Insertion of One and Two Arsenic Atoms into Calix[4]arenes[†]

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The insertion of arsenic into the base of the *p*-Rcalix[4]arenes (R = *tert*-butyl, H) via tris(dimethylamino)arsine proceeds smoothly to give monoarsenic (**5a**, **5b**) and diarsenic (**6a**, **6b**) derivatives depending on whether the calix[4]arene:arsine ratio is 1:1 or 1:2, respectively (where **a** denotes R = *tert*-butyl and **b**, R = H). The monoarsenic species have the arsenic bonded to three of the four phenolic units of the calix[4]arene with the fourth containing a hydroxyl. The diarsenic species have two $AsNMe_2$ groups, each bonded to two adjacent phenolic units in a 1,2-alternate conformation. If moisture is present in the initial calix[4]arene starting materials, hydrolysis products (**7a**, **7b**) are formed. These contain As–O–As bridges between the four phenolic units in a cone conformation. X-ray data: **5a**, $P\bar{1}$, $a = 9.821(2)$ Å, $b = 13.913(3)$ Å, $c = 16.884(4)$ Å, $\alpha = 100.52(2)°$, $\beta = 101.39(2)°$, $\gamma = 90.23(2)°$, $Z = 2$; **6b**, $P2_1/n$, $a = 8.685(3)$ Å, $b = 10.482(3)$ Å, $c = 15.597(3)$ Å, $\beta = 101.37(2)°$, $Z = 2$; **7a**, $P2_1/c$, $a = 13.067(4)$ Å, $b = 20.385(5)$ Å, $c = 18.652(5)$ Å, $\beta = 96.90(2)°$, $Z = 4$; **7b**, $P\bar{1}$, $a = 10.303(4)$ Å, $b = 11.175(3)$ Å, $c = 11.339(2)$ Å, $\alpha = 117.12(2)°$, $\beta = 102.29(2)°$, $\gamma = 92.12(2)°$, $Z = 2$.

Our studies on the insertion of main-group elements into macrocycles is leading to an understanding of the factors that influence structure and reactivity of particular macrocycle/main-group element combinations. For example, when phosphorus is inserted into *p*-Rcalix[4]arenes[2] (R = *tert*-butyl, H) via tris(dimethylamino)phosphine, a six-coordinate zwitterionic species **1** is initially formed (Scheme 1).[3] Subsequent transformations lead to species in which phosphorus is five-, four-, and three-coordinate. In this particular system, the constraint of the calix[4]arene backbone appears to stabilize phosphorus geometries with 90° O–P–O bond angles in addition to the usual (approximately) trigonal and tetrahedral structures. In an effort to probe the effect of central atom size on the chemistry of calix[4]arene/main-group element compounds, we herein report the first experiments on the insertion of arsenic.

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 dry box prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents tris(dimethylamino)arsine,[4] *p-tert*-butylcalix[4]arene–toluene,[5] and Hcalix[4]arene[6] were synthesized by literature methods. When indicated, oven-dried samples of the calix[4]arenes were dried at 110–120 °C for at least 12 h. 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 for the oven-dried samples. All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer (equipped with a Tecmag computer system) resonating at 200.132 (^{1}H) MHz. ^{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.

Synthesis of 5a. A stirred suspension of oven-dried *p-tert*-butylcalix[4]arene (260 mg, 0.401 mmol) in benzene (2 mL) was treated dropwise with tris(dimethylamino)arsine (80 μL, 0.43 mmol). This mixture turned clear and then became cloudy again. After stirring for 4 d, the resulting mixture was filtered. The solid was washed with benzene and pumped dry to yield **5a** as a white, air-sensitive solid (236 mg, 82%), mp 346–348 °C. Anal. Calcd for $C_{44}H_{53}O_4As$: C, 75.17; H, 7.44. Found: C, 75.11; H, 7.60. ^{1}H NMR ($CDCl_3$): δ 1.18 (s, 9 H), 1.28 (s, 9 H), 1.35 (s, 18 H), 3.54 (d, $^2J_{HH}$ = 15 Hz, 2 H), 3.65 (d, $^2J_{HH}$ = 17 Hz, 2 H), 4.24 (d, $^2J_{HH}$ = 17 Hz, 2 H), 4.54 (d, $^2J_{HH}$ = 15 Hz, 2 H), 4.74 (s, OH, 1 H), 7.11, 7.15, 7.18 (8H total).

Synthesis of 6a. A stirred suspension of oven-dried *p-tert*-butylcalix[4]arene (260 mg, 0.401 mmol) in benzene (2 mL) was treated dropwise with tris(dimethylamino)arsine (154 μL, 0.83 mmol). This mixture turned clear and then became cloudy again. After stirring for 4 d, the resulting mixture was filtered. The solid was washed with benzene and pumped dry to yield **6a** as a white, air-sensitive, crystalline 1:1 benzene complex (349 mg, 99%), mp 382–383 °C. Anal. Calcd for $C_{48}H_{64}N_2O_4As_2 \cdot C_6H_6$: C, 67.49; H, 7.31; N, 2.91. Found: C, 67.55; H, 7.12; N, 2.58. ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 36 H), 2.27 (s, 12 H), 3.29 (d, $^2J_{HH}$ = 12 Hz, 2 H), 3.99 (s, 4 H), 4.69 (d, $^2J_{HH}$ = 12 Hz, 2 H), 6.93 (d, $^4J_{HH}$ = 2 Hz, 4 H), 7.16 (d, $^4J_{HH}$ = 2 Hz, 4 H).

