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Reaction of *p*-*tert*-Butylcalix[4]arene with Dichlorodimethylsilane and Subsequent Alkylation. A Disproportionation Reaction?

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Treatment of *p*-*tert*-butylcalix[4]arene with dichlorodimethylsilane yields a single product, *p*-*tert*-butylcalix[4]arene$SiMe_2(OH)_2$ (**4**), in which one dimethylsilyl group bridges adjacent oxygens. Subsequent treatment of **4** with butyllithium and methyl trifluoromethanesulfonate yields two products, *p*-*tert*-butylcalix[4]arene$(SiMe_2)_2$ (**5**) and a lithium triflate complex of *p*-*tert*-butylcalix[4]arene$(OMe)_4$, **6**·LiO_3SCF_3. No evidence is found for the expected product *p*-*tert*-butylcalix[4]arene$SiMe_2(OMe)_2$ (**7**). This can be viewed as a formal disproportionation reaction of **7**, although the mechanism of the formation of **5** and **6** likely does not involve initial formation of **7**. A large difference in the ^{1}H NMR resonances for the nonequivalent methylsilyl groups in both **4** and **5** is found. This is attributed to the proximity of one methyl group to the π system of the aromatic rings of the calix[4]arene backbone. The structures of **4** and **5** were determined by X-ray diffraction.

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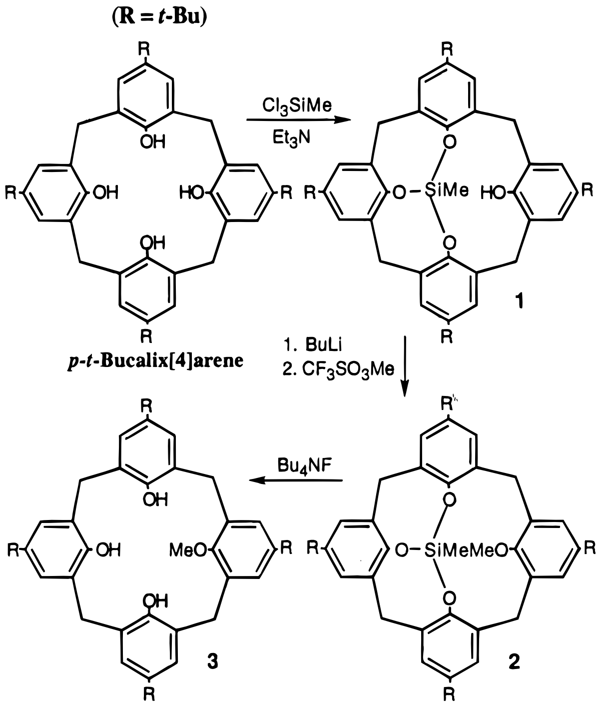
Our investigations of the insertion of main-group elements into calix[4]arenes have led to novel structures and reactions in which phosphorus exhibits coordination numbers from 6 through 3.[1] More recently, we have found that arsenic[2] and silicon[3] can also be inserted into calix[4]arenes. In fact, the MeSi group could be used as a novel protecting group to synthesize a monosubstituted calix[4]arene according to Scheme 1. In an attempt to extend the use of silicon as a protecting group to synthesize "1,2"-disubstituted calix[4]arenes, we have encountered an unusual reaction that can be viewed as a disproportionation which we herein report.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques, unless otherwise indicated. Solvents were dried using standard procedures and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents butyllithium (1.6 M in hexanes), methyl trifluoromethanesulfonate, dichlorodimethylsilane, 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 starting material *p*-*tert*-butylcalix[4]arene·toluene was synthesized by literature methods.[4] 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]arene 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. All NMR spectra were recorded on either an IBM/Bruker WP200SY multinuclear NMR spectrometer (equipped with a Tecmag computer system) resonating at 200.132 (^{1}H) MHz or on a 400 MHz Bruker AVANCE DRX Multinuclear NMR Spectrometer resonating at ^{1}H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si. 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.

