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Two Organometallic Fragments Inclusioned in a 1,3-Alternate Calix[4]arene Tetraphosphane: Evidence for Transition Metal–Arene Interaction through the Cavity

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The preparation of an 1,3-alternate calix[4]arene tetraphosphane ligand, 25,26,27,28-tetrakis{2-(diphenylphosphino)-ethoxy}calix[4]arene (**4**), is described. Ligand **4** is obtained in four steps in 17% overall yield. Reaction of **4** with $AgBF_4$ produced the encapsulated two silver complex $[Ag_2\{(P,P,P,P)\text{-tetraphencalix[4]arene}\}](BF_4)_2$. The solid-state structure shows that the encapsulated silver undergoes a substantial π-interaction by two opposite arene rings. Rhodation of **4** employing $[Rh(cot)_2]BF_4$ yielded the encapsulated complex with a bent coordination mode. Two organometallic fragments inclusioned inside a 1,3-alternate calix[4]arene tetraphosphane was also achieved by the reaction of **4** with $[PtH(PPh_3)_2(thf)]^+$. Full characterization includes X-ray structural studies of compounds **4**–**6**.

Introduction

Metallic calix[4]arenes have been topics of intensive study due to their host−guest chemistry,[1] catalysis,[2] supramolecular chemistry,[3] function as inclusion hosts for ions,[4] and even molecular recognition.[5] These structures can vary in shape, size, and the number of metal fragments that comprise the calix[4]arene. The recent synthetic development of the functionalization of calix[4]arenes has led to the isolation of cavity-shaped podands displaying highly selective complexation properties. It was found that the affinity of a calixarene toward a metal ion depends on the conformation of the calix[4]arene.[6] While most of the research was performed on alkali-metal and alkaline-earth-metal ions, transition metal complexes of the parent calixarenes have not been explored extensively.[7] Introduction of an organometallic fragment into the interior of the calixarene cavity appears particularly interesting because such architectures could possess the capability to promote metal-centered reactions.[8] Matt and co-workers[9] recently communicated the directed positioning of organometallic fragments by penetrating the hydrophobic calixarene cavity. One of the most popular synthetic tools for such macrocycles is the phosphorus functionalization of calix[4]arenes using anchoring phosphines tethered at distal phenols units or directly connected to the upper rim. So far, most studies have focused on calix[4]arenes with one,[10] two,[11] and four phosphorus[12] centers located at the lower rim and some on the upper rim of the macrocycle. We have recently reported the metallic

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macrocycle with a 1,3-alternate calix[4]arene diphosphorus-containing ligand.[13] However, nothing is known of the 1,3-alternate calix[4]arene tetraphosphane of the type **3** and its chemistry. Such 1,3-alternate calix[4]arene ligand is of particular importance because two sites of the cavity can be used to incorporate reactive metallic fragments. Here we report a new, high-yield strategy for synthesizing the direct bimetallic macrocycles positioned inside the mouth of the cavity.

Results and Discussion

1,3-Alternate Tetraphosphinated Calix[4]arene Ligand. Our strategy for the synthesis of such macrocycles utilizes the coordinative properties of the 1,3-alternate calix[4]arene tetraphosphane located on two distal carbon atoms of the lower and upper rim. Tetraphosphane **4** is conveniently synthesized in four steps from the nonsubstituted calix[4]arene: calix[4]arene reacted with 8 equiv of ethyl bromoacetate in the presence of excess Cs_2CO_3 in acetone to give **1** in the 1,3-alternate conformation. The reduction of **1** with $LiAlH_4$, followed by tosylation using *para*-toluenesulfonyl chloride, gave 1,3-alternate calix[4]arene tetratosylated product **3**. The calix[4]arene tetratosylate **3** was found to be in the 1,3-alternate conformation judging from a singlet peak at δ 3.65 for the methylenic protons of the ArCH_2Ar bridge in the ^1H NMR spectrum and a single peak at δ 37.0 for the ArCH_2Ar bridge carbon in the ^{13}C NMR spectrum. Tetraphosphorylation of **3** with $KPPh_2$ resulted in formation of **4** in 82% yield after column chromatography (Scheme 1). A similar preparation of tethering $CH_2CH_2PPh_2$ groups has been reported by the Reinhoudt group.[14] Ligand **4** is a crystalline solid that is stable in air and soluble in $CHCl_3$, toluene, and THF. Spectroscopic data for **4** are completely consistent with its proposed structure. One resonance at 3.52 ppm in the ^1H NMR spectrum and one peak at 32.6 ppm in the ^{13}C NMR spectrum for the methylene bridge are observed. The ^{31}P NMR spectrum of **4** shows a singlet at −27.3 ppm. This value is comparable to those observed for the lower rim 1,3-diphosphino calix[4]arene and 1,3-alternate diphosphinated calix[4]arene.[15] The structure of **4** was established by single-crystal X-ray analysis and is shown in Figure 1. The crystallographic data and processing parameters are given in Table 1. The molecule of **4** possesses a crystallographic 2-fold axis that the middle of four aryl groups goes through. The interesting feature of the molecular structure of **4** is that the aryl rings bearing the phosphorus units (P(1) and P(4)) are splayed outward with the aryl rings moving upward and the aryl rings with other phosphorus unit (P(2) and P(3)) are pinched together with the aryl rings moving downward. The phosphorus lone pairs are directed toward the interior of the cavity. A similar geometric configuration was observed in another diphosphinated calix[4]arene.[16]

