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Transition Metal Rimmed-Calixresorcinarene Complexes

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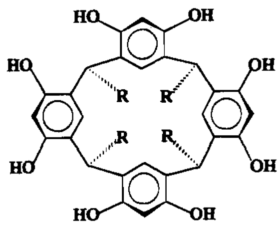
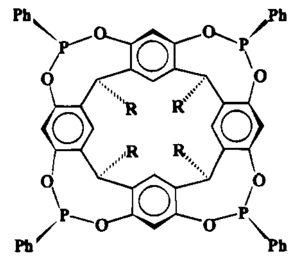
A bowl-shaped calixresorcinarene **1** has been derivatized to incorporate four phosphonite units to give a phosphonito-cavitand **2** and eight phosphinite units to give phosphinito-calixresorcinarene **3**. These derivatives have been used as multidentate ligands to incorporate transition metals on the upper rim of the calixresorcinarene bowl. Several gold(I) complexes and platinum(II) complexes have been synthesized. The chlorogold(I) complex of **2**, **2**$(AuCl)_4$, was characterized by an X-ray structure determination [crystal data: $C_{84}H_{68}Au_4Cl_4P_4O_8{\cdot}0.5CH_2Cl_2{\cdot}2.5CH_3CN{\cdot}H_2O$, fw = 2422.16, triclinic, $P\bar{1}$, a = 15.271(5) Å, b = 28.399(8) Å, c = 11.060(5) Å, α = 93.40(3)°, β = 111.21(3)°, γ = 98.41(2)°, V = 4390.8 Å^3, Z = 2, R = 0.0534, R_w = 0.0504]. This complex is shown to contain three AuCl units around the upper rim of the bowl with the fourth AuCl unit folded inside the cavity. The gold(I)-rimmed bowl forms inclusion complexes with amines and alkali metal cations but not with other potential substrates.

Introduction

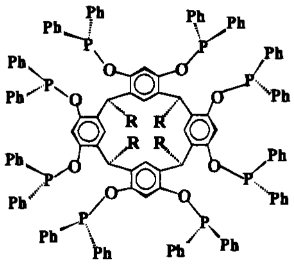
One strategy for making use of host−guest chemistry for shape- and/or size-selective catalysis is to derivatize the host molecule with transition metal atoms capable of catalytic activation of guest molecules, and this has led to increasing interest in transition metal complexes of macrocyclic ligands.[1−4] The calixresorcinarenes **1**, which are easily prepared by condensation of resorcinol with various aldehydes,[5] are bowl-shaped compounds that can serve as hosts for small guest molecules and cations.[6−8] The first transition metal complexes derived from **1** were reported in the preliminary communication of this work.[4] This article reports details of the successful derivatization of the calixresorcinarene to give a phosphonito-cavitand **2** with four PhP units and a phosphinito-calixresorcinarene **3** with eight PPh_2 units around its upper rim. The strong coordinating ability of **2** and **3** made it possible to introduce transition metals, such as Au and Pt, to the upper rim of the calixresorcinarene to give transition metal-rimmed bowl complexes, which have the potential to accept small guest molecules and ions.[9]



R = CH_2CH_2Ph
1



R = CH_2CH_2Ph
2



R = CH_2CH_2Ph
3

Previous research has been focused on the derivatization of the calix-4-arenes with phosphorus donors to bind to late transition metal acceptors, and much interesting chemistry has resulted.[1] The advantage of the approach in the present work is that the transition metals are naturally introduced at the open face of the calixresorcinarene and so inclusion chemistry directly involving the transition metals is more likely to occur.

Results and Discussion

1. Preparation and Characterization of Phosphonito-Derived Cavitand 2.

Although the OH groups[1,2] and aryl rings[10] of a calixresorcinarene can act as coordination sites, the

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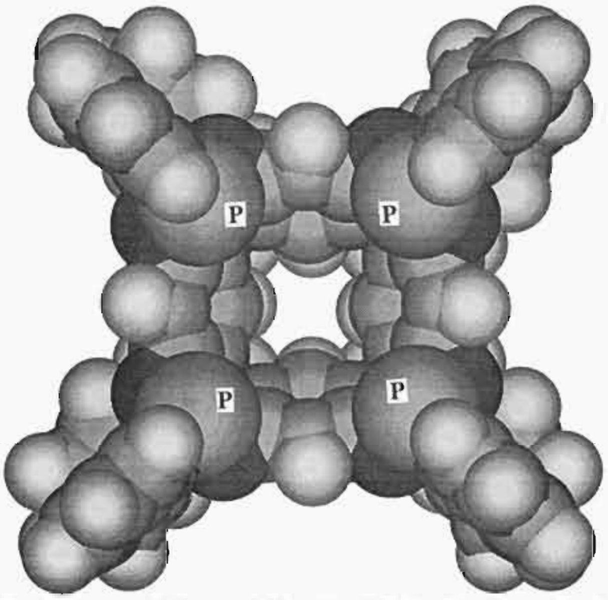


Figure 1. Space-filling model of cavitand 2, showing the natural cavity and orientation of the phosphorus donors.

Table 1. Molecular Mechanics Calculations for the Six Possible Conformers of 2

	compound 2					
	A	B	C (*trans*)	D (*cis*)	E	F
MMX energy	126.61	134.12	146.32	148.41	149.60	153.21
% difference	0	5.93	15.57	17.22	18.16	21.00

introduction of soft donors, such as phosphorus(III) or sulfur(II), is highly desirable if late transition metals are to be strongly bound to the macrocyclic system. Thus, treatment of the resorcinol-derived calixresorcinarene 1, which has a frozen cone conformation, with phenylphosphonous chloride in the presence of pyridine as base gave a new phosphorus(III) calixresorcinarene derivative, 2. All the spectroscopic data indicate that 2 maintains the cone conformation and so has a bowl-shaped architecture with a cavity deeper than that of its precursor 1 as shown in Figure 1.

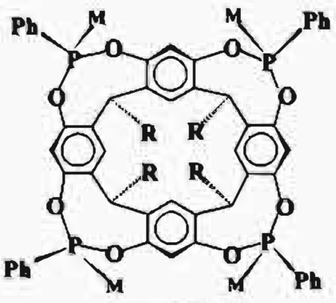
However, it should be noted that there are six possible isomeric forms for the cavitand **2**, even when it is in the cone conformation. The lone pair of electrons on the phosphorus atoms of 2 could be directed either outward or inward with respect to the middle of the bowl (Figure 2). Molecular mechanics calculations[11] (Table 1) indicated that the isomer with all phenyl groups directed outward and lone pairs directed inward would be preferred, and this stereochemistry is consistent with the observation of a single ^{31}P NMR resonance for 2 and with all of the chemistry described below.

