

Phosphorus-Based *p*-tert-Butylcalix[5]arene Ligands

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New calix[5]arene trivalent phosphorus derivatives have been synthesized which should be excellent ligands with which to study and control the interaction of a ligand atom with a metal. The larger cavity of the calix[5]arene (compared to calix[4]arene) provides a good balance between constraint and flexibility. Treatment of *p*-tert-butylcalix[5]arene with 2 equiv of either tris(dimethylamino)phosphine or dichlorophenylphosphine inserts two RP moieties into the calix[5]arene framework to give calix[5](PR)₂(OH) (**1**, R = Me₂N; **2**, R = Ph). Further treatment of **1** with 4 equiv of HCl gives calix[5](PCl)₂(OH) (**3**). Heating a solution of the monophosphorus compound calix[5](PNMe₂)(OH)₃ (**4**) releases dimethylamine to yield both monomeric calix[5](P)(OH)₂ (**6**) and dimeric {calix[5](P)(OH)₂}₂ (**7**), the latter having a tubelike geometry. X-ray crystallographic studies confirm the structures and show that **1** and **2** have approximate cone conformations while **3** has an approximate 1,2-alternate conformation. The orientations of the phosphorus lone pairs and oxygen atoms in all derivatives provide a framework for both soft and hard ligand interactions within the calix[5]arene.

Because of their ease of synthesis, most calixarene research has focused on the even-numbered members of the family, particularly the calix[4]arenes and, to a lesser extent, the calix[6]- and calix[8]arenes.¹ Our work² has taken advantage of the constraint of the small cavity of the calix[4]arene to stabilize high-coordinate main-group element geometries and study their transformations within the cavity. However, in most cases, the cavity is too small to study the interaction of two atoms within the framework. To that end, we reported³ the control of a phosphorus/metal interaction within the cavity of a calix[5]arene.⁴ We believe that this cavity has the ideal balance between constraint and flexibility to study

and control such interactions. In addition, we recently reported⁵ insertion of one and two bridging silyl groups into *p*-tert-butylcalix[5]arene to investigate the conformational effects of such bridging. We herein report the insertion of trivalent phosphorus moieties into the calix[5]arene framework to yield derivatives that should be able to bind both soft and hard donor atoms to a single metal.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, unless otherwise indicated. Solvents were dried using standard procedures, distilled under a nitrogen atmosphere, and either used immediately or stored in a nitrogen atmosphere, and either used immediately or stored in a nitrogen atmosphere prior to use. The reagents dichlorophenylphosphine and hydrogen chloride (anhydrous, 1.0 M in ethyl ether) were obtained from Sigma-Aldrich and used without further purification. The reagents tris(dimethylamino)phosphine⁶ and *p*-tert-butylcalix[5]arene⁷ were synthesized by literature procedures. All NMR spectra were recorded on a Bruker AVANCE DRX-400 multinuclear NMR spectrometer resonating at 400.137 MHz (¹H) and 161.979 MHz

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(^{31}P). ^1H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si . ^{31}P NMR resonances were measured relative to external 85% H_3PO_4 . Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from Complete Analysis Laboratories, Inc. (E + R Microanalytical Division), Parsippany, NJ, or Desert Analytics, Tucson, AZ, or on a CE Elantech Thermo-Finnigan Flash 1112 CHN elemental analyzer. Elemental analyses calculated with solvent included were determined by NMR integrations.

Synthesis of 1. A stirred solution of *p*-*tert*-butylcalix[5]arene (0.600 g, 0.740 mmol) in toluene (30 mL) was treated dropwise with tris(dimethylamino)phosphine (0.241 g, 1.48 mmol). The reaction mixture was stirred for 2 d after which the mixture was filtered to remove a small amount of insoluble material. The volatiles were removed from the filtrate under vacuum.

The white residue was washed with hexane (3×1 mL) and dried under vacuum yielding **1** as a white, air-stable powder (0.570 g, 80%). Samples suitable for elemental analysis and X-ray structure determination were obtained by recrystallization from hot toluene. Mp: 252–254 °C. Anal. Calcd for $\text{C}_{59}\text{H}_{78}\text{N}_2\text{O}_5\text{P}_2 \cdot 1.5\text{C}_7\text{H}_8$: C, 76.20; H, 8.28. Found: C, 76.47; H, 8.27. ^1H NMR (CDCl_3 , ppm): 1.14 (s, 18H, t-Bu), 1.17 (s, 18H, t-Bu), 1.35 (s, 9H, t-Bu), 2.88 (pseudo-t, 12H, NMe_2), 3.33 (d, 1H, CH_2 , $^2J_{\text{HH}} = 15.2$ Hz), 3.40 (d, 2H, CH_2 , $^2J_{\text{HH}} = 15.0$ Hz), 3.44 (d, 2H, CH_2 , $^2J_{\text{HH}} = 14.5$ Hz), 4.34 (d, 1H, CH_2 , $^2J_{\text{HH}} = 15.1$ Hz), 4.52 (d, 2H, CH_2 , $^2J_{\text{HH}} = 14.0$ Hz), 4.54 (d, 2H, CH_2 , $^2J_{\text{HH}} = 14.1$ Hz), 6.78 (t, 1H, OH, $J_{\text{PH}} = 8.5$ Hz), 6.83 (d, 2H, CH, $^4J_{\text{HH}} = 2.2$ Hz), 7.00 (d, 2H, CH, $^4J_{\text{HH}} = 2.3$ Hz), 7.02 (d, 2H, CH, $^4J_{\text{HH}} = 2.3$ Hz), 7.24 (d, 2H, CH, $^4J_{\text{HH}} = 2.2$ Hz), 7.30 (s, 2H, CH). ^{31}P NMR (CDCl_3 , ppm): 129. ν_{OH} (Nujol, cm^{-1}): 3384 (broad).