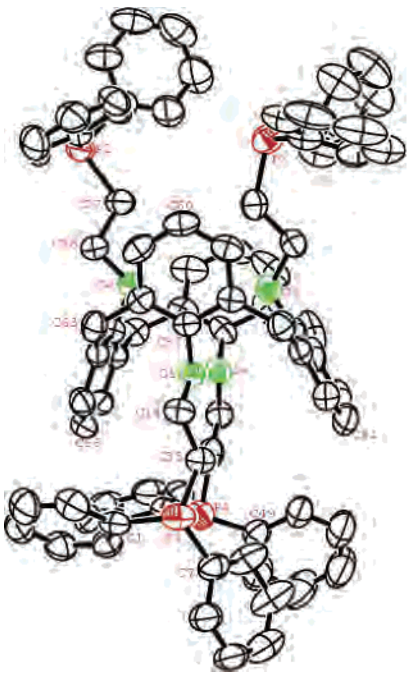

Figure 1. ORTEP drawing of ligand **4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−C(1) 1.832(2), P(1)−C(13) 1.843(2); C(1)−P(1)−C(13) 99.36(10), P(1)−C(13)−C(14) 113.06(16).

Scheme 1

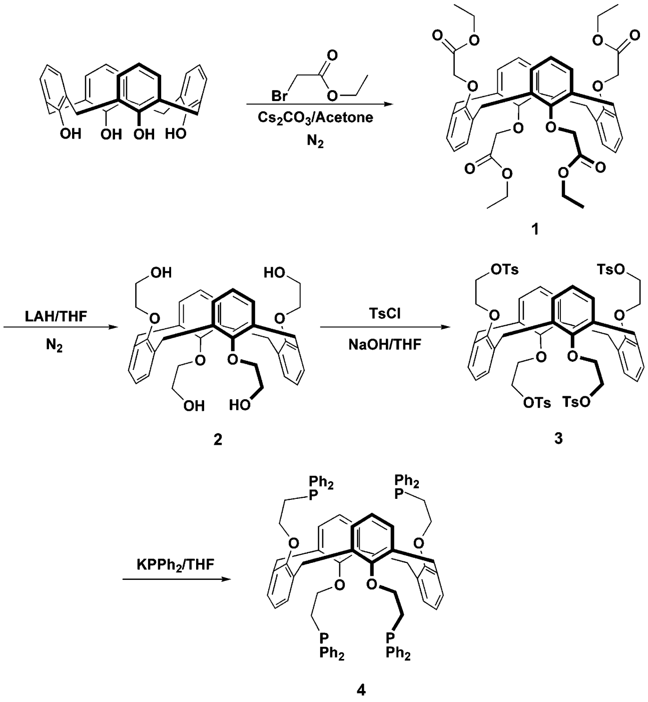

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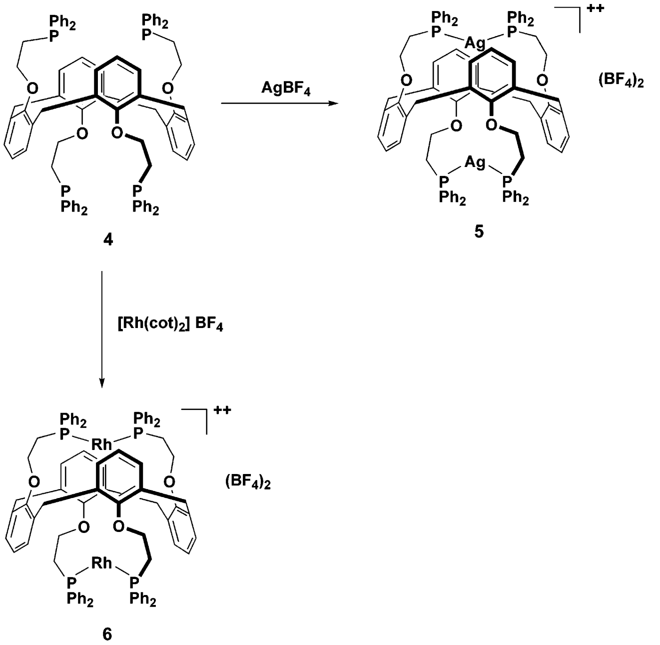
Table 1. Crystal and Structure Refinement Data for **4**−**6**

