

Main-Group-Element Calix[4]arenes: Variable Coordination and Conformational Isomerism at Phosphorus and Silicon

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Treatment of calix[4]arene (**1b**) with trichloromethylsilane yields two conformers of calix[4]SiMe(OH), the cone **2b-C** and the partial cone **2b-PC**. These are isolated and structurally characterized, and their thermodynamic activation parameters are determined in solution [$E_a = 117(3)$ kJ/mol, $\Delta H = 5(4)$ kJ/mol]. Similar parameters are found for the *p*-tert-butylcalix[4]arene analogues **2a-C** and **2a-PC**. Deprotonation of **2b** with butyllithium yields calix[4]SiMe(OLi) (**8b**). The structure of **8b** is solvent dependent: **8b** contains a five-coordinate silicon in THF and a four-coordinate silicon in benzene. Similar behavior is found for the *p*-tert-butylcalix[4]arene analogues. The five-coordinate phosphorus analogue of the anion in **8**, *p*-tert-butylcalix[4]PMe (**11a**), is synthesized from the phosphonium triflate salt *p*-tert-butylcalix[4]PMe(OH)OTf (**10a(OTf)**) via treatment with butyllithium. The structure of **11a** shows the geometry around phosphorus to be very close to a pure trigonal bipyramid. The X-ray structure of **10a(OTf)** cannot be obtained, but its iodide analogue **10a(I)** is synthesized and structurally characterized. The cation in **10a(I)** adopts the partial cone conformation in the solid state, similar to **2b-PC**. Treatment of **8b** with methyl trifluoromethanesulfonate yields the methyl phenyl ether calix[4]SiMe(OMe) (**3b**). This species and its *p*-tert-butyl analogue **3a** are structurally characterized. Both adopt the partial cone conformation. The SiMe group in **3b** can be removed via treatment with fluoride to yield the monomethylated calix[4]arene **4b** in 50–60% overall yield based on **1b**.

Our recent investigations¹ into the insertion of main-group elements into calixarenes have led to novel structures and reactions in which several coordination geometries are observed. The calixarenes provide two properties seldom found in the same system: constraint and flexibility. The constraint is derived from the size of the central cavity, while the flexibility arises from the ease of conformational mobility of the calixarene backbone. In this paper, we report calix[4]arene derivatives containing both four- and five-coordinate silicon and phosphorus, conformational isomerism of several of these species, and a unique solvent-dependent coordination change for silicon.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or with standard Schlenk techniques, unless otherwise indicated. Solvents were dried using standard procedures, distilled under a nitrogen atmosphere, and either used immediately or stored in the drybox prior to use, except for anhydrous 1,2-dichlorobenzene, which was used without further purification. Glassware was oven-dried at 140 °C overnight prior to use. The reagents butyllithium (1.6 M in hexanes), methyl trifluoromethanesulfonate, tetrabutylammonium fluoride (1.0 M in THF),

trichloromethylsilane, tris(dimethylamino)methylsilane, iodomethane, and triethylamine were purchased commercially and used without further purification, except for triethylamine, which was dried over potassium hydroxide and distilled prior to use. The reagents *p*-tert-butylcalix[4]arene–toluene (**1a**–toluene)² and calix[4]arene (**1b**)³ were synthesized by literature methods. In all cases, oven-dried (110–120 °C for at least 12 h, either in the oven or under vacuum) samples of the calix[4]arenes were used. In addition to removing moisture, drying also removes greater than 80% of the toluene from *p*-tert-butylcalix[4]arene. Stoichiometric calculations for *p*-tert-butylcalix[4]arene omit toluene. The *p*-tert-butylcalix[4]arene phosphite **7a**^{1c} was synthesized by a published procedure. All ¹H NMR spectra were recorded on either an IBM/Bruker WP200SY multinuclear NMR spectrometer (equipped with a Tecmag computer system) resonating at 200.132 MHz or a Bruker AVANCE DRX400 multinuclear NMR spectrometer resonating at 400.135 MHz. ¹H resonances were measured relative to residual proton solvent peaks and referenced to Me₄Si. All ²⁹Si and ³¹P NMR spectra were recorded on the Bruker AVANCE DRX400 multinuclear NMR spectrometer resonating at 79.494 and 161.978 MHz, respectively. ²⁹Si NMR samples contained Cr(acac)₃, and spectra were recorded using the INEPTND sequence. ²⁹Si resonances were referenced to external Me₄Si, and ³¹P resonances were referenced to external 85% H₃PO₄. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from E + R Microanalytical Laboratories, Inc., Corona, NY. When solvent is included in the calculated elemental analysis, it is based on (integrated) peaks for the solvent appearing in the ¹H NMR spectrum of the sample analyzed.

Monomethyl Ether of Methylsilyl Calix[4]arene (3b). A stirred solution of calix[4]arene (**1b**) (1.25 g, 2.94 mmol) in toluene (60 mL)

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was treated dropwise with triethylamine (0.894 g, 8.85 mmol), giving a white precipitate. Trichloromethylsilane (0.445 g, 2.98 mmol) was then added dropwise, and the reaction mixture was stirred for about 24 h. The resulting mixture was filtered, and the volatiles were pumped off from the filtrate. The residue was washed with hexane and pumped dry to yield 0.958 g of a white solid. ^1H NMR analysis of this mixture showed it to contain the partial cone (**2b-PC**) and cone (**2b-C**) conformers in an approximate 2:1 ratio. This solid was redissolved in benzene (30 mL), and the solution was treated with butyllithium (1.3 mL, 2.1 mmol). The resulting solution was stirred for 4 h, during which a white precipitate formed. Methyl trifluoromethanesulfonate (0.342 g, 2.08 mmol) was then added dropwise, and the mixture was stirred overnight. The resulting mixture was filtered, and the volatiles were pumped off from the filtrate, leaving a yellow residue. This residue was washed with hexane (3×1 mL) to yield **3b** as a white air-stable compound (0.925 g, 67% based on **1b**). Analytically pure samples were obtained by recrystallization from toluene. Mp: 278–280 °C. Anal. Calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4\text{Si}$: C, 75.29; H, 5.48. Found: C, 75.20; H, 5.45. ^1H NMR (C_6D_6): δ -0.25 (s, 3 H), 2.78 (s, 3 H), 3.33 (d, $^2J_{\text{HH}} = 14$ Hz, 2 H), 3.53 (d, $^2J_{\text{HH}} = 16$ Hz, 2 H), 3.99 (d, $^2J_{\text{HH}} = 16$ Hz, 2 H), 4.62 (d, $^2J_{\text{HH}} = 13$ Hz, 2 H), 6.58–7.05 (12 H total).

Monomethyl Ether of Calix[4]arene (4b). A stirred solution of (unrecrystallized) **3b** (0.655 g, 1.37 mmol) in THF (40 mL) was treated dropwise with tetrabutylammonium fluoride (1.0 M in THF, 1.4 mL, 1.4 mmol), and stirring was continued overnight. The resulting solution was poured into water, and the mixture was extracted with ether. The ether layer was washed twice with dilute HCl and then with water until the washings were neutral. The washed ether layer was dried (MgSO_4) and filtered, and the volatiles were pumped off from the filtrate to give **4b** as a white air-stable solid (0.48 g, 78%). Mp: 260–262 °C (lit. 276–277 °C). The ^1H NMR spectrum (CDCl_3) agrees with that previously reported.⁴

Partial Cone Conformer of Methylsilyl Calix[4]arene (2b-PC). A stirred solution of **1b** (0.560 g, 1.32 mmol) in toluene (80 mL) was treated dropwise with triethylamine (0.400 g, 3.95 mmol), giving a white precipitate. Trichloromethylsilane (0.203 g, 1.36 mmol) was then added dropwise, and the reaction mixture was stirred for about 24 h. The resulting mixture was filtered, and the volatiles were pumped off from the filtrate. The residue was washed with hexane (3×2 mL) and pumped dry to yield 0.49 g of a white solid. Recrystallization from toluene yielded **2b-PC** as a white, air-stable solid (0.30 g, 50%). Mp: 312–314 °C. Anal. Calcd for $\text{C}_{29}\text{H}_{24}\text{O}_4\text{Si}$: C, 74.97; H, 5.21. Found: C, 75.48; H, 5.51. ^1H NMR (C_6D_6): δ -0.29 (s, 3 H), 3.33 (d, $^2J_{\text{HH}} = 14$ Hz, 2 H), 3.51 (d, $^2J_{\text{HH}} = 16$ Hz, 2 H), 3.92 (d, $^2J_{\text{HH}} = 16$ Hz, 2 H), 4.21 (s, 1 H, OH), 4.59 (d, $^2J_{\text{HH}} = 14$ Hz, 2 H), 6.69–7.03 (12 H total).