Synthesis of 2. Dichlorophenylphosphine (170 μL , 0.224 g, 1.25 mmol) was added to a stirred solution of *p*-*tert*-butylcalix[5]arene (0.50 g, 0.62 mmol) in toluene (20 mL). The resulting mixture was treated dropwise with triethylamine (349 μL , 0.254 g, 2.50 mmol) and immediately filtered. The volatiles were pumped off the filtrate. The residue was dissolved in ether (20 mL) and filtered. The solvent was pumped off, and the resulting residue was washed with hexane (1 mL) and pumped dry yielding **2** as an analytically pure, white powder (0.29 g, 46%). (If the reaction is allowed to proceed for longer periods of time, more impurities appear.) This compound decomposes during an extended period of air exposure. Mp: 238–240 °C. Anal. Calcd for $\text{C}_{67}\text{H}_{76}\text{O}_5\text{P}_2$: C, 78.64; H, 7.49. Found: C 78.47; H, 7.69. ^1H NMR (CDCl_3 , ppm): 1.16 (s, 18H, t-Bu), 1.18 (s, 18H, t-Bu), 1.37 (s, 9H, t-Bu), 3.10 (d, 1H, CH_2 , $^2J_{\text{HH}} = 14.8$ Hz), 3.47 (d, 2H, CH_2 , $^2J_{\text{HH}} = 14.2$ Hz), 3.49 (d, 2H, CH_2 , $^2J_{\text{HH}} = 14.5$ Hz), 3.99 (d, 1H, CH_2 , $^2J_{\text{HH}} = 15.0$ Hz), 4.57 (d, 2H, CH_2 , $^2J_{\text{HH}} = 13.9$ Hz), 4.64 (d, 2H, CH_2 , $^2J_{\text{HH}} = 14.2$ Hz), 6.82 (d, 2H, CH, $^4J_{\text{HH}} = 2.4$ Hz), 7.05 (d, 2H, CH, $^4J_{\text{HH}} = 2.4$ Hz), 7.07 (d, 2H, CH, $^4J_{\text{HH}} = 2.4$ Hz), 7.35 and 7.45 [m, 11H, CH (PPH) and OH], 7.78 (m, 4H, overlapping CH). ^{31}P NMR (CDCl_3 , ppm): 154. ν_{OH} (KBr, cm^{-1}): 3357 (broad).

Synthesis of 3. A stirred solution of **1** (0.20 g, 0.21 mmol) in toluene (5 mL) was treated dropwise with hydrogen chloride (anhydrous, 1.0 M in ethyl ether, 0.80 mL, 0.80 mmol) via a microliter syringe over a period of 20 min. The resulting mixture was stirred overnight and then filtered. The volatiles were pumped off from the filtrate and the resulting solid stirred overnight in hexane. The solid was filtered off and pumped dry to yield **3** as an air-stable white powder (0.10 g, 53%). Samples suitable for elemental analysis and X-ray structure determination were obtained by recrystallization from a hot hexane/toluene mixture (adding only enough toluene to ensure dissolution) and keeping the solution at

–30 °C. Mp: 269–272 °C. Anal. Calcd for $\text{C}_{55}\text{H}_{66}\text{Cl}_2\text{O}_5\text{P}_2$: C, 70.28; H, 7.08. Found: C, 70.87; H, 6.87. All peaks in the ^1H NMR spectrum are broad. ^1H NMR (CDCl_3 , ppm): 1.23 (27H, t-Bu), 1.33 (18H, t-Bu), 3.44, 3.55, 3.64 (6H, overlapping CH_2), 4.30, 4.41 (4H, overlapping CH_2), 4.96 (1H, OH), 6.88 (2H, CH), 7.06 (2H, CH), 7.18 (4H, overlapping CH), 7.37 (2H, CH). ^{31}P NMR (CDCl_3 , ppm): 156. ν_{OH} (KBr, cm^{-1}): 3538 (sharp).

