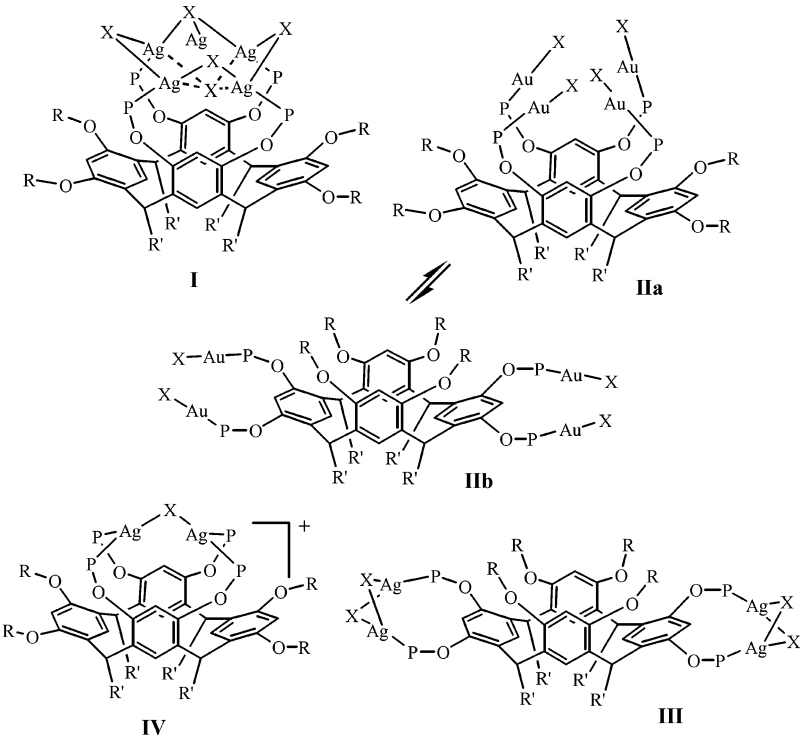
two-coordinate linear gold halide units, and these complexes exist in a boat conformation and undergo easy conformational exchange in solution (**IIa/IIb**).[6] Silver complexes of the type **III** are formed when the anions ($X = CF_3COO^-$, $CF_3SO_3^-$) are more weakly binding than halide; complex **III** can undergo intermolecular association to form a coordination polymer of a resorcinarene.[6d] The tetraphosphinite ligands have a low tendency to form chelate complexes to two silver(I) centers as in **IV**, and no examples of chelate complexes with linear P−M−P coordination are known.[6] The chelation in **IV** involves pairs of phosphorus donors on *different* aryl groups and so can only occur when the aryl groups with the phosphinite substituents are in the upright position.

To explore further the chemistry of the ligands based on the resorcinarene scaffold, the diphenylphosphinite units in compounds **1**−**5** were oxidized by sulfur to give the corresponding diphenylthiophosphinate compounds **6**−**10** (Scheme 1), and the coordination chemistry of these new sulfur-donor ligands has been investigated. There are many known transition-metal complexes of phosphine sulfides, but reports of thiophosphinates are scarce and there are no examples incorporating the resorcinarene skeleton.[7,8] Indeed, there are only a few reports of transition-metal complexes of resorcinarenes bearing sulfur donors affixed to the upper rim of the macrocyclic skeleton.[5] The tetrakis(thiophosphinate) ligands **6**−**10** were found to exhibit considerably different coordination chemistry in comparison to the tetraphosphinite resorcinarene parent compounds **1**−**5** reported previously.[6,9] One of the new gold(I) complexes is shown to form a supramolecular polymer in the solid state, through formation of secondary Au···Au interactions,[9] and the structures and dynamic properties were studied in solution by using variable-temperature NMR spectroscopy.

Results and Discussion

Synthesis of the Thiophosphinate Ligands and the Structure of Compound 6. Reaction of the tetrakis(diphenylphosphinite) resorcinarene compounds **1**−**5** with elemental sulfur readily produced the sulfide derivatives **6**−**10** as outlined in Scheme 1. The compounds **6**−**10** were characterized by ^1H and ^{31}P NMR spectroscopy, by elemental

Chart 1



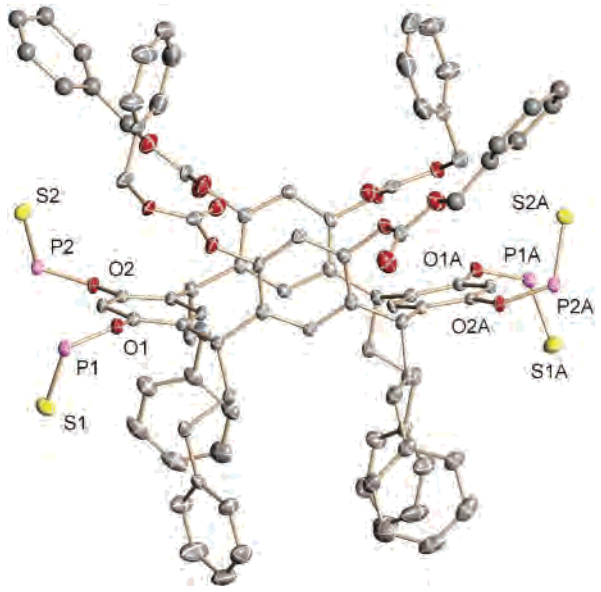


Figure 1. View of the structure of compound **6**. The phenyl rings of the thiophosphinate groups have been removed for clarity. Selected bond distances (Å) and angles (deg): P1−S1, 1.920(2); P2−S2, 1.928(2); P1−O1, 1.610(3); P2−O2, 1.617(3); O1−P1−S1, 116.3(1); O2−P2−S2, 115.7-(1).

analyses, and in the case of compound **6** by X-ray structure determination. The thiophosphinate derivatives were all obtained as air-stable white solids that are soluble in chlorinated solvents and in THF.

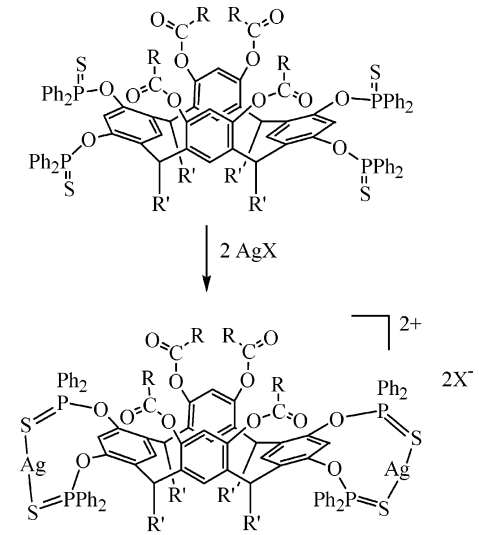
The structure of the tetrakis(thiophosphinate) compound **6** (R = OCH_2Ph in Scheme 1) was determined crystallographically, and a view of the structure is shown in Figure 1. The resorcinarene skeleton of **6** adopts a boat conformation, with the thiophosphinate-derivatized rings in a flattened position and the acylated rings in an upright position, similar to the parent tetraphosphinite compound **1**.[6a] Some conformational parameters are listed in Table 1. The angle between the planes of the arene rings carrying the benzyl carbonate substituents is 15° (fold angle Θ_1, showing that these arene rings are upright and close to parallel), while the angle between the planes of the arene rings bearing the diphenylthiophosphinate groups is 162° (fold angle Θ_2, showing that these arene rings are in the flattened position and close to parallel). The resorcinarene skeleton is only slightly twisted, as is seen by the dihedral angles between opposing arene rings (Φ_1 = 11° and Φ_2 = 10°; Table 1). The two thiophosphinate groups bound to a given arene group are oriented with one sulfur atom above the ring and the other below (Figure 1). This is in contrast to the parent tetraphosphinite compound **1**, in which the phosphorus atom lone pairs are oriented in the same direction.[6a] Compound **6** has crystallographically imposed C_2 symmetry.

Table 1. Conformational Parameters (Fold and Twist Angles, deg) for the Structurally Characterized Ligand **6** and Complexes **14a**, **18**, and **19**[a]

complex	Θ_1	Θ_2	Φ_1	Φ_2
6	15	162	11	10
14a	4	139	1	1
18a	4	153	10	12
18b	2	154	10	13
19	186	−17[b]	5	0

[a] Θ_1 and Θ_2 are the fold angles between the arene rings carrying the ester groups and the thiophosphinate groups, respectively, and Φ_1 and Φ_2 are the corresponding twist (dihedral) angles. [b] The negative sign indicates an inward tilt.