[†] Dedicated to Dr. Dilip Vishwanath Khasnis (1955–1995), my co-worker and my friend.

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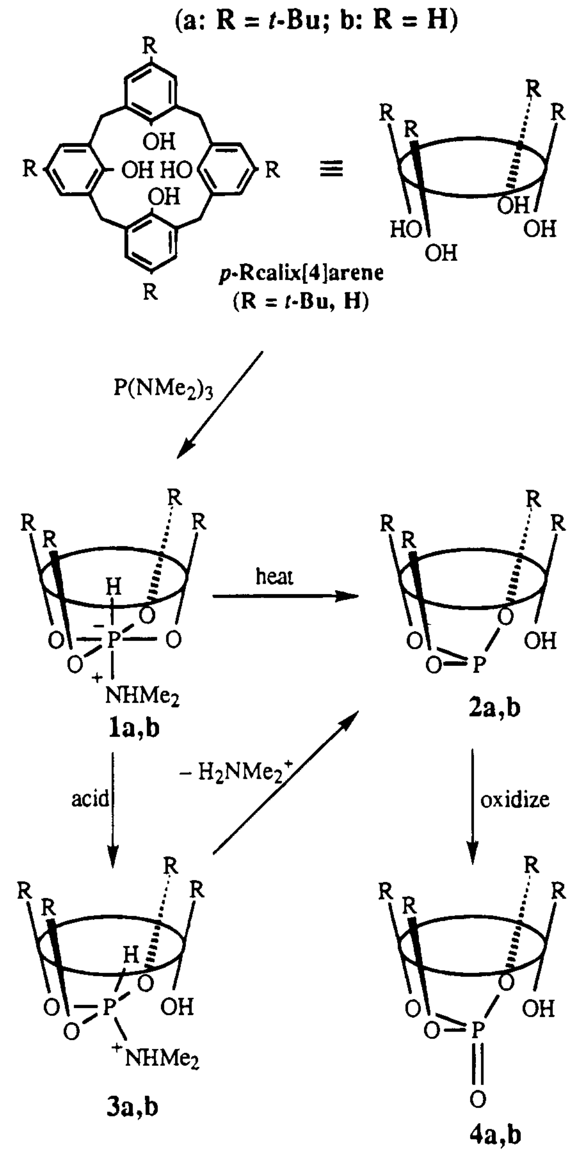
Scheme 1



Synthesis of 5b. A stirred suspension of oven-dried Hcalix[4]arene (127 mg, 0.299 mmol) in benzene (2 mL) was treated dropwise with tris(dimethylamino)arsine (60 μL, 0.32 mmol). This mixture was refluxed for 3 h. The volatiles were then pumped off and the residue recrystallized from hot benzene yielding **5b** as colorless, air-sensitive crystals (84 mg, 57%), mp 302–304 °C. Anal. Calcd for $C_{28}H_{21}O_4As$: C, 67.75; H, 4.26. Found: C, 67.87; H, 4.19. ^{1}H NMR ($CDCl_3$): δ 3.56 (d, $^2J_{HH}$ = 15 Hz, 2 H), 3.70 (d, $^2J_{HH}$ = 17 Hz, 2 H), 4.25 (d, $^2J_{HH}$ = 17 Hz, 2 H), 4.55 (d, $^2J_{HH}$ = 15 Hz, 2 H), 4.90 (s, OH, 1 H), 6.83–7.20 (m, 12 H total). The same product can be obtained if the reaction is carried out at ambient temperature for 4 d; however, the recrystallized yield in this case is 36%.

Synthesis of 6b. A stirred suspension of oven-dried Hcalix[4]arene (127 mg, 0.299 mmol) in benzene (2 mL) was treated dropwise with tris(dimethylamino)arsine (115 μL, 0.622 mmol). After this was stirred for 4 d, the resulting mixture was filtered. The solid was washed with benzene and hexane and pumped dry to yield **6b** as white, air-sensitive crystals (180 mg, 91%), mp 316–318 °C dec. Anal. Calcd for $C_{32}H_{32}O_4N_2As_2\cdot{}^1/_6C_6H_6$: C, 59.03; H, 4.95; N, 4.17. Found: C, 59.25; H, 4.97; N, 3.80. ^{1}H NMR ($CDCl_3$): δ 2.33 (s, 12 H), 3.35 (d, $^2J_{HH}$ = 12 Hz, 2 H), 4.02 (s, 4 H), 4.72 (d, $^2J_{HH}$ = 12 Hz, 2 H), 6.82–7.15 (m, 12 H total).