Synthesis of 6. A stirred solution of **4** (1.2 g, 1.4 mmol) in toluene (40 mL) was refluxed in toluene for 15 h. The reaction mixture was cooled and filtered to remove the insoluble dimer. The volatiles were pumped off from the filtrate, and the resulting solid was washed with hexane. The solid was recrystallized from hot toluene yielding **6** as a white, air-stable powder (0.56 g, 48%). Mp: 324–328 °C. Anal. Calcd for $\text{C}_{55}\text{H}_{67}\text{O}_5\text{P}$: C, 78.73; H, 8.05. Found: C, 78.37; H, 8.05. ^1H NMR (CDCl_3 , ppm): 1.20 (18H, t-Bu), 1.25 (9H, t-Bu), 1.36 (18H, t-Bu), 3.75 (br d, 2H, CH_2), 3.86 (br d, 2H, CH_2 , $^2J_{\text{HH}} = 16.4$ Hz), 4.02 (br d, 2H, CH_2), 4.13 (overlapping s, 2H, CH and br d, 2H, CH_2), 4.47 (s, 2H, OH), 6.95 (br s, 2H, CH), 7.04 (s, 2H, CH), 7.17 (s, 2H, CH), 7.20 (s, 2H, CH), 7.27 (s, 2H, CH). ^{31}P NMR (CDCl_3 , ppm): 124. ν_{OH} (KBr, cm^{-1}): 3498 (sharp).

Synthesis of 7. A stirred solution of **4** (0.200 g, 0.226 mmol) in toluene (5 mL) was refluxed in toluene for 15 h. The reaction mixture was cooled and filtered to separate the insoluble dimer **7** as a white, air-stable powder (0.020 g, 11%). Mp: >400 °C. Anal. Calcd for $\text{C}_{110}\text{H}_{134}\text{O}_{10}\text{P}_2$: C, 78.73; H, 8.05. Found: C, 78.51; H, 8.00. ^1H NMR (CDCl_3 , ppm): 0.36 (18H, t-Bu), 1.03 (36H, t-Bu), 1.30 (36H, t-Bu), 2.50 (d, 4H, CH_2 , $^2J_{\text{HH}} = 15.9$ Hz), 3.31 (d, 2H, CH_2 , $^2J_{\text{HH}} = 12.6$ Hz), 3.61 (d, 4H, CH_2 , $^2J_{\text{HH}} = 16.5$ Hz), 4.09 (d, 4H, CH_2 , $^2J_{\text{HH}} = 16.0$ Hz), 4.65 (d, 2H, CH_2 , $^2J_{\text{HH}} = 12.0$ Hz), 4.75 (s, 4H, OH), 5.06 (d, 4H, CH_2 , $^2J_{\text{HH}} = 16.4$ Hz), 6.55 (s, 4H, CH), 6.58 (s, 4H, CH), 6.68 (s, 4H, CH), 6.94 (s, 4H, CH), 7.06 (s, 4H, CH). ^{31}P NMR (CDCl_3 , ppm): 137. ν_{OH} (KBr, cm^{-1}): 3471.

Single-Crystal X-ray Diffraction Studies. All crystal samples are colorless and, except for **6**, were grown from toluene solutions. Crystals of **6** were grown from a mixture of toluene and benzene. Data for **1–3** were collected on a Bruker P4 diffractometer which was equipped with a conventional scintillation counter, while data for **6** and **7** were collected on a Bruker APEX system with a CCD area detector. The crystals used in the experiments were coated with mineral oil under a low-temperature nitrogen stream. Crystallographic data are summarized in Table 1. All structures were solved by direct methods and subsequent difference Fourier syntheses and refined by full-matrix least-squares methods against F^2 .⁸ Solvate toluene molecules were found in each of crystal lattices, while benzene molecules appeared in structure **6**, as well. Most solvent molecules, as well as some methyl groups of the *tert*-butyls, are positionally disordered. These disordered atoms were refined with occupancy and distance restraints. All non-hydrogen atoms were refined anisotropically, while H atoms were constrained with a riding model. Selected bond distances and angles are listed in Table 2. The structure of **7** could not be well-refined.⁹ Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for each structure reported in this paper, are presented in CIF format in the Supporting Information.

Results and Discussion

Synthesis. Insertion of two PNMe_2 or PPh moieties into the calix[5]arene framework proceeds at ambient temperature in reasonable yields according to Scheme 1. The reaction

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Table 1. Crystal Data^a

	1	2	3	6
empirical formula	C ₅₉ H ₇₈ N ₂ O ₅ P ₂ ·C ₇ H ₈	C ₆₇ H ₇₆ O ₅ P ₂ ·2C ₇ H ₈	C ₅₅ H ₆₆ O ₅ Cl ₂ P ₂ ·C ₇ H ₈	2C ₅₅ H ₆₇ O ₅ P·C ₇ H ₈ ·1/2C ₆ H ₆
fw	1049.31	1207.49	1032.05	1809.30
cryst system	monoclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> , Å	13.886(4)	17.269(1)	14.353(1)	13.744(1)
<i>b</i> , Å	24.733(6)	24.363(1)	14.612(1)	17.404(1)
<i>c</i> , Å	18.573(4)	17.584(1)	14.916(1)	21.924(2)
α, deg	90	90	102.288(7)	89.395(1)
β, deg	104.74(2)	109.621(5)	102.074(8)	84.826(1)
γ, deg	90	90	96.007(8)	83.546(1)
<i>V</i> , Å ³	6169(3)	6968.4(6)	2925.3(3)	5189.8(7)
<i>Z</i>	4	2	2	2
ρ _{calcd} , g cm ⁻³	1.130	1.151	1.161	1.158
μ, mm ⁻¹	0.119	0.113	0.210	0.101
extinctn coeff ^b	0.0020(3)	0.0055(6)		
R ₁ [<i>I</i> > 2σ(<i>I</i>)] ^c	0.062	0.076	0.087	0.083
wR ₂ (all data) ^c	0.153	0.223	0.260	0.208