2. Gold- and Platinum-Rimmed Cavitands. The space-filling model of 2 indicates that it has a deeper cavity than its precursor **1** (Figure 1), and so it should have a strong ability to engulf guests. However, the phosphorus donors in compound **2** are too far apart (~6.6 Å) to chelate to metals and so they can only act as terminal ligands toward transition metals. Thus, treatment of **2** with [AuCl(SMe$_2$)] gave **4a**, X = Cl, by replacement of SMe$_2$ ligands on gold by the phosphorus donors of **2**. The complexes **4b**, X = Br, and **4c**, X = I, were prepared by reactions of **4a** with NaBr and KI, respectively. In each case, the ^{31}P NMR spectra of **4** contained only one resonance, consistent with the expected stereochemistry with all phenyl groups directed outward and all AuX groups inward.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **4a**

Au(1)−Cl(1)	2.270(6)	Au(2)−Cl(2)	2.95(6)
Au(3)−Cl(3)	2.297(6)	Au(4)−Cl(4)	2.291(6)
Au(1)−P(1)	2.212(6)	Au(2)−P(2)	2.191(6)
Au(3)−P(3)	2.223(6)	Au(4)−P(4)	2.210(6)
P(1)−O(1)	1.59(1)	P(1)−O(2)	1.62(1)
P(2)−O(3)	1.60(1)	P(2)−O(4)	1.63(1)
P(3)−O(5)	1.60(1)	P(3)−O(6)	1.61(1)
P(4)−O(7)	1.63(1)	P(4)−O(8)	1.60(1)
P(1)−C(111)	1.77(2)	P(2)−C(211)	1.79(2)
P(3)−C(311)	1.75(2)	P(4)−C(411)	1.76(1)
O(1)−C(12)	1.42(2)	O(2)−C(24)	1.40(2)
O(3)−C(22)	1.38(2)	O(4)−C(34)	1.39(2)
O(5)−C(32)	1.43(2)	O(6)−C(44)	1.41(2)
O(7)−C(42)	1.38(2)	O(8)−C(14)	1.40(2)
Cl(1)−Au(1)−P(1)	166.9(2)	Cl(2)−Au(2)−P(2)	164.2(2)
Cl(3)−Au(3)−P(3)	167.7(2)	Cl(4)−Au(4)−P(4)	166.6(2)
Au(1)−P(1)−O(1)	122.6(5)	Au(1)−P(1)−O(2)	110.1(5)
Au(2)−P(2)−O(3)	123.2(6)	Au(2)−P(2)−O(4)	110.2(5)
Au(3)−P(3)−O(5)	111.9(5)	Au(3)−P(3)−O(6)	110.8(5)
Au(4)−P(4)−O(7)	111.4(5)	Au(4)−P(4)−O(8)	122.6(6)
Au(1)−P(1)−C(111)	114.9(5)	Au(2)−P(2)−C(211)	116.7(5)
Au(3)−P(3)−C(311)	125.3(5)	Au(4)−P(4)−C(411)	115.1(5)
O(1)−P(1)−O(2)	105.7(7)	O(3)−P(2)−O(4)	103.2(7)
O(5)−P(3)−O(6)	104.6(7)	O(7)−P(4)−O(8)	104.8(7)
O(1)−P(1)−C(111)	101.1(7)	O(2)−P(1)−C(111)	99.7(7)
O(3)−P(2)−C(211)	99.8(7)	O(4)−P(2)−C(211)	100.8(7)
O(5)−P(3)−C(311)	100.9(7)	O(6)−P(3)−C(311)	101.1(7)
O(7)−P(4)−C(411)	100.1(7)	O(8)−P(4)−C(411)	99.9(7)
P(1)−O(1)−C(12)	131(1)	P(1)−O(2)−C(24)	118(1)
P(2)−O(3)−C(22)	125(1)	P(2)−O(4)−C(34)	120(1)
P(3)−O(5)−C(32)	117(1)	P(3)−O(6)−C(44)	115(1)
P(4)−O(7)−C(42)	119(1)	P(4)−O(8)−C(14)	127(1)

The proposed structure was confirmed by an X-ray structure determination of complex **4a**.0.5CH$_2$Cl$_2$·2.5CH$_3$CN·H$_2$O. The structure of **4a** is shown in Figure 3, and selected bond distances and angles are given in Table 2. The "bowl" is in the conformation predicted by the MMX calculation, namely that with all phenyl groups directed outward from the center of the bowl. Each phosphorus is a member of an eight-membered PO$_2$C$_5$ ring, and these rings adopt an extended chair conformation. Each gold(I) center is two-coordinate with PAuCl coordination. Three of the AuCl units form a "picket fence" around the upper rim of the calixresorcinarene bowl while the fourth AuCl unit is folded into the center of the bowl and so occupies the cavity normally available to a guest molecule. As a result, the solvent molecules can only occupy regions of space between and not inside the potential host molecules. The Au−Cl and Au−P distances are in the normal ranges, 2.270(6)−2.297(6) Å and 2.191(6)−2.223(6) Å, respectively. The P−Au−Cl units are all somewhat distorted from linearity [range of angles P−Au−Cl = 164.2(2)−167.7(2)°], apparently as a result of repulsive interactions between different AuCl units. For example, the shortest nonbonded Au−Cl distance is Au(3)−Cl(2) = 3.359(8) Å, and the repulsive interaction on Cl(2) leads to the angle P(2)−Au(2)−Cl(2) = 164.2(2)°. The



R = CH$_2$CH$_2$Ph
M = AuX, 4 (X = Cl, Br, I)
M = PtCl$_2$(SMe$_2$), 5

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[11] PCMODEL Molecular Modeling Software, version 4.2, Serena Software, 1992.

