Six-, Five-, Four-, and Three-Coordinate Phosphorus in Calix[4]arenes

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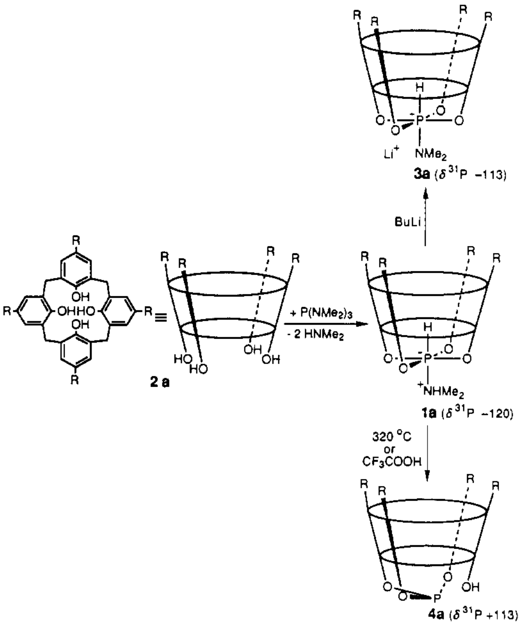
The conversion of the hexacoordinate zwitterionic phosphorus compound (*p*-*tert*-butylcalix[4]arene)P(H)NHMe$_2$ (**1a**) to the tricoordinate hydroxyphosphite (OH) (*p*-*tert*-butylcalix[4]arene)P (**4a**) proceeds through a pentacoordinate intermediate **5a** which can be spectroscopically characterized. This intermediate contains three calixarene P–O bonds; in addition, a proton and dimethylamine remain attached to the phosphorus. No evidence is found for a pentacoordinate species in which all four calixarene oxygens are bound to the phosphorus. Treatment of **1a** with methyl trifluoromethanesulfonate leads to **4a** and trimethylammonium trifluoromethanesulfonate. Treatment of **1a** with butyllithium followed by addition of methyl trifluoromethanesulfonate leads to **6a**, the trimethylamine analog of **1a**. Oxidation of the phosphorus in **4a** with *tert*-butyl hydroperoxide gives the phosphoryl derivative **7a**. If the *tert*-butyl groups in the starting calixarene are replaced with hydrogens, the analogous unsubstituted compounds **1b**, **4b**, and **7b** can all be synthesized and isolated under similar reaction conditions. Both **1a** and **1b** can be converted to **4a** and **4b**, respectively, by heating in the solid state or in solution; however, significantly higher temperatures are necessary for conversion of the *tert*-butyl analog. The species **4** can be deprotonated with potassium *tert*-butoxide to give the potassium salt **9**; spectra suggest that the overall geometry of **9** is similar to **4** except for the absence of the hydroxyl proton. However, when **4** is treated with butyllithium, a mixture of two products is formed. One, **10**, is the lithium analog of **9**. The other, **11**, appears to be a hexacoordinate derivative in which the bottom of the basket has reclosed via attack of the butyl anion on phosphorus and proton transfer from oxygen back to phosphorus. The X-ray crystal structures of **1b** and **7b** were obtained. The structure of **1b** shows the geometry about phosphorus to be distorted octahedral, with the calixarene in the cone conformation and the phosphorus lying 0.14 Å above (inside the basket) the plane of the four calixarene oxygens. The P–H bond is inside the basket, and the P–N bond is trans to it. In **7b**, the calixarene backbone lies somewhere between a partial cone and 1,2-alternate conformation. The phosphorus is bound to three calixarene oxygens. X-ray data: **1b**, $P\bar{1}$, a = 11.677(3) Å, b = 14.055(4) Å, c = 18.824(7) Å, α = 90.47(3)°, β = 101.85(3)°, γ = 112.19(2)°, Z = 2; **7b**, $P2_1/c$, a = 15.064(5) Å, b = 15.424(4) Å, c = 13.073(3) Å, β = 108.52(2)°, Z = 4.

Our interest in calixarenes stems from our efforts to stabilize high-coordinate geometries around main-group elements by their incorporation into macrocycles and to study the reactivity of these species.[2] Moreover, the variable coordination that we have observed with phosphorus in calix[4]arenes should lead to different conformations of the calixarene backbone, an important aspect of the chemistry of these unique macromolecules that have potential to be important as complexing agents, biomimics, physiological compounds, and catalysts.[3]

We recently reported the synthesis and preliminary reactivity of **1a** (Scheme 1).[4–6] The initial synthesis of **1a** involves loss of two moles of dimethylamine during the treatment of *p*-*tert*-butylcalix[4]arene **2a** with tris(dimethylamino)phosphine. At this point, the "bottom of the basket" closes to yield the observed zwitterionic hexacoordinate phosphorus species. The coordinated dimethylamine can be deprotonated to yield **3a**, while treatment with either trifluoroacetic acid (in solution) or heat (in the solid-state) yields the open trivalent phosphite **4a**.

Scheme 1. **a**, R = *tert*-Butyl; **b**, R = H.



We herein report a more detailed study of **1a** and its derivatives, as well as the synthesis, reactivity, and structures of several corresponding unsubstituted (R = H) species. (The notation **a** and **b** in compound numbers denotes R = *tert*-butyl and H, respectively.) This study demonstrates that the coordination number of phosphorus can vary from six through three when incorporated into the macrocycle, while X-ray structural analyses

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show that the phosphorus coordination has a marked effect on the conformation of the calix[4]arene.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Model DL-001-S-P drybox or by 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 $HBF_4{\cdot}Et_2O$, methyl trifluoromethanesulfonate, *tert*-butyl hydroperoxide (3.0 M in 2,2,4-trimethylpentane), tris(dimethylamino)methylsilane, potassium *tert*-butoxide (1.0 M in THF), and butyllithium (1.6 M in hexanes) were purchased commercially and used without further purification. The starting materials **2a**,[3] **2b**,[7] and tris(dimethylamino)phosphine[8] were synthesized and purified according to literature procedures. All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer resonating at 200.132 (^1H), 50.327 (^{13}C), and 81.026 (^{31}P) MHz. ^1H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si. ^{13}C resonances were measured relative to solvent peaks and referenced to Me_4Si. ^{31}P resonances were measured relative to external 85% H_3PO_4. ^{13}C NMR spectra are proton-decoupled unless otherwise indicated. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY, or on a Carlo Erba Strumentazione Model 1106 elemental analyzer. Thermal gravimetric analyses were performed by Oneida Research Services, Inc., using an Omnitherm (PL Thermal Sciences) 1500 TGA.