^a Graphite monochromatized Mo Kα radiation, λ = 0.710 73 Å. ^b See ref 8. ^c R₁ = Σ||F_o| - |F_c||/Σ|F_o|, wR₂ = {Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)]^{1/2}, where w = 1/[σ²(F_o²) + (aP)² + bP], P = [2F_c² + F_o²]/3.

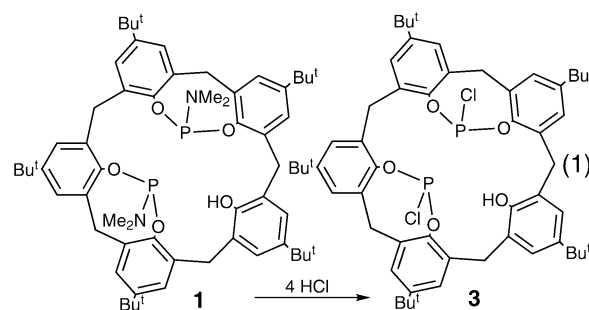
Table 2. Selected Interatomic Distances (Å) and Angles (deg)

1		2		3		6	
P(1)–O(3)	1.647(3)	P(1)–O(3)	1.625(4)	P(1)–O(3)	1.633(3)	P(1)–O(2)	1.6287(19)
P(1)–N(1)	1.672(4)	P(1)–O(2)	1.650(4)	P(1)–O(2)	1.645(3)	P(1)–O(1)	1.6292(18)
P(1)–O(2)	1.681(4)	P(1)–C(71)	1.805(6)	P(1)–Cl(1)	2.050(2)	P(1)–O(3)	1.642(2)
P(2)–O(4)	1.646(4)	P(2)–O(4)	1.648(4)	P(2)–O(4)	1.597(3)	P(1)–O(4)	4.151(2)
P(2)–N(2)	1.646(5)	P(2)–O(5)	1.661(4)	P(2)–O(5)	1.640(4)	P(1)–O(5)	4.717(2)
P(2)–O(5)	1.655(3)	P(2)–C(81)	1.823(6)	P(2)–Cl(2)	2.064(2)		
N(1)–C(3)	1.449(7)	P(1)–P(2)	3.810(2)	P(1)–P(2)	3.859(2)		
N(1)–C(4)	1.461(7)	P(1)–O(1)	3.214(4)	P(1)–O(1)	4.681(4)		
N(2)–C(6)	1.435(7)	P(2)–O(1)	3.093(4)	P(2)–O(1)	3.357(4)		
N(2)–C(5)	1.466(7)						
P(1)–P(2)	3.726(2)						
P(1)–O(1)	2.925(4)						
P(2)–O(1)	3.268(4)						

1		2		3		6	
O(3)–P(1)–N(1)	95.4(2)	O(3)–P(1)–O(2)	103.08(19)	O(3)–P(1)–O(2)	102.45(17)	O(2)–P(1)–O(1)	101.45(9)
O(3)–P(1)–O(2)	101.11(18)	O(3)–P(1)–C(71)	105.0(2)	O(3)–P(1)–Cl(1)	94.35(13)	O(2)–P(1)–O(3)	98.88(9)
N(1)–P(1)–O(2)	99.1(2)	O(2)–P(1)–C(71)	98.3(3)	O(2)–P(1)–Cl(1)	95.39(13)	O(1)–P(1)–O(3)	93.87(9)
O(4)–P(2)–N(2)	108.3(2)	O(4)–P(2)–O(5)	102.62(19)	O(4)–P(2)–O(5)	103.1(2)		
O(4)–P(2)–O(5)	99.94(18)	O(4)–P(2)–C(81)	95.1(2)	O(4)–P(2)–Cl(2)	101.63(15)		
N(2)–P(2)–O(5)	98.3(2)	O(5)–P(2)–C(81)	96.2(2)	O(5)–P(2)–Cl(2)	95.69(15)		
C(21)–O(2)–P(1)	119.8(3)	C(21)–O(2)–P(1)	111.1(3)	C(21)–O(2)–P(1)	116.2(3)		
C(31)–O(3)–P(1)	118.4(3)	C(31)–O(3)–P(1)	128.6(3)	C(31)–O(3)–P(1)	119.0(3)		
C(41)–O(4)–P(2)	128.1(3)	C(41)–O(4)–P(2)	117.7(3)	C(41)–O(4)–P(2)	138.2(3)		
C(51)–O(5)–P(2)	113.1(3)	C(51)–O(5)–P(2)	115.7(3)	C(51)–O(5)–P(2)	121.6(3)		
C(3)–N(1)–C(4)	111.8(5)						
C(3)–N(1)–P(1)	123.2(4)						
C(4)–N(1)–P(1)	113.8(4)						
C(6)–N(2)–C(5)	114.8(5)						
C(6)–N(2)–P(2)	127.1(4)						
C(5)–N(2)–P(2)	116.8(4)						