Scheme 2



R = OCH_2Ph **11a** X = CF_3SO_3 **11b** X = PF_6
R = 4-$C_6H_4CH_3$ **12a** X = CF_3SO_3 **12b** X = PF_6
R = C_4H_3S **13a** X = CF_3SO_3 **13b** X = PF_6
R = OCH_2CCH **14a** X = CF_3SO_3 **14b** X = PF_6

R' = CH_2CH_2Ph

Synthesis and Structure of Silver(I) Complexes. The disilver(I) complexes **11**−**14** were prepared by the reaction of compounds **6**−**9** with 2 equiv of silver triflate or silver hexafluorophosphate, as outlined in Scheme 2. Attempts to prepare tetrasilver complexes (one silver for each thiophosphinate group) were unsuccessful. The disilver(I) complexes were isolated as white solids.

The structure of the disilver complex **14a** was determined crystallographically and is shown in Figure 2. It provides a benchmark for characterization of the disilver complexes **11a**−**14b**. The resorcinarene skeleton adopts a boat conformation in which the arene rings bearing the thiophosphinate groups are in the flattened position and the acylated arene rings are upright (Figure 2). The angle between the planes

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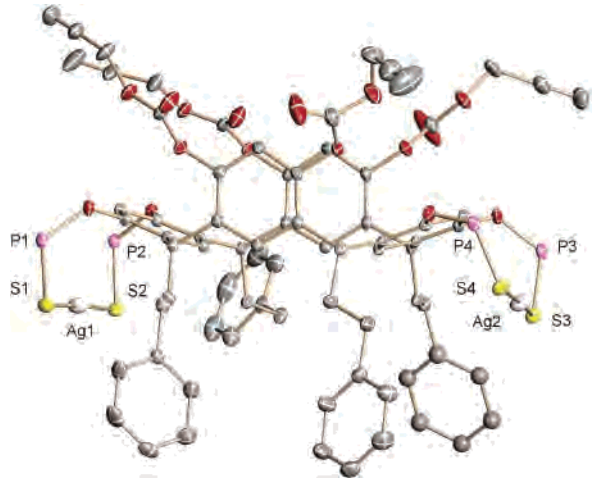


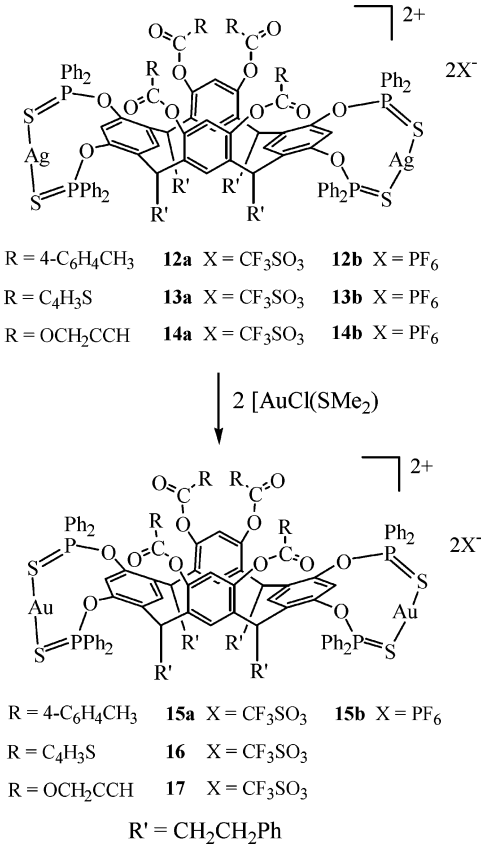
Figure 2. View of the structure of complex **14a**. The phenyl rings of the thiophosphinate groups have been removed for clarity. Oxygen atoms are shown in red. Selected bond distances (Å) and angles (deg): P1−S1, 1.971(2); P2−S2, 1.967(2); P3−S3, 1.957(2); P4−S4, 1.960(2); Ag1−S1, 2.450(1); Ag1−S2, 2.491(2); Ag2−S3, 2.454(2); Ag2−S4, 2.449(2); S1−Ag1−S2, 175.69(4); S3−Ag2−S4, 174.37(4); P1−S1−Ag1, 109.72(7); P2−S2−Ag1, 95.03; P3−S3−Ag2, 102.07(7); P4−S4−Ag2, 108.15(7).

made by the upright arene rings (fold angle Θ_1) is 4°, while the angle between the planes of the flattened arene rings (fold angle Θ_2) is 139°. There is little twisting distortion of the resorcinarene skeleton as seen by the dihedral angles between opposing arene rings ($\Phi_1 = 1°$ and $\Phi_2 = 1°$; Table 1). The conformation of the resorcinarene skeleton is similar to that of the ligand **6**, but the orientation of the thiophosphinate groups is different.

There are two silver atoms present in the structure of complex **14a**, and each is chelated by two sulfur atoms of the thiophosphinate groups of the same arene ring. The coordination geometry of the silver atoms is close to linear in each case [S1−Ag1−S2 = 175.69(4)°; S3−Ag2−S4 = 174.37(4)°]. We have previously shown that weakly coordinating anions such as triflate can be used to generate coordination polymers and capsule complexes of resorcinarenes.[6d,f] However, in **14a** the closest approach of an anion to either of the silver atoms is 2.72(1) Å between an oxygen atom of a triflate anion and Ag2. Furthermore, the near-ideal linear geometry of the silver atoms suggests that there is only a weak interaction between the silver cations and the triflate anions and so no extended structure was observed for complex **14a**. Similar structures are expected for the disilver(I) complexes with noncoordinating hexafluorophosphate anions.

The chelation of the silver atoms by the resorcinarene ligand in complex **14a** is significantly different from the chelating mode in the disilver(I) complexes of the parent tetraphosphinite resorcinarene ligands.[6] It was found that chelation by the tetraphosphinite ligands could only occur in the conformation in which the arene rings bearing the phosphinite groups were upright because the bite distance of the tetraphosphinite resorcinarene ligands in the reverse conformation is not suitable for chelation (Chart 1).[6] Thus, it is clear that the addition of the sulfur atoms significantly

Scheme 3



R = 4-$C_6H_4CH_3$ **12a** X = CF_3SO_3 **12b** X = PF_6
R = C_4H_3S **13a** X = CF_3SO_3 **13b** X = PF_6
R = OCH_2CCH **14a** X = CF_3SO_3 **14b** X = PF_6

R = 4-$C_6H_4CH_3$ **15a** X = CF_3SO_3 **15b** X = PF_6
R = C_4H_3S **16** X = CF_3SO_3
R = OCH_2CCH **17** X = CF_3SO_3

R' = CH_2CH_2Ph

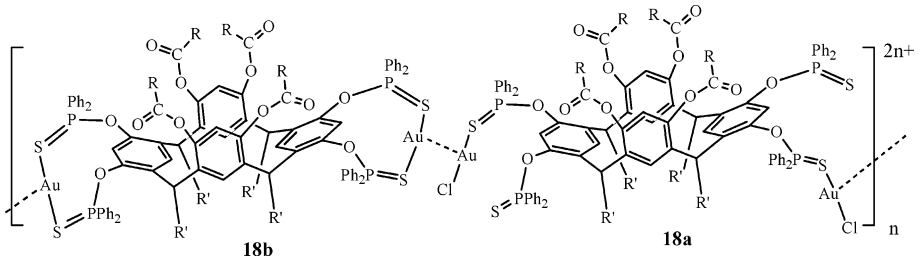
alters the bite distances in the resorcinarene ligands and has a dramatic effect on the preferred mode of chelation.

Synthesis and Structure of Gold(I) Complexes. Several digold(I) complexes were prepared by the reaction of the disilver complexes **12**−**14** with 2 equiv of [AuCl(SMe_2)], as outlined in Scheme 3. These reactions occur with precipitation of silver chloride and displacement of the dimethyl sulfide ligand from gold. The digold(I) complexes **15**−**17** (Scheme 3) were isolated as white solids.

The reaction of 4 equiv of [AuCl(SMe_2)] with the tetrathiophosphinate compound **7** resulted in a complex mixture of products, as analyzed by ^1H and ^{31}P NMR spectroscopy. However, recrystallization of the bulk solid gave the selective formation of pale-yellow crystals, which were shown by X-ray structure determination to have the structure [Resorcinarene($OC(O)C_6H_4Me$)$_4$($OP(S)Ph_2$)$_4$-{$AuCl$}$_2$]·[Resorcinarene($OC(O)C_6H_4Me$)$_4$($OP(S)Ph_2$)$_4$$Au_2$]-[$AuCl_2$]$_2$ (**18**; Chart 2 and Figures 3 and 4), where Resorcinarene = (C_6H_2CH{CH_2CH_2Ph})$_4$.