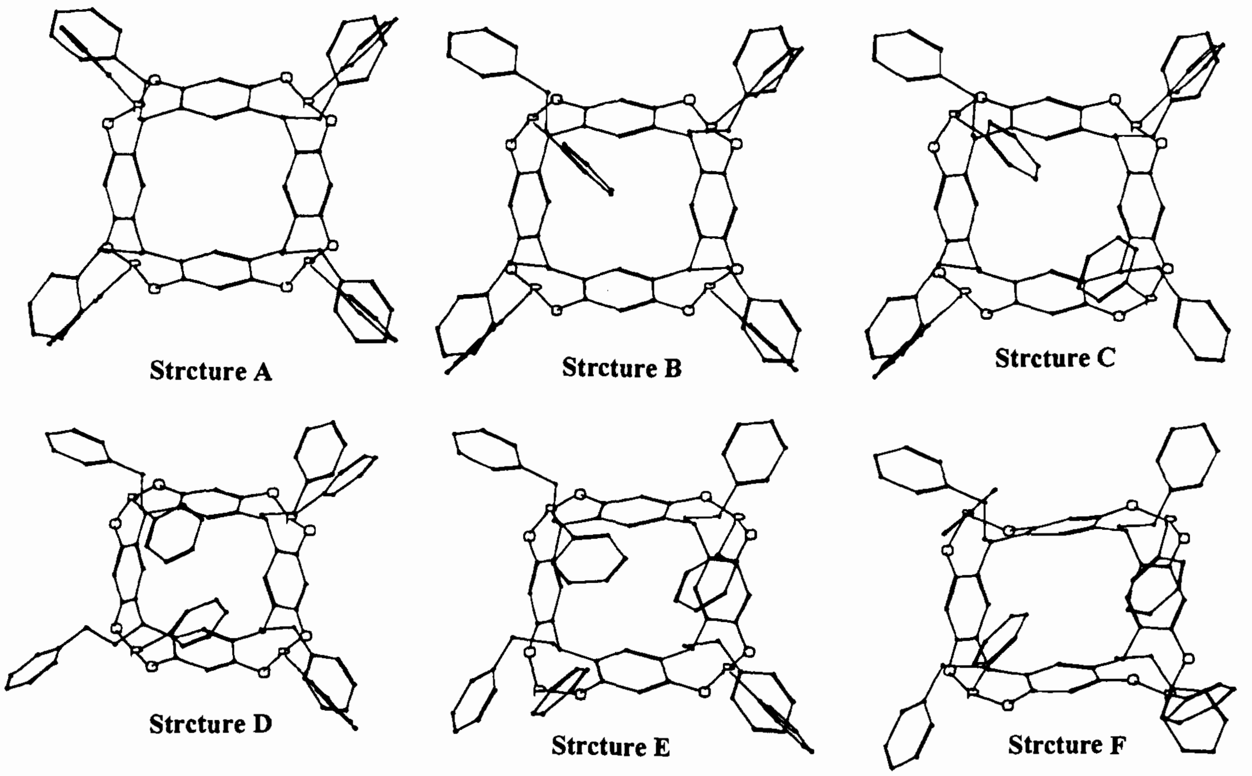

Figure 2. Structures of six possible conformers of compound **2** in their lowest energy conformations as determined by MMX calculations.

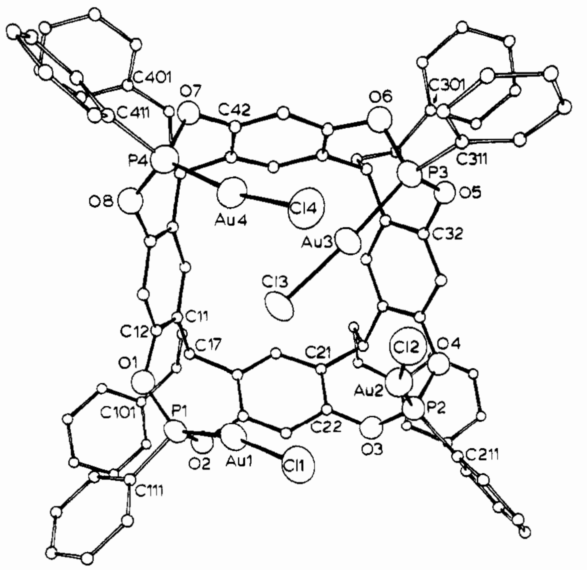

Figure 3. Top view of the structure of gold complex **4a**, showing 50% probability ellipsoids.

geometry imposed by the ligand prevents close $Au\cdots Au$ contacts of the kind commonly observed in gold(I) complexes.[9b] In the natural geometry of the bowl ligand, the four AuCl units would collide above the center of the bowl, and so the molecule must distort to avoid this situation. This leads to several unusual bond angles in the complex. As mentioned, the Au(3)Cl(3) group folds into the center of the bowl and this gives rise to a large angle Au(3)−P(3)−C(311) = 125.3(5)°. The Au(2)-Cl(2) and Au(4)Cl(4) units lean toward the vacant space above Au(3) and this causes large angles Au(2)−P(2)−O(3) = 123.2(6)°, P(2)−O(3)−C(22) = 125(1)°, Au(4)−P(4)−O(8) = 122.6(6)°, and P(4)−O(8)−C(14) = 127(1)°. The Au(1)Cl(1) group leans toward Au(2) and so the larger angles are Au(1)−P(1)−O(1) = 122.6(5)° and P(1)−O(1)−C(12) = 131(1)°. The range of angles Au−P−O = 110.1(5)-123.2(6)°, Au−P−C = 114.9(5)−125.3(5)°, and P−O−C = 115(1)−131(1)° emphasize the extent of these distortions. The geometry of the $PhPO_2$ units is much more constant as shown by the much narrower ranges of angles O−P−O = 103.2(7)−105.7(7)° and O−P−C(Ph) = 99.7(7)−101.7(7)°.

Since all PAuCl units are equivalent on the NMR time scale even at −80 °C, it is clear that the Au(3)Cl(3) unit can easily move to the periphery of the bowl and so exchange with the other AuCl units. A structure with no AuCl unit folded into the bowl would require more twisting of the AuCl units and probably a flattening of the bowl structure. In such a conformation, small guest molecules could be admitted. Attempts to modify the complex with other anions such as $CCPh^-$, NO_3^-, and CN^- were unsuccessful.

The ligand **2** reacted with 4 equiv of $[PtCl_2(SMe_2)_2]$, with displacement of only one SMe_2 ligand from each platinum atom, to give **5**. Complex **5** has effective C_4 symmetry, as shown by the presence of a single resonance in the ^{31}P NMR spectrum. The presence of a single phosphorus donor on each platinum in **5** was most easily demonstrated by recording the ^{195}Pt NMR spectrum, which appeared as a doublet due to the coupling $^1J(PtP)$ = 4966 Hz. The remaining SMe_2 ligand was readily identified in the ^1H NMR spectrum by a singlet with satellites due to coupling to ^{195}Pt with $^3J(PtH)$ = 52 Hz, and the magnitude of this coupling shows that the SMe_2 ligand is *trans* to chloride rather than phosphorus.[12] Hence each platinum is shown to have the *cis*-$PtCl_2PS$ coordination. This reaction illustrates clearly that the ligand **2** cannot chelate to platinum(II). Complex **5** is expected to have significant steric hindrance between the $PtCl_2(SMe_2)$ units, and so a greater degree of distortion of the natural bowl geometry is expected compared to the case of **4**.