Synthesis of 7b. A stirred suspension of undried Hcalix[4]arene (127 mg, 0.299 mmol) in benzene (2 mL) was treated dropwise with tris(dimethylamino)arsine (60 μL, 0.32 mmol). This mixture was refluxed for 3 h. The volatiles were then pumped off and the residue recrystallized from hot benzene yielding **7b** as colorless, air-sensitive crystals (58 mg, 33%), mp 360–362 °C. A trace of free Hcalix[4]arene remained in the purified product. Anal. Calcd for $C_{28}H_{20}O_5As_2$: C, 57.36; H, 3.44. Found: C, 58.13; H, 3.52. ^{1}H NMR ($CDCl_3$): δ 3.27 (d, $^2J_{HH}$ = 13 Hz, 2 H), 3.68 (d, $^2J_{HH}$ = 16 Hz, 2 H), 3.85 (d, $^2J_{HH}$ = 16 Hz, 2 H), 4.56 (d, $^2J_{HH}$ = 13 Hz, 2 H), 6.68 – 7.22 (m, 12 H total).

Reaction of Undried *p-tert*-Butylcalix[4]arene–toluene with Tris(dimethylamino)arsine. Mixtures of **5a** and **7a** were obtained in varying ratios, as well as sometimes other impurities. We were able to crystallize out **7a** on several occasions and did obtain its X-ray crystal structure. In a typical procedure, a stirred suspension of undried *p-tert*-butylcalix[4]arene–toluene (140 mg, 0.189 mmol) in benzene (5 mL) was treated dropwise with tris(dimethylamino)arsine (50 μL, 0.27 mmol). After this was stirred for 2 d, the resulting mixture was filtered and the filtrate pumped to dryness. A ^{1}H NMR spectrum of the residue indicated a mixture of **5a** and **7a**. Concentration of a benzene solution of the mixture led to crystals of **7a** suitable for X-ray crystallography. ^{1}H NMR of **7a** (C_6D_6): δ 1.11 (s, 36 H), 3.29 (d, $^2J_{HH}$ = 13 Hz, 2 H), 3.45 (d, $^2J_{HH}$ = 16 Hz, 2 H), 3.71 (d, $^2J_{HH}$ = 16 Hz, 2 H), 4.81 (d, $^2J_{HH}$ = 13 Hz, 2 H), 6.89 (s, 4 H), 7.06 (s, 4 H).

X-ray Structure Determination and Refinement. Crystals of all four compounds were grown from benzene solutions and mounted on a Siemens R3m/V diffractometer under a low-temperature nitrogen stream. The crystals of **5a** and **7a** were coated with dried mineral oil before mounting. Final unit cell parameters for all structures, given in Table 1, were obtained by a least-squares fit of the angles of 24 accurately centered reflections (18° < 2θ < 27° for **5a**, 16° < 2θ < 28° for **6b**, 16° < 2θ < 29° for **7a**, 18° < 2θ < 29° for **7b**). Data-collection conditions are listed in Table 1. Data were collected using graphite-monochromated Mo Kα radiation (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. A semiempirical absorption correction was applied for all samples with the minimum and maximum transmission factors indicated in Table 1. The structures were solved by heavy-atom methods and subsequent difference Fourier syntheses using the *SHELXTL-Plus* package.[7] Scattering factors were taken from common sources.[8] Full-matrix, least-squares refinements were performed in each case. The weight had the form $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$, with the g values listed in Table 1. Final cycles of refinement converged at the indicated values of $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. Important bond distances and bond angles are listed in Table 2.

Structure of 5a. One and one-half benzene solvate molecules were found in an asymmetric unit. The benzene molecules were disordered and were elastically restrained during the final cycles of refinement. The lattice solvent molecules were located on the opposite sides of the two flat aromatic rings [containing C(1) and C(21)]. See Supplementary Material for a drawing showing the solvent molecules. The closest contact distances between **5a** and the solvent molecules were C(52)- - -C(31) 3.495 Å and C(59)---O(3) 3.458 Å. Except for the hydroxyl hydrogen H(1), all hydrogen atoms were located by using a "riding model"; H(1) was located in a DF map. On the basis of the distances O(1)–H(1) 1.21 Å, O(2)- - -H(1) 1.93 Å, O(4)- - -H(1) 2.12 Å, O(1)- - -O(2) 2.911(8) Å, and O(1)- - -O(4) 2.956 Å, an intramolecular hydrogen-bond can be proposed. The parameters of H(1) were not refined. The arsenic atom is "centrally" located in the calix[4]arene: the deviations from plane I [C(1), C(4), C(21), C(24)] and plane II [C(11), C(14), C(31), C(34)] are 0.003 Å and 0.014Å, respectively. Planes I and II are essentially perpendicular: the dihedral angle between planes is 90.4°.