Cone Conformer of Methylsilyl Calix[4]arene (2b-C). A stirred solution of **1b** (0.500 g, 1.32 mmol) in benzene (50 mL) was treated dropwise with tris(dimethylamino)methylsilane (0.620 g, 3.54 mmol). The reaction mixture was stirred for 3 h and then refluxed overnight under a sweep of nitrogen to help remove the generated dimethylamine. The volatiles were then pumped off. ^1H NMR analysis of this crude product showed the presence of both **2b-PC** and **2b-C** in an approximate 60:40 ratio. However, other impurities were also observed in the mixture. The crude product was then dissolved in toluene, and the mixture was filtered. Crystallization of the filtrate led this time to **2b-C** as a white, air-stable compound (0.25 g, 45%). Mp: 317–319 °C. Anal. Calcd for $\text{C}_{29}\text{H}_{24}\text{O}_4\text{Si}$: C, 74.97; H, 5.21. Found: C, 74.82; H, 5.26. ^1H NMR (C_6D_6): δ 0.72 (s, 3 H), 3.21 (d, $^2J_{\text{HH}} = 14$ Hz, 4 H), 4.11 (d, $^2J_{\text{HH}} = 14$ Hz, 2 H), 4.56 (d, $^2J_{\text{HH}} = 14$ Hz, 2 H), 4.77 (s, 1 H, OH), 4.59 (d, $^2J_{\text{HH}} = 14$ Hz, 2 H), 6.13–6.99 (12 H total).

Heating of 2b in the Solid State. In a nitrogen-filled tube, a sample of **2b-PC** and **2b-C** in an approximate 2:1 ratio was heated at 200 °C in an oil bath for 1 h. An ^1H NMR spectrum of this sample showed no change. Heating another sample of this isomer mixture at 230 °C for 1 h showed greater than 95% conversion to **2b-C**.

Heating of the Methylsilyl *p*-tert-Butylcalix[4]arene Partial Cone Conformer (2a-PC) in the Solid State. In a nitrogen-filled tube, a sample of **2a-PC** was heated at 280 °C in an oil bath for 3 h. An ^1H NMR spectrum of this sample showed no change. Heating another sample of this isomer mixture at 310 °C for 1.5 h showed some conversion to the cone conformer but also substantial decomposition.

Five-Coordinate Methylsilyl *p*-tert-Butylcalix[4]arene (8a). A stirred slurry of **2a** (0.475 g, 0.690 mmol) in toluene (10 mL) was treated dropwise with butyllithium (430 μL , 0.690 mmol), and the reaction mixture was stirred overnight. The precipitate was collected by filtration, washed with hexane (3×2 mL), and pumped dry to yield a white solid (0.350 g, 73%). Analytically pure samples were obtained by recrystallization from toluene. Mp: 230 °C dec. Anal. Calcd for $\text{C}_{45}\text{H}_{55}\text{O}_4\text{SiLi}\cdot\text{C}_7\text{H}_8$: C, 79.36; H, 8.07. Found: C, 78.92; H, 8.22. ^1H NMR ($\text{THF}-d_8$): δ 0.66 (s, 3 H, SiMe), 1.20 (s, 36 H, *t*-Bu), 3.13 (d, $^2J_{\text{HH}} = 12$ Hz, 4 H, CH_2), 4.59 (d, $^2J_{\text{HH}} = 12$ Hz, 4 H, CH_2), 6.94 (s, 8 H, aromatic).

Five-Coordinate Methylsilyl Calix[4]arene (8b). A stirred solution of **2b** (isomer mixture, 0.300 g, 0.640 mmol) in toluene (10 mL) was treated dropwise with butyllithium (400 μL , 0.640 mmol), and the reaction mixture was stirred overnight. The precipitate was collected by filtration, washed with hexane (3×2 mL), and pumped dry to yield a white solid (0.25 g, 82%). Mp: 210 °C dec. This sample could not be isolated free of impurities for an accurate elemental analysis. ^1H NMR ($\text{THF}-d_8$): δ 0.76 (s, 3 H, SiMe), 3.16 (d, $^2J_{\text{HH}} = 13$ Hz, 4 H, CH_2), 4.63 (d, $^2J_{\text{HH}} = 13$ Hz, 4 H, CH_2), 6.48 (t, $^3J_{\text{HH}} = 7$ Hz, 4 H, CH), 6.87 (d, $^3J_{\text{HH}} = 7$ Hz, 8 H, CH).

Solvent Study of 8. The initial precipitate of **8a** (from toluene) was dissolved in $\text{THF}-d_8$. This gave rise to the ^1H NMR spectrum reported above (with some minor impurity peaks). The $\text{THF}-d_8$ was then pumped off and the residue dissolved in C_6D_6 . The resulting ^1H NMR spectrum was complex (see Figure 7c). The C_6D_6 was then pumped off and the residue redissolved in $\text{THF}-d_8$. The ^1H NMR spectrum returned to the original (Figure 7d) with a few more impurities present. The experiment was repeated with the following changes: the initial sample of **8a** was the recrystallized product and the solvents were cycled in the order $\text{C}_6\text{D}_6/\text{THF}-d_8/\text{C}_6\text{D}_6$. The initial C_6D_6 -dissolved sample appeared to be **8a-open-PC**. ^1H NMR (C_6D_6): δ -0.60 (s, 3 H), 1.09 (s, 9 H), 1.26 (s, 9 H), 1.31 (s, 18 H), 3.27 (d, $^2J_{\text{HH}} = 15$ Hz, 2 H), 3.50 (d, $^2J_{\text{HH}} = 16$ Hz, 2 H), 4.04 (d, $^2J_{\text{HH}} = 15$ Hz, 2 H), 4.53 (d, $^2J_{\text{HH}} = 16$ Hz, 2 H), 7.01–7.16 (aromatic, overlapping with C_6D_6 and toluene peaks present in sample). Pumping off the C_6D_6 and redissolving the residue in $\text{THF}-d_8$ yielded an ^1H NMR spectrum identical to Figure 7b (or 7d). Pumping off the $\text{THF}-d_8$ and redissolving the residue in C_6D_6 yielded a spectrum identical to Figure 7c. Similar behavior was found for **8b**, except that **8b** was only very slightly soluble in benzene.

***p*-tert-Butylcalix[4]arene Phosphonium Triflate [10a(OTf)].** A stirred slurry of *p*-tert-butylcalix[4]arene phosphite (**7a**) (3.17 g, 4.68 mmol) in toluene (50 mL) was treated with methyl trifluoromethanesulfonate (1.54 g, 9.37 mmol), and the suspension was refluxed for 12 h. The slurry became a clear, dark pink solution after several hours, and then an off-white precipitate appeared. After cooling, the precipitate was isolated by filtration and pumped dry to yield **10a(OTf)** as an off-white powder (3.44 g, 74%). ^1H NMR analysis of this mixture showed it to contain **10a(OTf)-PC** and **10a(OTf)-C** in an approximate 9:1 ratio. Mp: 312–314 °C. Anal. Calcd for $\text{C}_{46}\text{H}_{56}\text{O}_7\text{PSF}_3$: C, 65.70; H, 6.71. Found: C, 64.47; H, 6.62. All carbon analyses for these salts were consistently low. A portion of this product (1.89 g) was boiled in toluene. The hot slurry was filtered, and the insoluble material was isolated by filtration and pumped dry to yield a white powder (1.54 g, 82%). NMR spectra showed it to be a single product, **10a(OTf)-PC**. Anal. Calcd for $\text{C}_{46}\text{H}_{56}\text{O}_7\text{PSF}_3$: C, 65.70; H, 6.71. Found: C, 64.06; H, 6.79. ^1H NMR (CDCl_3): δ 1.27 (s, 9 H), 1.29 (s, 9 H), 1.34 (s, 18 H), 1.54 (d, $^2J_{\text{PH}} = 18$ Hz, 3 H), 3.69 (d, $^2J_{\text{HH}} = 15$ Hz, 2 H), 3.88 (d, $^2J_{\text{HH}} = 17$ Hz, 2 H), 4.38 (d, $^2J_{\text{HH}} = 17$ Hz, 2 H), 4.50 (d, $^2J_{\text{HH}} = 15$ Hz, 2 H), 5.09 (s, 1 H, OH), 7.15, 7.26, 7.28, 7.31 (8 H total). ^{31}P NMR (CDCl_3): δ 39. A small amount of a clear white crystalline substance (0.082 g, 4%) formed in the filtrate overnight. The solvent was decanted, and the crystalline solid was pumped dry. This was also a single product but the other isomer **10a(OTf)-C**. Anal. Calcd for $\text{C}_{46}\text{H}_{56}\text{O}_7\text{PSF}_3$: C, 65.70; H, 6.71. Found: C, 63.47; H, 7.50. ^1H NMR