3. Host−Guest Properties of the Transition Metal-Rimmed Cavitands. The selective recognition of biogenic amines is of fundamental interest in biomimetic chemistry.[13] A

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[12] (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643. (b) Verkade, J. G.; Mosbo, J. A. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987.

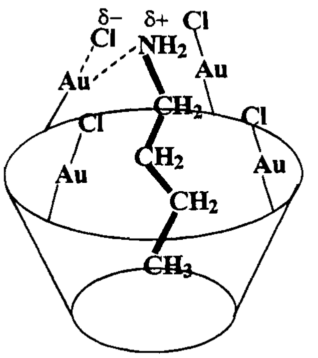

Figure 4. Proposed nature of amine inclusion by gold complex **4a**.

primary aim has been the design and synthesis of functionalized macrocycles which can recognize, or show catalytic activity toward, biologically interesting ammonium guests.[14–16] The host–guest interaction is assumed to be due mainly to complexation through N–H⋯O=C(host) hydrogen bonds and RNH_3^+ ⋯ O=C(host) charge–dipole interactions.

Attempts to find simple organic guest molecules that form endo-calix complexes with **4** were unsuccessful because the potential guests, such as PhCN, MeCN, PhCCH, HCCH, and Bu^tCCH, did not form complexes which were detectable by spectroscopic methods.[6] It is possible that the AuCl which folds inside the bowl could block access into the cavity or that binding is too weak to give selective inclusion in competition with inclusion of solvent molecules. However, amines, which are expected to have a stronger interaction with gold, were proved to be admitted into the bowl as guests. The ^1H NMR spectra of a mixture of **4** and RNH_2 were significantly different from those of the pure host and guest compounds. All guest ^1H NMR peaks broadened due to fast exchange between internal and external guest molecules. In general, the changes in the ^1H NMR parameters between the free amine and **4a**·NH_2R were similar to those between RNH_2 and RNH_3^+. It is implied that the guest donates its lone pair to one or more gold(I) atoms in **4a**. Furthermore, when ammonium was used as a potential guest, no obvious chemical shift changes were observed for either guest or host molecule, indicating that no inclusion complex was formed. It is suggested that the amines are included in **4** as shown in Figure 4, on the basis of the ^1H NMR spectra. Thus, for an amine with the skeleton $C^1C^2C^3C^4NH_2$, the protons on C^3 and C^4 are located in the deshielding area generated by the calixresorcinarene phenyl rings whereas protons on C^1 and C^2 extend into the shielding area. When an amine with a bulky R group is used, only external complexes are formed with only minor chemical shift changes in the ^1H NMR spectra for either the guest or host molecules (Table 3). This is consistent with the model proposed since bulky alkyl groups cannot gain access to the cavity but could still form external complexes.

Table 3. Amine Inclusion by Host Complex **4a**

guest	^1H NMR data, δ/ppm for complexed amine (free amine)
Bu^nNH_2	$-CH_2NH_2$, 3.34 (2.70); $-CH_2CH_2NH_2$, 1.61 (1.41); $-CH_2CH_2NH_2-$, 1.33 (1.40); $-CH_3$, 0.88 (0.92)
Pr^nNH_2	$-CH_2NH_2$, 3.34 (2.66); CH_3CH_2-, 1.54 (1.46); $-CH_3$, 0.87 (0.91)
Pr^iNH_2	$-CHCH$ 3.41 (3.12); CH_3, 1.19 (1.08)
Bu^iNH_2	$-CH_2NH_2$, 2.61 (2.50); $(CH_3)_2CH-$, 1.77 (1.58); $-CH_3$, 0.92 (0.89)

Table 4. Percent Extraction of Alkali Picrates in CH_2Cl_2 at 25 °C by Transition Metal Calixresorcinarene Derivatives **4a** and **5**[a]

	% picrate salt extracted					
ligands	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
4a	52.6	63.5	70.0	60.8	56.3	58.6
5	45.1	69.7	74.3	47.4	32.8	26.2

[a] Aqueous phase: [metal chloride] = 0.1 M; [picric acid] = 8.1×10^{-5} M. Organic phase: [ligand] = 8.1×10^{-5} M.

The liquid–liquid extraction[17a] of alkali metal cations by the transition metal rimmed cavitands, **4a** and **5**, has been studied. The results are shown in Table 4, and they indicate that the whole group of alkali metal ions can be extracted by **4a** and **5**. The alkali cation selectivity of these complexes is quite different from that of other calixresorcinarene derivatives, which normally have a strong affinity for Cs^+.[17b] These transition metal-rimmed cavitands show a greater affinity for K^+ than for the other alkali metal ions. Attempts to grow crystals of either the amine or alkali metal cation inclusion complexes have not been successful, and further speculation about the nature of the binding is probably not justified.

4. Preparation of "Octopus" Phosphinito-Calixresorcinarene Derivatives. Calixresorcinarene 1 has a total of eight OH groups around its upper rim. It should also be possible for 1 to react with $ClPPh_2$ to give an open octaphosphinito macrocyclic ligand. Thus, treatment of 1 with excess of $ClPPh_2$ in the presence of pyridine gave the desired product 3 with eight phosphinito groups attached to the upper rim of the calixresorcinarene.

The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two singlets of equal intensity at $\delta = 108$ and 104.4. The observation of two ^{31}P resonances was unexpected, and so molecular mechanics calculations were carried out in an attempt to define the stereochemistry of **3**. These calculations[11] indicated that the bulky PPh_2 groups force the bowl to adopt a flattened cone conformation in order to minimize steric repulsions between adjacent PPh_2 groups. Several conformers with different orientations of the PPh_2 groups have almost equal energy, but there is a preference for structures in which alternating PPh_2 groups are directed inward or outward with respect to the center of the flattened bowl. A possible structure is illustrated in Figure 5. Presumably, restricted rotation of the Ph_2PO units due to steric hindrance leads to the observation of two ^{31}P resonances, one for the inward- and one for the outward-directed PPh_2 groups.

5. Coordination Chemistry of [Calixresorcinarene-$(OPPh_2)_8$], 3. The complexing behavior of 3 was explored. It is interesting to note that the PPh_2 groups on the upper rim of 3 are fairly close (4.5–5.5 Å) and have some flexibility. Hence, unlike the situation for 2, they could act either as monodentate ligands toward eight different metal centers or as chelate ligands toward four metal centers. When 3 was treated with $AuCl(SMe_2)$ in CH_2Cl_2, it acted as a terminal ligand to give a "gilded octopus molecule", 6, in which each gold(I) center is two-coordinate. For this complex, only one ^{31}P resonance was observed, showing that it adopts a more symmetrical conformation than the parent ligand. Since addition of AuCl groups will not reduce steric hindrance to rotation of PPh_2 groups, it is proposed that all AuCl groups are directed inward with respect to the flattened bowl. This may allow weak Au··Au bonding between neighboring AuCl units.