Structure of 6b. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in calculated positions with fixed isotropic temperature factors (U = 0.08 Å^2). The molecule possesses a center of symmetry which is located at the midpoint on the line between As and As(a) ($-x$, $-y$, $2 - z$). The six atoms As, As(a), N,

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Table 1. Crystallographic Data

	5a	**6b**	**7a**	**7b**
formula	$C_{44}H_{45}O_4As\cdot1.5(C_6H_6)$	$C_{32}H_{32}N_4O_4As_2$	$C_{44}H_{42}O_5As\cdot2(C_6H_6)$	$C_{28}H_{20}O_5As_2$
fw	837.9	658.4	966.9	586.3
color	colorless	colorless	colorless	colorless
habit	plates	prisms	plates	plates
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a, Å	9.821(2)	8.685(3)	13.067(4)	10.303(4)
b, Å	13.913(3)	10.482(3)	20.385(5)	11.175(3)
c, Å	16.884(4)	15.597(3)	18.652(5)	11.339(2)
α, deg	100.52(2)			117.12(2)
β, deg	101.39(2)	101.37(2)	96.90(2)	102.29(2)
γ, deg	90.23(2)			92.12(2)
V, Å^3	2221.8(9)	1391.8(7)	4932(2)	1121.7(6)
Z	2	2	4	2
D_{calcd}, g cm^{-3}	1.253	1.571	1.302	1.736
μ_{calcd}, mm^{-1}	0.810	2.442	1.395	3.020
cryst dimens, mm	0.15 × 0.25 × 0.10	0.15 × 0.30 × 0.10	0.15 × 0.25 × 0.35	0.30 x 0.20 × 0.05
T, K	230	230	230	230
scan type	ω	ω	ω	2θ
scan width, deg	1.20 plus Kα-separation	1.20 plus Kα-separation	1.20 plus Kα-separation	1.20 plus Kα-separation
2θ range, deg	3.5−40.0	3.5−44.0	3.5−40.0	3.5−42.0
decay, %	none	none	none	none
no. of data collcd	5064	1839	4982	2579
no. of unique data	4720	1704	4535	2406
no. of obsd reflctns, $F > 6.0\sigma(F)$	3414	973	2525	1885
no. params refined	524	181	414	316
transm fctrs (min, max)	0.576, 0.714	0.716, 0.825	0.851, 0.955	0.521, 0.985
GOF	2.08	0.87	1.75	1.42
g	0.001	0.001	0.0005	0.001
R	0.068	0.033	0.061	0.040
R_w	0.088	0.039	0.069	0.053

N(a), C(7), and C(7a) are essentially coplanar with the mean deviation from the best plane 0.019 Å.

Structure of 7a. Two independent benzene molecules of solvation were found in the structure. One of these molecules [labeled C(70)−C(75)] is located inside the calix[4]arene basket and oriented almost parallel to the plane of C(1), C(4), C(21), and C(24). See the supplementary material for a drawing showing the solvent molecule inside the basket. The closest contact distance between this benzene molecule and **7a** is [C(74)- - -C(13)] 3.564 Å. One of the *tert*-butyl groups [C(41)−C(44)] was disordered and its geometry elastically restrained during the final stages of refinement. Except for the methyl carbons of the disordered *tert*-butyl group [C(42)−C(44)], all non-hydrogen atoms were anisotropically refined. The oxygen atom (O) bridging the two arsenics is positioned below the center of the calix[4]arene basket and is almost on the the two planes described by C(1), C(4), C(21), C(24) and C(11), C(14), C(31), C(34). It is 2.824 Å below the plane of C(1), C(11), C(21), C(31). All hydrogen atoms were included by using a riding model.

Structure of 7b. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in calculated positions with fixed isotropic temperature factors (U = 0.08 Å^2). The position of the bridging oxygen atom (O) is essentially the same as in **7a**.

Results

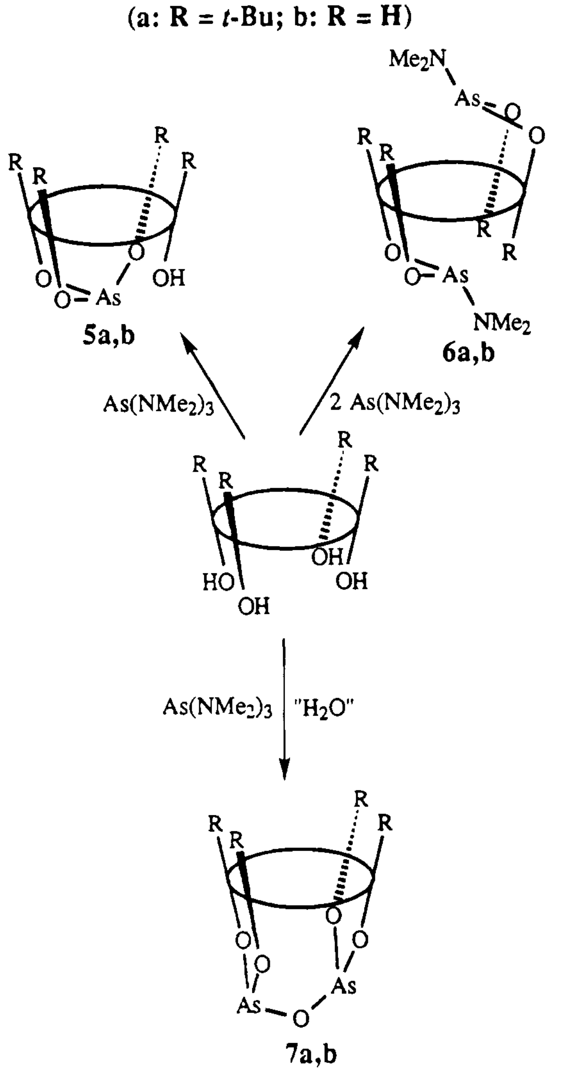
The reaction between *p*-*tert*-butylcalix[4]arene and tris(dimethylamino)arsine in a 1:1 molar ratio yields a single compound **5a** (Scheme 2). The ^{1}H NMR spectrum of **5a** has three peaks in the *tert*-butyl region in a 1:1:2 ratio, as well as four doublets in the methylene region. This spectrum is inconsistent with the symmetry expected for the arsenic analog of **1a**. In addition, a hydroxyl resonance is observed at δ 4.74, corresponding to a single proton. This spectrum is similar to that of the three-coordinate phosphorus species **2a**,[3b] and in fact, **5a** was confirmed to be the arsenic analog of **2a** by X-ray analysis (see below). If a similar reaction is carried out in a 1:2 ratio, another product **6a** is isolated. This product shows only one *tert*-butyl resonance in the ^{1}H NMR spectrum and two doublets and one singlet (in a 1:1 ratio) in the methylene region.