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Table 1. Crystal Data and X-ray Experimental Details

	2b-PC	11a	3a	3b	10a(I)
formula	C ₂₉ H ₂₄ O ₄ Si	C ₄₅ H ₅₅ O ₄ P·2C ₄ H ₈ O	C ₅₃ H ₆₆ O ₄ Si·C ₇ H ₈	C ₃₀ H ₂₆ O ₄ Si	C ₄₅ H ₅₆ O ₄ P·5CH ₃ I
fw	464.6	835.07	795.2	478.6	1528.4
space group	P1	R $\bar{3}$	P1	C2/c	P2 ₁ /c
<i>a</i> , Å	9.655(1)	44.267(4)	12.756(2)	30.614(6)	13.328(2)
<i>b</i> , Å	11.115(1)	44.267(4)	13.006(3)	9.354(2)	21.560(4)
<i>c</i> , Å	11.345(1)	13.311(1)	15.291(3)	19.691(3)	20.720(4)
α , deg	72.95(1)	90	92.61(2)	90	90
β , deg	73.98(1)	90	103.85(2)	123.80(1)	104.18(1)
γ , deg	87.95(1)	120	112.01(2)	90	90
<i>V</i> , Å ³	1117.5(3)	22 589(3)	2258(1)	4631(3)	5773(2)
<i>Z</i>	2	18	2	8	4
<i>D</i> _{calcd} , mg m ⁻³	1.381	1.11	1.170	1.373	1.759
abs coeff, mm ⁻¹	0.141	0.10	0.097	0.138	0.294
λ , Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
<i>T</i> , K	220	228	220	220	220
<i>R</i> ^a	0.033	0.101	0.052	0.046	0.068
<i>Rw</i> ^b or <i>Rw</i> ^c	0.049 (<i>R_w</i>)	0.256 (<i>R_{w2}</i>) ^d	0.124 (<i>R_{w2}</i>) ^e	0.055 (<i>R_w</i>)	0.164 (<i>R_{w2}</i>) ^f

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + 0.001(F_o)^2]$. ^c $R_{w2} = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $P = (F_o^2 + 2F_c^2)/3$. ^d $w = 1/[\sigma^2(F_o^2) + (0.0180P)^2 + 154P]$. ^e $w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 1.70P]$. ^f $w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 70.3P]$.

(CDCl₃): δ 1.03 (s, 9 H), 1.22 (s, 9 H), 1.33 (s, 18 H), 2.98 (d, ²*J*_{PH} = 17 Hz, 3 H), 3.57 (d, ²*J*_{HH} = 15 Hz, 2 H), 3.67 (d, ²*J*_{HH} = 15 Hz, 2 H), 4.39 (d, ²*J*_{HH} = 15 Hz, 2 H), 4.86 (d, ²*J*_{HH} = 15 Hz, 2 H), 6.82, 7.14, 7.21, 7.31 (8 H total), 8.33 (s, 1 H, OH). ³¹P NMR (CDCl₃): δ 34.

***p*-tert-Butylcalix[4]arene Phosphorane (11a).** A stirred slurry of **10a(OTf)** (0.530 g, 0.630 mmol) in ether (ca. 7 mL) was treated dropwise with butyllithium (1.6 M in hexanes, 394 μ L, 0.630 mmol) via syringe. The solution became clearer and yellowed slightly. Stirring was continued for 12 h. Pumping off the volatiles and recording spectra of the crude product indicated formation of **11a** with only minor impurities present. Analytically pure samples were prepared as follows. The crude reaction mixture was filtered, and the volume of the filtrate was reduced under vacuum. This induced formation of a white powder, which was isolated by filtration and pumped dry to yield 0.140 g (22%) of the product. Mp: 222 °C dec. X-ray-quality crystals of this sample were grown by slow cooling of a hot THF solution, yielding a sample containing two molecules of THF for each molecule of **11a**. ¹H NMR (CDCl₃): δ 1.27 (s, 36 H), 1.83 (m, 8 H, THF), 2.28 (d, ²*J*_{PH} = 17 Hz, 3 H), 3.43 (d, ²*J*_{HH} = 14 Hz, 4 H), 3.73 (m, 8 H, THF), 4.50 (d, ²*J*_{HH} = 14 Hz, ⁵*J*_{PH} = 2 Hz, 3 H), 7.10 (s, 8 H). ³¹P NMR (CDCl₃): δ -33. The crystals were then pumped dry to remove the THF. Anal. Calcd for C₄₅H₅₅O₄P: C, 78.23; H, 8.02. Found: C, 77.74; H, 8.54.

Heating of 10a(OTf) in Solution. Attempts to obtain reliable information on the heating of **10a(OTf)-PC** in solution were hindered by its poor solubility in some solvents (benzene and toluene) and decomposition in others (hot chloroform and THF). A solution of **10a(OTf)-C** in CDCl₃ was heated overnight at 82 °C. No change was observed in its ¹H NMR spectrum.

***p*-tert-Butylcalix[4]arene Phosphonium Iodide [10a(I)].** A mixture of **7a** (0.200 g, 0.295 mmol) and iodomethane (1 mL) was heated in a sealed tube in an oil bath at 115 °C for 6 h. The tube was left in the dark for 5 d, during which crystals formed. One of these crystals was selected for the X-ray analysis reported below. The remainder of the crystals were then collected by filtration, pumped dry, and dissolved in less than 1 mL of hot chloroform. Hexane was slowly added to induce crystallization, yielding **10a(I)** as a white solid (0.160 g, 60%). Mp: 199–201 °C (melts to a red liquid). ¹H NMR (CDCl₃): δ 1.28 (s, 9 H), 1.29 (s, 9 H), 1.35 (s, 18 H), 1.73 (d, ²*J*_{PH} = 18 Hz, 3 H), 3.70 (d, ²*J*_{HH} = 15 Hz, 2 H), 3.88 (d, ²*J*_{HH} = 17 Hz, 2 H), 4.46 (d, ²*J*_{HH} = 17 Hz, 2 H), 4.62 (d, ²*J*_{HH} = 15 Hz, 2 H), 5.03 (s, 1 H, OH), 7.15, 7.26, 7.28, 7.33 (8 H total). ³¹P NMR (CDCl₃): δ 40. As with the triflate salt, accurate elemental analyses could not be obtained for this compound.

NMR Kinetics Studies. A sample of **2a-PC** (44.6 mg, 64.7 mmol) was dissolved in 1,2-dichlorobenzene in a 5 mL volumetric flask. One drop of toluene was added as an internal integration standard and the solution diluted to volume. Very gentle heating was necessary for complete dissolution. This solution (0.0129 M) was syringed into 4

mm nitrogen-filled tubes which were then flame-sealed. An identical procedure was used to prepare samples of 0.0341 M **2b-C**. These samples were heated at 110, 120, 130, 140, and 150 °C at various intervals to follow the kinetics. ¹H NMR spectra were recorded by inserting each sealed tube into a 5 mm NMR tube containing a small amount of D₂O as a lock solvent. Changes were monitored by integration of the Si–Me resonances for the partial cone and cone conformers. For consistency, both the R = H and R = *tert*-butyl derivatives are considered as cone \rightleftharpoons partial cone equilibria, although the reaction actually measured for R = *tert*-butyl is the reverse. For plots of ln(*x*_c - *x*) vs *t*, points were plotted for about 15–90% of complete reaction. The precision of the data obtained for **2b** is significantly better than that for **2a**; this is not surprising, considering the limited solubility of **2a**.