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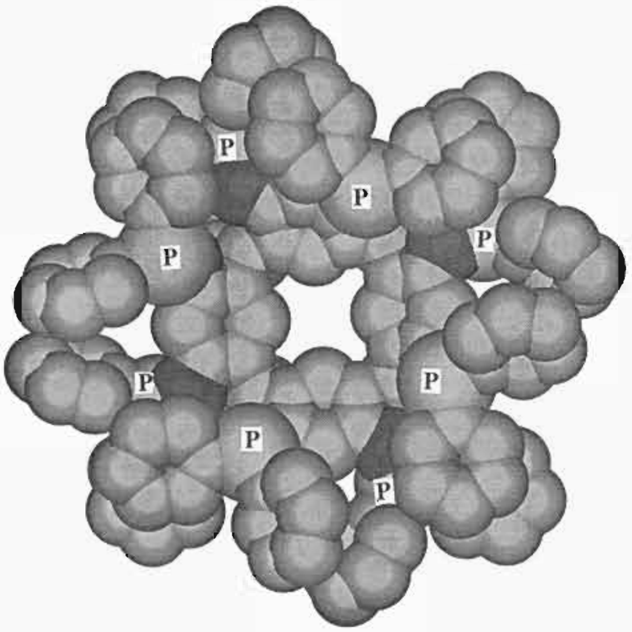
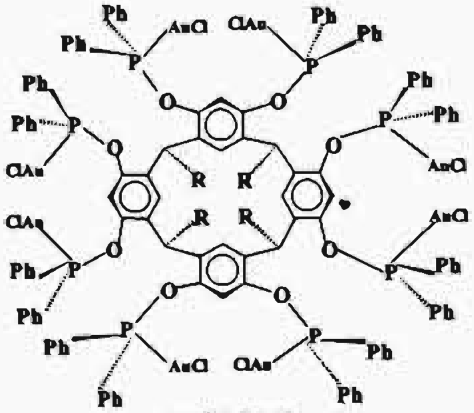


Figure 5. Space-filling model of phosphinito-calixresorcinarene **3**.



R = CH_2CH_2Ph

6

Ligand **3** reacted with $[PtCl_2(SMe_2)_2]$ to give complex **7**. There are four possible ways for the ligand to chelate metals as shown in Figure 6, structures **G**–**J**. It is possible to have *cis*- or *trans*-chelation by pairs of phosphorus atoms attached to the same aryl rings to give eight-membered rings (structures **G**, **H**) as well as *cis*- or *trans*-chelation by phosphorus atoms attached to adjacent aryl rings to give 10-membered rings (structures **I**, **J**). Molecular mechanics calculations indicated that the product **G**, involving *cis*-chelation by phosphorus atoms on the same aryl ring to give eight-membered rings, has much lower angle strain and steric hindrance than the other three possibilities. Complex **7** gave a singlet in the ^{31}P NMR spectrum, indicating that all phosphorus atoms are equivalent. The *cis*-chelation is readily proved by the magnitude of the coupling constant $^1J(PtP)$ = 4431 Hz, consistent with a phosphinite *trans* to chloride but too high for a phosphinite *trans* to phosphorus.[12]

The peaks in the ^{1}H NMR spectra of **6** and **7** are broad, probably because of the equilibration of different conformers, and this effect made it difficult to study the inclusion chemistry of these compounds by ^{1}H NMR techniques.

Conclusions

The functionalization of calixarenes at the lower rim by introducing phosphorus(III) donors is now well-established, and much interesting coordination chemistry has been developed for the resulting tetraphosphinite ligands.[1] This work shows that functionalization of the upper rim of calixresorcinarenes can be carried out similarly for tetraphosphonite and octaphosphinite ligands and that an extensive and novel coordination chemistry can be developed from these macrocyclic ligands. It is particularly noteworthy that the transition metals are naturally introduced at the upper rim of the "bowl" and so host–guest chemistry involving the metal atoms is expected. The demonstration of amine inclusion with a tetragold(I) derivative provides the first example of such chemistry. Most host–guest chemistry involves neutral or cationic guests since the hosts often bind through their donor groups, but the transition metals at the upper rim are expected to enhance the inclusion of anionic and nucleophilic guest ions and molecules, such as the amines studied here.

Experimental Section

The complexes $[AuCl(SMe_2)]$,[18] $[PtCl_2(SMe_2)_2]$,[19] and calixresorcinarene **1**[5] were prepared by literature methods. All the experiments were carried out by using standard Schlenk techniques. NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts were measured relative to deuterated solvent peaks but were reported relative to tetramethylsilane. ^{31}P NMR chemical shifts were determined relative to 85% H_3PO_4 as external standard. IR spectra were recorded on a Bruker IFS32 FTIR spectrometer with Nujol mulls. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Mass spectra were recorded by using a FINNIGAN MAT 8230 mass spectrometer.

[Calixresorcinarene(O_2PPh)$_4$], 2. A suspension of **1** (1.81 g, 2 mmol) in a mixture of dry ether (100 mL) and pyridine (2.5 mL) was cooled to −40 °C, and then phenylphosphonous chloride (1.1 mL, 8.1 mmol) was added slowly. The mixture was stirred for 4 h and then allowed to warm to room temperature. The mixture was stirred for another 24 h, and then hexane (50 mL) was added to the mixture. The white precipitate was collected by filtration, washed with hexane (3 × 20mL) and dried under vacuum. The solid was then washed with water (2 × 200 mL) and dried under vacuum immediately. Compound **2** (2.15 g), which was mixed with a small amount of pyridinium chloride impurity, is suitable for further reactions. Small amounts of pure sample can be obtained by column chromatography with Et_2O/hexane (1:1) as eluent; it must be stored under inert atmosphere and appears to be very hygroscopic. Typical spectroscopic data follow. NMR in CD_2Cl_2: $\delta(^{31}P\{^1H\})$ = 166.3 [s]; $\delta(^1H)$ = 2.68 [br s, 16H, CH_2CH_2Ph], 4.86 [br, dt, 4H, $CH(CH_2)_2Ph$], 6.75 [t, 4H, Ar *H*, ortho to O], 7.09–7.30 [m, 20H, C_6H_5], 7.41 [s, 4H, Ar *H*, meta to O], 7.48–7.58 [m, 12H, PC_6H_5, para and meta to P], 7.80–7.79 [m, 8H, PC_6H_5, ortho to P]. EI-MS: *m/e* = 1328.394, calc for $C_{84}H_{68}O_8P_4$ 1328.386.