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

	5a		
As-O(2)	1.770 (5)	As-O(3)	1.801 (5)
As−O(4)	1.779(6)	O(1)−C(1)	1.388(11)
O(2)−C(11)	1.383(10)	O(3)−C(21)	1.375(10)
O(4)−C(31)	1.381(9)		
O(2)−As−O(3)	97.3(2)	O(2)−As−O(4)	85.0(3)
O(3)−As−O(4)	96.0(2)	As−O(2)−C(11)	120.3(5)
As−O(3)−C(21)	113.1(5)	As−O(4)−C(31)	122.2(5)
	6b		
As−O(1)	1.837(4)	As−O(2)	1.827(5)
As−N	1.774(7)	O(1)−C(1)	1.384(8)
O(2)−C(11)	1.376(9)	N−C(21)	1.447(11)
N−C(22)	1.454(11)		
O(1)−As−O(2)	98.5(2)	O(1)−As−N	96.8(2)
O(2)−As−N	93.9(3)	As−O(1)−C(1)	120.8(4)
As−O(2)−C(11)	125.0(4)	As−N−C(21)	118.6(6)
As−N−C(22)	123.1(5)	C(21)−N−C(22)	115.9(7)

	7a	**7b**
As(1)−O	1.776(8)	1.771(6)
As(1)−O(1)	1.779(8)	1.783(5)
As(1)−O(4)	1.813(8)	1.786(5)
As(2)−O	1.745(8)	1.759(4)
As(2)−O(2)	1.804(8)	1.803(5)
As(2)−O(3)	1.771(8)	1.799(6)
O(1)−C(1)	1.378(14)	1.371(10)
O(2)−C(11)	1.393(14)	1.399(9)
O(3)−C(21)	1.379(15)	1.360(8)
O(4)−C(31)	1.386(14)	1.395(11)
O−As(1)−O(1)	95.2(4)	94.0(2)
O−As(1)−O(4)	98.7(4)	100.8(3)
O(1)−As(1)−O(4)	95.6(3)	97.2(2)
O−As(2)−O(2)	99.8(4)	100.4(2)
O−As(2)−O(3)	94.9(3)	96.3(2)
O(2)−As(2)−O(3)	96.8(4)	95.4(2)
As(1)−O−As(2)	133.3(5)	132.8(3)
As(1)−O(1)−C(1)	121.3(7)	125.0(3)
As(2)−O(2)−C(11)	123.5(7)	123.3(4)
As(2)−O(3)−C(21)	122.8(7)	117.1(6)
As(1)−O(4)−C(31)	124.3(7)	124.8(4)

Scheme 2



In addition, a singlet corresponding to two dimethylamino groups is observed. These data support a structure in which two arsenic atoms, each containing a dimethylamino group, have been inserted into the calix[4]arene framework. Moreover, the NMR spectrum strongly suggests that the molecule adopts the 1,2-alternate conformation for the calix[4]arene, since the methylene pattern is a "textbook" example of this conformation.[2a]

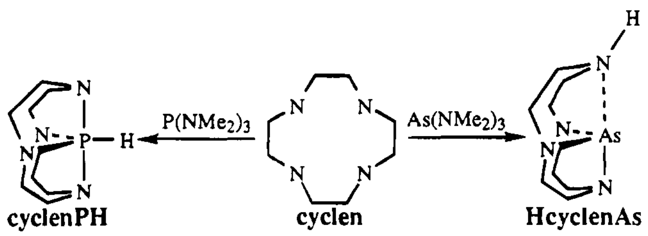
The above results are obtained when the *p-tert*-butylcalix[4]arene is oven-dried to remove any moisture before reaction. If undried samples of the calix[4]arene are used, the reaction follows a different course. In addition to **5a**, another compound **7a** is also produced. This latter species has a single *tert*-butyl resonance in the ^{1}H NMR spectrum but four doublets in the methylene region. No resonances due to either dimethylamino groups or hydroxyls are observed. X-ray analysis (see below) showed this compound to be a hydrolysis product containing an As−O−As unit bridging the four oxygens at the base of the calix[4]arene.