X-ray Structure Determinations and Refinements. Crystals of **2b-PC**, **11a**, **3a**, and **3b** are colorless, while those of **10a(I)** are orange. All diffraction data were collected on a Bruker P3 diffractometer, except data for **11a**, which was collected on a P4 diffractometer. The crystals used in the experiments were coated with mineral oil under a low-temperature nitrogen stream. Pertinent crystallographic data and the conditions for the data collections are summarized in Table 1. Final unit cell parameters were obtained by least-squares fits of the angles of 24–30 accurately centered reflections in the range 15° < 2 θ < 30°. Three standard reflections monitored after every 150 reflections did not show any significant change in intensity during the data collection. The data were corrected for Lorentz and polarization effects. ψ -Scan absorption studies were carried out on structure **10a(I)** with *T*_{min} and *T*_{max} of 0.729 and 0.978, respectively. No absorption corrections were applied to the other structures. The structure of **10a(I)** was solved by heavy-atom methods, while the other structures were solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL-Plus package.⁵ Full-matrix least-squares refinements were performed. Scattering factors, as well as anomalous-dispersion corrections for heavy atoms, were taken from literature sources.⁶ Structures **2b-PC** and **3b** were refined on the basis of *F*, while structures **3a**, **10a(I)**, and **11a** were refined on the basis of *F*² (SHELXL-93).⁷ In structure **2b-PC**, the methyl hydrogen atoms of C(1) were located on a riding model while the other hydrogen atoms were located in difference Fourier maps and were isotropically refined sharing a common thermal parameter (*U* = 0.038 Å²). Solvated toluene molecules were found in the crystal lattice of **3a**, and THF was found in that of **11a**. In the structure of **10a(I)**, the iodine ion, I(1), is discretely located with the contact distance I(1)···O(1) = 3.432(8) Å. There are five indepen-

(5) Sheldrick, G. M. *SHELXTL-Plus*; Siemens Analytical X-ray Instruments: Madison, WI, 1990.

(6) *International Tables for X-ray Crystallography*; Kynock Press: Birmingham, U.K., 1974; Vol. IV.

(7) Sheldrick, G. M. *SHELXL-93: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

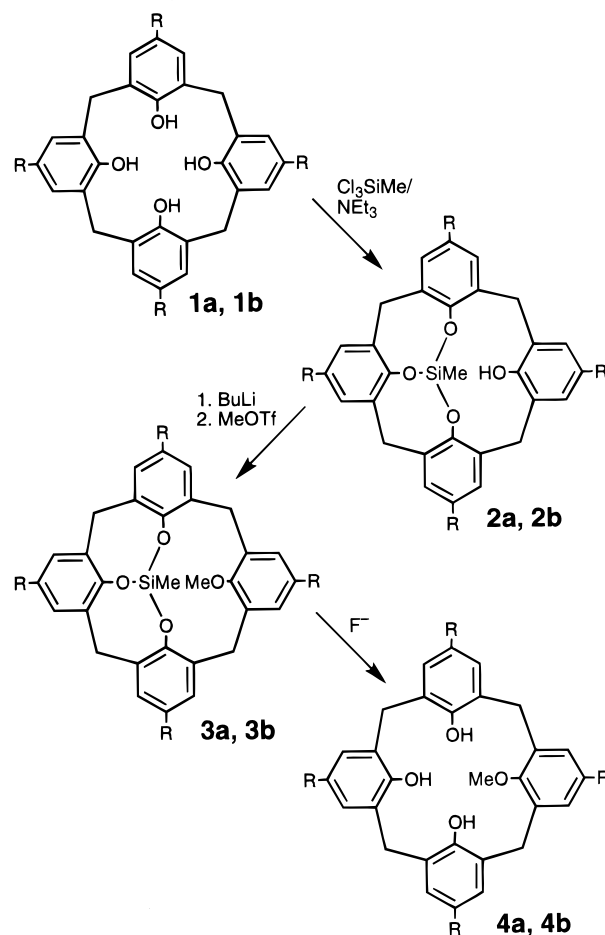
Table 2. Interatomic Distances (Å) and Angles (deg)

	2b-PC	11a	3a	3b	10a(I)
E—O(1)		1.717(6)			
E—O(2)	1.636(1)	1.609(6)	1.623(2)	1.621(4)	1.537(8)
E—O(3)	1.643(1)	1.730(6)	1.631(2)	1.627(7)	1.559(8)
E—O(4)	1.636(1)	1.611(5)	1.618(2)	1.604(5)	1.545(8)
E—C(1)	1.824(2)	1.779(8)	1.816(3)	1.809(10)	1.742(12)
C(1) - - C(11)	4.252(3)		4.168(4)	4.10(1)	3.97(2)
C(1) - - C(12)	4.075(3)		3.967(4)	3.98(1)	3.97(2)
C(1) - - C(13)	3.780(3)		3.765(4)	3.74(1)	3.77(2)
C(1) - - C(14)	3.648(3)		3.777(4)	3.66(2)	3.59(2)
C(1) - - C(15)	3.759(3)		3.852(4)	3.75(2)	3.50(2)
C(1) - - C(16)	4.057(3)		4.051(4)	3.99(1)	3.68(2)
O(1)—E—O(2)		91.6(3)			
O(1)—E—O(3)		177.0(3)			
O(1)—E—O(4)		90.8(3)			
O(2)—E—O(3)	108.3(1)	90.2(3)	107.48(10)	107.2(3)	108.8(4)
O(2)—E—O(4)	108.8(1)	121.8(3)	110.41(10)	109.4(3)	109.3(4)
O(3)—E—O(4)	107.7(1)	90.3(3)	107.07(11)	110.0(3)	110.2(4)
O(1)—E—C(1)		89.3(4)			
O(2)—E—C(1)	108.3(1)	114.9(4)	113.43(13)	114.2(4)	114.4(5)
O(3)—E—C(1)	108.5(1)	87.8(4)	110.67(13)	109.0(4)	106.7(5)
O(4)—E—C(1)	115.0(1)	123.3(4)	107.61(13)	107.1(3)	107.4(5)
E—O(1)—C(11)		121.2(5)			
E—O(2)—C(21)	138.5(1)	139.9(5)	137.7(2)	139.0(5)	129.3(7)
E—O(3)—C(31)	116.3(1)	121.9(5)	115.7(2)	114.6(5)	117.8(7)
E—O(4)—C(41)	138.6(1)	126.8(5)	137.4(2)	141.5(5)	135.3(7)

dent MeI molecules crystallized in the lattice. Among the five MeI's, three are disordered; e.g., the site occupancy of I(4) is 72%, while that of I(4') is 28%. In the structure of **11a**, the methyl groups of three *tert*-butyls and the two solvated THF's are disordered. C(18), C(19), and C(20) each have 61% occupancy, while C(181), C(191), and C(201) each have 39%. Similar occupancies are found for C(28) and C(281), etc. The above-mentioned disordered moieties were all elastically constrained during the final stages of refinement. Hydrogen atoms of **3a**, **3b**, and **11a** were all located on a riding model. The final values of *R* and weighted *R* (*R_w* or *R_{w2}*) are listed in Table 1, while selected interatomic distances and angles are given in Table 2. Complete crystallographic data are supplied in the Supporting Information, including X-ray data for **2b-C** showing disorder at the silicon.