param	**4**	**5**	**6**
empirical formula	$C_{84}H_{76}O_4P_4$	$C_{84}H_{76}Ag_2B_2F_8O_4P_4$	$C_{84}H_{76}B_2F_8O_4P_4Rh_2$
fw	1273.33	1662.76	1652.84
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$\bar{2}/c$	$C2/c$
a (Å)	11.125(2)	18.7622(14)	18.7027(16)
b (Å)	11.133(2)	13.7204(10)	13.6292(10)
c (Å)	31.458(6)	32.702(2)	32.470(3)
α (deg)	95.350(4)	90	90
β (deg)	95.120(4)	97.9780	98.371(2)
γ (deg)	115.772(3)	90	90
V (Å^3)	3456.6(11)	8336.9(11)	8188.6(11)
Z value	2	4	4
D_{calc} (g/cm^3)	1.223	1.460	1.478
F(000)	1344	3728	3712
μ(Mo Kα) (mm^{-1})	0.161	0.742	0.680
temp (K)	298	293	233
2θ range (deg)	3.94−56.70	3.70−56.66	3.72−56.84
no. of reflcns measd	21 796	29 783	41 147
no. of observns ($I > 2\sigma(I)$]	15 719	10 374	10 212
R	0.0515	0.0555	0.0552
R_w	0.1135	0.1404	0.1441
goodness-of-fit	0.950	0.883	1.030

Scheme 2



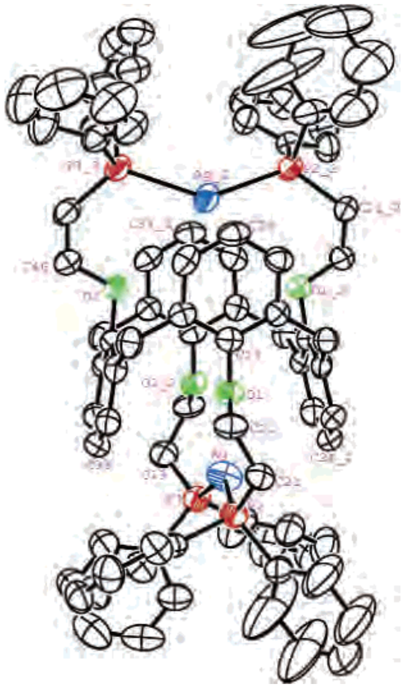


Figure 2. ORTEP drawing of complex **5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, two CH_2Cl_2, and two BF_4 atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ag−P(1) 2.4342(12), Ag−P(2) 2.4261(13), Ag−C(33) 3.545, Ag−C(26_2) 2.981; P(1)−Ag−P(2) 139.77(4).

Inclusion of Silver Ion inside a Calix[4]arene Cavity. Tetraphosphane **4** was found to be a good model to incorporate organometallic fragments inside the cavity. For example ligand **4** reacts in a 1:2 stoichiometric ratio with $AgBF_4$ to provide the new macrocycle **5** in almost quantitative yield (Scheme 2). Consistent with this structural formulation, the ^{31}P NMR of **5** exhibits a resonance at −12.7 ppm with two doublets ($J^{107}{}_{Ag-P} = 530$ Hz, $J^{109}{}_{Ag-P} = 604$ Hz), which is characteristic of a Ag(I) complex with a bent coordination geometry.[17] ^{1}H NMR spectroscopy and mass spectrometry also support this proposed formulation. The solid-state structure of **5** is consistent with its assigned solution structure (Figure 2). The shape of the calix[4]arene may be viewed as a pinched cone; the dihedral angle between the distal aryl rings bearing the phosphorus unit is 21.02(0.22)°. Complex **5** has a bent geometry with the bond angle of P(1)−Ag−P(2) being 139.77(4)°. The solid-state structure shows that two of the carbon atoms [C(33), 3.545 Å; C(26_2), 2.981 Å] lie sufficiently close to the silver so as to undergo a substantial interaction by two opposite arene rings. The previous investigations established that π-base receptors which feature cation−π interactions such as 1,3-alternate calix[4]arene always display a high affinity for Ag^+ and Cs^+.[18] Accordingly, this result implies that the Ag^+ complex with 1,3-alternate conformers may be stabilized not only by

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the interaction with two phosphines but also by π-donor participation of two benzene rings.