The complex **18** is constructed of two different components, one neutral and the other dicationic. The neutral component **18a** (Figure 3, top) has two S−Au−Cl units, one at each end of the resorcinarene ligand, and two noncoordinated sulfur atoms. The coordination geometry of the gold(I) centers is linear, with the S−Au−Cl bond angles being 178.4(2)° and 177.1(2)°. In the dicationic component **18b** (Figure 3, bottom), the gold(I) centers have linear S−Au^+−S coordination [bond angles of 172.2(2)° and 172.1(2)°], with chelation of each gold(I) center by two sulfur donors of the thiophosphinate groups on the same arene ring of the

Chart 2



macrocyclic skeleton. Thus, the dicationic component is analogous to the dications in the disilver(I) and digold(I) complexes **11**−**17** (Scheme 3). The anions present in the solid-state structure of **18**, which were highly disordered, were identified as $[AuCl_2]^-$. There are no interactions between the resorcinarene molecules and the dichloroaurate(I) anions or between the anions themselves, which merely fill space in the crystal lattice. It is noteworthy that only two gold atoms are taken up by each resorcinarene unit even though there are labile dichloroaurate(I) anions present. In both components, the resorcinarene skeleton adopts a boat conformation in which the thiophosphinate-derivatized arene rings are in the flattened position, while the acylated rings are upright. The conformational parameters are similar for each of the two different molecules, as seen by the near-identical fold and dihedral angles (Table 1).

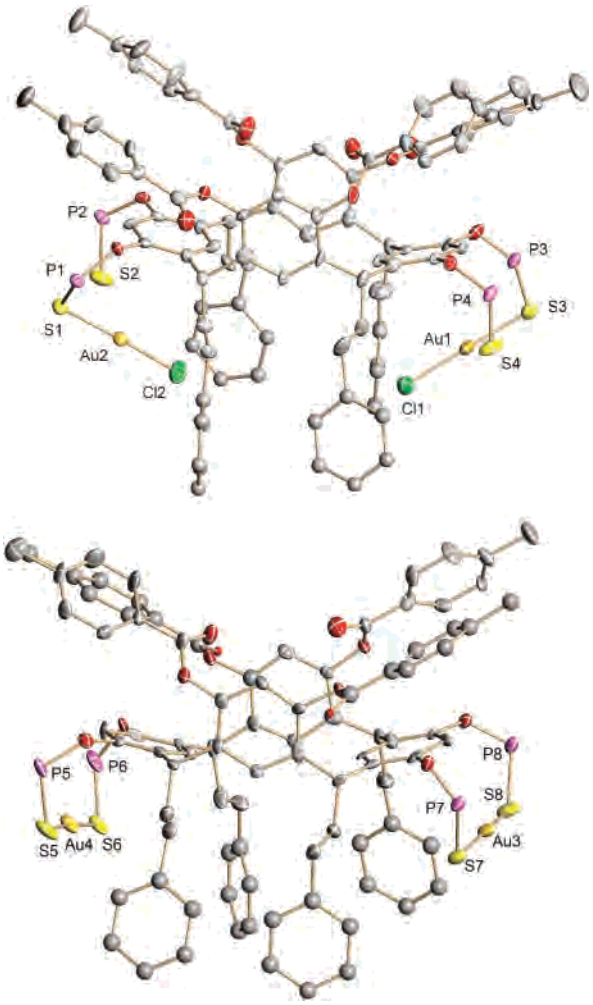


Figure 3. (top) View of the linear S−Au−Cl-containing component of complex **18a**. (bottom) View of the chelate S−Au−S-containing component of complex **18b**. In both cases, the phenyl rings of the thiophosphinate groups have been removed for clarity. The $[AuCl_2]^-$ anions are not shown. Oxygen atoms are shown in red. Selected bond distances (Å) and angles (deg): Au1−Cl1, 2.283(5); Au1−S3, 2.280(5); Au2−Cl2, 2.274(5); Au2−S1, 2.283(5); Au3−S7, 2.295(5); Au3−S8, 2.313(5); Au4−S5, 2.301(5); Au4−S6, 2.272(6); S3−Au1−Cl1, 178.4(2); S1−Au2−Cl2, 177.1(2); S7−Au3−S8, 172.2(2); S5−Au4−S6, 172.2(2).

The presence of the two different components in the solid state for complex **18** results in the remarkable polymeric structure depicted in Figure 4. The two different molecules are linked via Au···Au interactions at each end, so that each complex molecule or ion forms two intermolecular aurophilic bonds. The Au···Au distances, which occur between a chelate S−Au−S and a linear S−Au−Cl group, are nearly identical [Au1···Au4 = 3.023(1) Å; Au2···Au3 = 3.026(1) Å] and are indicative of a strong aurophilic attraction in each case.[9] Thus, the presence of these aurophilic attractions between the chelated S−Au−S gold centers and the linear S−Au−Cl gold centers results in an infinite, alternating pattern of the two different components **18a** and **18b**, which make up the solid-state structure of complex **18**. It is probable that the formation of the favorable Au···Au attractions provides the driving force for the selective crystallization of these two specific components from the complex mixture of compounds present in solutions of **18**. Clearly, the diverse coordination ability of the thiophosphinate ligand, which can accommodate both a linear Au−Cl unit and a chelated gold cation, allows for the formation of this supramolecular resorcinarene coordination polymer.

Synthesis and Structure of Palladium(II) Complexes. The palladium(II) chloride complexes **19**−**21** (Chart 3) were prepared by the reaction of 2 equiv of $PdCl_2$ with the thiophosphinate ligands; no further reaction of the thiophosphinate ligands with $PdCl_2$ could be effected. The complexes **19**−**21**, which are obtained as brown solids, were all characterized by elemental analysis and ^1H and ^{31}P NMR spectroscopy. The identity of the complexes was confirmed via the elucidation of the single-crystal structure of complex **19**. It is interesting to note that the parent tetraphosphinite ligands **1**−**5** do not react with solid $PdCl_2$ even after several days of reaction time.

The structure of the palladium(II) complex **19** is shown in Figure 5. The resorcinarene skeleton of complex **19** adopts the boat conformation in which the thiophosphinate-derivatized arene rings are in the *upright* position rather than in the *flattened* position seen in complexes **14** and **18**. Further-

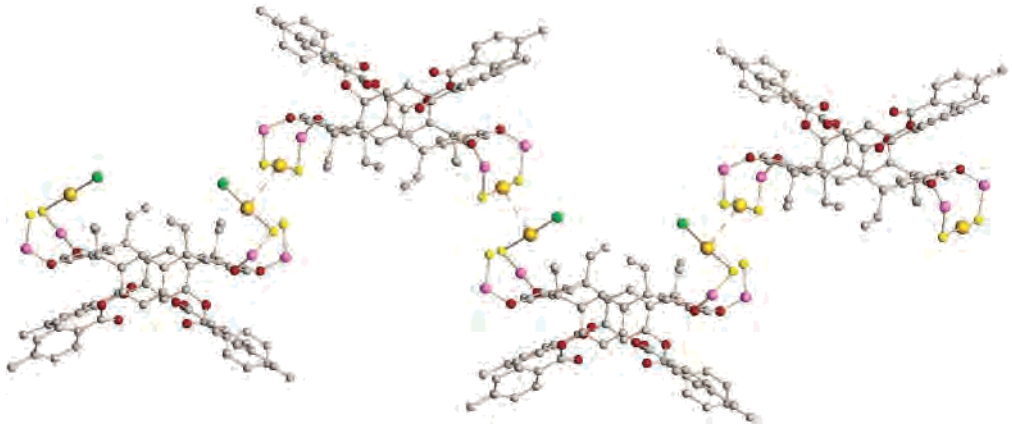
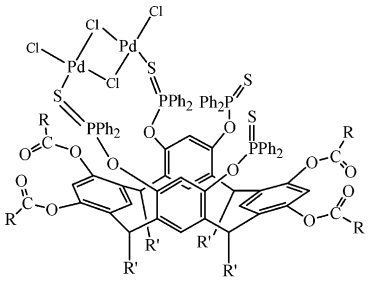


Figure 4. View of the polymeric structure of complex **18** formed by intermolecular aurophilic bonding [intermolecular distances (Å): Au1···Au4, 3.023(1); Au2..Au3A, 3.026(1)]. The phenyl rings of the thiophosphinate and phenethyl groups have been removed for clarity.