Results

We previously reported⁸ isolation of a monoalkylated *p-tert*-butylcalix[4]arene via the reaction sequence shown in Scheme 1 (*R* = *tert*-butyl). We now find that similar products are formed with the *R* = H analogue **1b**. (Throughout this paper, the designations **a** and **b** refer to *tert*-butyl and hydrogen substituents, respectively, at the para positions of the calix[4]arene phenolic groups.) The yield of the final monomethylated calix[4]arene **4b** is 50–60%, based on **1b**. However, there is one significant difference in the overall schemes between the *tert*-butyl and non-*tert*-butyl derivatives, and it is in the first silylation step: **2a** appears to be a single conformer (the partial cone **2a-PC**), whereas **2b** is formed as a mixture of both the partial cone **2b-PC** and cone **2b-C** conformers.⁹ The conformational formulations of these products are consistent with their ¹H NMR spectra, in each of which the diastereotopic protons on the methylene groups give rise to four doublets of equal intensity. In addition, a singlet is observed for the hydroxyl proton in each spectrum. However, the methyl group on the silicon appears at vastly different chemical shifts for **2b-PC** and **2b-**

Scheme 1^a

^a **a**: *R* = *t*-Bu. **b**: *R* = H.

(8) Shang, S.; Khasnis, D. V.; Burton, J. M.; Santini, C. J.; Fan, M.; Small, A. C.; Lattman, M. *Organometallics* **1994**, *13*, 5157.

(9) These notations refer to calix[4]arene conformations with all four hydroxyls pointing in the same direction (cone) and three pointing in one direction with the fourth flipped (partial cone). See: (a) Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, U.K., 1998. (b) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, U.K., 1989.

C: -0.29 and 0.72 ppm, respectively. Such a difference was observed previously,^{1c} and the more upfield signal was attributed to the shielding of the methyl group when found "above" an aromatic ring.

We confirmed the conformations of these derivatives by X-ray crystallography. In **2b-PC** (Table 2 and Figure 1), C(1) does

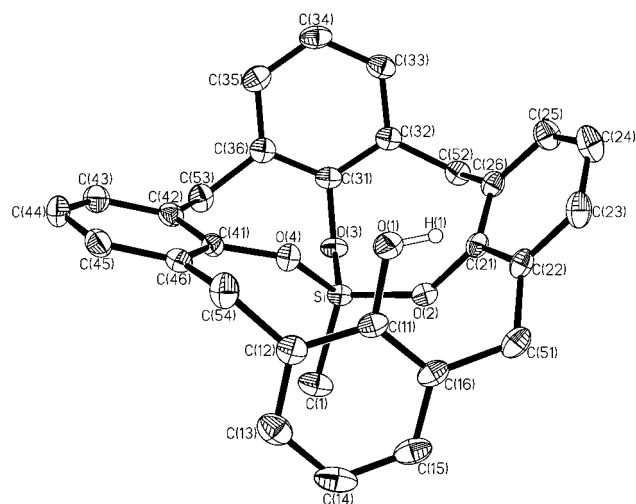
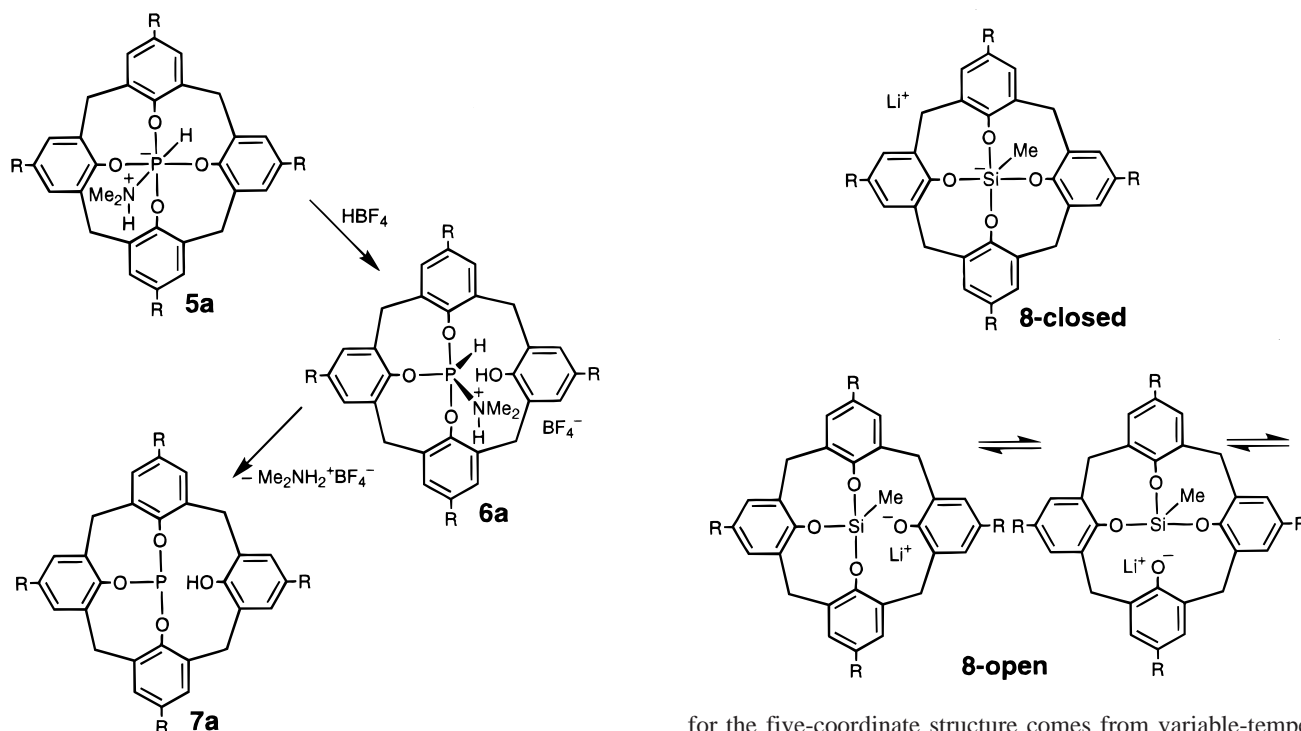


Figure 1. Molecular structure and atom-numbering scheme for **2b-PC**. Thermal ellipsoids correspond to 40% probability.

Scheme 2^a



^a R = *t*-Bu.

lie above the phenolic ring, but not directly above the ring centroid: the nonbonded C(1) to C(13), C(14), and C(15) distances range from 3.65 to 3.78 Å, while the C(1) to C(11), C(12), and C(16) distances range from 4.06 to 4.25 Å. The geometry about silicon in **2b-PC** is distorted tetrahedral with all of the angles around silicon between 108 and 109°, except for the O(4)–Si–C(1) angle, which is 115°. This larger angle is likely the result of the “upward twist” of O(4) relative to O(2) and O(3).¹⁰ The Si–O bond lengths are normal and comparable to those of other calixarene structures,¹¹ while the Si–C (1.82 Å) bond length is on the short end of normal Si–C bond lengths. The X-ray data for **2b-C** show disorder at the

silicon, and little will be said of its structure other than that the phenolic ring is flipped relative to that in **2b-PC**. Data for **2b-C** can be found in the Supporting Information.

A cone conformation for **2b-C**, with all four oxygens on the same “side” as the silicon, suggests that the calix[4]arene might be able to stabilize a five-coordinate silicon atom. A five-coordinate phosphorus was previously reported for **6a** (Scheme 2);^{1c} however, **6a** was observed only as an intermediate by NMR spectroscopy. It is possible that deprotonation of **2** might lead to a species in which all four oxygens are bound to an anionic five-coordinate silicon. We isolated the lithium salt of **2a** (Scheme 1, product after addition of butyllithium but before addition of methyl trifluoromethanesulfonate). The ¹H NMR spectrum of this product in THF-*d*₈ shows a singlet for the *tert*-butyl groups and two doublets for the methylene groups. Similarly, two doublets are observed for the methylene groups in the R = H analogue. Significantly, the latter salt appears to be a single species even though the precursor **2b** is a mixture of isomers. These spectra can be interpreted in terms of either a five-coordinate silicon anion, **8-closed**, or a four-coordinate anion, **8-open**, with rapidly exchanging Si–O bonds. Evidence

for the five-coordinate structure comes from variable-temperature ¹H NMR spectroscopy, which shows only two signals in the methylene region down to –100 °C, although the “doublets” are quite broad at this temperature (see Figure 2 for the spectra of **8b**). There is certainly no indication of four doublets as would be expected for **8-open**. As further evidence for the **8-closed** structure, we examined the ²⁹Si NMR spectra of the silylated calix[4]arenes; these data are shown in Table 3. The chemical shifts for **2** are in an expected region (i.e., close to the signals of the related triphenoxydimethylsilane). After deprotonation, the chemical shifts move upfield. Such a change is expected for increased coordination at silicon; for example, the ²⁹Si NMR chemical shift for five-coordinate silatrane **9** is upfield of the four-coordinate triethoxydimethylsilane. Taken together, these data strongly suggest a five-coordinate silicon.