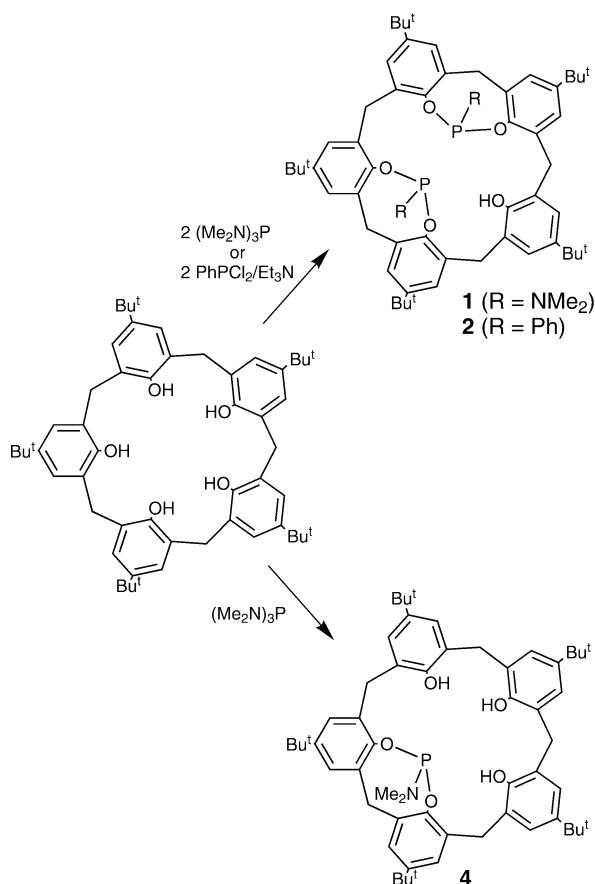
with the aminophosphine is slow, while the chlorophosphine is very fast. In fact, extended reaction times reduce the yield of **2**, and the best yields are obtained if the reaction is stopped as soon after triethylamine addition as possible. While the P–C bond is relatively inert, the P–N bond in aminophos-

phines is known to be cleaved with hydrogen halides, and treatment of **1** with 4 mol of anhydrous HCl does produce the dichloro analogue **3** via formation of dimethylamine hydrochloride (eq 1).

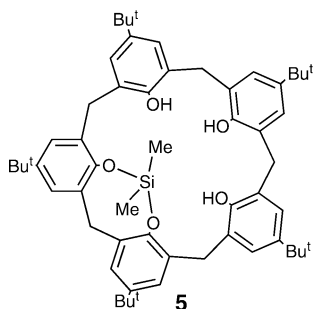


(9) Data for **7**: C₁₁₀H₁₃₄O₁₀P₂·6C₇H₈; fw 1115.46; space group *P*2₁/*c*; *a* = 19.181(4), *b* = 30.530(7), *c* = 11.169(3) Å; β = 101.202(4); *V* = 6416(2) Å³; *Z* = 2; *d* = 1.155 Mg/m³; μ = 0.094 mm⁻¹. Data were collected on a Bruker APEX diffractometer at 100 K, Mo Kα radiation, with 2θ = 2.54–56.94°. The structure was solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL program package (Sheldrick, G. M. *SHELXTL*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1990). The dimeric calix(5)arene molecule possesses a center of symmetry located at the center of the dimer. Six toluene molecules (per dimer) were found in the lattice. The final refinement parameters R₁ [*I* > 2σ(*I*)] = 0.167 and wR₂ (all data) = 0.373.

Scheme 1

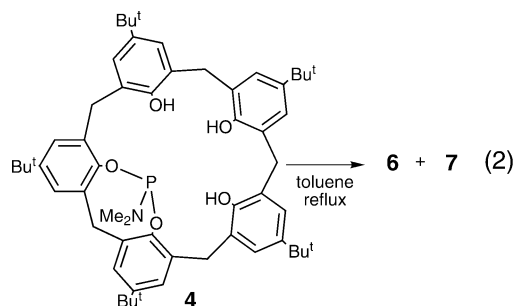


Attempts to synthesize a mono-PPh derivative (using 1:1 molar ratios of dichlorophenylphosphine:calixarene or lower) led to **2** and unreacted *p*-*tert*-butylcalix[5]arene, along with small amounts of unidentified phosphorus-containing products. This contrasts with our successful insertion of a single PNMe₂ to give **4**³ (Scheme 1) and a single SiMe₂ [via (Me₂N)₂SiMe₂] to yield **5**.⁵ Attempts to isolate a mono P–Cl compound were unsuccessful as well; treatment of **4** with 2 mol of HCl led to mixtures.