Chart 3



19 R = OCH_2Ph **20** R = 4-$C_6H_4CH_3$ **21** R = C_4H_3S
R' = CH_2CH_2Ph

more, there are significant differences in the conformational parameters of the resorcinarene skeleton (Table 1). The upright rings are tilted significantly inward, as is seen by the fold angle Θ_2 of −17°, and the flattened rings are tilted past the ideal 180° angle for a boat conformation, with the fold angle Θ_1 being 186°.

In complex **19**, two sulfur atoms of the thiophosphinate groups on opposing upright arene rings bind to a $Pd_2Cl_2(\mu\text{-}Cl)_2$ unit, while the remaining two sulfur atoms are not

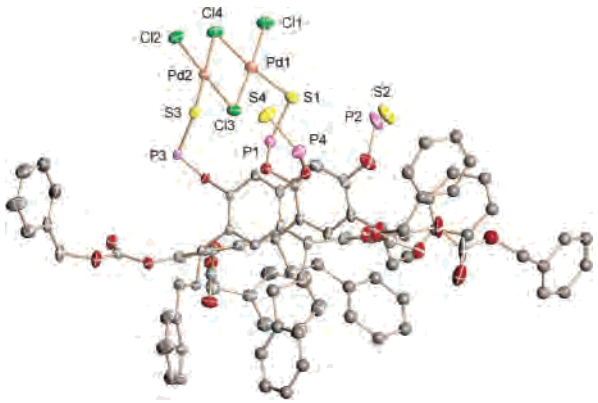
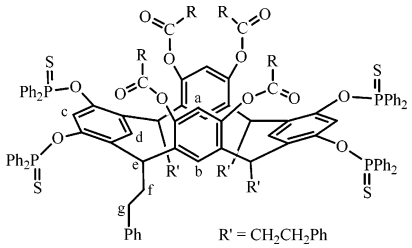


Figure 5. View of the structure of complex **19**. The phenyl rings of the thiophosphinate groups have been removed for clarity. Oxygen atoms are shown in red. Selected bond distances (Å) and angles (deg): Pd1−S1, 2.288(2); Pd1−Cl1, 2.280(2); Pd1−Cl3, 2.339(2); Pd1−Cl4, 2.355(2); Pd2−S3, 2.285(2); Pd2−Cl2, 2.277(2); Pd2−Cl3, 2.336(2); Pd2−Cl4, 2.337(2); S1−Pd1−Cl1, 86.24(8); S1−Pd1−Cl3, 96.50(7); Cl1−Pd1−Cl4, 91.51(8); Cl3−Pd1−Cl4, 85.89(7); S3−Pd2−Cl2, 85.51(8); S3−Pd2−Cl3, 96.78(7); Cl2−Pd2−Cl4, 91.33(8); Cl3−Pd2−Cl4, 86.38(7).

Chart 4. NMR Labeling Scheme



R' = CH_2CH_2Ph

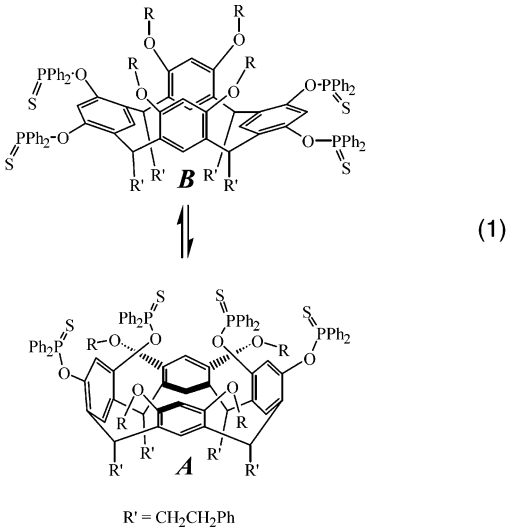
coordinated. Presumably, the bulk of the $Pd_2Cl_2(\mu\text{-}Cl)_2$ moiety prevents the coordination of a second such unit, due to unfavorable steric interactions. The two palladium centers each exhibit square-planar coordination geometry. The Pd−Cl bond distances for the bridging chlorides are similar [2.336(2)−2.355(2) Å] and are significantly longer than the two terminal chloride bonds [2.277(2)−2.280(2) Å]. There is a slight folding between the two square planes made by the atoms coordinated to the palladium centers, with the angle between the Cl1−S1−Cl3−Cl4 plane and the Cl2−S3−Cl3−Cl4 plane being 168°. Similar folding has been observed in other complexes of the general formula [$Pd_2Cl_2(\mu\text{-}Cl)_2L_2$].[10]

NMR Studies and Dynamics of the Compounds in Solution. The ^1H and ^{31}P NMR spectra of compounds **6**−**9** (Scheme 1 and Chart 4) were consistent with the presence of a single conformer with effective C_{2v} symmetry. For example, a single resonance was observed for the bridging methine protons (CH^e; Chart 4) as well as a single phosphorus resonance. However, the NMR data for compound **10** were consistent with the presence of two components, each with effective C_{2v} symmetry, and this observation prompted a detailed study of the solution NMR spectra.

It has been well 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 4) because CH^d in the flattened ring is more shielded.[6,11] The resonances for CH^b and CH^d can be assigned from the $^1H-^{13}C$ gHMBC and $^1H-^{31}P$ gHMBC

(10) Grossman, O.; Azerraf, C.; Gelman, D. *Organometallics* **2006**, *25*, 375 and references cited therein.

correlated NMR spectra.[6c] For compound **6**, the resonance for H^d is more shielded ($\delta = 6.23$) than the resonance for H^b ($\delta = 7.56$), indicating that the conformation adopted by the resorcinarene skeleton in solution is that in which the thiophosphinate-derivatized arene rings are flattened and the acylated arene rings are upright. This is also the conformation of complex **6** in the solid state (Figure 1), so the conformations are similar in both solution and the solid state. The conformation of complex **7** in solution was the same as that for **6** (conformation **B** in eq 1), as determined by the NMR method. For compound **10**, it was established that the two species present in solution are the conformers **A** and **B** (eq 1; R = $C_6H_{11}CO$). We suggest that the bulky cyclohexyl substituents present in compound **10** have two effects. First, the $C_6H_{11}CO_2$ substituents are similar in size to the $OPPh_2S$ substituents, so that conformers **A** and **B** (eq 1) have similar energies. Second, the bulky $C_6H_{11}CO_2$ substituents increase the energy barrier to the fluxionality depicted in eq 1, and so the interconversion between conformers is slower than that in compounds **6**−**9**. Variable-temperature NMR studies were performed on compounds **6**−**9**, but no evidence for the fluxionality of eq 1 was observed at temperatures down to 193 K. It seems likely that compounds **6**−**9** undergo boat−boat transitions in solution but with considerably less of conformer **A** and with a lower energy barrier to this fluxionality than that observed for compound **10**.



(1)

The ^1H and ^{31}P NMR data for the disilver and digold complexes **11a**−**17** were consistent with the presence of a single species with effective C_{2v} symmetry in each case. Thus, only a single resonance for H^e (Chart 4) and a single phosphorus resonance were observed. No silver couplings to the phosphorus resonances were observed for any of the disilver complexes. The $^1H-^{13}C$ gHMBC and $^1H-^{31}P$ gHMBC correlated NMR spectra were collected for several of the complexes, and in each case, it was determined that the resorcinarene skeleton of the complexes adopts conformation **B** (eq 1) in solution, which is in accordance with the solid-state structure of complex **14a**. Variable-temperature NMR studies were performed on several of the complexes, and the spectra remained virtually unchanged down to 193 K, thus providing no evidence for the fluxionality depicted in eq 1. This is not surprising because the chelation of the silver or gold centers by the sulfur atoms, as is seen in the solid-state structure of **14a**, would enforce geometric restraints on the resorcinarene ligand and so inhibit boat−boat transitions.

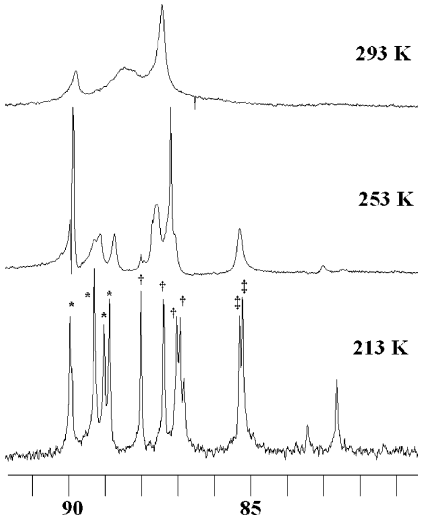


Figure 6. Variable-temperature ^{31}P NMR spectra of complex **18**. In the 213 K spectrum, the phosphorus atoms that are exchange-coupled are indicated.