Scheme 1



Synthesis of 4. A stirred suspension of *p*-*tert*-butylcalix[4]arene (0.800 g, 1.23 mmol) in toluene (40 mL) was treated

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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dropwise with dichlorodimethylsilane (0.161 g, 1.23 mmol). Then, triethylamine (0.250 g, 2.46 mmol) was added dropwise. The reaction mixture was stirred for 1 d. The resulting mixture was filtered, and the volatiles were pumped off from the filtrate. The residue was dissolved in hexane and filtered, and the filtrate was stored at −30 °C yielding **4** as a white air-stable solid (0.52 g, 60%). Mp: 195−197 °C. Anal. Calcd for $C_{46}H_{60}O_4Si$: C, 78.36; H, 8.58. Found: C, 78.16; H, 9.07. ^1H NMR (C_6D_6): δ −0.81 (s, 3 H, CH_3Si), 0.32 (s, 3 H, CH_3Si), 1.23 (s, 18 H, t-Bu), 1.28 (s, 18 H, t-Bu), 3.37 (d, $^2J_{HH}$ = 14 Hz, 1 H), 3.54 (d, $^2J_{HH}$ = 14 Hz, 1 H), 3.79 (d, $^2J_{HH}$ = 16 Hz, 2 H), 4.07 (d, $^2J_{HH}$ = 14 Hz, 1 H), 4.27 (d, $^2J_{HH}$ = 16 Hz, 2 H), 4.37 (d, $^2J_{HH}$ = 15 Hz, 1 H), 6.33 (s, OH, 2 H), 6.99−7.18 (8 H total). ^{13}C NMR ($CDCl_3$): δ −3.1 (CH_3Si), 2.5 (CH_3Si), 31.49 [$C(CH_3)_3$], 31.53 [$C(CH_3)_3$], 31.7 (CH_2), 33.9 [$C(CH_3)_3$], 34.0 [$C(CH_3)_3$], 35.5 (CH_2), 37.5 (CH_2), 125.0, 125.3, 125.5, 126.3, 126.6, 128.5, 128.6, 129.3, 143.2, 144.6, 149.4, 149.5.

Synthesis of 5. A stirred solution of **4** (0.700 g, 0.993 mmol) in benzene (50 mL) was treated dropwise with butyllithium (1.24 mL, 1.98 mmol). The reaction mixture was stirred overnight during which time a large amount of insoluble material formed. Then, methyl trifluoromethanesulfonate (0.329 g, 2.00 mmol) was added dropwise and the mixture stirred overnight. Only a small amount of undissolved material remained which was separated by filtration. The volatiles were then pumped off from the filtrate yielding a yellow residue. The ^1H NMR spectrum of this crude product indicated the presence of primarily **5** and **6**·LiO_3SCF_3 with only small amounts of impurities. The crude product was washed with hexane (3 × 1 mL) and recrystallized from toluene yielding **5** as colorless air-stable crystals (0.20 g, 53%). Mp 392−394 °C. Anal. Calcd for $C_{48}H_{64}O_4Si_2$: C, 75.74; H, 8.47. Found: C, 75.94; H, 8.27. ^1H NMR (C_6D_6): δ −1.30 (s, 6 H, CH_3Si), 0.37 (s, 6 H, CH_3Si), 1.34 (s, 36 H, t-Bu), 3.36 (d, $^2J_{HH}$ = 14 Hz, 2 H), 4.10 (s, 4 H), 4.52 (d, $^2J_{HH}$ = 14 Hz, 2 H), 7.07−7.11 (8 H total). ^{13}C NMR ($CDCl_3$): δ −3.1 (CH_3Si), 4.1 (CH_3Si), 31.5 [$C(CH_3)_3$], 33.9 [$C(CH_3)_3$], 35.6 (CH_2), 39.9 (CH_2), 125.1, 126.4, 129.4, 130.2, 144.0, 149.5.