Reaction of 1a with Tetrafluoroboric Acid. A stirred solution of **1a** (34 mg, 0.047 mmol) in CD_2Cl_2 (1.5 mL) was treated dropwise with 85% $HBF_4{\cdot}Et_2O$ (10 μL, 0.058 mmol). The mixture was stirred for 5 min during which time the solids went into solution. The solution was then transfered to an NMR tube and the reaction monitored by ^1H and ^{31}P NMR spectroscopy. After a total of 15 min of reaction time, the ^{31}P NMR spectrum showed primarily the peak due to **5a** at δ −21(d, $^1J_{PH}$ = 706 Hz). The ^1H NMR spectrum of **5a** shows the following data: δ 1.11 (s, 9 H), 1.28 (s, 18 H), 1.29 (s, 9 H), [3.43 (d)], 3.50 (dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{PH}$ = 9.9 Hz), [3.54 (dd, $^5J_{PH}$ = 2.0 Hz)], 4.37 (dd, $^2J_{HH}$ = 13.4 Hz, $^5J_{PH}$ = 6.4 Hz, 2 H), 4.70 (dd, $^2J_{HH}$ = 12.9 Hz, $^5J_{PH}$ = 1.9 Hz, 2 H), 5.02 (d, $^1J_{PH}$ = 709 Hz, 1 H), 6.96, 7.13 (d, $^4J_{HH}$ = 2 Hz), 7.30 (d, $^4J_{HH}$ = 2 Hz), 7.31 (8H total aromatic), 7.5 (br, NH). The N–H coupling was confirmed by homonuclear decoupling in which the peak at δ 7.5 was irradiated. The methylene peaks in square brackets are approximations due to overlap with the dimethylamino resonance (see Figure 1). After 4 h reaction time, spectra indicated about a 40:60 **4a**:**5a** ratio. After 16 h, this ratio increased to about 90:10. The reaction is complete in 24 h.

Reaction of 1a with Methyl Trifluoromethanesulfonate. A stirred solution of **1a** (70 mg, 0.097 mmol) in dichloromethane (3 mL) was treated dropwise with methyl trifluoromethanesulfonate (12 μL, 0.11 mmol). The mixture was refluxed for 24 h during which time a white precipitate formed. The mixture was filtered, and the volatiles were pumped off from the filtrate to yield **4a** (55 mg, 84%), identified by spectral comparison with a previously synthesized sample.

Synthesis of 6a. A stirred slurry of **1a** (154 mg, 0.213 mmol) in THF (3 mL) was treated dropwise with butyllithium (1.6 M in hexanes, 140 μL, 0.22 mmol). Stirring was continued for 30 m after the addition was complete. The resulting clear solution was treated dropwise with methyl trifluoromethanesulfonate (26 μL, 0.23 mmol) and stirred for 20 m. The volatiles were then pumped off and the residue dissolved in about 15 mL of dichloromethane, filtered, and concentrated to about 5 mL. About 30 mL of ether was then added to precipitate the product which was separated by filtration, washed with ether, and pumped dry to yield **6a** as a white, air-stable solid (99 mg, 63%). Mp: 320–322 °C dec. Anal. Calcd for $C_{47}H_{62}NO_4P$: C, 76.70; H, 8.49; N, 1.90. Found: C, 76.35; H, 8.62; N, 1.87. The compound decomposes slowly in solution. ^1H NMR (CD_2Cl_2): δ 1.22 (s, 36 H), 3.11 (dd, $^2J_{HH}$ = 11.4 Hz, $^5J_{PH}$ = 2.0 Hz, 4 H), 3.56 (d, $^3J_{PH}$ = 7.7 Hz, 9 H), 4.35 (d, $^1J_{PH}$ = 697.3 Hz, 1 H), 4.65 (dd, $^2J_{HH}$ = 11.4 Hz, $^5J_{PH}$ = 6.8 Hz, 4 H), 7.03 (s, 8 H). ^{31}P NMR (CD_2Cl_2): δ −113 ($^1J_{PH}$ = 697 Hz).

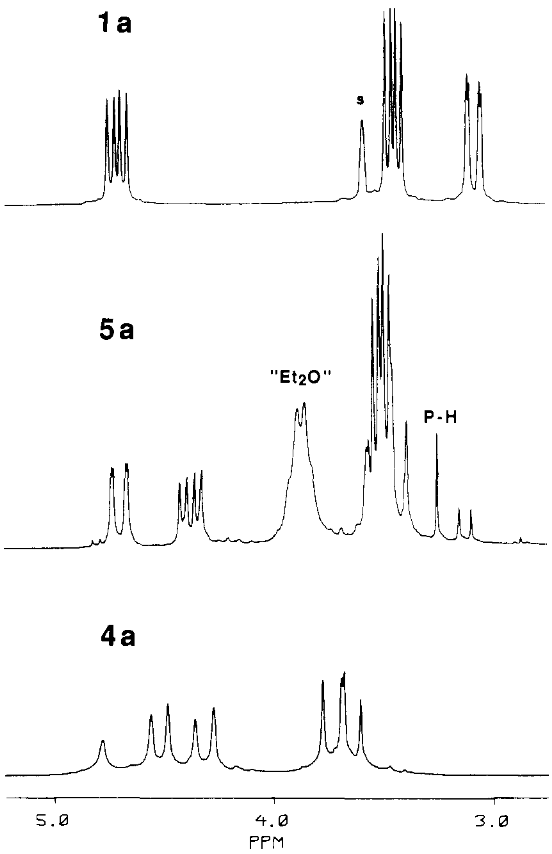

Figure 1. Portion of the ^1H NMR spectra of **1a** (THF-d_8), **5a** (CD_2Cl_2), and **4a** (CD_2Cl_2). Labels: s is peak due to THF-d_8; "Et_2O" is due to $HBF_4{\cdot}Et_2O$; P–H is right-hand portion of P–H resonance. The resonance at δ 4.74 in the spectrum of **4a** is due to the hydroxyl proton.