The ^1H and ^{31}P NMR spectra obtained for bulk samples of **18** were very complex. The variable-temperature ^{31}P NMR spectra are shown in Figure 6. At room temperature, several broad resonances are observed, suggesting that ligand exchange or fluxionality was occurring in solution. At 213 K, a complex spectrum containing 14 resonances is observed, as shown in Figure 6, with two of these resonances overlapped at ca. $\delta = 90$. A ^{31}P g-COSY NMR experiment demonstrated that many of the resonances were exchange-coupled, with two sets of four resonances and one set of two resonances showing coupling in the g-COSY spectrum (Figure 6). Identical NMR data were obtained for the batch of crystals of **18** from which the X-ray crystal was selected, clearly indicating that two components present in the solid-state structure of **18** must undergo an exchange process in solution. Presumably, this exchange involves the transfer of AuCl and/or Au^+ between the thiophosphinate resorcinarene ligands, arising from the high lability of the P═S−Au bonds. In the low-temperature ^{31}P NMR spectrum shown in Figure 6, the resonance at $\delta = 82.5$ is due to the free ligand **7** and the uncoupled singlet resonance at $\delta = 89.9$ is assigned to the symmetrical structure **18b** (Chart 2), based on the similarity of the chemical shift to those of the analogous gold(I) complexes **15a** and **15b**, each of which has a single resonance in the ^{31}P NMR spectrum at $\delta = 89.7$. The presence of the free ligand **7** suggests that there may also be unsymmetrical complexes containing one or three gold atoms, but it was not possible to establish the identity of any of the unsymmetrical complexes. We note that complex

(11) (a) Shivanyuk, A.; Paulus, E. F.; Böhmer, V.; Vogt, W. *J. Org. Chem.* **1998**, *63*, 6448. (b) Shivanyuk, A.; Paulus, E. F.; Rissanen, K.; Kolehmainen, E.; Böhmer, V. *Chem.—Eur. J.* **2001**, *7*, 1944.

18a is expected to give two ^{31}P NMR resonances. Perhaps the selective crystallization of **18a** and **18b** from the complex mixture present in solution occurs because the intermolecular Au···Au interactions are stronger than those in other potential structures.[9]

The ^{1}H and ^{31}P NMR spectra for the palladium complexes **19**−**21** were consistent with the presence of a single species with effective C_s symmetry in each case, which is in accordance with the solid-state structure obtained for complex **19**. For example, two equal-intensity resonances were observed for the bridging methine protons as well as two equal-intensity phosphorus resonances. The ^{1}H−^{13}C gHMBC and ^{1}H−^{31}P gHMBC correlated NMR spectra for complex **19** established that the resorcinarene skeleton of the complex adopts conformation **A** in solution, which is in accordance with the solid-state structure. Similar results were obtained for complex **20**. No evidence for the fluxionality depicted in eq 1 was obtained for any of the palladium complexes. This absence of fluxionality is not surprising because the $Pd_2Cl_2(\mu\text{-}Cl)_2$ unit bridges between opposite aryl rings of the resorcinarene skeleton (Figure 5) and so locks them into position. There was no evidence for easy exchange between free and coordinated thiophosphinate groups or for the presence of the potential isomer formed by coordination of all thiophosphinate groups by cleavage of the chloride bridges in **19**.

Conclusions

The new tetrathiophosphinate resorcinarene ligands gave a considerably different coordination chemistry in comparison to the parent tetraphosphinite ligands described previously (Chart 1).[6] These differences may be attributed to a combination of the weaker ligating ability of the thiophosphinate groups and to differences in bite distances. For example, the tetrathiophosphinate ligands **6**−**10** were found to form chelate complexes with both silver(I) and gold(I), in which linear S−M−S units were present (**11**−**17**; Scheme 2) and the chelation involves pairs of thiophosphinate donors on the *same* aryl group, which is in the flattened position (Scheme 2 and Figure 2). This is in contrast to the tetraphosphinite ligands **1**−**5**, for which chelation has only been observed when the aryl groups with the phosphinite substituents are in the upright position.[6]

The ability of the tetrathiophosphinite ligands to act as either chelate or terminal ligands while in conformation **B** (eq 1) is illustrated in the solid-state structure of complex **18**, which contains both the chelate form in $[LAu_2]^{2+}$ and the terminal ligand form in $[L(AuCl)_2]$. This complex **18** undergoes supramolecular association to form the first example of a resorcinarene coordination polymer of gold(I).[6]

Although the thiophosphinate sulfur donors generally coordinate more weakly than the phosphinite phosphorus donors of Chart 1, it is interesting that, in contrast to the parent phosphinite ligands, the thiophosphinate ligands were capable of forming palladium complexes by direct reaction with solid $PdCl_2$. It seems that the thiophosphinate ligands provide a good platform for binding the *cis*-$Pd_2Cl_2(\mu\text{-}Cl)_2$ unit present in the solid-state structure of complex **19** (Figure 5), whereas the parent phosphinite ligands do not. The coordination chemistry of the tetrathiophosphinate resorcinarene ligands is versatile and differs very significantly from the tetraphosphinite ligands from which they are easily derived. In addition, the work further establishes the value of the resorcinarene skeleton in forming polydentate ligands with very unusual and interesting coordination chemistry.[1−6]

Experimental Section

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled, dried, and degassed prior to use. NMR spectra were recorded using a Varian Inova 400 spectrometer. The tetraphosphinite resorcinarene ligands **1**−**5** and the complex $[AuCl(SMe_2)]$ were prepared as reported elsewhere.[6a,12] In the formulas below, the resorcinarene skeleton $(C_6H_2CH\{CH_2CH_2Ph\})_4$ is represented as Resorcinarene. The proton resonances of the resorcinarene skeleton are identified according to the labeling scheme shown in Chart 4.

Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OP(S)Ph$_2$)$_4$ (6). A solution of **1** (2.0 g, 0.92 mmol) and S_8 (0.118 g, 0.46 mmol) in CH_2Cl_2 (50 mL) was stirred for 12 h. The solution was concentrated and filtered through Celite, and a white solid was precipitated with diethyl ether. The solid was washed with MeOH and diethyl ether and recrystallized from CH_2Cl_2/diethyl ether to give colorless needles of **6**, which turn to white powder upon drying. Yield: 2.08 g, 98%. NMR (CD_2Cl_2): δ(^{1}H) 2.12 [m, 4H, *H*^{f}], 2.23 [m, 8H, *H*^{f}, *H*^{g}], 2.49 [m, 4H, *H*^{g}], 4.62 [m, 4H, *H*^{e}], 4.80 [s, br, 8H, OC*H*$_2$Ph], 6.23 [s, 2H, *H*^{d}], 6.81 [s, 2H, *H*^{a}], 7.07 [s, 2H, *H*^{c}], 7.56 [s, 2H, *H*^{b}], 6.86−7.94 [m, 80H, *Ph*]; δ(^{31}P) 81.1 [s]. Anal. Calcd for $C_{140}H_{116}O_{16}P_4S_4$: C, 72.90; H, 5.07. Found: C, 72.53; H, 5.07.

Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OP(S)Ph$_2$)$_4$ (7). This was prepared similarly from ligand **2** (2.10 g, 0.99 mmol) and S_8 (0.127 g, 0.495 mmol). Yield: 2.05 g, 92%. NMR (CD_2Cl_2): δ(^{1}H) 2.04 [m, 4H, *H*^{f}], 2.19 [m, 8H, *H*^{f}, *H*^{g}], 2.46 [m, 4H, *H*^{g}], 2.49 [s, 12H, C$_6$H$_4$C*H*$_3$], 4.57 [m, 4H, *H*^{e}], 6.36 [s, 2H, *H*^{d}], 6.62 [s, 2H, *H*^{c}], 7.01 [s, 2H, *H*^{a}], 7.71 [s, 2H *H*^{b}], 6.73−7.86 [m, 76H, *Ph*, C$_6$*H*$_4$-CH$_3$]; δ(^{31}P) 82.1 [s]. Anal. Calcd for $C_{140}H_{116}O_{12}P_4S_4$: C, 74.98; H, 5.21. Found: C, 74.59; H, 4.96.

Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OP(S)Ph$_2$)$_4$ (8). This was prepared similarly from ligand **3** (1.75 g, 0.84 mmol) and S_8 (0.108 g, 0.42 mmol). Yield: 1.45 g, 78%. NMR (CD_2Cl_2): δ(^{1}H) 2.06 [m, 4H, *H*^{f}], 2.19 [m, 8H, *H*^{f}, *H*^{g}], 2.51 [m, 4H, *H*^{g}], 4.58 [m, 4H, *H*^{e}], 6.27 [s, 2H, Ar−*H*], 6.71−7.82 [m, 78H, *Ph*, Ar−*H*, C$_4$*H*$_3$S]; δ-(^{31}P) 81.8 [s]. Anal. Calcd for $C_{128}H_{100}O_{12}P_4S_8$: C, 69.55; H, 4.56. Found: C, 69.21; H, 4.60.

Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OP(S)Ph$_2$)$_4$ (9). This was prepared similarly from ligand **4** (1.09 g, 0.55 mmol) and S_8 (0.071 g, 0.276 mmol). Yield: 1.01 g, 88%. NMR (CD_2Cl_2): δ(^{1}H) 2.12 [m, 4H, *H*^{f}], 2.27 [m, 8H, *H*^{f}, *H*^{g}], 2.49 [m, 4H, *H*^{g}], 2.56 [t, 4H, $^{4}J_{HH}$ = 2 Hz, OCH$_2$C≡C*H*], 4.51 [m, 8H, $^{2}J_{HH}$ = 16 Hz, OC*H*$_2$C≡CH], 4.56 [m, 4H, *H*^{e}], 6.14 [s, 2H, Ar−*H*], 6.98−7.65 [m, 66H, Ar−*H*, *Ph*]; δ(^{31}P) 81.1 [s]. Anal. Calcd for $C_{124}H_{100}O_{16}P_4S_4$: C, 70.98; H, 4.80. Found: C, 70.61; H, 4.91.

Resorcinarene(OC(O)C$_6$H$_{11}$)$_4$(OP(S)Ph$_2$)$_4$ (10). This was prepared similarly from ligand **5** (2.12 g, 1.02 mmol) and S (0.142 g, 0.55 mmol). Yield: 1.40 g, 62%. NMR (CD_2Cl_2): δ(^{1}H) (**A**, **B**) 1.10−2.62 [m, *H*^{f}, *H*^{g}, C$_6$*H*$_{11}$], 6.81−8.02 [m, Ar−*H*, *Ph*]; (**A**) 4.71

(12) (a) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 411. (b) Brandys, M.-C.; Jennings, M. C.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **2000**, 4601.

[m, 4H, H^e], 6.57 [s, 2H, H^b], 7.01 [s, 2H, H^a], 7.15 [s, 2H, H^c], 7.71 [s, 2H, H^d]; (**B**) 4.51 [m, 4H, H^e], 6.24 [s, 2H, H^d], 6.69 [s, 2H, H^a], 7.24 [s, 2H, H^c], 7.61 [s, 2H, H^b]; $\delta(^{31}P)$ (**A**) 83.2 [s]; (**B**) 81.9 [s]. Anal. Calcd for $C_{136}H_{132}O_{12}P_4S_4$: C, 73.89; H, 6.02. Found: C, 73.55; H, 6.09.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][CF$_3$SO$_3$]$_2$ (11a). A solution of **6** (0.050 g, 0.022 mmol) and $AgCF_3SO_3$ (0.011 g, 0.043 mmol) in CH_2Cl_2 (5 mL) was stirred for 15 min in a darkened flask. The solution was filtered through Celite, and a white solid was precipitated with *n*-hexane and recrystallized from dichloroethane/*n*-hexane. Yield: 0.047 g, 76%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.29 [m, 8H, H^f], 2.47, 2.65 [m, 8H, H^g], 4.59 [m, 4H, H^e], 4.85 [m, 8H, $^2J_{HH}$ = 12 Hz, OCH_2Ph], 6.14 [s, 2H, H^c], 6.65 [s, 2H, H^d], 7.03 [s, 2H, H^a], 7.71 [s, 2H, H^b], 6.94−7.86 [m, 80H, *Ph*]; $\delta(^{31}P)$ 91.0 [s]. Anal. Calcd for **11a**·CH_2Cl_2, $C_{143}H_{118}Ag_2Cl_2F_6O_{22}P_4S_6$: C, 59.12; H, 4.09. Found: C, 58.61; H, 4.05.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][PF$_6$]$_2$ (11b). This was prepared similarly from **6** (0.080 g, 0.037 mmol) and $AgPF_6$ (0.019 g, 0.075 mmol). Yield: 0.074 g, 71%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.29 [m, 8H, H^f], 2.50, 2.71 [m, 8H, H^g], 4.60 [m, 4H, H^e], 4.88 [m, 8H, $^2J_{HH}$ = 12 Hz, OCH_2Ph], 6.12 [s, 2H, H^c], 6.72 [s, 2H, H^d], 7.09 [s, 2H, H^a], 7.72 [s, 2H, H^b], 6.97−7.85 [m, 80H, *Ph*]; $\delta(^{31}P)$ 92.8 [s, P(S)], −143.2 [m, PF_6^-]. Anal. Calcd for $C_{140}H_{116}Ag_2F_{12}O_{16}P_6S_4$: C, 59.79; H, 4.16. Found: C, 59.46; H, 4.05.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][CF$_3$SO$_3$]$_2$ (12a). This was prepared similarly from **7** (0.078 g, 0.035 mmol) and $AgCF_3SO_3$ (0.018 g, 0.07 mmol). Yield: 0.062 g, 64%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.20, 2.35 [m, 8H, H^f], 2.48, 2.73 [m, 8H, H^g], 2.62, [s, 12H, $C_6H_4CH_3$], 4.57 [m, 4H, H^e], 5.74, 6.72, 7.69 [s, 6H, Ar−*H*], 6.90−7.97 [m, 78H, Ar−*H*, *Ph*, $C_6H_4CH_3$]; $\delta(^{31}P)$ 92.1 [s]. Anal. Calcd for $C_{142}H_{116}Ag_2F_6O_{18}P_4S_6$: C, 61.87; H, 4.24. Found: C, 61.98; H, 4.47.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][PF$_6$]$_2$ (12b). This was prepared similarly from **7** (0.080 g, 0.036 mmol) and $AgPF_6$ (0.018 g, 0.071 mmol). Yield: 0.077 g, 78%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.26 [m, 8H, H^f], 2.52, 2.79 [m, 8H, H^g], 2.64, [s, 12H, $C_6H_4CH_3$], 4.62 [m, 4H, H^e], 5.72, 6.81, 7.83 [s, 6H, Ar−*H*], 6.92−7.98 [m, 78H, Ar−*H*, *Ph*, $C_6H_4CH_3$]; $\delta(^{31}P)$ 93.9 [s, P(S)], -143.2 [m, PF_6^-]. Anal. Calcd for **12b**·0.5$ClCH_2CH_2Cl$, $C_{141}H_{118}Ag_2ClF_{12}O_{12}P_6S_4$: C, 60.53; H, 4.25. Found: C, 60.12; H, 4.30.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][CF$_3$SO$_3$]$_2$ (13a). This was prepared similarly from **8** (0.080 g, 0.036 mmol) and $AgCF_3SO_3$ (0.019 g, 0.074 mmol). Yield: 0.078 g, 80%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.14, 2.28 [m, 8H, H^f], 2.44, 2.71 [m, 8H, H^g], 4.59 [m, 4H, H^e], 5.90, 6.67, 6.92 [s, 6H, Ar−*H*], 6.86−8.06 [m, 74H, *Ph*, Ar−*H*, C_4H_3S]; $\delta(^{31}P)$ 92.3 [s]. Anal. Calcd for $C_{130}H_{100}Ag_2F_6O_{18}P_4S_{10}$: C, 57.31; H, 3.70. Found: C, 56.94; H, 3.56.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][PF$_6$]$_2$ (13b). This was prepared similarly from **8** (0.080 g, 0.036 mmol) and $AgPF_6$ (0.018 g, 0.071 mmol). Yield: 0.082 g, 84%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.24 [m, 8H, H^f], 2.48, 2.75 [m, 8H, H^g], 4.60 [m, 4H, H^e], 5.88, 6.73 [s, 4H, Ar−*H*], 6.88−8.06 [m, 76H, *Ph*, Ar−*H*, C_4H_3S]; $\delta(^{31}P)$ 93.8 [s, P(S)], −143.1 [m, PF_6^-]. Anal. Calcd for $C_{128}H_{100}Ag_2F_{12}O_{12}P_6S_8$: C, 56.60; H, 3.71. Found: C, 56.38; H, 3.53.

[Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][CF$_3$SO$_3$]$_2$ (14a). This was prepared similarly from **9** (0.080 g, 0.038 mmol) and $AgCF_3SO_3$ (0.020 g, 0.078 mmol). Yield: 0.074 g, 75%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.30 [m, 8H, H^f], 2.37, 2.61 [m, 8H, H^g], 2.83 [t, 4H, $^4J_{HH}$ = 2 Hz, OCH$_2$C≡CH], 4.51 [m, 4H, H^e], 4.59 [s, br, 8H, OCH_2C≡CH], 6.30, 6.51 [s, 4H, Ar−*H*], 6.94−8.01 [m, 64H, Ar−*H*, *Ph*]; $\delta(^{31}P)$ 91.4 [s]. Anal. Calcd for $C_{126}H_{100}Ag_2F_6O_{22}P_4S_6$: C, 57.94; H, 3.86. Found: C, 58.12; H, 4.03.

[Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OP(S)Ph$_2$)$_4${Ag$_2$}][PF$_6$]$_2$ (14b). This was prepared similarly from **9** (0.080 g, 0.038 mmol) and $AgPF_6$ (0.019 g, 0.075 mmol). Yield: 0.073 g, 74%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.27 [m, 8H, H^f], 2.45, 2.62 [m, 8H, H^g], 2.78 [s, br, OCH$_2$C≡CH], 4.51 [m, 4H, H^e], 4.59 [m, 8H, $^2J_{HH}$ = 16 Hz, $^4J_{HH}$ = 2 Hz, OCH_2C≡CH], 6.25, 6.59 [s, 4H, Ar−*H*], 6.94−7.96 [m, 64H, Ar−*H*, *Ph*]; $\delta(^{31}P)$ 93.1 [s], −143.2 [m, PF_6^-]. Anal. Calcd for **14b**·$ClCH_2CH_2Cl$, $C_{126}H_{104}Ag_2Cl_2F_{12}O_{16}P_6S_4$: C, 55.99; H, 3.88. Found: C, 55.71; H, 3.86.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OP(S)Ph$_2$)$_4${Au$_2$}][CF$_3$SO$_3$]$_2$ (15a). To a solution of **12a** (0.098 g, 0.036 mmol) in CH_2Cl_2 (5 mL) in a darkened flask was added [AuCl(SMe$_2$)] (0.021 g, 0.071 mmol), resulting in an immediate precipitation of AgCl. The solution was stirred for 15 min and filtered through Celite, and a white solid was precipitated with *n*-hexane. Yield: 0.080 g, 76%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.29 [m, 8H, H^f], 2.53, 2.80 [m, 8H, H^g], 2.62, [s, 12H, $C_6H_4CH_3$], 4.67 [m, 4H, H^e], 5.92 [s, 2H, H^c], 6.76 [s, 2H, H^d], 6.89 [s, 2H, H^a], 7.86 [s, 2H, H^b], 6.92−7.96 [m, 76H, *Ph*, $C_6H_4CH_3$]; $\delta(^{31}P)$ 89.7 [s]. Anal. Calcd for **15a**·0.5(*n*-hexane), $C_{145}H_{123}Au_2F_6O_{18}P_4S_6$: C, 58.49; H, 4.16. Found: C, 57.98; H, 3.93.

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OP(S)Ph$_2$)$_4${Au$_2$}][PF$_6$]$_2$ (15b). This was prepared similarly from **12b** (0.120 g, 0.043 mmol) and [AuCl(SMe$_2$)] (0.026 g, 0.088 mmol). Yield: 0.092 g, 73%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.32 [m, 8H, H^f], 2.50, 2.83 [m, 8H, H^g], 2.63, [s, 12H, $C_6H_4CH_3$], 4.68 [m, 4H, H^e], 5.93 [s, 2H, H^c], 6.78 [s, 2H, H^d], 6.91 [s, 2H, H^a], 7.87 [s, 2H, H^b], 6.92−7.98 [m, 78H, *Ph*, $C_6H_4CH_3$]; $\delta(^{31}P)$ 89.7 [s, P(S)], −143.2 [m, PF_6^-]. Anal. Calcd for $C_{140}H_{116}Au_2F_{12}O_{12}P_6S_4$: C, 57.46; H, 4.00. Found: C, 57.25; H, 4.15.

[Resorcinarene(OC(O)C$_4$H$_3$S)$_4$(OP(S)Ph$_2$)$_4${Au$_2$}][CF$_3$SO$_3$]$_2$ (16). This was prepared similarly from **13a** (0.099 g, 0.036 mmol) and [AuCl(SMe$_2$)] (0.021 g, 0.071 mmol). Yield: 0.070 g, 67%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.29 [m, 8H, H^f], 2.55, 2.77 [m, 8H, H^g], 4.67 [m, 4H, H^e], 6.12 [s, 2H, H^c], 6.67 [s, 2H, H^d], 6.92 [s, 2H, H^a], 7.83 [s, 2H; H^b], 6.71−8.04 [m, 72H, *Ph*, C_4H_3S]; $\delta(^{31}P)$ 89.1 [s]. Anal. Calcd for $C_{130}H_{100}Au_2F_6O_{18}P_4S_{10}$: C, 53.79; H, 3.47. Found: C, 53.97; H, 3.45.

[Resorcinarene(OC(O)OCH$_2$C≡CH)$_4$(OP(S)Ph$_2$)$_4${Au$_2$}][CF$_3$SO$_3$]$_2$ (17). This was prepared similarly from **14a** (0.099 g, 0.038 mmol) and [AuCl(SMe$_2$)] (0.022 g, 0.075 mmol). Yield: 0.083 g, 78%. NMR (CD_2Cl_2): $\delta(^1H)$ 2.30 [m, 8H, H^f], 2.45, 2.65 [m, 8H, H^g], 2.81 [s, br, 4H, OCH$_2$C≡CH], 4.52 [m, 8H, $^2J_{HH}$ = 16 Hz, OCH_2C≡CH], 4.56 [m, 4H, H^e], 6.43 [s, 2H, H^c], 6.57 [s, 2H, H^d], 7.12 [s, 2H, H^a], 7.63 [s, 2H, H^b], 6.98−8.04 [m, 60H, *Ph*]; $\delta(^{31}P)$ 89.5 [s].

[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OP(S)Ph$_2$)$_4${Au}$_2$][AuCl$_2$]$_2$·[Resorcinarene(OC(O)C$_6$H$_4$CH$_3$)$_4$(OP(S)Ph$_2$)$_4${AuCl}$_2$] (18). A solution of **7** (0.100 g, 0.045 mmol) and [AuCl(SMe$_2$)] (0.053 g, 0.180 mmol) in CH_2Cl_2 (10 mL) in a darkened flask was stirred for 16 h. The yellow solution was filtered through Celite, and a light-yellow solid was precipitated with *n*-hexane. Yield: 0.084 g, 63%. NMR (CD_2Cl_2, 193K): $\delta(^{31}P)$ 83.2, 85.2, 85.3, 86.8, 86.9, 87.0, 87.4, 88.0, 88.9, 89.1, 89.3, 89.9, 90.0. Anal. Calcd for **18**·3$ClCH_2CH_2Cl$, $C_{286}H_{244}Au_6Cl_{12}O_{24}P_8S_8$: C, 55.62; H, 3.98. Found: C, 55.44; H, 3.72.