However, heating a solution of **4** (in toluene) to reflux led to a particularly interesting reaction. Two products were observed having significantly different solubilities. The major product **6**, isolated in about 50% yield, is soluble in toluene, while the minor product **7**, isolated in about 10% yield, is totally insoluble in toluene at ambient temperature. ¹H NMR spectra (see below and Experimental Section) indicate that no dimethylamino moiety is present in either species, and

both compounds analyze to identical compositions in which dimethylamine has been lost from **4**. Loss of dimethylamine should result in formation of a third phosphorus–oxygen bond.



NMR Spectra. For derivatives **1** and **2**, all peaks in the ¹H NMR spectra are sharp. There are three singlets for the *tert*-butyl groups in a 2:2:1 ratio. The methylene region shows the expected six doublets (geminal coupling due to nonequivalent methylene hydrogens), with two of the doublets being half the intensity of the others. These latter doublets, due to the unique methylene bridging group, are separated by about 1 ppm. This is usually a good indication of overall C_s symmetry for the molecule. Most of the peaks in the ¹H NMR spectrum of **3** are broad, implying greater flexibility for this derivative, perhaps due to the lower steric requirements of the chloride. The *tert*-butyl resonances appear as two peaks in a 3:2 ratio, with the larger area peak significantly broader. The methylene region is grouped into two broad signals, with overlapping maxima at δ 3.44, 3.55, 3.64 and 4.30, 4.41. These regions integrate to 6:4, respectively. While broad, it is clear the general methylene pattern is significantly different from that for **1** and **2**, since there is no large separation between signals for the two protons on the unique bridging methylene group. This suggests a different conformation for this compound.

The single most unusual feature in the above spectra is the hydroxyl resonance in **1**: this appears as a 1:2:1 triplet at δ 6.78. The corresponding resonance in the dichloro compound **3** is a singlet at δ 4.96. In **2**, no separate peak is observed, although integration suggests it lies under the PPh peak at δ 7.35. The only plausible explanation for the observed splitting in **1** is a through-space interaction with the two phosphorus atoms. Indeed, a ¹H{³¹P} NMR spectrum (Figure 1) reveals that this is the case, since the resonance collapses to a singlet.

As mentioned above, the ¹H NMR spectra of **6** and **7** indicate loss of dimethylamine which is expected to result in formation of a third phosphorus–oxygen bond. However, it is possible that this reaction could be intra- or intermolecular. In **6**, most peaks are sharp except for the methylene region. There are the three characteristic *tert*-butyl resonances (2:2:1 ratio), and the aromatic region shows five singlets for the ring protons, both characteristic of overall C_s symmetry. In the methylene region, the protons on the unique bridging methylene group appear as a sharp singlet while the others appear as broad doublets. The spectrum of **7** exhibits similar patterns in the *tert*-butyl and aromatic regions, but the

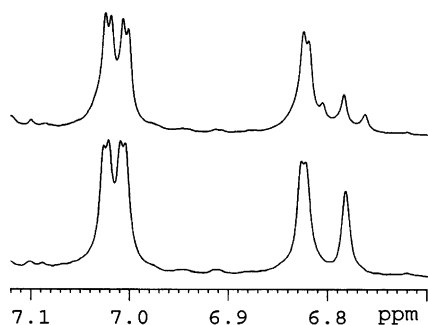


Figure 1. Selected portion of the ^1H NMR spectrum of **1**: normal spectrum (top); phosphorus-decoupled spectrum (bottom).

methylene peaks are very sharp, with a similar splitting pattern as found for **1** and **2**. This suggests that **7** has a significantly more rigid structure than **6**. In fact, **6** results from intramolecular phosphorus–oxygen bond formation while **7** is the result of an intermolecular reaction leading to a dimeric tubelike structure with C_{2h} symmetry.