Inclusion of Rhodium inside a Calix[4]arene Cavity. Tetraphosphane **4** seems to be an ideal scaffold to test the suitability of specific phosphino ether coordination environments for complexing Rh(I). Treatment of **4** with a Rh(I) precursor (formed by the reaction between $[\{Rh(cot)_2Cl\}_2]$ (cot = cycloctene) and $AgBF_4$) readily afforded the two 18-membered rhodium(I) calix[4]arene **6** (Scheme 2). Complex **6** was characterized by ^1H and ^{31}P NMR, mass spectroscopy, and elemental analysis. The initial indication of the dinuclear formulation for **6** stemmed from the observation of an ion in the mass spectrum at *m*/*z* 1478, a fragmentation attributable to the loss of two BF_4^- groups. Two doublets in the ^1H NMR spectrum (4.20 and 3.45 ppm, $J = 11.2$ Hz), one peak at 30.4 ppm in the ^{13}C NMR spectrum for the methylene bridge, and one upfield resonance at -12.4 ppm ($\sim$15 ppm downfield with respect to the tetraphosphane **4**) with a characteristic coupling constant of $J_{Rh-P} = 538.2$ Hz in the ^{31}P NMR spectrum[19] proved that a pinched cone conformation is maintained in **6**. These values compares with those reported for system for which rhodium–arene interaction has been documented in the 1,3-alternate calix[4]arene.[13] This implies that above 1,3-alternate conformers also provide the well-preorganized cavity for Rh^+ binding. Furthermore, the solid-state structure of **6**, which was determined by a single-crystal X-ray analysis (Figure 3), is consistent with our structural formulation of **6** in solution. The coordination geometry of Rh(I) consists of a bent configuration. Interestingly, P1–Rh–P2 angle [139.42(3)°] is such that the rhodium metal is pushed into the cavity. The close rhodium–carbon distance (2.970–3.450 Å) on the opposite arene rings indicates that the rhodium ion has a substantial interaction with two benzene rings. It is noteworthy that the calix[4]-arene-derived diphosphines bearing auxiliary groups control the degree of encapsulation of the chelated metal atom.[20]

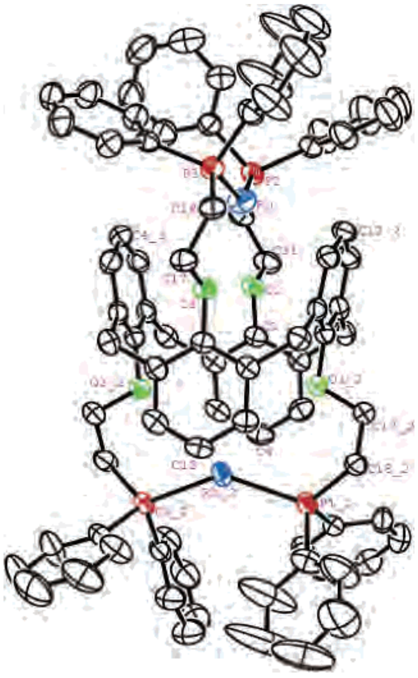
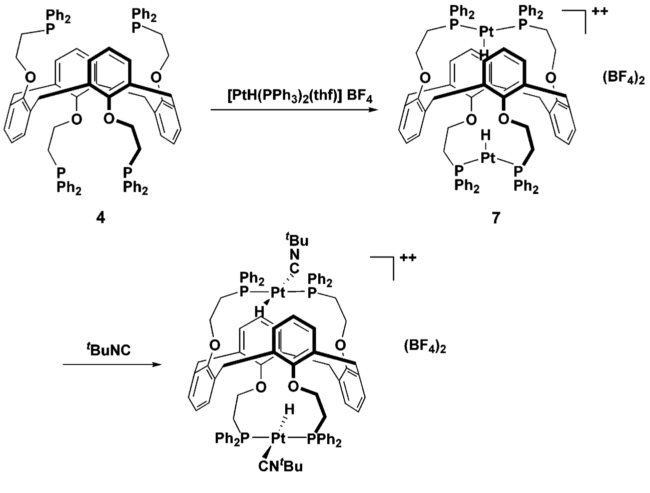


Figure 3. ORTEP drawing of complex **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, two CH_2Cl_2, and two BF_4 atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–P(1) 2.4229(10), Rh–P(2) 2.4237(9), Rh–C(12_2) 2.970, Rh–C(4_2) 3.450; P(1)–Rh–P(2) 139.42(3).