Synthesis of 7a. A stirred slurry of **4a** (210 mg, 0.310 mmol) in ether (5 mL) was treated dropwise with *tert*-butylhydroperoxide (3.0 M in 2,2,4-trimethylpentane, 100 μL, 0.300 mmol). The mixture was stirred for 18 h. The resulting slightly turbid solution was filtered and concentrated to about 1 mL. The product was precipitated with about 20 mL of hexane, filtered, and pumped over P_2O_5 to yield **6a** as a white, hygroscopic solid (130 mg, 63%). Mp: 338–340 °C dec. Anal. Calcd for $C_{44}H_{53}O_5P{\cdot}H_2O$: C, 74.34; H, 7.80. Found: C, 74.39; H, 8.09. ^1H NMR (C_6D_6): δ 0.99 (s, 9 H), 1.23 (s, 18 H), 1.44 (s, 9 H), 3.27 (d, $^2J_{HH}$ = 14.4 Hz, 2 H), 3.71 (d, $^2J_{HH}$ = 16.2 Hz, 2 H), 3.86 (s, OH, 1 H), 4.12 (d, $^2J_{HH}$ = 16.2 Hz, 2 H), 4.57 (d, $^2J_{HH}$ = 14.4 Hz, 2 H), 7.09, 7.15 (overlapping with C_6D_6), 7.35 (8 H total aromatic). ^{31}P NMR (C_6D_6): δ −23.

Synthesis of 1b. A stirred solution of **2b** (530 mg, 1.25 mmol) in benzene (20 mL) was treated dropwise with $P(NMe_2)_3$ (250 μL, 1.38 mmol). After the mixture was stirred for 18 h, the resulting precipitate was filtered, washed with benzene, and pumped dry, yielding **1b** as a white, air-stable solid. The product was pumped for 48 h over P_2O_5 to remove water (present from the starting material **2b**) and the last traces of benzene to give the pure product (410 mg, 66%). Mp: 367–74 °C. Anal. Calcd for $C_{46}H_{60}NO_4P$: C, 72.42; H, 5.67; N, 2.82. Found: C, 70.97; H, 5.45; N, 2.69. ^1H NMR ($CDCl_3$): δ 3.19 (dd, $^2J_{HH}$ = 11.7 Hz, $^5J_{PH}$ = 2.1 Hz, 4 H), 3.56 (dd, $^3J_{HH}$ = 5.9 Hz, $^3J_{PH}$ = 9.4 Hz, 6 H), 4.68 (d, $^1J_{PH}$ = 731.3 Hz, 1 H), 4.69 (dd, $^2J_{HH}$ = 11.7 Hz, $^5J_{PH}$ = 6.7 Hz, 4 H), 6.3 (br, NH, 1 H), 6.72 (td, $^3J_{HH}$ = 7.4 Hz, $^6J_{PH}$ = 2.7 Hz, 4 H), 7.01 (d, $^3J_{HH}$ = 7.4 Hz, 8 H). ^{31}P NMR ($CDCl_3$): δ −118 (d, $^1J_{PH}$ = 730 Hz). The product above can be recrystallized from THF/hexane. In this case **1b**·THF is formed, and a somewhat better analysis is obtained. Anal. Calcd for $C_{46}H_{60}NO_4P{\cdot}C_4H_8O$: C, 71.69; H, 6.37; N, 2.46. Found: C, 71.14; H, 6.23; N, 2.41. A sample of **1b**·THF was used for the thermal gravimetric analysis.

Synthesis of 4b. A 25-mL round-bottom flask fitted with an outlet to a nitrogen bubbler was charged with solid **1b** (726 mg, 1.46 mmol). The flask was heated in an oil bath at 150 °C for 4 h, yielding **4b** as a white, air-stable solid (647 mg, 98%). Mp: 359 °C. Anal. Calcd for $C_{28}H_{21}O_4P$: C, 74.33; H, 4.68. Found: C, 74.02; H, 4.80. ^1H NMR ($CDCl_3$): δ 3.61 (d, $^2J_{HH}$ = 15.0 Hz, 2 H), 3.72 (d, $^2J_{HH}$ = 16.9 Hz, 2

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H), 4.33 (d, $^2J_{HH}$ = 16.9 Hz, 2 H), 4.59 (d, $^2J_{HH}$ = 15.0 Hz, 2 H), 5.4 (br, OH, 1 H), 6.8–7.2 (comp m, 12 H). ^{31}P NMR (THF-d_8): δ 116.

Synthesis of 7b. A stirred slurry of **4b** (132 mg, 0.292 mmol) in ether (5 mL) was treated dropwise with *tert*-butyl hydroperoxide (3.0 M in 2,2,4-trimethylpentane, 100 μL, 0.300 mmol). The mixture was stirred for about 18 h during which time a yellow solid precipitated. About 10 mL of hexane were added to precipitate any further product. The solid was then separated by filtration and washed with hexane. Dissolution in THF (5 mL) and reprecipitation with hexane (20 mL) followed by pumping over P_2O_5 yielded **6b** as a white, air-stable solid (150 mg, 100%). Mp: 318–320 °C dec. Anal. Calcd for $C_{28}H_{21}O_5P$: C, 71.79; H, 4.52. Found: C, 71.36; H, 4.69. ^{1}H NMR (CDCl$_3$): δ 3.55 (d, $^2J_{HH}$ = 14.5 Hz, 2 H), 3.79 (d, $^2J_{HH}$ = 16.3 Hz, 2 H), 4.27 (d, $^2J_{HH}$ = 16.3 Hz, 2 H), 4.49 (d, $^2J_{HH}$ = 14.5 Hz, 2 H), 5.1 (br, OH, 1 H), 6.9–7.2 (comp m, 12 H). ^{31}P NMR (C$_6$D$_6$): δ –22.

Thermal Gravimetric Analyses of 1. For **1a**, a 4.59-mg sample was heated from 40 to 300 °C at 10 deg/min under a nitrogen purge at an indicated flow rate of 35 mL/min. The sample lost 6.35% of its mass (calculated 6.23% for loss of dimethylamine). For **1b**·THF, a 9.03 mg sample was heated from 40 to 200 °C at 10 deg/min under a nitrogen purge at an indicated flow rate of 35 mL/min. The sample lost 18.5% of its mass (calcd 20.1% for loss of dimethylamine and THF). Initial mass loss for **1a** and **1b** occurs at about 220 and 110 °C, respectively. The full reports with thermograms are available as supplementary material.