The analogous unsubstituted calix[4]arene (R = H) compounds, **5b**, **6b**, and **7b** are synthesized in a similar manner. X-ray structures of **6b** and **7b** were obtained (see below).

Discussion

There are some similarities, but several important differences, in the calix[4]arene chemistry of phosphorus and arsenic. No arsenic analog of the six-coordinate phosphorus species **1** is observed. Several reasons account for this. As mentioned in the Introduction, the calix[4]arene framework appears to have the proper constraint to support 90° O−P−O bond angles around phosphorus. The larger arsenic, with its substantially longer bonds to oxygen (ca. 0.15 Å on average),[9] apparently does not "fit" into the oxygen plane. In addition, the As−H bond is significantly weaker than the P−H bond (by ca. 75 kJ/mol).[10] Thus, with arsenic, the initial reaction goes all the way to **5** by elimination of the entire three moles of dimethylamine. This chemistry can be compared to the analogous reactions with the tetraamino macrocycle cyclen (Scheme 3). For phosphorus, cyclenPH exists as a 10-P-5 phosphorane.[11] The cyclen macrocycle has the correct bite for the nitrogens to occupy two axial and two equatorial positions in a distorted trigonal bipyramidal (tbp) geometry around phosphorus. A somewhat similar geometry is found for the (approximate) 10-As-4 species HcyclenAs,[12] except no As−H bond is formed. Instead, the proton remains on one of the axial nitrogens resulting in a long transannular N(H)- - -As interaction. Here, again, the position of the proton is probably due to the relatively weak As−H bond energy compared to N−H (by ca. 142 kJ/mol).[10] Thus, it appears that cyclen may have greater flexibility than the calix[4]arene, since the former macrocycle is able to accommodate both phosphorus and arsenic in somewhat similar "hypervalent" geometries.

Scheme 3



Since arsenic does not get "trapped" in the base of the calix[4]arene, it was expected that increasing the amount of tris(dimethylamino)arsine in the reaction might insert more than one arsenic. Indeed, changing the calix[4]arene:tris(dimethylamino)arsine molar ratio from 1:1 to 1:2 inserts two $AsNMe_2$ groups in a 1,2 alternate conformation. Such a conformation minimizes steric interactions between the dimethylamino groups. This result contrasts with that of phosphorus, where increasing the amount of tris(dimethylamino)phosphine has no effect on the outcome of the reaction.

As shown above, if water is present in the starting calix[4]arene, the hydrolysis products **7** form. In an effort to get some insight into the formation of **7**, we attempted several controlled reactions with the *p-tert*-butyl derivatives. It is tempting to speculate that one way in which **7** forms is by the reaction of **6** with water. However, **7** forms whether the ratio of calix[4]arene to arsine is 1:1 or 1:2. Moreover, in a separate experiment in either $CDCl_3$ or C_6D_6, **7a** is not detected when **6a** is treated with water; rather, the free calix[4]arene is observed upon hydrolysis. This occurs whether water is present in a 1:1 molar ratio or in excess. Under similar conditions, no reaction is

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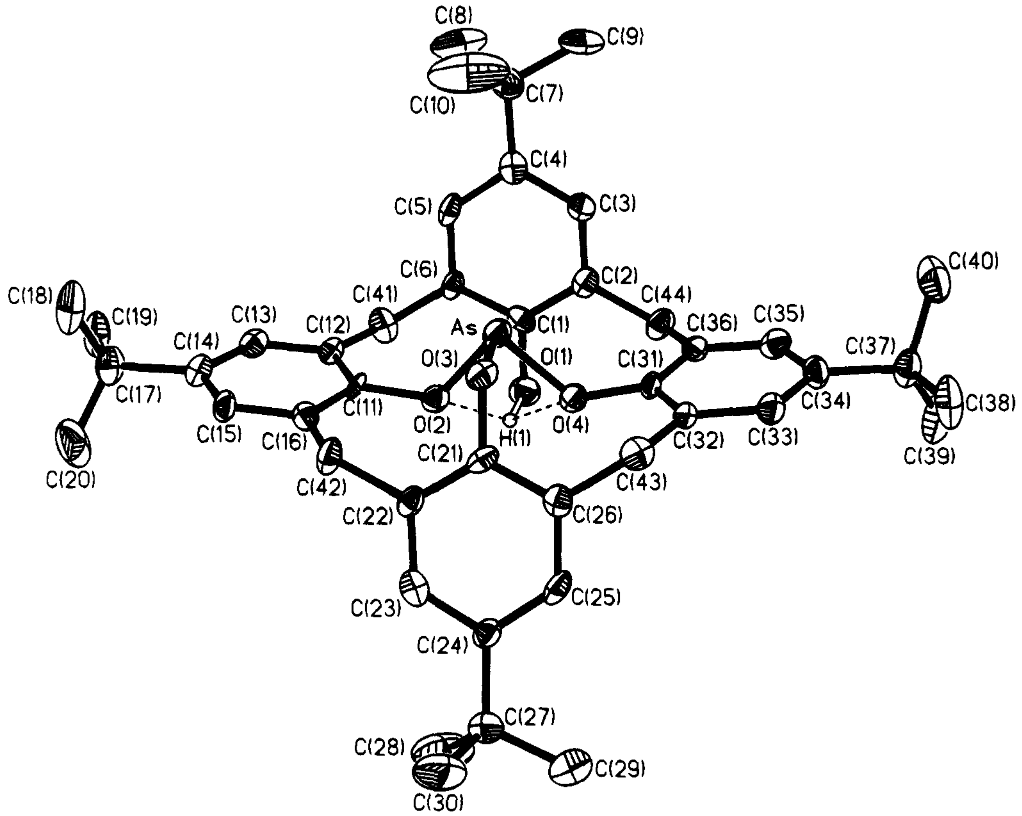