Inclusion of Platinum Hydride inside a Calix[4]arene Cavity. Although the above two examples serve to indicate that the Ag^+ and Rh^+ fragments are positioned into the calix-[4]arene cavity, additional evidence of such systems was then sought. Initially, we attempted to react tetraphoshane **4** with $[PtHCl(PPh_3)_2]$ and $[PtH(PPh_3)_3]^+$, but the ligand **4** failed to react with the metal complexes. However, reaction of **4** with $[PtH(PPh_3)_2(thf)]BF_4$ (formed by the reaction of $[PtHCl(PPh_3)_2]$ with $AgBF_4$ in THF) gave the new platinum complex **7** (Scheme 3). This compound was spectroscopically characterized, and all data are consistent with the formulated structure. For example, the ^1H NMR spectrum in CD_2Cl_2 shows a resonance at -6.24 ppm (t with Pt satellites, $J_{H-P} = 156$ Hz, $J_{H-Pt} = 684$ Hz) for the hydride coordinated to platinum.

Scheme 3



The hydride resonance has shifted 2.6 ppm upfield from that for the $[PtH(PPh_3)_2(thf)]^+$ ion, which is indicative of the high shielding effect of the 1,3-alternate calix[4]arene. The ^{31}P NMR spectrum of **7** in CD_2Cl_2 displays a single resonance at 3.6 ppm with ^{195}Pt satellites. The J_{P-Pt} coupling constant of 3359 Hz is typical for a cis geometry about the platinum atom.[21] NMR studies clearly showed that the hydride ligand is situated into the cavity induced around the platinum center. The complex **7** is quite inert toward cis/trans isomerization and extrusion of the Pt–H bond. Such

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rigidity of the ligand backbone is essential for obtaining high selectivity in the catalytic reaction.[22] Indeed, the extrusion reaction of Pt−H with CO and PPh_3 does not take place in our case. However, the reaction of **7** with a stronger π-donor ligand such as ${}^tBuNC$ took place to give the square planar complex **8**. The chelate complex **8** was readily characterized by ^1H, ^{13}C, and ^{31}P NMR, FAB-MS, and IR spectroscopies. The ^{31}P NMR spectrum of **8** exhibited one resonance at 23.1 ppm ($^1J_{Pt-P}$ = 2834 Hz). A trans arrangement for the phosphino ligands in a typical square-planar Pt(II) environment is proposed on the basis of the $^1J_{Pt-P}$ value for complex **8**.[23] The ^1H NMR pattern of hydrido ligand appears as a triplet with platinum satellites ($J_{H-P} = 19.2$ Hz, $J_{H-Pt} = 926$ Hz) at −12.82 ppm. The chemical shift and coupling constants of **8** resemble the values for the *trans*-$[PtH(PPh_3)_2L]$.[24] The IR spectrum of **8** exhibits one strong $\nu(C{\equiv}N)$ absorption band at 2187 cm^{-1} and one $\nu(Pt-H)$ absorption band at 1962 cm^{-1}. All these results clearly indicate that **8** has a trans configuration with the Pt−H unit extruded from the cavity. The fact that **8** can still react with strong π-donor ligands suggests that the Pt−H fragment is not completely shielded from the solution.

In summary, a novel 1,3-alternate calix[4]arene tetraphosphane was prepared. The ligand was found to be an effective reactant to introduce metal units inside the cavity. The dimetallic Ag(I) and Rh(I) complexes of the 1,3-alternate tetraphosphino calix[4]arene exhibit a chelate coordination of the phosphorus ligands with the directed positioning of the metal ions inside a calix[4]arene cavity. The Pt−H fragment of Pt(II) complex formed by the reaction of 1,3-alternate calix[4]arene tetraphosphane with $[PtH(PPh_3)_2(thf)]BF_4$ was found to be entrapped inside the interior of the cavity. Work is now in progress to demonstrate specific catalytic reactions.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. THF, toluene, and ether were distilled from sodium benzophenone. *n*-Hexane, CH_2Cl_2, and pentane were dried and distilled from CaH_2. Acetone was freshly distilled from the appropriate drying agents under nitrogen. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.00, 75.44, and 121.44 MHz, respectively. Chemical shifts were referenced relative to TMS and H_3PO_4. The IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Calixarene,[25] $[Rh(cot)_2Cl]_2$,[26] $[Rh(CO)_2Cl]_2$,[27] and *trans*-$[PtH(thf)(PPh_3)_2]BF_4$[9] were synthesized according to procedures reported in the literature.