Synthesis of 4a via Sublimation. A sublimation apparatus was charged with **1a** (2.25 g, 3.12 mmol). The apparatus was connected to a high-vacuum line (1×10^{-5} Torr) and heated at 250–300 °C for about 2 h until all of the solid had sublimed. Yield: 1.94 g (92%) of pure **4a**. The volatiles from the sublimation were collected in a liquid nitrogen trap on the vacuum line and identified by IR spectroscopy as dimethylamine (3.09 mmol, 99% based on **1a**).

Thermal Reactions of 1 in Solution. The following samples were prepared in 10-mm NMR tubes and kept under nitrogen: a suspension of **1a** (31 mg, 0.043 mmol) in dioxane (2.0 mL) and a solution of **1b** (20 mg, 0.040 mmol) in dioxane (2.0 mL). The samples were capped with septa pierced by a needle leading to a nitrogen bubbler and immersed in an oil bath maintained between 100 and 107 °C. At this temperature, most of **1a** goes into solution. Spectra were monitored as described in Results and Discussion. The non-*tert*-butyl derivative converts smoothly from **1b** to **4b** with no observed intermediates in the ^{31}P NMR spectra. However, an unidentified intermediate at δ 1 is observed in the conversion of **1a** which is still present after the final heating (19 h total).

Deprotonation Studies. A stirred solution of **4b** (40.0 mg, 0.0884 mmol) in THF (3 mL) was treated dropwise with potassium *tert*-butoxide (1.0 M in THF, 100 μL, 1.0 mmol). The resulting solution was stirred for 1 h. Hexane was added to precipitate the product **9b** which was then pumped dry and redissolved in THF-d_8. ^{1}H NMR (THF-d_8): δ 2.95 (d, $^2J_{HH}$ = 14.5 Hz, 2 H), 3.64 (d, $^2J_{HH}$ = 16.6 Hz, 2 H), 4.23 (d, $^2J_{HH}$ = 16.6 Hz, 2 H), 4.94 (d, $^2J_{HH}$ = 14.6 Hz, 2 H), 5.85 (t, $^3J_{HH}$ = 7.2 Hz), 6.22 (t, $^3J_{HH}$ = 7.4 Hz), 6.56 (d, $^3J_{HH}$ = 7.2 Hz), 6.77 (d, $^3J_{HH}$ = 7.4 Hz), 6.8–7.1 (comp m) [12 H total aromatic]. ^{31}P NMR: δ 115. A stirred solution of **4b** (66.0 mg, 0.146 mmol) in ether (5 mL) was treated dropwise with butyllithium (1.6 M in hexanes, 105 μL, 0.17 mmol). The resulting mixture was stirred for 18 h. The solid was separated by filtration and washed with ether and benzene to yield a solid weighing 55 mg. Spectroscopic analysis showed this to be a mixture of **10b** and **11b** in an approximate 1:1 ratio. **10b**: ^{1}H NMR (THF-d_8): δ 3.26 (d, $^2J_{HH}$ = 14.9 Hz, 2 H), 3.70 (d, $^2J_{HH}$ = 17.0 Hz, 2 H), 4.24 (d, $^2J_{HH}$ = 16.8 Hz, 2 H), 4.72 (d, $^2J_{HH}$ = 14.3 Hz, 2 H), 6.26 (t, $^3J_{HH}$ = 7.3 Hz), 6.94 (d, $^3J_{HH}$ = 7.3 Hz), 7.02 (d, $^3J_{HH}$ = 7.6 Hz), 7.10, 7.14 (due to overlapping resonances with **11b**, all aromatic peaks could not be assigned and accurate integrations were difficult). ^{31}P NMR: δ 115. **11b**: ^{1}H NMR (THF-d_8): δ 1.04 (t, butyl), 1.5 (m, butyl), 2.4 (m, butyl), 2.86 (dd, $^2J_{HH}$ = 10.9 Hz, $^5J_{PH}$ not observed, 4 H), 4.74 (PH, estimated from overlapping peaks), 4.97 (dd, $^2J_{HH}$ = 3.4 Hz, $^5J_{PH}$ = 10.7 Hz, 4 H), 6.36 (t, $^3J_{HH}$ = 7 Hz), 6.80 (d, $^3J_{HH}$ = 7 Hz) (due to overlapping resonances with **10b**, accurate aromatic integrations were difficult). ^{31}P NMR: δ –101 (d, $^1J_{PH}$ = 864 Hz).

X-ray Structure Determination and Refinement. Colorless crystals of **1b** (recrystallized from benzene) and **7b** (recrystallized from chloroform/ether) were mounted on a Siemens R3m/V diffractometer under a low-temperature nitrogen stream. Final unit cell parameters, given in Table 1, were obtained by a least-squares fit of the angles of 25 accurately centered reflections ($16° < 2\theta < 27°$ for **1b**, $18° < 2\theta < 29°$ for **7b**). Data collection conditions are listed in Table 1. 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. A semiempirical absorption correction was applied for **7b**, with the minimum and maximum transmission factors of 0.8165 and 0.8863, respectively. Both structures were solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL-Plus package.[9] Scattering factors were taken from common sources.[10] Blocked, full-matrix refinements were performed in each case. All non-hydrogen atoms in each structure were anisotropically refined. Important bond distances and bond angles are listed in Table 2. Further detailed information is provided as supplementary material.

Table 1. Crystallographic Data for **1b** and **7b**

	1b	**7b**
formula	$[C_{30}H_{28}NO_4P]_2 \cdot 1.5C_6H_6$	$[C_{28}H_{21}O_5P] \cdot HCCl_3$
fw	1112.2	587.8
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.677(3)	15.064(5)
b, Å	14.055(4)	15.424(4)
c, Å	18.824(7)	13.073(3)
α, deg	90.47(3)	90.00
β, deg	101.85(3)	108.52(2)
γ, deg	112.19(2)	90.00
V, Å^3	2287(2)	2880(1)
Z	2	4
D_{calcd}, g cm^{-3}	1.325	1.356
abs coeff, mm^{-1}	0.134	0.410
crystal dimens, mm	0.25 × 0.35 × 0.15	0.30 × 0.35 × 0.20
scan type	$\omega/2\theta$	$\omega/2\theta$
scan speed in ω; min, max	5.0, 25.0	8.0, 30.0
2θ range, deg	3.5–38.0	3.5–42.0
T, K	230	230
decay, %	no	no
no. of data collcd	7734	3436
no. of obsd reflcns, $I > 3.0\sigma(I)$	5254	2174
no. of params refined	730	380
GOF	2.04	2.60
g	0.0006	0.0005
$\Delta\rho$(max,min), e/Å^3	0.27, –0.27	0.83, –0.38
R	0.062	0.067
R_w	0.078	0.085