Isolation of 6·LiO_3SCF_3. The volume of the above supernatant was reduced, and colorless crystals of **6**·LiO_3SCF_3 were obtained (0.12 g, 25%). Mp: 253−255 °C. The ^1H NMR spectrum indicated 1 mol of toluene present in the sample. Anal. Calcd for $C_{49}H_{64}O_7F_3SLi{\cdot}C_7H_8$: C, 70.28; H, 7.71. Found: C, 70.56; H, 7.61. ^1H NMR (CD_2Cl_2): δ 1.19 (s, 36 H, t-Bu), 3.40 (d, $^2J_{HH}$ = 12 Hz, 4 H), 4.17 (s, 12 H, OCH_3), 4.30 (d, $^2J_{HH}$ = 12 Hz, 4 H), 7.13 (s, 8 H). ^{13}C NMR (CD_2Cl_2): δ.31.4 [$C(CH_3)_3$], 31.9 (CH_2), 34.5 [$C(CH_3)_3$], 64.8 (CH_3), 126.4, 134.8, 148.7, 152.1. ^7Li NMR (CD_2Cl_2): δ −1.28. ^{19}F NMR (CD_2Cl_2): δ −77.

X-Ray Structure Determination and Refinement. Colorless crystals of **4** and **5**, coated with mineral oil, were mounted on a Siemens R3m/V diffractometer under a low-temperature nitrogen stream. The pertinent crystallographic data and conditions for data collection are summarized in Table 1. Final unit cell parameters were obtained by a least-squares fit of the angles of 24 accurately centered reflections (**4**, 16° < 2θ < 30°; **5**, 14° < 2θ < 26°). Intensity data were collected in the ranges specified in Table 1 using graphite monochromated Mo Kα (λ = 0.710 73 Å). 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, but no absorption study was applied. The structure was solved by direct methods using the SHELXTL-Plus package.[5] Full-matrix least-squares refinement was performed. Scattering factors were taken from literature sources.[6] Structure **5** was refined on F, while structure **4** was on F^2 (SHELXL93),[7] and all reflections were used in the refinement. Both **4** and **5** have a 1,2-alternate configuration (Figures 1 and 2). In **4** the two hydroxyl groups form an intramolecular hydrogen bonding interaction with O(1)−H(1) 0.83(4) Å, H(1)···O(2) 1.96(5) Å, O(1)···O(2) 2.779(5) Å, O(1)−H(1)···O(2) 166(4)°. Structure **5** possesses a center of symmetry which is located at the midpoint of Si···Si(a). The lattice of **4** included a disordered solvent toluene. The hydroxyl, aromatic, and methylene H's of **4** were located in difference Fourier maps and were isotropically refined, while methyl-H's of **4** as well as all H atoms of **5** were on calculated positions. Final cycles of refinement converged at $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.067 and 0.044 for **4** and **5**, respectively. The weighted R-index of **5** has the form $wR = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.053$, where $w = [\sigma^2(F_o) + 0.0010(F_o)^2]^{-1}$, while that of **4** is $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o)^4]^{1/2} = 0.147$, where $w = 1/[\sigma^2(F_o{}^2) + (0.0593P)^2 + 4.8158P]$ and $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 1. Crystallographic Data for 4 and 5

	4	**5**
formula	$[C_{46}H_{60}O_4Si]{\cdot}0.5[C_7H_8]$	$C_{48}H_{64}O_4Si_4$
fw	751.10	761.2
space group	$P\bar{1}$	$P2_1/c$
a, Å	9.368(2)	11.490(2)
b, Å	13.559(2)	15.566(3)
c, Å	18.919(4)	12.769(2)
α, deg	71.01(1)	90.00
β, deg	78.31(2)	108.51(2)
γ, deg	81.30(4)	90.00
V, Å^3	2215.7(7)	2165.1(7)
Z	2	2
$D_{calcd,}$ g cm^{-3}	1.126	1.168
abs coeff, mm^{-1}	0.095	0.124
cryst dmns, mm	0.35 × 0.25 × 0.15	0.25 × 0.35 × 0.10
scan type	ω	ω
scan sp in ω, deg/min: min, max	5.0, 25.0	8.0, 30.0
2θ range, deg	3.0−44.0	3.0−42.0
T, K	220	220
decay, %	no	no
data collcd	5837	2473
obsd reflcns, $F > 6.0\sigma(F)$	4803 [$F > 4.0\sigma(F)$]	2335
params refined	562	244
GOF	0.967	1.13
$\Delta\rho$(max, min), e/Å^3	0.50, −0.31	0.22, −0.22
R	0.067	0.044
wR	0.147 [wR_2]	0.052