25,26,27,28-Tetrakis(ethylacetoethoxy)calix[4]arene, 1,3-Alternate (1). To a refluxing suspension of calix[4]arene (2.00 g, 4.53 mmol) and Cs_2CO_3 (8.87 g, 27.0 mmol) in dry acetone (150 mL) was added dropwise a solution of ethyl bromoacetate (6.05 g, 36.2 mmol) in dry acetone (50 mL) over 3 h under nitrogen atmosphere. The reaction mixture was refluxed for an additional 24 h. After cooling of the reaction to room temperature, the salt was filtered off and the solvent was removed in vacuo. The reaction mixture was extracted three times with 50 mL of CH_2Cl_2, washed twice with water, and dried over anhydrous $MgSO_4$, and then the solvent was removed in vacuo. The crude product was chromatographed on silica gel using a mixture of ethyl acetate and *n*-hexane (1:5) as an eluent. Recrystallization from CH_2Cl_2/*n*-hexane (1:30, v/v) gave a white crystalline solid **1** in 29% yield (1.02 g). Mp: 118−119 °C. IR (KBr pellet): 2921, 1771, 1439, 1181, 1092, 1048, 760 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.16 (d, 8 H, ArH_m), 6.71 (t, 4 H, ArH_p), 4.23 (q, 8 H, OCH_2CH_3), 4.04 (s, 8 H, $ArCH_2Ar$), 3.78 (s, 8 H, $ArOCH_2$), 1.33 (t, 12 H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 169.5, 155.4, 133.4, 130.3, 122.8, 69.6, 60.7, 35.5, 14.1. Anal. Calcd for $C_{44}H_{48}O_{12}$: C, 68.74; H, 6.29. Found: C, 68.73; H, 6.40.

25,26,27,28-Tetrakis(2-hydroxyethoxy)calix[4]arene, 1,3-Alternate (2). To a suspension of LAH (0.172 g, 4.68 mmol) in THF (100 mL) was added dropwise a solution of **1** (0.901 g, 1.17 mmol) in THF, and the mixture was stirred at room-temperature overnight. Excess LAH was quenched by the addition of water, and the solvent was removed in vacuo. The resulting solid was extracted with methylene chloride (100 mL), and the organic layer was washed three times with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. Recrystallization from CH_2Cl_2/*n*-hexane (1:30, v/v) gave 0.69 g (98% yield) of **2** as white crystals. Mp: 264 °C (dec). IR (KBr pellet, cm^{-1}): 3342, 2932, 1454, 1199, 1087, 1036, 925, 889, 822, 627 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.10 (d, 8 H, ArH_m), 6.95 (t, 4 H, ArH_p), 3.96 (s, 8 H, $ArCH_2Ar$), 3.61 (t, 8 H, $ArOCH_2CH_2OH$), 3.25 (t, 8 H, $ArOCH_2CH_2OH$). ^{13}C NMR ($CDCl_3$): δ 156.1, 133.3, 130.5, 122.7, 71.4, 60.8, 38.1 ppm. Anal. Calcd for $C_{36}H_{40}O_8$: C, 71.98; H, 6.71. Found: C, 71.95; H, 6.74.

25,26,27,28-Tetrakis(2-hydroxyethoxy)calix[4]arene Tetratosylate, 1,3-Alternate (3). To a solution of **2** (1.00 g, 1.83 mmol) and *p*-toluenesulfonyl chloride (2.79 g, 14.6 mmol) in 100 mL of THF was added dropwise a solution of NaOH (3.66 g, 91.5 mmol) in 5 mL of water at 0 °C. The solution was warmed to room temperature and stirred for additional 24 h. After removal of THF in vacuo, the crude product was extracted several times with CH_2Cl_2 (100 mL) and water (100 mL). Recrystallization from ethyl acetate gave 1.74 g (79% yield) of tetratosylate **3** as a white solid. Mp: 197−199 °C. IR (KBr pellet, cm^{-1}): 2926, 1598, 1461, 1361, 1176, 1094, 991, 925, 823, 768, 662 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.78 (d, 8 H, ArH, tosyl), 7.37 (d, 8 H, ArH, tosyl), 6.92 (d, 8 H, ArH_m), 6.60 (t, 4 H, ArH_p), 3.65 (s, 8 H, $ArCH_2Ar$), 3.64 (t, 8 H, $ArOCH_2CH_2O$), 3.50 (t, 8 H, $ArOCH_2CH_2O$), 2.47 (s, 12 H, $ArCH_3$, tosyl). ^{13}C NMR ($CDCl_3$): δ 155.2, 145.0, 133.5, 129.9, 129.5, 127.9, 123.1, 67.7, 67.5, 37.0, 21.6. Anal. Calcd for $C_{64}H_{64}O_{16}S_4$: C, 63.14; H, 5.30. Found: C, 63.17; H, 5.30.