Structure of 1b. There are two independent calix[4]arene molecules and 1.5 benzene molecules in an asymmetric unit. Both calix[4]arene molecules are geometrically the same. The symmetrical center of the lattice is located at the center of one of the benzene molecules. No significant interaction between the calix[4]arene and benzene molecules was found [closest distances from benzene to calixarene: C(25)···C(94) ($1.0 - x$, $1.0 - y$, $1.0 - z$) 3.62 Å, O(3)···C(98) ($-1.0 + x$, $-1.0 + y$, z) 3.54 Å, C(31)···C(98) ($-1.0 + x$, $-1.0 + y$, z) 3.66 Å]. The phosphorus-[H(1), H(2)] and nitrogen-bonded hydrogen atoms were located from difference Fourier maps, while other hydrogen atoms were placed at idealized positions. H(1) and H(2) are located inside their calix[4]arene baskets. The P(1) atom is 0.141 Å above the best plane of O(1), O(2), O(3), and O(4), while P(2) is 0.144 Å above that of O(5), O(6), O(7), and O(8). The weight had the form $\omega = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ where g = 0.0006. Final cycles of refinement converged at $R = \sum//F_o/ - /F_c// /\sum/F_o/$ = 0.062, $R_w = [\sum w(/F_o/ - /F_c/)^2/\sum w(F_o)^2]^{1/2}$ = 0.078, *GOF* = 2.04 for 2726 observed reflections [$I > 3.0\sigma(I)$].

Structure of 7b. After the calix[4]arene backbone was assigned, it seemed two solvated chloroform molecules appeared on difference Fourier maps. The very short distance between the chloroform molecules [Cl(1)···Cl(11) = 1.88 Å, Cl(2)···Cl(21) = 1.82 Å] indicated the chloroform molecules were disordered and these sites were partially occupied. The refinement showed the site occupancy factor for one chloroform molecule [C(38), Cl(1), Cl(2), and Cl(3)] was 60%, while the site occupancy factor for another one was 40%. The disordered molecules were elastically restrained during final refinements. No significant interaction was found between the calix[4]arene and chloroform molecules. All aromatic and methylene hydrogen atoms were placed in calculated positions, while the hydroxyl hydrogen was identified from a difference Fourier map. No

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Table 2. Bond Lengths (Å) and Bond Angles (deg)[a]

	1b (Molecule 1)		
P(1)–O(1)	1.731(7)	P(1)–O(2)	1.730(7)
P(1)–O(3)	1.700(7)	P(1)–O(4)	1.693(7)
P(1)–N(1)	1.895(8)	O(1)–C(11)	1.379(11)
O(2)–C(21)	1.381(15)	O(3)–C(31)	1.403(15)
O(4)–C(41)	1.382(12)	N(1)–C(2)	1.486(17)
N(1)–C(3)	1.494(12)		
O(1)–P(1)–O(2)	90.2(3)	O(1)–P(1)–O(3)	170.1(3)
O(2)–P(1)–O(3)	89.6(3)	O(1)–P(1)–O(4)	89.3(4)
O(2)–P(1)–O(4)	171.1(3)	O(3)–P(1)–O(4)	89.4(3)
O(1)–P(1)–N(1)	82.9(4)	O(2)–P(1)–N(1)	83.0(4)
O(3)–P(1)–N(1)	87.2(4)	O(4)–P(1)–N(1)	88.1(4)
P(1)–O(1)–C(11)	122.6(8)	P(1)–O(2)–C(21)	120.0(6)
P(1)–O(3)–C(31)	124.6(5)	P(1)–O(4)–C(41)	121.1(7)
P(1)–N(1)–C(2)	117.1(6)	P(1)–N(1)–C(3)	119.6(8)
C(2)–N(1)–C(3)	108.4(7)		
	1b (Molecule 2)		
P(2)–O(6)	1.712(7)	P(2)–O(5)	1.727(7)
P(2)–O(8)	1.718(9)	P(2)–O(7)	1.723(7)
O(5)–C(51)	1.384(14)	P(2)–N(4)	1.916(10)
O(7)–C(71)	1.382(18)	O(6)–C(61)	1.370(15)
N(4)–C(5)	1.487(19)	O(8)–C(81)	1.392(17)
N(4)–C(6)	1.476(14)		
O(5)–P(2)–O(7)	170.5(4)	O(5)–P(2)–O(6)	88.9(3)
O(5)–P(2)–O(8)	89.7(4)	O(6)–P(2)–O(7)	90.2(3)
O(7)–P(2)–O(8)	89.7(4)	O(6)–P(2)–O(8)	170.2(4)
O(6)–P(2)–N(4)	87.5(4)	O(5)–P(2)–N(4)	88.0(4)
O(8)–P(2)–N(4)	82.8(4)	O(7)–P(2)–N(4)	82.6(4)
P(2)–O(6)–C(61)	120.5(6)	P(2)–O(5)–C(51)	122.8(8)
P(2)–O(8)–C(81)	120.1(10)	P(2)–O(7)–C(71)	122.9(6)
P(2)–N(4)–C(6)	118.2(8)	P(2)–N(4)–C(5)	117.2(6)
C(5)–N(4)–C(6)	106.5(9)		
	7b		
P–O(1)	1.569(4)	P–O(2)	1.574(4)
P–O(3)	1.551(4)	P–O(5)	1.448(5)
O(1)–C(1)	1.440(7)	O(2)–C(11)	1.398(8)
O(3)–C(21)	1.419(8)	O(4)–C(31)	1.368(8)
O(1)–P–O(2)	104.8(2)	O(1)–P–O(3)	105.7(2)
O(2)–P–O(3)	106.4(2)	O(1)–P–O(5)	117.3(2)
O(2)–P–O(5)	110.5(2)	O(3)–P–O(5)	111.5(3)
P–O(1)–C(1)	126.3(4)	P–O(2)–C(11)	120.4(3)
P–O(3)–C(21)	140.1(4)		