[Calixresorcinarene($OPPh_2$)$_8$], 3. Calixresorcinarene **1** (1.81 g, 2 mmol) was suspended in a solution of diethyl ether (100 mL) with pyridine (5 mL). The solution was cooled at −78 °C, and Ph_2PCl (3.1 mL, 16 mmol) was slowly added. The mixture was stirred at −78 °C for 2 h; then it was allowed to warm to room temperature and stirred for another 36 h. Hexane (50 mL) was added to the mixture. The solid was filtered off and washed with hexane twice. The product was extracted from the solid by benzene (50 mL). The benzene was evaporated, and a white solid of **3** was obtained. Yield: 2.1 g, 44.2%. Anal. Calc for **3**, $C_{156}H_{128}O_8P_8$: C, 78.8; H, 5.4; P, 10.4. Found: C, 78.4; H, 5.9; P, 10.7. NMR in C_6D_6: $\delta(^{31}P\{^1H\})$ = 108.0 [s] and 104.4 [s] in 1:1 intensity ratio; $\delta(^1H)$ = 2.3–2.7 [br, 16H, CH_2CH_2-Ph], 4.3 [br, 4H, $CH(CH_2)_2Ph$], 6.7–7.8 [m, 108H, Ar*H*]. IR: ν_{OH} absent.

[Calixresorcinarene(O_2PPh·AuCl)$_4$], 4a. A mixture of [AuCl-(SMe_2)] (0.20 g, 0.68 mmol) and **2** (0.23 g, 0.17 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 2 h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. A light yellow solid was obtained, which was washed with MeCN and dried under vacuum. Yield: 0.32 g, 82%. Anal. Calc for **4a**, $C_{84}H_{68}Au_4Cl_4O_8P_4$: C, 44.7; H, 3.0; Cl, 6.3. Found: C, 45.0; H, 2.8; Cl, 6.2. NMR in

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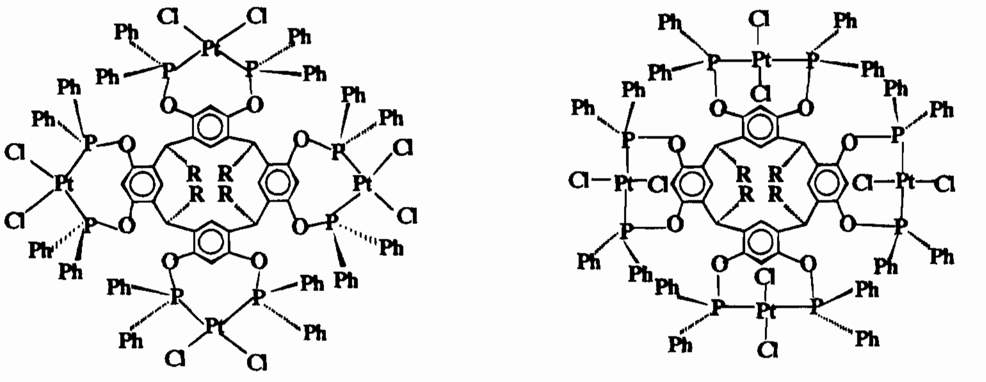
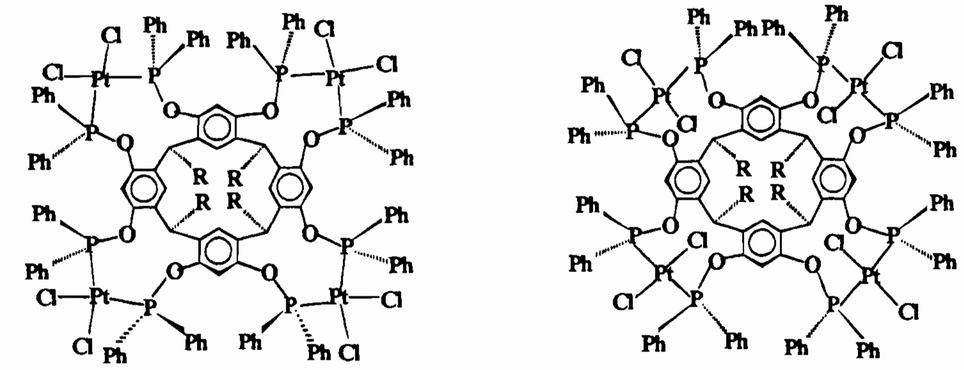


Structure G **Structure H**



Structure I **Structure J**

Figure 6. Structures of four possible isomers of compound **7**.

$CDCl_3$: $\delta(^{31}P\{^1H\})$ = 144 [s]; $\delta(^1H)$ = 2.70−2.82 [m, br, 16H, CH_2CH_2Ph], 4.74 [br, 4H, $CH(CH_2)_2Ph$], 6.93 [t, $^4J(PH)$ = 1.8 Hz, 4H, Ar *H*, ortho to O], 7.15−7.21 [m, 8H, C_6H_5], 7.26−7.35 [m, 12H, C_6H_5], 7.51 [s, 4H, Ar *H*, meta to O], 7.49−7.65 [m, 12H, PC_6H_5, para and meta to P], 7.98−8.10 [m, 8H, PC_6H_5, ortho to P]. FAB-MS: *m*/*e* = 2026, calc for M^+ − (AuCl) 2026.

X-ray Structure Determination of **4a**·$0.5CH_2Cl_2$·$2.5CH_3CN$·H_2O. Solvated single crystals of **4a** were grown from CH_2Cl_2/MeCN. They readily lost solvent in air. A large crystal was cut and then sealed in a capillary tube with mother liquor. The crystal density was determined by the neutral buoyancy method, using a mixture of CCl_4/CH_2Br_2.