25,26,27,28-Tetrakis(2-(diphenylphosphino)ethoxy)calix[4]arene, 1,3-Alternate, (*P*,*P*,*P*,*P*)-Tetraphencalix[4]arene (4). To a stirred THF solution (20 mL) of 3 (200 mg, 0.16 mmol) was added $KPPh_2$ (0.72 mmol) at 0 °C. The temperature was warmed to room temperature, and the solution was stirred for 15 h at that

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temperature. The solvent was removed and washed with pentane (3 × 5 mL). Column chromatography on silica gel with ethyl acetate/hexane (1:2) as an eluent ($R_f = 0.8$) gave a white solid in 82% yield. Mp: 202 °C. ^{1}H NMR ($CDCl_3$): δ 7.36−7.27 (m, 40H, P*Ph*), 6.64 (d, 8H, $J = 6.9$ Hz), 6.55 (t, 4H, $J = 6.9$ Hz), 3.52 (s, 8H, ArC*H$_2$*Ar), 3.46 (t, 8H, $J = 6.9$ Hz, OC*H$_2$*), 1.86 (t, 8H, PC*H$_2$*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.6, 154.2, 139.1, 137.6, 133.8 (d), 130.2, 128.3 (d), 122.6, 73.6, 32.6, 28.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −27.3. Anal. Calcd for $C_{84}H_{76}O_4P_4$: C, 79.23; H, 6.02. Found: C, 79.01; H, 5.96.

[Ag{(*P,P,P,P*)-tetraphencalix[4]arene}](BF$_4$)$_2$ (5). To a stirred THF solution (10 mL) of **4** (0.12 g, 0.094 mmol) was added $AgBF_4$ (0.037 g, 0.188 mmol) dissolved in THF (10 mL). The solution was stirred for 12 h at room temperature. The solution was evaporated and washed with ether (3 × 5 mL). Recrystallization using CH_2Cl_2/THF gave **5** as white crystals in 70% yield. Mp: 332 °C. ^{1}H NMR (CD_2Cl_2): δ 7.58−7.52 (m, 40H, P*Ph*), 6.82 (d, 8H, $J = 6.6$ Hz), 6.52 (t, 4H, $J = 6.65$ Hz), 4.12 and 3.04 (AB spin system, $J = 13.2$ Hz, ArC*H$_2$*Ar), 3.68 (m, 8H, OC*H$_2$*), 1.52 (m, 8H, PC*H$_2$*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 158.6, 156.4, 140.3, 137.4, 134.4 (d), 131.6, 127.9 (d), 123.6, 74.2, 33.4, 28.8. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −12.7 (dd, $J^{107}{}_{\mathrm{Ag-P}} = 530$ Hz, $J^{109}{}_{\mathrm{Ag-P}} = 604$ Hz). FAB-MS: *m/z* 1488 [(M − 2BF$_4$)$^+$]. Anal. Calcd for $C_{84}H_{76}Ag_2B_2F_8O_4P_4$: C, 60.68; H, 4.61. Found: C, 60.32; H, 4.48.

[Rh$_2${(*P,P,P,P*)-tetraphencalix[4]arene}](BF$_4$)$_2$ (6). To a stirred THF solution (10 mL) of $[Rh(cot)_2Cl]_2$ (74 mg, 0.103 mmol) and $AgBF_4$ (40 mg, 0.21 mmol) was added **4** (0.12 g, 0.094 mmol) dissolved in CH_2Cl_2 (10 mL). The solution was stirred for 12 h at room temperature and filtered. The solution was evaporated and washed with toluene (2 × 5 mL) and ether (3 × 5 mL). Recrystallization using CH_2Cl_2/Et_2O gave **6** as reddish-yellow crystals in 59% yield. Mp: 191 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.62−7.32 (m, 40H, P*Ph*), 6.94 (d, 8H, $J = 6.8$ Hz), 6.64 (t, 4H, $J = 6.8$ Hz), 4.20 and 3.45 (AB spin system, 8H, $J = 11.2$ Hz, ArC*H$_2$*Ar), 3.45 (m, 8H, OC*H$_2$*), 1.62 (m, 8H, PC*H$_2$*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 158.2, 155.6, 139.6, 137.8, 133.4 (d), 131.6, 129.3 (d), 128.1, 73.8, 30.4, 28.2. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −12.4 (d, $J_{\mathrm{Rh-P}} = 538.2$ Hz). FAB-MS: *m/z* 1478 [(M − 2BF$_4$)$^+$]. Anal. Calcd for $C_{84}H_{76}B_2F_8O_4P_4Rh_2$: C, 61.04; H, 4.63. Found: C, 60.92; H, 4.48.