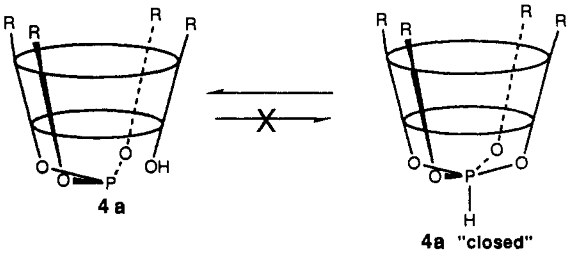
[a] For **1b**, there are two independent molecules in an asymmetric unit (see text). Both are listed in this table, but Figure 2 illustrates molecule 1.

attempts were made to locate hydrogen atoms on disordered chloroform molecules. Fixed isotropic temperature factors (U = 0.08 Å^2) were assigned to all hydrogen atoms. Intermolecular hydrogen-bonding, via hydroxyl hydrogen atoms and doubly-bonded oxygens, O(4)–H(4o) = 1.06 Å, H(4o)···O(5″) = 1.79 Å, O(4)–H(4o)···O(5″) = 149°, O(4)···O(5″) = 2.753 Å (double prime denotes = x, $^1/_2 - y$, $^1/_2 + z$), was formed between calix[4]arene molecules. Final cycles of refinement converged at R = 0.067, R_w = 0.85, GOF = 2.60 for 2174 observed refections [$I > 3.0\sigma(I)$]. The extreme features left on the final difference Fourier maps were a peak of height of 0.83 e/Å^3 and a negative feature of –0.38e/Å^3.

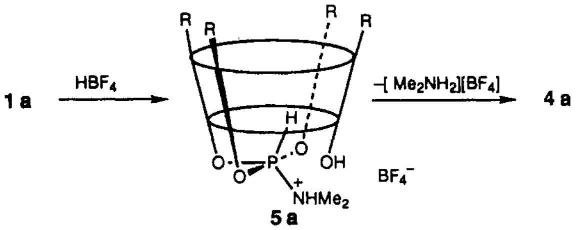
Results and Discussion

Synthesis and Reactivity. The hexacoordinate derivative **1a** is quite unusual and demonstrates that main-group "hypervalent" atoms can lock the calix[4]arene into the cone conformation by binding all four oxygens, an ability previously reserved for transition metals[11] and lanthanides.[12] In fact, **1a** can be considered a stable intermediate in the synthesis of **4a**, since heating evolves the last mole of dimethylamine to give the latter product.

Loss of dimethylamine from **1a**, whether as the gas (in the solid-state) or as the dimethylammonium salt (in solution), leads to cleavage of one of the phosphorus-oxygen bonds.[5] This suggests that the calix[4]arene macrocycle is unable to form a pentacoordinate P-H phosphorane (eq 1) with all four oxygens bound to phosphorus, unless it is an intermediate in the reaction. We found no evidence for any intermediates in the solution reaction with trifluoroacetic acid; however, when tetrafluoroboric acid is used, an intermediate **5a** is observed which can be spectroscopically characterized. This species has a ^{31}P NMR signal at δ –21 with a large proton coupling of 706 Hz, indicative of a direct P–H bond. The ^{31}P chemical shift is 99 ppm downfield of **1a** and in the region expected for a pentacoordinate phosphorus. The ^{1}H NMR spectrum of this intermediate indicates a much less symmetrical geometry for **5a** than for **1a**; for example, the *tert*-butyl region is split into a three-line pattern in a 1:2:1 ratio (see Experimental Section). In addition, there are four resonances for the methylene bridges of the calix[4]arene, some of which show coupling to phosphorus (Figure 1). However, in common with the spectrum of **1a**, a broad peak for N–H is found (at δ 7.5), and the four-line pattern (due to $^3J_{HH}$ and $^3J_{PH}$) from Me_2NH is also observed. These data suggest that the conversion of **1a** to **4a** with acid goes through an intermediate in which the phosphorus is bound to three of the oxygens of the calix[4]arene, as well as a proton and Me_2NH (eq 2). This conversion is clearly illustrated in Figure 1 which shows the methylene and dimethylamino region of the ^{1}H NMR spectra **1a**, **5a**, and **4a**.



(1)



(2)

The postulated geometry of **5a** is consistent with our results thus far. The calix[4]arene appears to stabilize high-coordinate structures with approximately 90° O–P–O bond angles but not with significantly smaller bond angles; this probably accounts for our inability to observe a square pyramidal O_4PH phosphorane (see X-ray Structures section). In principle, a square pyramidal geometry containing a planar O_4P base with delocalized 3-center/4-electron bonds is possible, particularly if the apical position contains hydrogen, the least sterically demanding substituent.[13] However, we have no evidence for such a species.

A possible mechanism for the conversion of **1a** to **4a** with acid involves initial protonation at oxygen leading to P–O bond rupture. This suggests that treatment of **1a** with strong electrophiles R$^+$ might lead to corresponding O-R derivatives of **4a**. However, this is not observed: treatment of **1a** with methyl trifluoromethanesulfonate yields **4a** and trimethylammonium triflate (eq 3). While several mechanisms would account for the products in eq 3, the most straightforward route is initial methyl/proton

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[11] (a) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465.

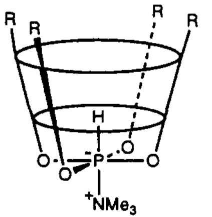
[12] Furphy, B. M.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H.; Wilner, F. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2217.

[13] We thank a reviewer for suggesting this possibility.

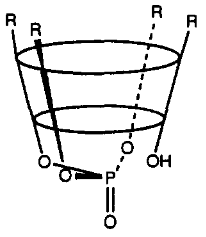
exchange at nitrogen, followed by P–O bond rupture and trimethylamine dissociation.

$$\mathbf{1a} + CF_3SO_3Me \rightarrow \mathbf{4a} + [Me_3NH][CF_3SO_3] \qquad (3)$$

Straightforward derivatives of both **1a** and **4a** can be synthesized. For example, treatment of **3a** with methyl trifluoromethanesulfonate yields **6a**, while oxidation of **4a** with *tert*-butyl hydroperoxide yields **7a**. In common with the other six-coordinate phosphorus derivatives,[4,5] long-range (five-bond) phosphorus–proton coupling to the diastereotopic methylene protons is observed in **6a**.