The data collection was carried on using an Enraf-Nonius CAD4F diffractometer using graphite-monochromated Mo Kα radiation.[20] Photoindexing and automatic indexing routines, followed by least-squares fits of 20 accurately centered reflections (25.0 < 2θ < 29.2°), gave cell constants and an orientation matrix. Intensity data were recorded in θ−2θ mode, at variable scan speeds (1.648−2.747° min^{-1}) and a scan width of (1.0 + 0.35 tan θ)°, with a maximum time per datum of 60 s. Background estimates were made by extending the scan by 25% on each side. Standard reflections 100, 011, and 020 were monitored every 180 min of X-ray exposure time and showed a 10.3% decay over the total period of 177 h. In all, 12 154 reflections and 198 standards were recorded. Corrections were made for Lorentz, monochromator and crystal polarization, background radiation effects, and decay using the Structure Determination Package[21] running on a PDP11/23+ computer. A *p* factor of 0.04 was included,[22] and a numerical absorption correction was applied using the program AGNOST.[23]

The structure was solved by a combination of MULTAN[24] and difference Fourier techniques. Refinement was by full-matrix least-squares techniques on *F*, using the SHELX-76 software[25] running on a CDC Cyber 2000. Scattering factors for neutral, non-hydrogen atoms were taken from ref 26. Anisotropic thermal parameters were refined for all the Au, P, and Cl atoms in the molecular core, while the thermal parameters of the remaining non-hydrogen atoms were refined isotropically. The solvent (one water and two acetonitrile) molecules were located in difference Fourier syntheses. Three disorder models (with occupancies 0.4, 0.3, and 0.3) were found for each acetonitrile solvent. The C−C and C−N bond lengths were constrained to 1.45 and 1.12 Å, respectively. Common isotropic thermal parameters were assigned for each disorder model and refined in the least-squares cycles. A subsequent difference Fourier map suggested that half a molecule of dichloromethane and half a molecule of acetonitrile appear to occupy the same region in the crystal lattice. The C−Cl bond lengths and the Cl−C−Cl angle in the CH_2Cl_2 molecule were fixed at 1.77 Å and 112°, respectively. The phenyl ring containing carbon atoms C(101) to

Table 5. Summary of the X-ray Structure Determination

formula, fw	$C_{84}H_{68}Au_4Cl_4P_4O_8$·$0.5CH_2Cl_2$·$2.5CH_3CN$·$H_2O$ 2422.16
crystal system, space group	triclinic, $P\bar{1}$
cell dimens (Å, deg)	*a* = 15.271(5) *b* = 28.399(8) *c* = 11.060(5) α = 93.40(3) β = 111.21(3) γ = 98.41(2)
cell volt (Å^3), *Z*	4390.8, 2
density (g cm^{-3}): obs, calc	1.87(5), 1.83
F(000)	2331.7
radiation, wavelength (Å)	Mo Kα, 0.710 73
abs coeff (cm^{-1})	117.97
final model: *R*, R_w^{a}	0.0534, 0.0504

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

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Table 6. Selected Atomic Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters for **4a**

atom	*x*	*y*	*z*	*U* (Å^2)[a]
Au(1)	7311.5(7)	3402.1(3)	4233.6(9)	44.1(4)*
Au(2)	7287.7(7)	1871.7(3)	4320.1(9)	46.4(4)*
Au(3)	4742.7(7)	1761.8(3)	3874.0(9)	44.9(4)*
Au(4)	3188.4(7)	2479.4(3)	2168.0(9)	45.6(4)*
Cl(1)	7565(5)	2941(2)	2690(6)	68(3)*
Cl(2)	6190(5)	1703(2)	2215(6)	64(3)*
Cl(3)	5504(5)	2548(2)	4291(7)	73(3)*
Cl(4)	3481(5)	1999(2)	672(6)	62(3)*
P(1)	7385(4)	3947(2)	5801(6)	39(2)*
P(2)	8375(4)	1827(2)	6234(6)	40(3)*
P(3)	4009(4)	1029(2)	3903(6)	38(2)*
P(4)	2558(4)	2895(2)	3291(6)	42(3)*
O(1)	6464(10)	4051(4)	6046(12)	42(4)
O(2)	8122(9)	3854(4)	7204(12)	40(4)
O(3)	8840(10)	2272(5)	7360(13)	44(4)
O(4)	7969(10)	1411(4)	6956(12)	40(4)
O(5)	4672(9)	758(4)	5019(12)	32(4)
O(6)	3089(9)	1051(4)	4269(12)	40(4)
O(7)	2065(9)	2553(4)	4083(12)	32(4)
O(8)	3161(10)	3354(4)	4324(13)	41(4)
C(11)	5858(14)	3557(6)	7380(18)	28(5)
C(12)	5712(13)	3737(6)	6209(18)	25(5)
C(13)	4844(13)	3646(6)	5196(18)	29(5)
C(14)	4053(14)	3385(7)	5325(19)	34(6)
C(15)	4122(14)	3191(7)	6489(19)	32(6)
C(16)	5053(13)	3279(6)	7493(17)	23(5)
C(21)	7823(14)	2496(7)	8469(19)	36(6)
C(22)	8352(15)	2604(7)	7671(20)	41(6)
C(23)	8439(14)	3059(7)	7286(18)	33(6)
C(24)	7982(14)	3388(7)	7593(18)	28(5)
C(25)	7401(14)	3289(7)	8267(19)	32(6)
C(26)	7360(13)	2852(6)	8752(17)	26(5)
C(31)	5222(15)	1301(7)	7021(19)	34(6)
C(32)	5450(14)	1048(6)	6068(18)	24(5)
C(33)	6311(14)	1080(6)	6005(18)	28(5)
C(34)	7066(14)	1385(7)	6993(19)	32(6)
C(35)	6924(14)	1654(7)	7982(19)	31(5)
C(36)	5990(14)	1605(6)	7950(19)	33(6)
C(41)	3196(14)	2395(7)	6116(18)	28(5)
C(42)	2573(13)	2236(7)	4826(18)	26(5)
C(43)	2524(14)	1799(7)	4238(20)	38(6)
C(44)	3079(15)	1490(7)	4924(20)	39(6)
C(45)	3651(14)	1604(7)	6265(19)	34(6)
C(46)	3675(13)	2069(6)	6802(18)	28(5)
C(17)	6825(14)	3655(7)	8484(19)	37(6)
C(18)	6729(15)	3703(7)	9833(19)	45(6)
C(19)	7593(22)	3971(11)	10909(30)	133(13)
C(27)	7775(14)	2001(7)	8949(18)	36(6)
C(28)	7743(15)	1996(7)	10385(19)	46(6)
C(29)	8728(18)	2116(9)	11392(24)	83(9)
C(37)	4243(14)	1253(7)	7033(19)	39(6)
C(38)	4230(15)	1261(7)	8404(19)	45(6)
C(39)	4407(2)	838(10)	9015(29)	123(12)
C(47)	3280(14)	2909(6)	6641(18)	32(6)
C(48)	3287(15)	2985(7)	8090(20)	50(7)
C(49)	2326(14)	2785(7)	8121(20)	48(7)

[a] Parameters marked with asterisks were assigned anisotropic thermal parameters giben as the isotropic equivalent displacement parameter defined as $U_{\mathrm{eq}} = {}^{1}/_{3}\Sigma_i\Sigma_j U_I J \cdot a^*_i \cdot a^*_j \cdot a_i \cdot a_j$.