(10) This twist places the geometry of the calix[4]arene backbone somewhere between the partial cone and the 1,2-alternate conformations. For simplicity, we ignore this twist when referring to the conformation.

(11) (a) Delaigue, X.; Hosseini, M. W.; Graff, R.; Kintzinger, J.-P.; Raya, J. *Tetrahedron Lett.* **1994**, 35, 1711. (b) Delaigue, X.; Hosseini, M. W.; De Cian, A.; Fischer, J.; Leize, E.; Kieffer, S.; Van Dorsselear, A. *Tetrahedron Lett.* **1994**, 34, 3285.

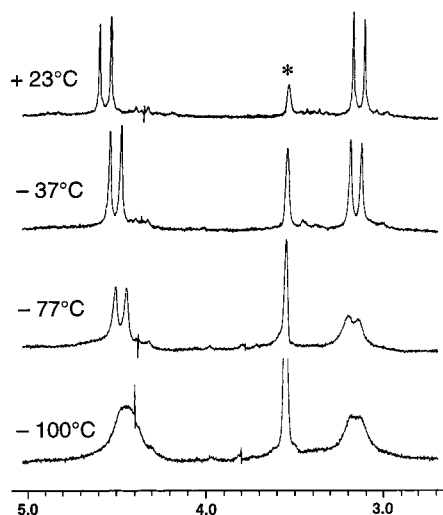
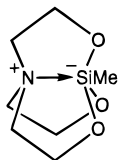


Figure 2. Variable-temperature ^1H NMR spectra of **8b** in the methylene region. * = $\text{THF-}d_8$ signal.

Table 3. ^{29}Si NMR Chemical Shift Data^a

compd	chem shift	compd	chem shift	compd	chem shift
2a-PC ^b	-50	(PhO) ₃ SiMe ^c	-54	(EtO) ₃ SiMe ^d	-45
2b-PC ^b	-50	8a ^b	-93	9 ^d	-65
2b-C ^b	-59	8b ^b	-84		

^a In ppm, relative to tetramethylsilane. ^b In THF/THF- d_8 solution. ^c Data from: Schraml, J.; Chvalovsky, V.; Magi, M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1981**, *46*, 377. ^d Data from: Harris, R. K.; Jones, J.; Ng, S. *J. Magn. Reson.* **1978**, *30*, 521. The structure of **9** is as follows:



We were unable to obtain an X-ray structure of either **8a** or **8b**. In an effort to shed further light on the structure of **8**, we attempted to synthesize the isoelectronic five-coordinate phosphorane. This work was done exclusively with R = *tert*-butyl. Methylation of **7a** with excess trifluoromethanesulfonate in refluxing toluene leads to the phosphonium salt **10a(OTf)** (Scheme 3). This compound forms primarily in the partial cone conformation with only a small amount of the cone conformation (about 10%). Treatment of **10a(OTf)** with butyllithium does, in fact, give the phosphorane **11a**. The ^1H NMR spectrum shows one singlet for the *tert*-butyl groups, two doublets for the methylene groups (one of which shows a small $^5J_{\text{PH}}$ value of 2 Hz), and a doublet for the phosphorus-bound methyl group. The ^{31}P resonance at -33 ppm is typical for five-coordinate phosphorus. We were able to structurally characterize this compound (Figure 3 and Table 2). The phosphorus is in a slightly distorted trigonal bipyramidal (tbp) geometry with O(1) and O(3) at the axial positions and O(2), O(4), and C(1) at the equatorial sites.

Discussion

Structures. In addition to the structures mentioned in the previous section, we obtained the X-ray structures of the methyl ethers **3a** and **3b**. While we were unable to obtain X-ray-quality crystals of the phosphonium triflate salt **10a(OTf)**, we were able to do so for the analogous iodide salt **10a(I)**, whose structure

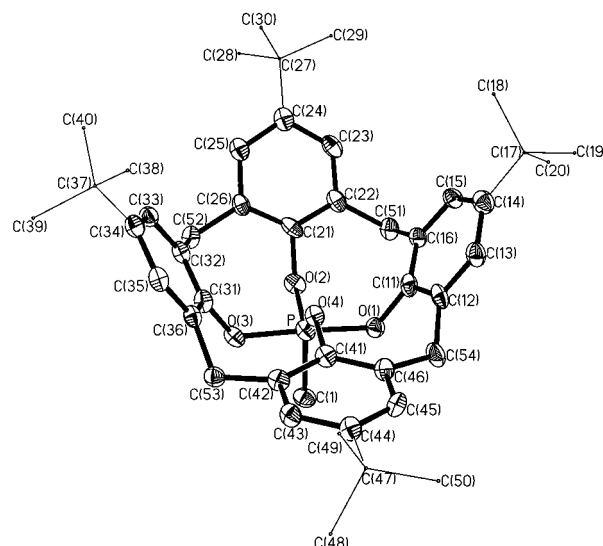
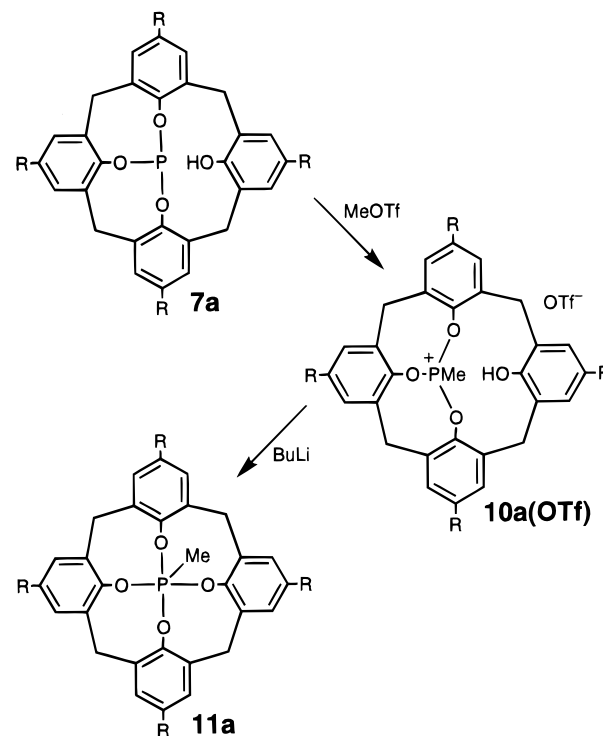


Figure 3. Molecular structure and atom-numbering scheme for **11a**. Thermal ellipsoids correspond to 40% probability.

Scheme 3^a



^a a: R = *t*-Bu.

we describe herein. These structures are illustrated in Figures 4–6, and selected distances and angles are listed in Table 2. The five structures obtained in this study provide data to (1) explain the relationship between four- and five-coordinate geometries in these calix[4]arenes, (2) compare isoelectronic Si and P structures, and (3) probe the effect of substitution. We will discuss these points in reverse order.