6 a



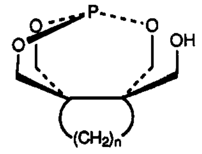
7 a

In order to see if the steric bulk of the *tert*-butyl substituents has any significant effect on reactivity, we utilized the unsubstituted calix[4]arene **2b** to synthesize several corresponding derivatives. Indeed, the R = H species **1b**, **4b**, and **7b** have each been isolated under similar reaction conditions. As in the case with the *tert*-butyl substituents, **4b** can be synthesized by heating **1b** in the solid-state or by treatment of **1b** with acid in solution. However, there is one significant difference between the two systems: heating to 320 °C is necessary for the isolation of **4a** from **1a** in the solid-state; **4b** is obtained from **1b** at 150 °C. Thermal gravimetric analyses (in a nitrogen atmosphere) confirm these differences: initial mass loss for **1a** and **1b** occur at about 220 and 110 °C, respectively. To see if these differences were due only to solid-state effects, we attempted to carry out the thermal conversions of **1a** and **1b** in solution; this was hampered by the general insolubility of **1a** in most solvents, even at elevated temperatures. It is moderately soluble in chloroform, dichloromethane, THF, and dioxane. We chose dioxane because of its higher boiling point. The reaction was conducted in an oil bath maintained around 100 °C. For the non-*tert*-butyl derivative, a trace amount of the open form **4b** is observed after heating for 1 h. After a total of 5.5 h, the conversion is about 75% complete; after a total of 10h, **1b** is no longer observed. For the *tert*-butyl derivative, **4a** is not observed until after heating for 10 h; even after a total of 19 h heating, some **1b** is still present [although other peaks are present as well (see Experimental Section)]. Thus, at least qualitatively, the same trend is found in solution as in the solid state.

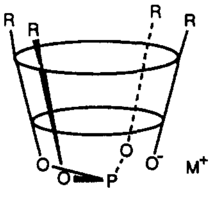
While the conversions of **1** to **4** take place thermally in both the solid-state and in solution, as well as by acid treatment in solution, the best way to isolate high-purity gram quantities of **4** is thermally without solvent. To obtain **4a**, **1a** is heated under high-vacuum (1×10^{-5} Torr) at about 300 °C until **4a** sublimes; for **4b**, simple heating of **1b** at 150 °C in an inert atmosphere yields a pure product. Attempts at obtaining pure samples of **4b** by sublimation of **1b** led to partial decomposition.

These calixarene derivatives are similar in many respects to the phosphorus[14] species of Verkade and co-workers, examples of which are **8**. However, the ligand backbones in **8** preclude any possibility of obtaining six-coordinate geometries, a key feature in the calixarene structures discussed here.

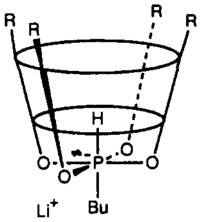
Although there appears to be no tendency for the formation of pentacoordinate 10-P-5 geometries, might deprotonation of **4** induce P–O bond formation and lead to tetracoordinate 10-P-4 phosphoranide anions? Treatment of **4b** with potassium *tert*-butoxide leads to a species **9b** with a resonance in the ^{31}P NMR spectrum at δ 115, only 1 ppm different than the starting material. However, no hydroxyl resonance is observed in the ^1H NMR spectrum of **9b**, and a significantly different pattern is found for the four methylene resonances compared to **4b**. These data suggest that the reaction resulted in deprotonation leading to the simple alkoxide, not the phosphoranide. Moreover, there appears to be no fluxionality, since four methylene resonances are observed. If the corresponding reaction is carried out with the more nucleophilic base butyllithium, a mixture of two products results; one, **10b** (δ 115), appears to be the lithium analog of **9b**. The other product **11b**, quite surprisingly, shows a peak in the ^{31}P NMR spectrum at δ −101 with a large P–H coupling constant of 864 Hz! Moreover, there are only two resonances due to the bridging methylene groups, one of which shows coupling to phosphorus. These data suggest that butyllithium has attacked phosphorus and reclosed the bottom of the basket via P–O bond formation and proton-transfer to phosphorus. In fact, it is well-known that alkyllithium reagents attack trivalent phosphorus leading to P–C bond formation.[15] However, for phosphite linkages, this is usually accompanied by P–O bond rupture. The fact that P–O bond cleavage does not occur in the present case implies that "basket-closing" is more facile and is further evidence for the stability associated with a hexacoordinate phosphorus in the oxygen plane of the calix[4]arene. Similar products are observed when the *tert*-butyl derivative **4a** is treated with the above bases; however, the reactions are not quite as clean, and the ^1H NMR spectra are more difficult to assign as completely.



8



9b (M = K)
10b (M = Li)



11 b

X-ray Structures. The structures of **1b** and **7b** were obtained and are illustrated in Figures 2 and 3, respectively. The molecules of **7b** are connected by intermolecular hydrogen-bonding between the hydroxyl hydrogens and the double-bonded oxygens; this is illustrated in Figure 4. Selected bond distances and angles are presented in Table 2. There are two different molecules of **1b** in an asymmetric unit (see Experimental Section). However, they have essentially the same geometry. Both sets of data are listed in Table 2, but Figure 2 illustrates molecule 1. In **1b**, the calix[4]arene backbone adopts what is commonly referred to as the cone conformation (all phenolic oxygens pointing in the same direction). The geometry about the phosphorus atom is distorted octahedral, with the phosphorus lying slightly above (0.14 Å) the plane of the four oxygens [sum of *cis*-O–P–O angles = 358.5(7)°]. Both the P–O and P–N bonds are long, which is common in hypervalent structures. The P–O bond lengths in **1b** are comparable to the longer P–O bonds found in axial positions of

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(14) Mason, M. R.; Duff, C. M.; Miller, L. L.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1992**, *31*, 2746 and references cited therein.

(15) (a) Davis, R. V.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 4983. (b) Williams, J. L. *Chem. Ind.* **1957**, 235. (c) Li, J.; Beak, P. *J. Am. Chem. Soc.* **1992**, *114*, 9206.