Figure 1. Computer-generated drawing of **5a** with thermal ellipsoids at 50%. All hydrogen atoms, except for the one involved in hydrogen-bonding, omitted for clarity.

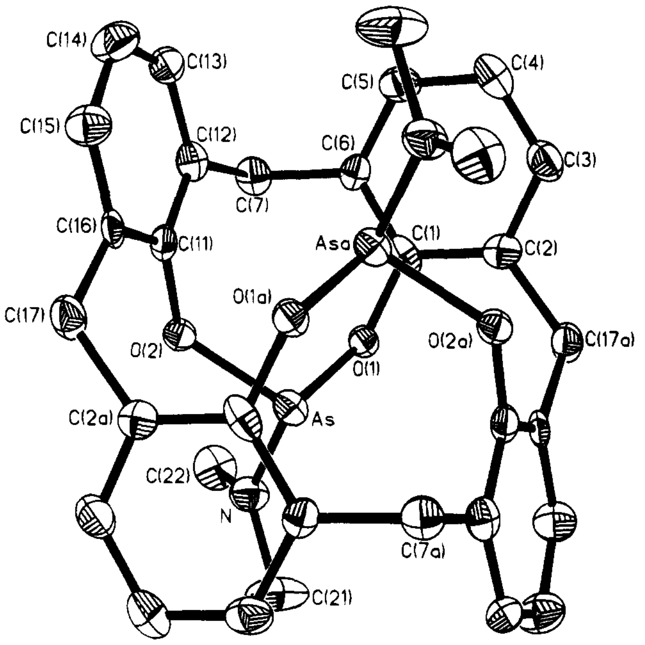

Figure 2. Computer-generated drawing of **6b** with thermal ellipsoids at 50%. All hydrogen atoms omitted for clarity.

observed with **5a**. It is known that tris(dimethylamino)arsine hydrolyzes to produce As_2O_3.[4] However, no reaction is observed when a mixture of oven-dried *p-tert*-butylcalix[4]arene and As_2O_3 is stirred overnight in C_6D_6. Thus, it appears that formation of **7** is due to partial hydrolysis of either tris(dimethylamino)arsine or an intermediate calix[4]arene/arsenic-containing species.

The X-ray structures of **5a**, **6b**, **7a**, and **7b** are illustrated in Figures 1–4, respectively. Selected bond distances and angles are listed in Table 2. The geometry around each of the arsenic atoms is pyramidal with reasonably small O–As–O (and O–As–N) angles, as expected. The sums of the three bond angles around each arsenic range from 289 to 292° with the exception of **5a** for which the sum is 278°, only slightly greater than the sum of three right angles. This is a result of the acute O(2)–As–O(4) of 85.0(3)° which is due to the solid-state hydrogen-bonding interaction from the phenolic hydroxyl group (Figure 1). Significantly, this interaction appears to be important in the solid-state only, since the hydroxyl resonance in the NMR spectrum occurs at δ 4.74, 0.3 ppm *upfield* of the corresponding signal in *p-tert*-butylphenol. Intramolecular hydrogen-bonding of the phenolic groups in calixarenes usually result in significant downfield shifts.[2a]

The (phenolic) As–O bond lengths range from 1.77 to 1.82 Å in the molecules and are about 0.2 Å longer than the P–O bond lengths in **4a** and about 0.1 Å longer than the hypervalent P–O bonds in **1a**. This lends further support to the argument that arsenic is too large to fit into the calix[4]arene plane, since the As–O bonds in a high-coordinate species should be even longer.

Three of the four calix[4]arene conformations are represented in these structures: **5a** adopts the (flattened) partial cone, **6b** the 1,2-alternate, and **7a** and **7b** the (slightly flattened) cone.

The structures of **7a** and **7b** allow comparison of the effect of substitution at the para position on geometry. As expected, there is little difference between the two structures with the largest As–O and O–C bond length differences being 0.03 and 0.02 Å, respectively. The largest bond angle differences are found in two of the As–O–C angles: the *tert*-butyl derivative has a 4° smaller As(1)–O(1)–C(1) angle and a 6° larger As(2)–O(3)–C(21) angle. This may be due to the presence of a benzene molecule within the cone in **7a** (see Experimental Section and supplementary material).