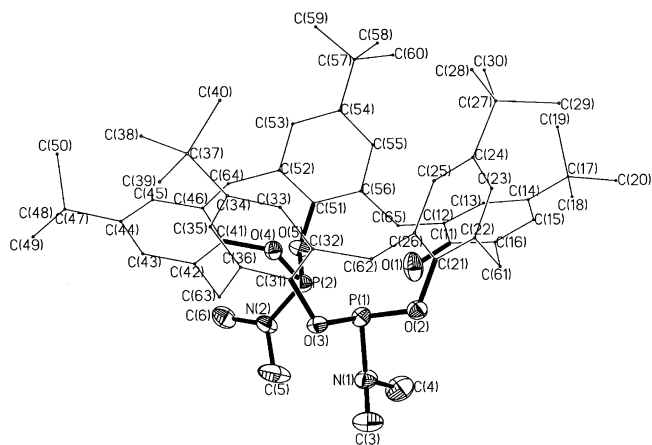
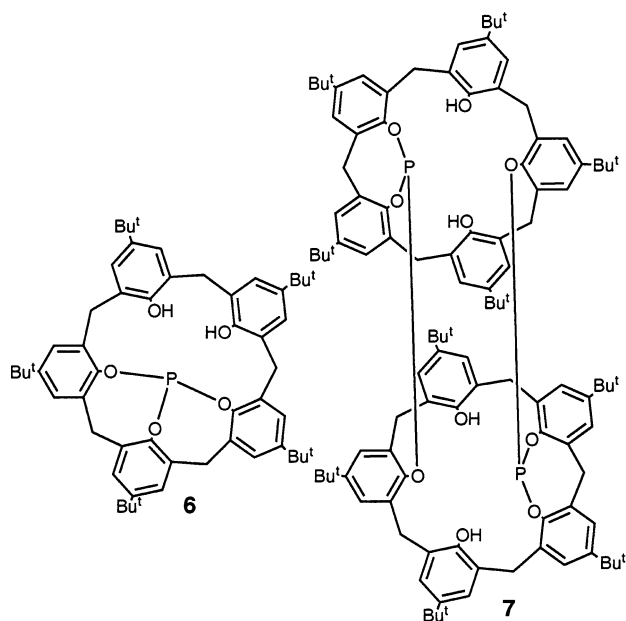


Figure 2. Molecular structure of **1**. Thermal ellipsoids are shown at 40% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.

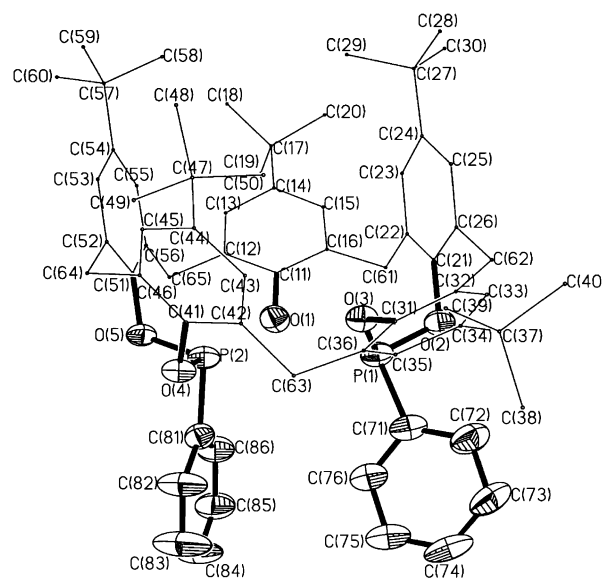


Figure 3. Molecular structure of **2**. Thermal ellipsoids are shown at 40% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.

Solid-State Structures. The X-ray structures of **1–3** and **6** are shown in Figures 2–5, respectively, and selected interatomic distances and angles are tabulated in Table 2. Unfortunately, the data for **7** could not be well-refined (see Experimental Section); however, the atom connectivity is clear and Figure 6 shows this connectivity. For the molecules with two phosphorus atoms, **1** and **2** are very similar in geometry, adopting approximate cone conformations with almost C_s symmetry, consistent with their solution ^1H NMR spectra. However, **3** adopts an approximate 1,2-alternate conformation. Although, the two phosphorus atoms in **3** are nonequivalent in the solid state due to the orientation of the free phenolic group, only one signal in the ^{31}P NMR spectrum is observed due, most likely, to rotation of this group through the annulus of the calixarene. Such motion would explain the broadness of the peaks in the ^1H NMR spectrum. In the solid state, there is a definite “sidedness”

to these structures. For example, in each molecule, one eight-membered phosphorus-containing ring adopts a boat-chair (BC) conformation [P(2) in **2** and P(1) in **1** and **3**], the most common conformation of eight-membered rings. The other phosphorus ring conformation is best described as a twisted boat (TB) in each structure. Differences also show up in the geometry of each phosphorus. The sum of the bond angles about the phosphorus in the BC rings is $292\text{--}296^\circ$, while this sum is $300\text{--}306^\circ$ in the TB rings. This results in shorter bond lengths for the atoms with larger sums due to the increased s-character in these bonds. It is unlikely that crystal packing forces would account for such similar features in the three structures; more likely, it is the constraint of the calix[5]arene that forces the different solid-state ring conformations. Support for this argument comes from the silicon derivatives of calix[5]arene.⁵ In the monosilyl compound **5**, the eight-membered ring containing silicon adopts the BC conformation; in the disilyl **8**, one ring is in the BC conformation while the other is in the TB. The structure of

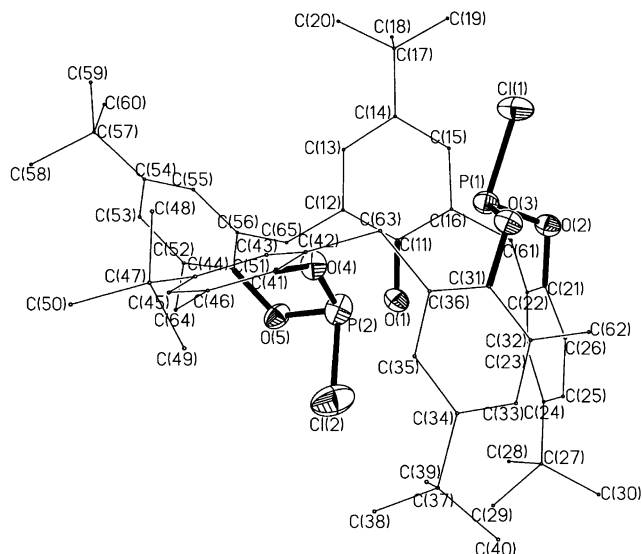


Figure 4. Molecular structure of **3**. Thermal ellipsoids are shown at 40% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.