[(PtH)$_2${(*P,P,P,P*)-tetraphencalix[4]arene}](BF$_4$)$_2$ (7). A mixture of $[PtHCl(PPh_3)_2]$ (0.13 g, 0.17 mmol) and $AgBF_4$ (0.034 g, 0.17 mmol) dissolved in THF (10 mL) was stirred for 30 min at room temperature. To that solution was added **4** (0.10 g, 0.079 mmol). The solution was stirred for 12 h and filtered. The solution was evaporated and washed with THF (3 × 5 mL). Recrystallization using CH_2Cl_2/Et_2O gave **7** as white crystals in 62% yield. Mp: 211 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.58−7.34 (m, 40H, P*Ph*), 6.82 (d, 8H, $J = 7.5$ Hz), 6.54 (t, 4H, $J = 7.5$ Hz), 4.15 and 3.14 (AB spin system, 8H, $J = 13.4$ Hz, ArC*H$_2$*Ar), 3.67 (m, 8H, OC*H$_2$*), 1.21 (m, 8H, PC*H$_2$*), −6.24 (t with Pt saterllites, 1H, $J_{\mathrm{H-P}} = 156$ Hz, $J_{\mathrm{H-Pt}} = 684$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 157.8, 156.8, 135.8, 134.1, 132.4 (d), 131.4, 130.3 (d), 129.2, 72.6, 31.6, 28.2. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 3.6 (s with Pt satellites, $J_{\mathrm{P-Pt}} = 3359$ Hz). FAB-MS: *m/z* 1665 [(M − 2BF$_4$)$^+$]. Anal. Calcd for $C_{84}H_{78}B_2F_8O_4P_4Pt_2$: C, 54.96; H, 4.27. Found: C, 55.24; H, 4.41.

[(PtH(CN^{t}Bu))$_2${(*P,P,P,P*)-tetraphencalix[4]arene}](BF$_4$)$_2$ (8). To a stirred CH_2Cl_2 solution (10 mL) of **7** (0.059 g, 0.027 mmol) was added ^{t}BuNC (0.02 mL, 0.14 mmol). The solution was stirred for 2 h at room temperature. The solution was evaporated. Recrystallization using CH_2Cl_2/hexane gave **8** as white solid in 93% yield. Mp: 187 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.53−7.37 (m, 40H, P*Ph*), 7.11−6.60 (m, 12H), 3.68 (s, 8H, ArC*H$_2$*Ar), 3.44 (m, 8H, OC*H$_2$*), 1.31 (s, 18H, CC*H$_3$*), 1.15 (m, 8H, PC*H$_2$*), −12.82 (t, $J_{\mathrm{H-P}} = 19.2$ Hz, $J_{\mathrm{H-Pt}} = 926$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2); δ 194.4, 157.6, 157.0, 146.2, 136.4, 135.8, 134.8, 134.2, 133.0 (d), 131.8, 130.2 (d), 128.8, 128.1, 72.6, 31.8, 29.4, 22.2, 9.8. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 23.1 ($^1J_{\mathrm{Pt-P}} = 2834$ Hz). FAB-MS: *m/z* 1831 [(M − 2BF$_4$)$^+$]. IR (KBr pellet, cm^{-1}) 2187 ($\nu_{\mathrm{C\equiv N}}$), 1962 ($\nu_{\mathrm{Pt-H}}$). Anal. Calcd for $C_{94}H_{96}B_2F_8N_2O_4P_4Pt_2$: C, 55.77; H, 4.88. Found: C, 55.72; H, 4.84.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **4**−**6** are given in Table 1. Crystals of **4**−**6** were grown from ethyl acetate/hexane, CH_2Cl_2/THF, and CH_2Cl_2/Et_2O, respectively. Crystals of **4**−**6** were mounted in thin-walled glass capillaries and sealed under argon. The data sets for **4**−**6** were collected on a Bruker Smart CCD detector single diffractometer. Mo Kα radiation ($\lambda = 0.7107$ Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELX-96 program and least-squares refinement using the SHELXL-Plus (5.1) software package. All non-hydrogen atoms in compounds **4**−**6** were refined anisotropically. All other hydrogen atoms were included in the calculated positions.

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Supporting Information Available: Tables listing crystallographic information, atomic coordinates and *U*(eq) values, and intramolecular bond distances and angles and crystallographic data in CIF format for **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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