Results and Discussion

Treatment of *p*-*tert*-butylcalix[4]arene with dichlorodimethylsilane yields a single product **4** in which the silicon bridges adjacent ("1,2"-bridged) oxygens (Scheme 2). No evidence is found for any "1,3"-bridged product, and **4** appears to exist as a single conformer. The identity of **4** is confirmed by its X-ray crystal structure which is illustrated in Figure 1. Selected bond distances and angles are listed in Table 2. The molecule adopts the 1,2-alternate confirmation. There is an intramolecular hydrogen-bonding interaction between the hydroxyl groups. The silicon is in a distorted tetrahedral geometry, and the Si−C and Si−O bond lengths are within the usual ranges.[8] Perhaps the most significant feature of the structure is the position of the "endo" methyl group [C(1)] on the silicon: it is above the centers of two of the calix[4]arene aromatic rings. One way to view this is by the distances between C(1) and the aromatic carbons. These range from about 3.7−3.9

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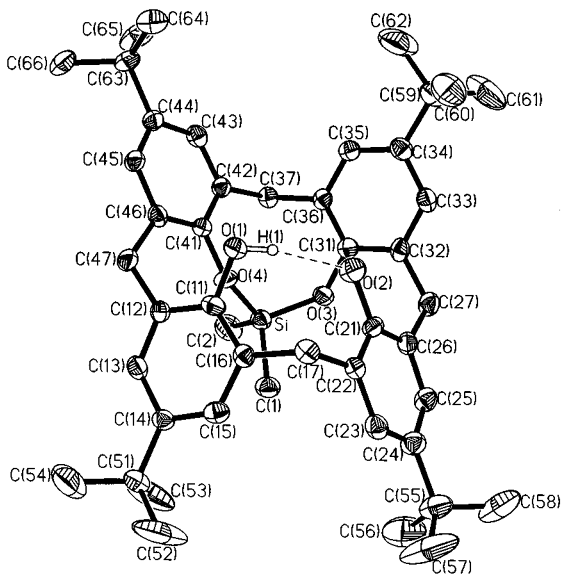
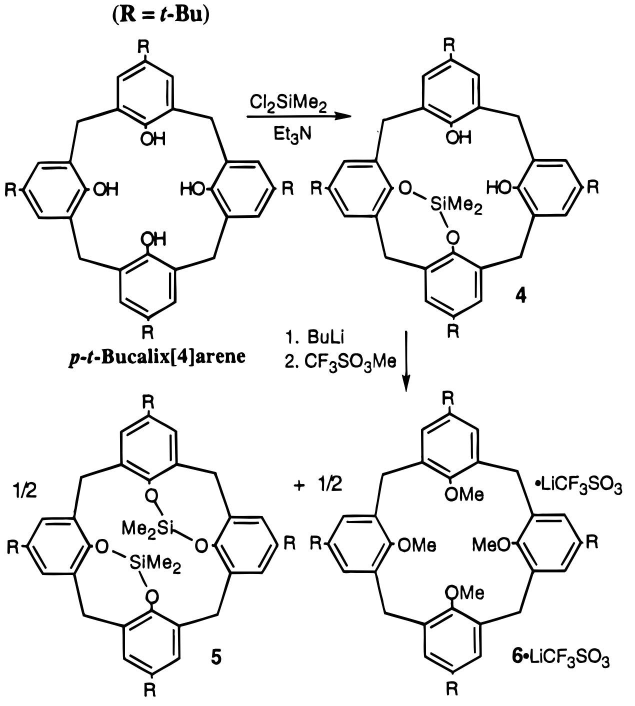


Figure 1. Perspective view of **4**. Hydrogen atoms are omitted for clarity.

Scheme 2



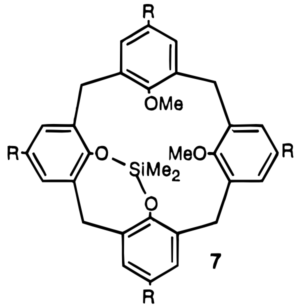
Å [C(11)–C(16)] and 3.6–4.2 Å [C(21)–C(26)]. The ring centroid–C(1)–ring centroid angle is 80.5°. This arrangement has a dramatic effect on the ^1H NMR chemical shift: the two methylsilyl resonances appear at δ 0.32 and −0.81 (C_6D_6), with the more upfield signal due presumably to the endo group. These resonances are even further apart in $CDCl_3$: δ 0.16 and −1.60. The two singlets in the *tert*-butyl region, six doublets in the methylene region, and a single hydroxyl resonance integrating to two protons are also consistent with the geometry.