C(106) showed high thermal parameters, indicating the possibility of further disorder. This disorder could not be resolved successfully, and therefore a common thermal parameter was assigned for all the carbon atoms in the ring and refined in the least-squares cycles.

With the use of 5233 observations with $I > 3\sigma(I)$ and utilizing weights of the form $w = k/\sigma^2(F_o) + gF^2$ where $k = 1.517$ and $g = 0.000\,24$, refinement of 445 variables converged at agreement factors $R = 0.0534$, $R_w = 0.0504$. Of the top 13 peaks in the final difference Fourier synthesis with electron densities in the range 1.40−0.91 e A^{-3}, nine were associated with Au atoms at distances of 0.25−1.31 Å; none were found near the solvent regions.

The experimental details and crystal data and the positional and *U*(equiv) thermal parameters are given in Tables 5 and 6. Tables of calculated hydrogen atom positonal parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibration, and weighted least-squares planes and dihedral angles have been included in the material.

[Calixresorcinarene(O$_2$PPh·AuX)$_4$], 4b (X = Br) and 4c (X = I). Bromide **4b** and iodide **4c** derivatives were synthesized by stirring the chloride derivative **4a** with an excess of the corresponding potassium halide in CH$_2$Cl$_2$ (1 h) followed by filtration and removal of solvent. No further purification was necessary. Yield: **4b**, 92%; **4c**, 93%. Anal. Calc for **4b**: $C_{84}H_{68}Au_4Br_4O_8P_4$: C, 41.4; H, 2.8. Found: C, 41.5; H, 2.9. NMR in CDCl$_3$: $\delta(^{31}P\{^1H\}) = 145.1$ [s]. Anal. Calc for **4c**, $C_{84}H_{68}Au_4I_4O_8P_4$: C, 38.4; H, 2.6. Found: C, 38.4; H, 2.7. NMR in CDCl$_3$: $\delta(^{31}P\{^1H\}) = 147.9$ [s].

[Calixresorcinarene(O$_2$PPh·PtCl$_2$SMe$_2$)$_4$], 5. A mixture of [PtCl$_2$(SMe$_2$)$_2$] (0.193 g, 0.495 mmol) and **2** (0.165 g, 0.124 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred at room temperature for 2 h. The CH$_2$Cl$_2$ and SMe$_2$ were removed completely under vacuum. The residue was redissolved in CH$_2$Cl$_2$ and crystallized by diffusion with MeCN. A yellow solid was obtained, which was washed with MeCN and dried under vacuum. Yield: 0.141 g, 43%. Anal. Calc for $C_{92}H_{92}Pt_4Cl_8O_8P_4S_4$: C, 41.8; H, 3.5. Found: C, 41.4; H, 3.5. NMR in CDCl$_3$: $\delta(^{31}P\{^1H\}) = 87.7$ [s, $^1J(PPt) = 4965$ Hz]; $\delta(^{195}Pt) = -2323$ [d, $^1J(PPt) = 4966$ Hz]; $\delta(^1H) = 2.72$ [s, $^3J(HPt) = 52$ Hz, SMe$_2$], 2.8−2.6 [m, br, 16H, C*H*$_2$C*H*$_2$Ph], 4.65 [t, 4H, $^3J(HH) = 7$ Hz, C*H*(CH$_2$)$_2$Ph], 7.84 [t, $^4J(PH) = 2$ Hz, 4H, Ar *H*, ortho to O], 7.0−7.2[m, 20H, C$_6$*H*$_5$, 7.17 [s, 4H, Ar*H*, meta to O], 7.4−7.6 [m, 12H, PC$_6$*H*$_5$, para and meta to P], 8.04 [m, 8H, PC$_6$*H*$_5$, ortho to P].

[Calixresorcinarene(OPPh$_2$AuCl)$_8$], 6. A mixture of [AuCl(SMe$_2$)] (0.20 g, 0.68 mmol) and [calixresorcinarene(OPPh$_2$)$_8$], **3** (0.20 g, 0.084 mmol), in CH$_2$Cl$_2$ (20 mL) was stirred at room temperature for 15 h. The CH$_2$Cl$_2$ and SMe$_2$ were removed completely under vacuum. The residue was redissolved in CH$_2$Cl$_2$ and crystallized by diffusion with toluene. A white solid was obtained and was washed with benzene and dried under vacuum. Yield: 0.27 g, 76%. Anal. Calc for $C_{156}H_{128}Au_8Cl_8O_8P_8$: C, 44.2; H, 3.1; P, 5.9. Found: C, 44.2; H, 3.0; P, 5.9. NMR in CDCl$_3$: $\delta(^{31}P\{^1H\}) = 87.5$ [s]; $\delta(^1H) = 2.68$ [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.45 [br, 4H, *H*(C*H*$_2$)$_2$Ph], 6.3 [br, 4H, Ar *H*, ortho to O], 7.2−7.88 [m, 104H, Ar *H*].

[Calixresorcinarene(OPPh$_2$)$_8$(*m*-PtCl$_2$)$_4$], 7a. A mixture of [PtCl$_2$(SMe$_2$)$_2$] (0.132 g, 0.34 mmol) and **3** (0.20 g, 0.084 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred at room temperature for 15 h. The CH$_2$Cl$_2$ and SMe$_2$ were removed completely under vacuum. The residue was redissolved in CH$_2$Cl$_2$ and crystallized by diffusion with benzene. A white solid was obtained, which was washed with benzene and dried under vacuum. Yield: 0.22 g, 76.2%. Anal. Calc for $C_{156}H_{128}Cl_8O_8P_8Pt_4$: C, 54.5; H, 3.8; P, 7.2. Found: C, 54.2; H, 3.7; P, 7.1. NMR in CDCl$_3$: $\delta(^{31}P\{^1H\}) = 84.9$ [s, $^1J(PtP) = 4431$ Hz]; $\delta(^1H) = 2.54$ [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.4−4.5 [br, 4H, C*H*(C*H*$_2$)$_2$Ph], 6.7−8.0 [m, 108H, Ar *H*].

Alkali Metal Cation Extraction. The receptor solution (5 mL) was shaken (3 min) with the picrate solution (5 mL) and percent extraction was measured from the absorbance at 357 nm of the resulting CH$_2$Cl$_2$ solution and aqueous solution.[17a] No picrate extraction was observed in the absence of ligands. The solution concentrations are given in Table 3.

Acknowledgment. We thank the NSERC (Canada) for financial support and Dr. N. C. Payne for access to X-ray facilities.

Supplementary Material Available: Tables of calculated hydrogen atom positional parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibration, weighted least-squares planes and dihedral angles, and complete atomic positional parameters (7 pages). Ordering information is given on any current masthead page.

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