Changing the para R substituent should have a minimal effect on the overall structure of calixarenes, and this is borne out in **3a** and **3b**. Bond distances and angles vary by no more than 0.02 Å and 3°, respectively. Nonbonded distances show greater variations with the larger distances, for the most part, in the R = *tert*-butyl molecule. These molecules show the same upward twist of one of the Si–O bonds as was found in **2b-PC**. In fact, this is a common structural feature in all of the four-

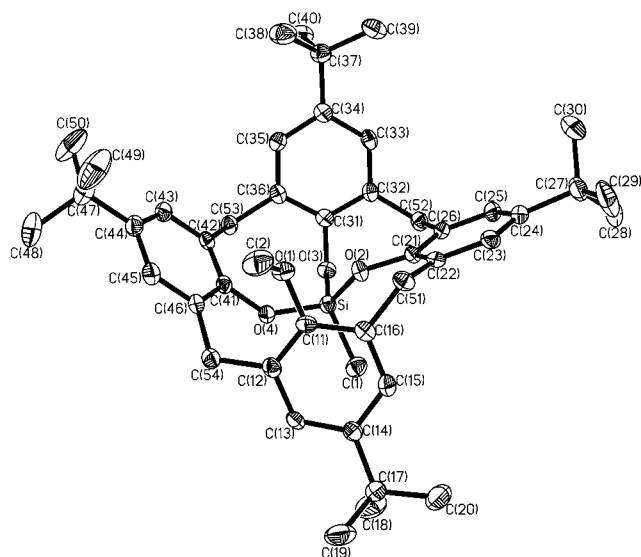


Figure 4. Molecular structure and atom-numbering scheme for **3a**. Thermal ellipsoids correspond to 40% probability.

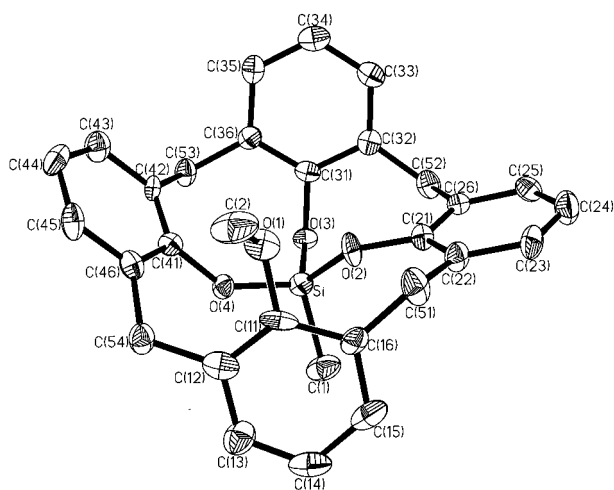


Figure 5. Molecular structure and atom-numbering scheme for **3b**. Thermal ellipsoids correspond to 40% probability.

coordinate derivatives: either the E–O(2) or E–O(4) bond shows this twist. The asymmetry is only observed in the solid state, since NMR spectra support a C_3 structure. This implies a rapid exchange of O(2) and O(4) in solution, and such a phenomenon was observed previously in similar molecules.^{1c} Comparison of the methoxy and hydroxy derivatives lacking *tert*-butyl groups, **3b** and **2b-PC**, again reveals only small differences, keeping in mind that the Si–O(2) bond shows the twist in **3b** and the Si–O(4) bond has this feature in **2b-PC**.

The phosphonium cation in **10a(I)** is isoelectronic with **2b-PC**, except for the presence of *tert*-butyl groups. It also adopts the partial cone conformation. Immediately obvious is that all the interatomic distances, both bonded and nonbonded, are smaller in the phosphonium salt. These bond distances are typical for phosphonium cations.¹² However, the same key features are present here as are observed for the silicon analogues: C(1) lies above the aromatic plane of the phenolic group, the P–O(2) bond shows the upward twist, and the P–O(2)–C(21) bond angle is larger than the other two P–O–C angles. The effect of the shielding of the aromatic ring on the *P*-methyl resonance is also similar: it is at 2.98 ppm for **10a-**

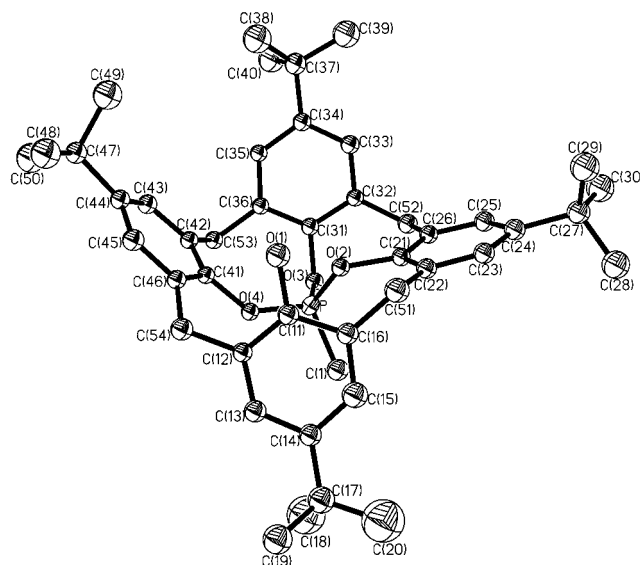


Figure 6. Molecular structure and atom-numbering scheme for the cation of **10a(I)**. Thermal ellipsoid (for P only) corresponds to 40% probability.

(OTf)-C and moves about 1.5 ppm upfield for the partial cone conformers [**10a(OTf)-C** and **10a(I)**].

Turning to the pentacoordinate phosphorane **11a**, the geometry about phosphorus is only slightly distorted from a trigonal bipyramid: the O(1)–P–O(3) angle is 177.0(3)°, all of the axial/equatorial bonds are within 2° of 90°, and the sum of the three equatorial angles is 360.0(6)°. As is common, the axial P–O bonds are longer than the equatorial ones. Even in this structure, one of the P–O bonds [P–O(4)] has the upward twist. It is interesting to postulate how **11a** is formed from **10a**. For example, after deprotonation of **10a**, P–O(2) might twist down and the phenoxy group simply rotate to form the fourth P–O bond. Alternatively, the phenoxy group might flip and then form the fourth P–O bond. The difference between these two pathways is that O(1) and O(3) in **10a** become equatorial in **11a** via the former route, whereas they end up in axial positions via the latter. Finally, as was found for the other structurally characterized species, the asymmetry created by the P–O twist is not observed in the ¹H NMR spectrum, since only one resonance is found for the *tert*-butyl groups. In this case, all of the P–O bonds are exchanging.

Conformational Isomerism. The fact that treating a mixture of **2b-PC** and **2b-C** with butyllithium led to a single species was our first indication that conformers can be interconverted in these derivatives. Moreover, the methyl ether derivative **3b** is formed exclusively in the partial cone conformation, although it is synthesized from this same conformer mixture (see the Experimental Section). We were able to isolate the cone and partial cone isomers of **2b**. The partial cone isomer is best isolated by crystallization of the filtered reaction mixture in Scheme 1. However, the pure cone isomer cannot be isolated from this mixture. If **2b** is synthesized using tris(dimethylamino)methylsilane instead of trichloromethylsilane, crystallization of this reaction mixture can give the cone isomer in reasonable yields (see the Experimental Section). Although this was the method used to originally isolate and structurally characterize **2b-C**, it is not the most reliable. Species **2b** undergoes an irreversible phase change in the solid state from the partial cone to the cone isomer. Heating a sample containing both isomers at 230 °C (mp > 300 °C) for 1 h yields a product that is greater than 95% **2b-C**. While this is an excellent method for isolation

Table 4. Kinetic and Thermodynamic Data for the Reaction **2-C** \rightleftharpoons **2-PC**

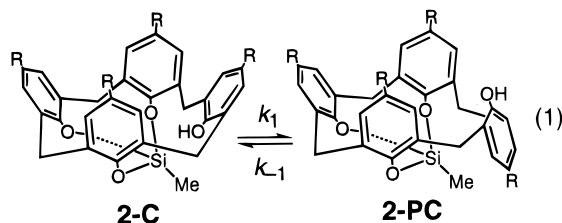
compd	K^a	T, K	k_1	k_{-1}
2a	1.69	383	0.00109	0.000646
	1.69	393	0.00388	0.00229
	1.80	403	0.00928	0.00516
	1.80	413	0.0216	0.0120
	1.74	422	0.0477	0.0274
2b	0.680	383	0.00115	0.00170
	0.705	393	0.00278	0.00395
	0.749	403	0.00645	0.00862
	0.758	413	0.0177	0.0233
	0.791	423	0.0353	0.0446

Derived Thermodynamic Quantities (kJ/mol)^b**2a:** $E_a = 128(5)$; $\Delta H = 2(7)$ **2b:** $E_a = 117(3)$; $\Delta H = 5(4)$

^a Equilibrium constants obtained by NMR integration. The values of K obtained for **2a** indicate the use of two significant figures. ^b Standard deviations in parentheses.

of the cone isomer for the non-*tert*-butyl derivative, it does not apply to the *tert*-butyl analogue. For **2a**, no change is observed for samples heated to 280 °C. Above this temperature, some conversion to the cone isomer is observed, but there is also some melting and decomposition. This is not surprising, since the presence of the *tert*-butyl groups should severely limit the ability of the phenolic group to rotate in the solid state.