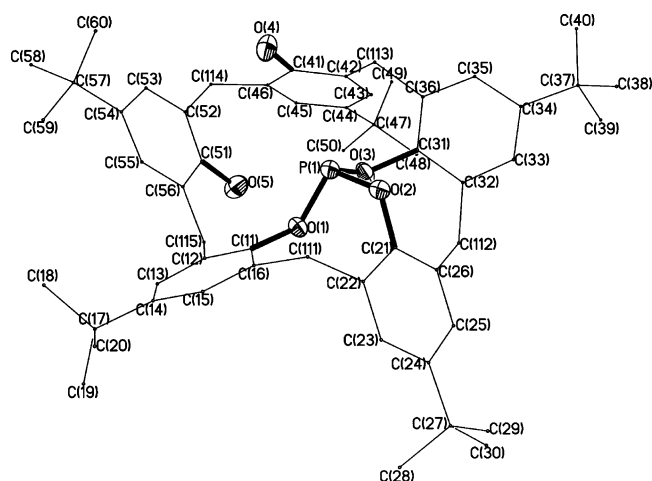
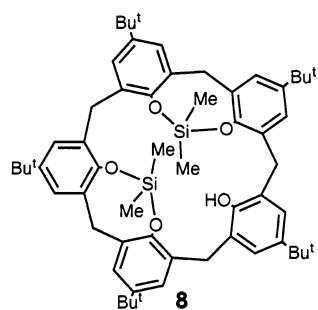


Figure 5. Molecular structure of **6**. Thermal ellipsoids are shown at 50% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.

the monophosphorus derivative **6** contains two fused eight-membered rings; both are best described as TB conformations.



Examination of the structures of **1** and **3** shows that the reaction to produce **3** results in retention of configuration at one phosphorus and inversion at the other. It has been proposed that the reaction of an aminophosphine with

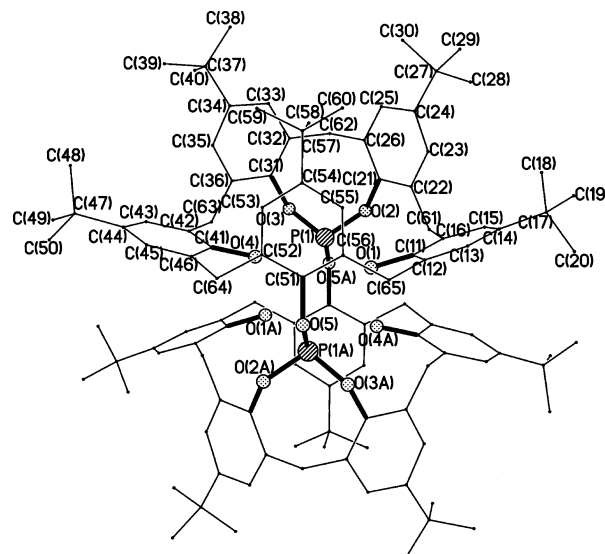


Figure 6. Molecular structure of **7** shown to illustrate atom connectivity. See Experimental Section.

hydrogen chloride is stereoselective, but racemization usually occurs, possibly via intermolecular exchange¹⁰ or reaction of the formed chlorophosphine with free HCl.¹¹ The steric constraint of the calixarene framework may also prevent retention at both phosphorus atoms.

The observed through-space phosphorus–proton coupling in **1** can also be rationalized by the solid-state geometries. The nonbonded P---O(1) distances average about 3.1 Å, almost 1 Å less than the average in **3** (Table 2).

These compounds are expected to be excellent ligands toward transition metals, particularly in light of work on metal binding of larger calixarenes.¹² Both phosphorus lone pairs are oriented to bind to a single metal in **1–3** with, perhaps, the metal “outside” the calixarene cavity with **1** and **2** and “inside” the cavity with **3**. In addition, the free phenolic oxygen may also interact. The monophosphorus compound **6** may serve a similar function as **4**, where both the phosphorus and oxygens bind to the metal. Finally, **7** may be a particularly novel ligand to trap metals deep inside its tube geometry. We are currently investigating these reactions. Preliminary data indicate that both phosphorus atoms in **1–3** do bind to a single metal in complexes with rhodium and platinum. In addition, the free phenolic group sometimes interacts with the metal as well. These results will be reported shortly.

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Supporting Information Available: A single file containing tables in CIF format for structures **1–3** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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