[Resorcinarene(OC(O)OCH$_2$Ph)$_4$(OP(S)Ph$_2$)$_4${Pd$_2$Cl$_2$(μ-Cl)$_2$}] (19). A solution of **6** (0.080 g, 0.035 mmol) and $PdCl_2$ (0.013 g, 0.073 mmol) in CH_2Cl_2 (5 mL) was stirred for 24 h. The resulting dark-yellow solution was filtered through Celite, and a brown solid was precipitated with *n*-hexane and recrystallized from $CHCl_3$/*n*-

Table 2. Crystallographic Data for Complexes **6**, **14a**, **18**, and **19**[a]

	6·5CH_2Cl_2·H_2O	**14a**·1.85$C_2H_4Cl_2$·0.35H_2O	**18**·4.75$C_2H_4Cl_2$·H_2O	**19**·4.5$CHCl_3$·0.5H_2O
formula	$C_{145}H_{126}Cl_{10}O_{17}P_4S_4$	$C_{129.7}H_{107.4}Ag_2Cl_{3.7}F_6O_{22.35}P_4S_6$	$C_{289.5}H_{251}Au_6Cl_{15.5}O_{25}P_8S_8$	$C_{144.5}H_{120.5}Cl_{17.5}O_{16.5}P_4Pd_2S_4$
fw	2747.08	2800.70	6365.42	3206.20
space group	*Pbcn*	$\bar{P}1$	*P*2(1)/*c*	$\bar{P}1$
a (Å)	33.460(7)	15.524(3)	27.102(5)	17.021(3)
b (Å)	17.535(4)	16.021(3)	28.513(6)	18.537(4)
c (Å)	24.043(5)	27.110(5)	37.424(8)	24.719(5)
α (deg)		103.40(3)		95.69(3)
β (deg)		98.20(3)	95.08(3)	93.33(3)
γ (deg)		101.04(3)		99.61(3)
V (Å^3)	14106(6)	6313(3)	28805(10)	7630(3)
Z	4	2	4	2
d_{calc} (g cm^{-3})	1.293	1.473	1.468	1.396
μ (mm^{-1})	0.364	0.616	3.351	0.698
R1, wR2 [$I > 2\sigma(I)$]	0.072, 0.212	0.065, 0.174	0.095, 0.266	0.085, 0.239
R indices (all data)	0.1306, 0.2447	0.0959, 0.1932	0.1618, 0.3163	0.1166, 0.2692

[a] Temperature = 150(2) K; wavelength = 0.710 73 Å.

hexane. Yield: 0.062 g, 67%. NMR (CD_2Cl_2): δ(^{1}H) 1.35, 1.57, 1.74, 1.89, 2.04, 2.34 [m, 16H, *H*^{f}, *H*^{g}], 3.54, 4.61 [m, 4H, *H*^{e}], 5.15, 5.19 [m, 8H, OC*H*$_2$Ph], 5.74, 5.82 [s, 2H, *H*^{b}], 7.20, 7.68 [s, 2H, *H*^{d}], 6.60−8.21 [m, 84H, *H*^{a}, *H*^{c}, *Ph*]; δ(^{31}P) 88.2 [s], 89.2 [s]. Anal. Calcd for **19**·0.5$CHCl_3$, $C_{140.5}H_{116.5}Cl_{5.5}O_{16}P_4Pd_2S_4$: C, 62.02; H, 4.32. Found: C, 61.82; H, 4.50.

[Resorcinarene(OC(O)C_4H_3S)$_4$(OP(S)Ph_2)$_4${Pd_2Cl_2(*μ*-Cl)$_2$}] (20). This was prepared similarly from **8** (0.080 g, 0.036 mmol) and $PdCl_2$ (0.013 g, 0.073 mmol). Yield: 0.078 g, 87%. NMR (CD_2Cl_2): δ(^{1}H) 1.18, 1.35, 1.79, 2.05, 2.26, 2.50 [m, 16H, *H*^{f}, *H*^{g}], 3.60, 5.00 [m, 4H, *H*^{e}], 5.92, 6.06 [s, 2H, *H*^{b}], 7.41, 7.71 [s, 2H, *H*^{d}], 6.50−8.16 [m, 76 H, *Ph*, *H*^{a}, *H*^{c}, C_4H_3S]; δ(^{31}P) 87.7 [s], 88.9 [s]. Anal. Calcd for **20**·$CHCl_3$, $C_{129}H_{101}Cl_7O_{12}P_4Pd_2S_8$: C, 57.71; H, 3.79. Found: C, 57.27; H, 3.71.

[Resorcinarene(OC(O)C_6H_{11})$_4$(OP(S)Ph_2)$_4${Pd_2Cl_2(*μ*-Cl)$_2$}] (21). This was prepared similarly from **10** (0.080 g, 0.036 mmol) and $PdCl_2$ (0.013 g, 0.073 mmol). Yield: 0.062 g, 67%. NMR (CD_2Cl_2): δ(^{1}H) 1.04−2.58 [m, 60H, *H*^{f}, *H*^{g}, C_6H_{11}], 3.51, 4.84 [m, 4H, *H*^{e}], 5.87, 6.00 [s, 2H, Ar−*H*], 6.62−8.16 [m, 70H, Ar−*H*, *Ph*]; δ(^{31}P) 87.4 [s], 88.2 [s]. Anal. Calcd for **21**·$CHCl_3$, $C_{137}H_{133}Cl_7O_{12}P_4Pd_2S_4$: C, 61.29; H, 4.99. Found: C, 60.86; H, 4.79.

X-ray Structure Determinations. A crystal suitable for X-ray analysis was mounted on a glass fiber. Data were collected at 150 K by using a Nonius-Kappa CCD diffractometer using *COLLECT* (B. V. Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius *DENZO* package. The data were scaled using SCALEPACK (B. V. Nonius, 1998). The *SHELX-TL* version 5.1 and *SHELX-TL* version 6.1 (G. M. Sheldrick) program packages were used to solve and refine the structures. The structures were all solved by direct methods. 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 2. All thermal ellipsoid diagrams are shown at 30% probability.

Compound 6. Crystals of [$C_{140}H_{116}O_{16}P_4S_4$]·5$CH_2Cl_2$·$H_2O$ were grown from diffusion of *n*-hexane into a dichloromethane solution. One of the O*CH*$_2$*Ph* groups was modeled as a 65:35 isotropic mixture with geometric restraints. One of the partial-occupancy solvent molecules was highly disordered and was modeled as a 25:25 isotropic mixture with geometric restraints. The molecule of adventitious water was modeled as a single isotropic oxygen atom.

Complex 14a. Crystals of [$C_{124}H_{100}Ag_2O_{16}P_4S_4$][$CF_3SO_3$]$_2$·1.85$ClCH_2CH_2Cl$·0.35$H_2O$ were grown from diffusion of *n*-hexane into a dichloroethane solution. There was disorder of two of the phenyl rings, which were modeled as 50:50 and 60:40 isotropic mixtures, respectively. One of the triflate anions was disordered and was modeled as a 75:25 isotropic mixture. The 25% portion was further disordered and was modeled as a 15:10 isotropic mixture of two anions inverted and superimposed in the same point in space. The solvent molecules were disordered and were modeled as isotropic mixtures with geometric restraints. The molecule of adventitious water was modeled as a single isotropic oxygen atom.

Complex 18. Crystals of [$C_{140}H_{116}Au_2O_{12}P_4S_4$][$AuCl_2$]$_2$[$C_{140}H_{116}Au_2Cl_2O_{12}P_4S_4$]·4.75$ClCH_2CH_2Cl$·$H_2O$ were grown from diffusion of *n*-hexane into a dichloroethane solution. There was a disorder of the entire structure present for complex **18**, which was refined to a 94:6 mixture. However, only the 6% occupancy gold atoms could be located for the minor component and were refined with isotropic thermal parameters; the remaining atoms were treated as 100%. All of the dangling phenethyl groups were disordered and were modeled with appropriate occupancies as isotropic mixtures with geometric restraints. Two of the tolyl substituents were modeled as 50:50 isotropic mixtures with geometric restraints. The solvents were disordered and were modeled with geometric restraints; only the chlorine atoms were refined with anisotropic thermal parameters. The chloroaurate anions were severely disordered. The first anion location was refined as a five-part disorder model in a 30:25:20:15:10 ratio. The second anion location was modeled as a four-part disorder in a 35:35:15:15 ratio. The gold chloride distances were restrained to be equal and allowed to refine, and only the gold atoms were refined with anisotropic thermal parameters.

Complex 19. Crystals of [$C_{140}H_{116}Cl_4O_{16}P_4Pd_2S_4$]·4.5$CHCl_3$·0.5$H_2O$ were grown from diffusion of *n*-hexane into a chloroform solution. The two uncoordinated Ph_2PS groups were highly disordered and were modeled as 45:30:25 and 75:25 mixtures, respectively. In both cases, geometric restraints were applied, and only the phosphorus and sulfur atoms of these highly disordered groups were modeled anisotropically. Three of the dangling phenethyl groups were disordered and were modeled as 50:50, 50:50, and 60:40 isotropic mixtures, respectively, with geometric restraints. One of the O*CH*$_2$*Ph* groups was modeled as a 55:45 isotropic mixture with geometric restraints. A second O*CH*$_2$*Ph* group showed evidence of disorder, but no suitable disorder model could be refined, and this group was refined at full occupancy with isotropic thermal parameters. One of the partial-occupancy solvent molecules was highly disordered and was modeled as a 40:35 isotropic mixture with geometric restraints and fixed coordinates

for the carbon atoms. The partial-occupancy solvent molecules were all modeled with isotropic thermal parameters. The molecule of adventitious water was modeled as a single isotropic oxygen atom.

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Supporting Information Available: Crystallographic tables in CIF format for compound **6** and complexes **14a**, **18**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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