NMR spectra of solutions of **2a**, **2b-PC**, and **2b-C** are unchanged after several hours at ambient temperature. However, at elevated temperatures in solution, conformer interconversion is observed. We studied this interconversion for both the R = *tert*-butyl and H species (eq 1) by ¹H NMR spectroscopy.



Temperatures above 100 °C were needed for the isomerization to proceed at reasonable rates. We selected 1,2-dichlorobenzene as the solvent because of its high boiling point and clear spectral window in the aliphatic region.

For the reversible, unimolecular reaction $A \rightleftharpoons B$, the integrated rate law is given by¹³ eq 2, where x_e is the equilibrium

$$\ln(x_e - x) = -(k_1 + k_{-1})t + \ln x_e \quad (2)$$

concentration of B, x is the concentration of B at time t , and k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively. Thus, a plot of $\ln(x_e - x)$ vs t is linear and has a slope equal to $-(k_1 + k_{-1})$. Since the equilibrium constant is known independently from the NMR integrals, the individual rate constants can be determined from the above slope and

$$K = k_1/k_{-1} \quad (3)$$

Kinetics experiments were run at five temperatures from 110 to 150 °C to obtain both rate and thermodynamic data for the cone \rightleftharpoons partial cone reaction. Representative plots (for R = H) of concentration change vs time, $\ln(x_e - x)$ vs t , and Arrhenius data are found in the Supporting Information. Table 4 sum-

marizes the various kinetic and thermodynamic data. It is clear from these data that K is close to unity and the two conformers do not differ materially in energy. For R = *tert*-butyl, these experiments were the first to show that **2a** can exist as both conformers, **2a-C** and **2a-PC**. The activation energy for isomer interconversion of about 120 kJ/mol is approximately twice the inversion barrier for **1a** and **1b**,⁹ which is not surprising, considering that a calix[4]arene with four free hydroxyl groups should be much more flexible than one in which three oxygens are tied to a single atom. We attempted a similar study with the phosphonium compound **10a(OTf)**. Heating **10a(OTf)-PC** in chloroform or THF led to decomposition. However, heating **10a(OTf)-C** in deuteriochloroform at 82 °C overnight showed no change in the NMR spectrum. While this temperature is about 20 °C lower than the lowest temperature used for the silyl studies, there should have been at least some change observed for comparable barriers. Either the activation energy for interconversion is significantly higher in **10a**, or the equilibrium is shifted toward the cone. The latter is highly unlikely, since the cone is the minor component in the original mixture. The higher activation energy may be the result of the shorter average P–O distances in **10a** compared to the Si–O distances in **2a-PC** or, perhaps, of ion pairing which restricts the ability of the phenolic group to rotate.

Variable Coordination. The isomerism described above is not the only change observed in solution. The structure of the lithium salt appears to be variable, depending on the solvent. This is best illustrated by following the appearance of the methylene region in the ¹H NMR spectra for the *tert*-butyl derivative shown in Figure 7. The top spectrum is that of **2a-PC** in C₆D₆ before lithiation. Treatment of **2a** with butyllithium in toluene yields a precipitate. Dissolving this precipitate in THF-*d*₈ leads to the ¹H NMR spectrum reported in the Experimental Section (Figure 7b). However, if the solvent is pumped off of this sample and the residue dissolved in C₆D₆, the spectrum in Figure 7c is observed. Pumping off the C₆D₆ and dissolving the residue in THF-*d*₈ yield the original spectrum (Figure 7d). If the solvent-cycling experiment starts with C₆D₆ instead of THF-*d*₈, the initial spectrum appears to be that of deprotonated **2a** in the partial cone conformation **8a-PC** (see the Experimental Section): three singlets are observed in the *tert*-butyl region in a 2:1:1 ratio, four doublets are observed in the methylene region, and a singlet is observed for the SiMe group at –0.60 ppm. Additionally, the ²⁹Si NMR chemical shift for this derivative (in benzene) is at –44 ppm, close to those for the other four-coordinate compounds (Table 3). However, after pumping off the C₆D₆ and dissolving the residue in THF-*d*₈, a spectrum similar to Figure 7b is observed. Finally, pumping

(13) Moore, John W.; Pearson, Ralph G. *Kinetics and Mechanism*, 3rd ed.; John Wiley & Sons: New York, 1981; p 304.

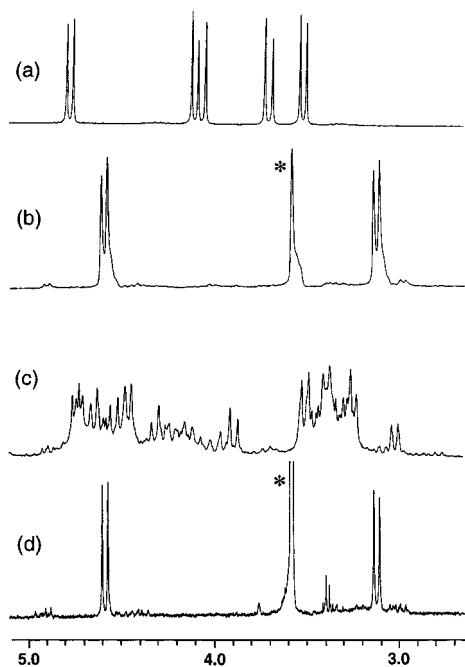


Figure 7. ^1H NMR spectra of **8a** in the methylene region illustrating solvent-dependent behavior: (a) **2a-PC** in C_6D_6 ; (b) **8a** initial precipitate dissolved in $\text{THF-}d_8$; (c) sample from (b) after removal of $\text{THF-}d_8$ and dissolution in C_6D_6 ; (d) sample from (c) after removal of C_6D_6 and dissolution in $\text{THF-}d_8$. * = $\text{THF-}d_8$ signal.

off the $\text{THF-}d_8$ and dissolving the residue in C_6D_6 yield a spectrum similar to Figure 7c.

It appears likely that the initial precipitate is **8a-open-PC**. The reaction in toluene simply deprotonates **2a-PC** with no change in conformation. However, in THF, the compound clearly contains a five-coordinate silicon. This geometry change must be due to the oxophilicity of the lithium cation. In benzene, the only oxygen source is the calixarene, and the lithium binds

to the phenoxy oxygen, preventing formation of the five-coordinate geometry. In THF, the solvent provides the oxygen source for the lithium, freeing the phenoxy oxygen to bind to the silicon. Removal of THF and again dissolution in benzene must then result in cleavage of a Si–O bond; however, this time, a mixture of products, most likely oligomeric, is formed. This process is reversible, and once again, removal of benzene and addition of THF re-form the pentacoordinate silicon.

Summary

Monomethylation of calix[4]arene (**1b**) via the use of an SiMe protecting group has been demonstrated. Moreover, the cone and partial cone isomers of **2b** have been isolated, and the barrier to their interconversion has been measured, yielding the energetics of flipping one phenol group through the annulus of a calix[4]arene when the other three oxygens are tied to a single atom. Stable five-coordinate silicon and phosphorus derivatives have been obtained, with the former showing solvent-dependent coordination at the silicon. Structural data allow comparison between isoelectronic silicon and phosphorus geometries as well as explain the relationship between four- and five-coordinate structures.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **2b-C**, **11a**, **3a**, and **10a(I)**, listings of X-ray experimental details, atomic coordinates, thermal parameters, and bond distances and angles for **2b-PC** and **3b**, and representative plots of concentration change vs time, $\ln(x_e - x)$ vs t , and Arrhenius data for **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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