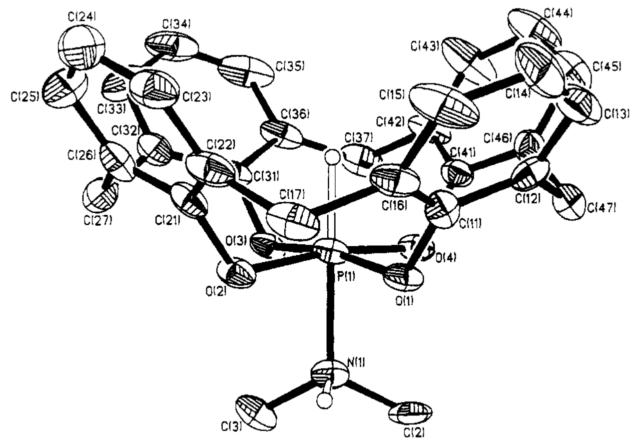


Figure 2. Computer-generated drawing of **1b** (molecule 1) with thermal ellipsoids at 50%. All hydrogen atoms, except for P–H, omitted for clarity.

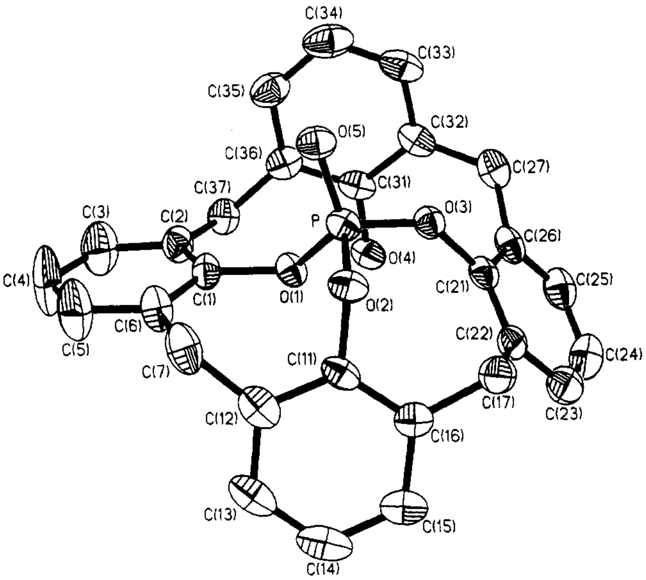
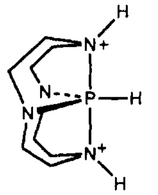
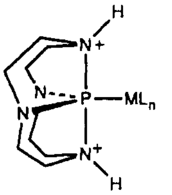


Figure 3. Computer-generated drawing of **7b** with thermal ellipsoids at 50%. All hydrogen atoms omitted for clarity.

trigonal bipyramidal geometries,[16] while the P–N bond length is similar to the axial P–N bonds found in cyclenPH$_3^{2+}$ (**12**)[17] and the platinum cationic complex **13** [ML$_n$ = *cis*-Cl$_2$(Ph$_3$P)Pt].[18]



12



13

Moreover, the P–O–C bond angles in **1b** are well within the usual range of P–O–Ph angles of about 120–128°.[19] Thus, there is little strain introduced by the calix[4]arene backbone when a hexacoordinate phosphorus is incorporated. In fact, the cone conformation of the calix[4]arene appears ideal to stabilize such a geometry for phosphorus. In **7b**, the calix[4]arene backbone does not adopt any of its idealized geometries but rather lies somewhere between a partial cone (one phenolic ring flipped) and 1,2-alternate (two adjacent phenolic rings flipped) conformation since O(1) is neither facing "up" nor "down" in the structure. The geometry about the phosphorus atom in **7b** is distorted tetrahedral. All four P—O bond lengths are within usual ranges for C(aromatic)—O—P=O derivatives,[16] and the (single bonded) O—P—O angles are quite similar to those found in (PhO)$_3$P=NSO$_2$Me (range 102° - 110°).[19c] In addition, the P–O(1)–C(1) and P–O(2)–C(11) angels are normal; however, the P–O(3)–C(21) is quite large. This larger angle must be due to the constraint of the methylene groups connecting the rings in the calix[4]arene backbone. The larger P–O(3)–C(21) angle implies that the tetracoordinate phosphorus may be in a more strained environment than the hexacoordinate one.

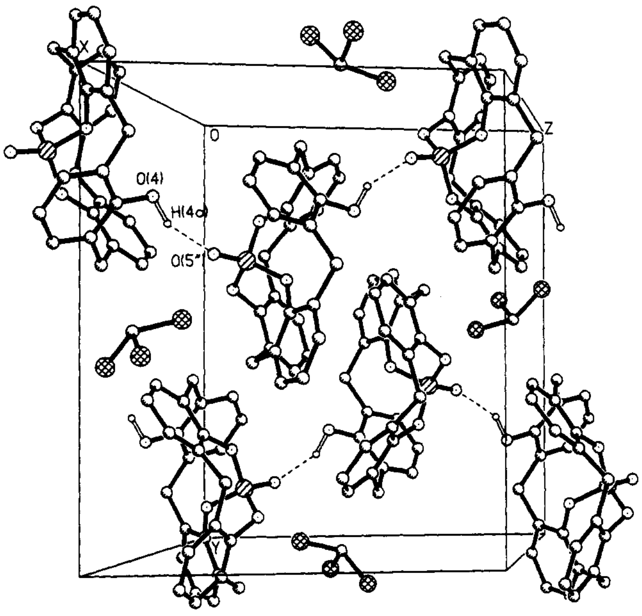


Figure 4. Computer-generated drawing of **7b** showing the crystal packing and hydrogen-bonding in the unit cell.

These structural data are consistent with our observations concerning the chemistry of these derivatives: the only pentacoordinate species that is observed is **5a**, not **4a "closed"**. In the latter derivative, the most likely structure would be a square pyramid (ideal trans basal angles of 150°) with the four oxygens at the basal positions and the hydrogen at the unique apical site. Such a geometry would most likely elongate the P–O bonds and distort the P–O–C angles to such an extent as to force P–O bond rupture (and lead to **4a**). For a trigonal bipyramid, the equatorial O–P–O angle would be too small to accommodate all four P–O bonds. In **5a**, the O–P–O angles are still 90°; thus, the phosphorus is still in a relatively unstrained environment. Moreover, the observed calix[4]arene conformations in the X-ray structures imply that the ligand backbone in **5a** also adopts the cone conformation.

We are currently studying the effect of the insertion of other main-group elements into calixarenes.

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Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement coordinates, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates for **1b** and **7b** and text and figures describing complete thermal gravimetric data for **1a** and **1b** (22 pages). Ordering information is given on any current masthead page.

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