This product appeared to be an ideal starting material for the synthesis of 1,2-disubstituted calix[4]arene derivatives. However, when **4** is treated with butyllithium and methylated (in a 1:2 molar ratio), no evidence is found for the expected dimethoxy analog of **4**. Rather, two species are observed in the ^1H NMR spectrum of the crude reaction mixture (Scheme 2). One product, **5**, shows two methylsilyl resonances at δ 0.37 and −1.30 in C_6D_6 (δ 0.32 and −1.68 in $CDCl_3$), indicating a similar arrangement for these groups in **5** as was found for **4**. However, integration of these signals reveals that there are two Me_2Si groups present, not one. In addition, there is one singlet for the *tert*-butyl groups and two doublets and one singlet in the methylene region; this is consistent with a 1,2-alternate confirmation[9] with overall C_{2h} symmetry. This was confirmed by X-ray analysis (see below). The other compound is the lithium triflate complex of the tetramethoxy calix[4]arene, **6**$\cdot LiO_3SCF_3$. The ^1H NMR spectrum of this complex shows a singlet for the *tert*-butyl groups, two doublets in the methylene region, and a singlet at δ 4.17 integrating to twelve protons, indicative of the cone conformation.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	Compound **4**		
Si–O(4)	1.621(3)	Si–O(3)	1.648(3)
Si–C(1)	1.826(5)	Si–C(2)	1.841(5)
O(1)–C(11)	1.372(5)	O(2)–C(21)	1.384(5)
O(3)–C(31)	1.374(5)	O(4)–C(41)	1.369(5)
O(4)–Si–O(3)	110.1(2)	O(4)–Si–C(1)	107.7(2)
O(3)–Si–C(1)	107.3(2)	O(4)–Si–C(2)	112.2(2)
O(3)–Si–C(2)	109.4(2)	C(1)–Si–C(2)	110.1(2)
C(31)–O(3)–Si	130.8(3)	C(41)–O(4)–Si	142.1(3)
	Compound **5**		
Si–C(1)	1.833(6)	Si–O(1)	1.643(4)
O(1)–C(11)	1.382(7)	Si–C(2)	1.851(5)
Si–O(2)	1.633(4)	O(2)–C(21)	1.381(7)
C(1)–Si–C(2)	108.7(3)	C(2)–Si–O(1)	111.1(2)
C(2)–Si–O(2)	111.7(2)	Si–O(1)–C(11)	138.5(3)
C(1)–Si–O(1)	106.9(2)	C(1)–Si–O(2)	107.9(2)
O(1)–Si–O(2)	110.4(2)	Si–O(2)–C(21)	143.3(4)

We do not know the mechanism of the formation of **5** and **6**. The reaction can be viewed as a disproportionation of the dimethoxy compound **7**. However, if **7** was formed and then yielded the observed products, might not **4** also disproportionate in a similar manner to form **5** and the starting material *p*-*tert*-butylcalix[4]arene? We do know that **5** does not form until after the addition of methyl trifluoromethanesulfonate, since we find no evidence for the presence of **5** when **4** is treated with only butyllithium. Both **4** and **5** exist in the 1,2-alternate conformation. We believe that the most likely pathway for the formation of **5** and **6** involves an intermediate in which the phenoxide on one calix[4]arene attacks the silicon on another, viz.