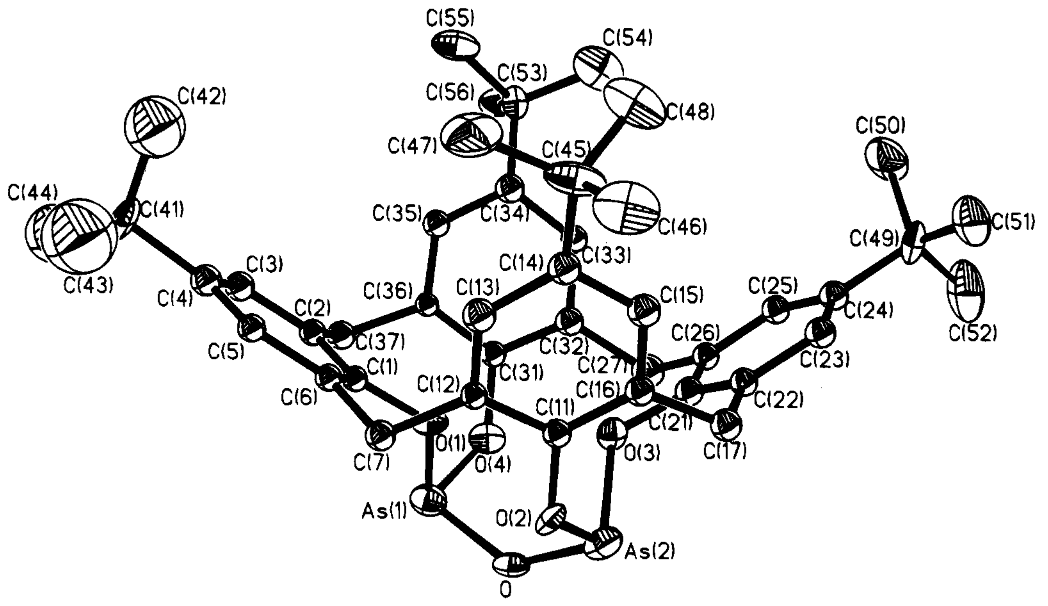

Figure 3. Computer-generated drawing of **7a** with thermal ellipsoids at 50%. All hydrogen atoms and benzene molecule within basket omitted for clarity.

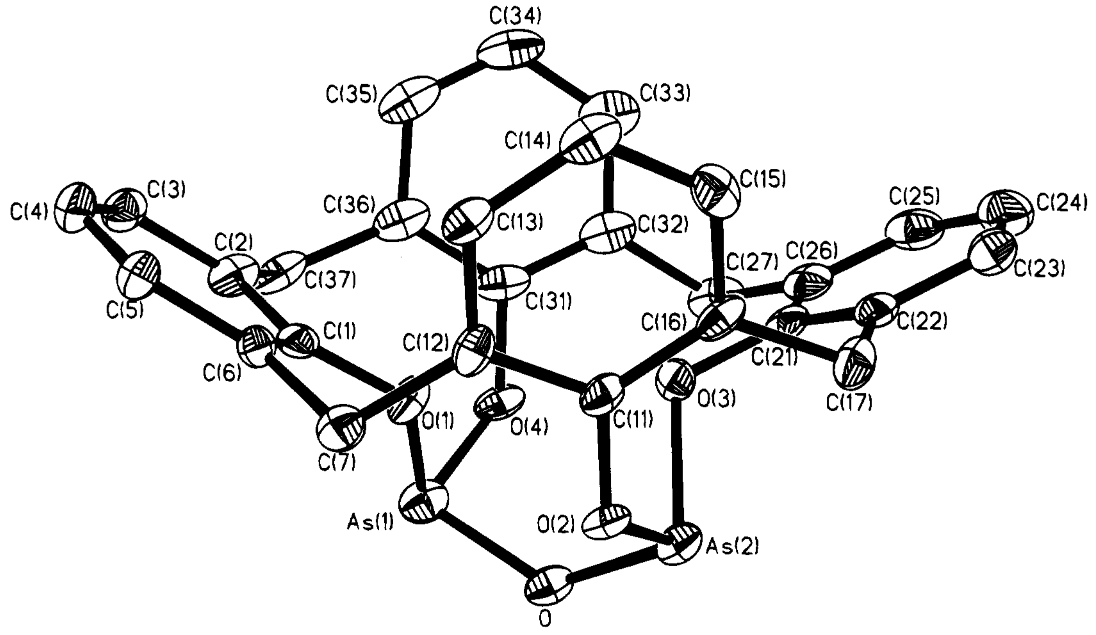

Figure 4. Computer-generated drawing of **7b** with thermal ellipsoids at 50%. All hydrogen atoms omitted for clarity.

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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 as well as computer-generated drawings of **5a** and **7a** showing solvated benzene (25 pages). Ordering information is given on any current masthead page.

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