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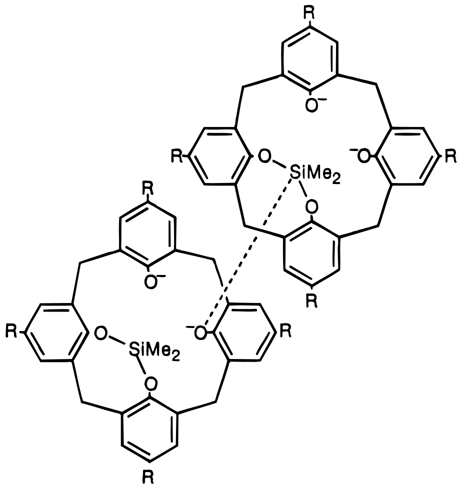


During methylation, the silyl group is "extracted" from one calix[4]arene to the other. In fact, the lithium may actually act as a template around which the tetramethoxy calix[4]arene forms, since it is postulated that alkali metal ions are symmetrically bound to the OMe groups of **6**.[10]

Mention should be made of the solvent-dependent stability of the complex **6**·LiO_3SCF_3. The ^{1}H NMR spectrum in CD_2Cl_2 remains unaltered after several days in solution. This spectrum is very similar to that observed for a sodium complex of **6**.[11] However, the spectra in both $CDCl_3$ and C_6D_6 show changes over time indicating decomposition of the complex. Moreover, the ^{1}H NMR spectrum of the complex bears no resemblance to that of uncomplexed **6**. The spectrum of the latter[12] was interpreted as **6** being in the partial cone conformation . Finally, the lithium triflate can be removed by washing with water. The resulting product now shows a ^{1}H NMR spectrum identical to that previously observed for uncomplexed **6**.[12]

The X-ray crystal structure of **5** is illustrated in Figure 2. Selected bond lengths and angles are listed in Table 1. The molecule adopts the 1,2-alternate conformation for the calix[4]arene backbone. The distances between C(1a) and the aromatic rings are 3.6−3.8 Å [C(11)−C(16)] and 3.7−3.9 Å [C(21)−C(26)] with the ring centroid−C(1a)−ring centroid angle being 83.5°. The silicon atoms are distorted tetrahedra, and the Si−C and Si−O bond lengths are within the usual ranges.[8] However, the Si−O−C angles in **5** of around 140° are quite large. In **4**, one Si−O−C angle is 142° while the other is a more usual 131°. These angles can be contrasted to those in diphenyldiphenoxysilane where the Si−O−C angles are 126 and 130°.[13] Steric hindrance appears to play a major role in these angles with an extreme example being 147° in the $-SiMe_2-O-C_6H_2(t\text{-}Bu)_3$ linkage.[14] Previous data on main-group element calixarenes from our laboratories[1,2] have shown E−O−C (E = P, As) of around 120° to be usual. In one case, however, one of the P−O−C angles in the phosphoryl derivative **8** was found to be 140°,[1e] suggesting that the calix[4]arene backbone can accommodate a large range of E−O−C bond angles. The constraint of the calix[4]arene backbone appears to require quite large angles in certain cases.

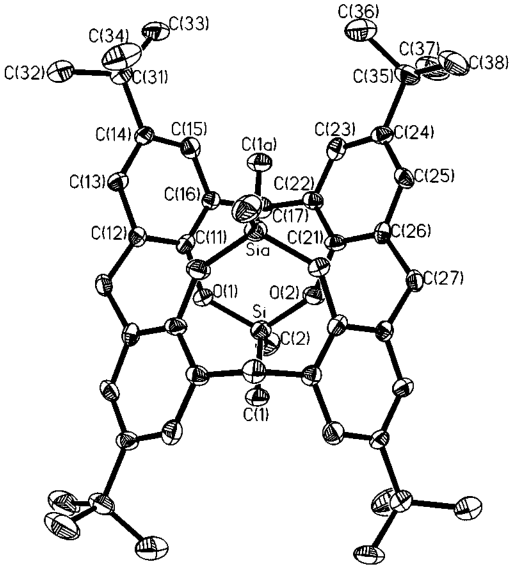
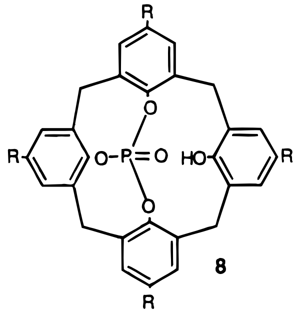


Figure 2. Perspective view of **5**. Hydrogen atoms are omitted for clarity.



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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coordinates, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates (12 pages). Ordering information is given on any current masthead page.

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