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Article

Synthesis and Characterization of Bismuth(III) and Antimony(III) Calixarene Complexes

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A series of calixarene bismuth and antimony complexes have been fully characterized by NMR, X-ray, IR, UV/vis, and elemental analysis. The reactions of $SbCl_3$ with the monosodium salt of *p-tert*-butylcalix[4]arene (**Bu^{t}C4**), **Bu^{t}C4**·Na, and the tetralithium salt of para-*tert*-butylcalix[4]arene, **Bu^{t}C4**·Li_4, afforded two diantimony calix[4]arene complexes **Bu^{t}C4**$(SbCl)_2$, with different ^{1}H NMR spectra and different THF coordination, but the same core structures. Other calix[4]arene antimony complexes (**HC4**$(SbCl)_2$ **2** and **AC4**$(SbCl)_2$ **3**, diantimony chloride complexes of calix[4]arene and *p*-allylcalix[4]arene) and calix[4]arene bismuth complexes (**Bu^{t}C4**$(BiCl_2)_2Li_2$ **4**, **HC4**$(BiCl_2)_2Li_2$·6DMSO **5**, and **AC4**$(BiCl_2)_2Li_2$·4THF **6**) were prepared by the reactions of MCl_3 (M = Sb or Bi) with **RC4**·Li_4 (R = Bu^t, H, or allyl) in a 2:1 molar ratio in THF. The same strategy was applied for **Bu^{t}C8** (*p-tert*-butylcalix[8]arene), and the desired bismuth complex [**Bu^{t}C8**$(BiCl_2)_4(\mu\text{-}Cl)_2Li_6$][4THF·7DME] **12** was successfully synthesized. Complex **12** contains a planar Bi_4 core with four terminal chlorine atoms, which adopt a *syn* arrangement with respect to the plane defined by four bismuth atoms, and orient away from each other. A calix[4]arene monobismuth complex **11** was prepared by the reaction of $Bi(OBu^t)_3$ with the 1,2-disubstituted benzyl ether of calix[4]arene. Complexes **1**−**6** contain central planar $M_2(\mu\text{-}O)_2$ (M = Sb or Bi) four-membered rings, similar to four-membered rings observed in other calix[4]arene main group metal complexes. Intramolecular bismuth-arene π interactions are observed in complexes **4**−**6** and **11** but not **12**.

Introduction

The coordination chemistry of bismuth and antimony is currently attracting great interest because of its myriad applications in organic and oxidation catalysis, medicine and biochemistry, superconductors, ferroelectrics, and many other oxide based materials.[1−25] Chemists are focusing much attention on the synthesis and identification of new bismuth and antimony aryloxides/alkoxides that are suitable for these applications.[1,2,4,6,7,26−28]

A number of bismuth alkoxides have now been reported (recently reviewed by Mehring[1]), but few bismuth aryloxides, or antimony alkoxides/aryloxides, have been structurally characterized. Evans et al. reported the first monomeric bismuth aryloxide $Bi(O\text{-}2,6\text{-}Me_2C_6H_3)_3$,[29] and Horley et al. more recently reported the first antimony aryloxide $Sb(O\text{-}2,6\text{-}Me_2C_6H_3)_3$.[28] Whitmire et al. reported the fluoride-containing bismuth aryloxides $[Bi(\mu\text{-}OC_6F_5)(OC_6F_5)_2(Solv)]_2$ (Solv = toluene, THF, cyclohexane),[30,31] and recently Turner et al. reported aminetris(phenoxide) bismuth and antimony complexes.[32] Our group has now synthesized and characterized an extensive series of bismuth aryloxides $Bi(OAr)_3$ by the reactions of simple phenols with bismuth amides.[33]

There has also been considerable and growing interest in the metal coordination chemistry of calixarenes and calixarene derivatives as poly(dentate) ligands because of their potential applications in homogeneous catalysis and model systems, supramolecular chemistry, and material sciences.[34−36] Transition metal complexes of calixarenes have received much attention over the last two decades,[36−46] but far fewer heavy main group complexes have been reported (e.g., M = As, Ge, Sn, Al, Zn).[34,47−55]

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We have a particular interest in the coordination chemistry of bismuth,[7,33,48,56,57] and have found that the chemistry of bismuth, and even of antimony, frequently differs from that of their lighter congeners. In 2004 we demonstrated that calixarene frameworks are able to accommodate bismuth and antimony.[48] In an expansion of these studies, we report herein the synthesis and X-ray characterization of a series of Bi(III) and Sb(III) calixarene complexes.

Experimental Section

All reactions were carried out in a nitrogen-filled glovebox, unless otherwise stated. Dry tetrahydrofuran, toluene, and hexane were distilled from sodium benzophenone ketyl. Other anhydrous solvents were purchased from Aldrich and stored over 4 Å activated molecular sieves. *p*-Hcalix[4]arene (**HC4**),[58] *p-tert*-butylcalix[4]arene (**Bu^{t}C4**),[59] *p*-allylcalix[4]arene (**AC4**),[60] *p-tert*-butylcalix[8]arene (**Bu^{t}C8**),[61] 1,3-dimethyl ether of *p-tert*-butylcalix[4]arene (**7**),[62] 1,3-dimethyl ether of p-Hcalix[4]arene (**8**),[63] 1,2-dibenzyl ether of *p*-Hcalix[4]arene (**9**),[64] Bi(OBu^t)$_3$,[29] **Bu^{t}C4**·Na,[65] and Bi[N(SiMe$_3$)$_2$]$_3$[66] were prepared by literature procedures. ClBi(NCy$_2$)$_2$ was prepared in our laboratory by the reaction of BiCl$_3$ with LiN(Cy)$_2$ in a 1:2 ratio in THF.[67] All other reagents were commercially available and used without further purification. The melting points of all compounds were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 400 °C thermometer calibrated against a thermocouple. The melting points are uncorrected. A melting temperature preceded by a ">" sign indicates that the compound starts to decompose at that temperature but appears to actually melt at some higher temperature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer

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Table 1. Summary of X-ray Data Collection Parameters

	Bu^{t}C4(BiCl)$_2$·2LiCl·6THF (**4**·6THF)	**HC4**(BiCl)$_2$·2LiCl·6DMSO (**5**·6DMSO)	**AC4**(BiCl)$_2$·2LiCl·4THF (**6**·6THF)
formula	$C_{74}H_{112}Bi_2Cl_4Li_2O_{10}$	$C_{40}H_{56}Bi_2Cl_4Li_2O_{10}S_6$	$C_{56}H_{68}Bi_2Cl_4Li_2O_8$
fw	1735.28	1462.85	1442.74
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
T, K	213(2)	213(2)	100(2)
a, Å	12.7418(8)	9.8018(5)	11.2898(18)
b, Å	13.1653(8)	11.2845(9)	17.171(3)
c, Å	13.6265(9)	13.0660(7)	15.211(2)
α, deg	114.8660(10)	90.8250(10)	90
β, deg	111.9260(10)	109.3610(10)	110.594(2)
γ, deg	90.1240(10)	99.9690(10)	90
V, Å^3	1889.2(2)	1338.88(12)	2760.3(7)
Z, Z'	1, 1	2, 1	2, 1
cryst dimens, mm	0.20 × 0.15 × 0.10	0.30 × 0.18 × 0.05	0.39 × 0.21 × 0.12
d_{calcd}, g/cm^{-3}	1.525	1.814	1.736
μ, mm^{-1}	4.847	7.045	6.621
$2\theta_{max}$, deg	56.34	56.26	55.00
T_{min}/T_{max}	0.612	0.422	0.800
N measd. [R_{int}]	13757 [0.0201]	9750 [0.0245]	17135 [0.0205]
N ind	8510	6061	6288
N obs ($I > 2(I)$)	7869	5810	5550
no. of params	401	289	325
R ($I > 2(I)$)	0.0295	0.0401	0.0245
R_w ($I > 2(I)$)	0.0758	0.1077	0.0607
GOF	1.046	1.098	1.051

	Bn$_2$C4(BiO^{t}Bu) (**11**)	**HC4**(SbCl)$_2$·2DMSO (**2**·2DMSO)	**Bu^{t}C8**(BiCl)$_4$·6LiCl·6DME·3THF (**12**)
formula	$C_{46}H_{43}Bi_1O_5$	$C_{32}H_{32}Cl_2O_6S_2Sb_2$	$C_{149}H_{238}Bi_4C_{110}Li_6O_{30}$
fw	884.78	891.10	3741.46
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2(1)$	$P2(1)/n$	$P\bar{1}$
T, K	100(2)	213(2)	218(2)
a, Å	11.0005(6)	9.5564(4)	16.0081(9)
b, Å	31.5851(18)	15.8074(7)	20.2527(10)
c, Å	11.2779(6)	11.0846(5)	28.0539(15)
α, deg	90	90	77.0410(10)
β, deg	112.4710(10)	98.8210(10)	77.5000(10)
γ, deg	90	90	75.9260(10)
V, Å^3	3622.4(3)	1654.65(13)	8470.5(8)
Z, Z'	4, 1	2, 1	2, 1
cryst dimens, mm	0.37 × 0.20 × 0.17	0.15 × 0.10 × 0.08	0.35 × 0.20 × 0.10
d_{calcd}, g/cm^{-3}	1.622	1.789	1.467
μ, mm^{-1}	4.916	1.963	4.364
$2\theta_{max}$, deg	55.02	55.34	56.30
T_{min}/T_{max}		0.806	0.594
N measd. [R_{int}]	30577 [0.0270]	14108 [0.0230]	61607 [0.0235]
N ind	15662	7286	38331
N obs ($I > 2(I)$)	14593	6745	26148
no. of params	937	263	1643
R ($I > 2(I)$)	0.0254	0.0351	0.0392
R_w ($I > 2(I)$)	0.0492	0.0787	0.1001
GOF	0.789	1.102	0.970

at 300 and 75 MHz, respectively. Analytical samples were dried in a drying pistol under vacuum for at least 24 h. Microanalyses were performed by Microanalysis Laboratory, University of Illinois, Urbana−Champaign, Urbana, IL. IR and UV/vis spectra were obtained with an Infinity Gold FTIR spectrometer and Agilent 8453 spectrophotometer respectively. Filtrations used a medium sintered glass filter.

Synthesis of Bu^{t}C4(SbCl)$_2$ (1). Method A.[48] To a solution of **Bu^{t}C4**·Na (0.27 g, 0.40 mmol) in THF was added a solution of $SbCl_3$ (0.18 g, 0.80 mmol), and a white suspension was obtained. The reaction mixture was stirred overnight at room temperature. Removal of insoluble material (**Bu^{t}C4**) gave a colorless solution. The solvent was reduced to half-volume, the solution put into the freezer (−35 °C) for several days, and colorless X-ray quality crystals of **1** (0.28 g, 69% yield) were obtained.

Method B. To a suspension of **Bu^{t}C4** (0.32 g, 0.50 mmol) in THF (8.0 mL) was added a solution of LiOBu^t (0.16 g, 2.0 mmol) in THF (3.0 mL), and a light yellow solution was formed. The reaction mixture was stirred overnight at room temperature. A solution of $SbCl_3$ (0.23 g, 1.0 mmol) in THF (3.0 mL) was added to the solution of calixarene lithium salt, and a white suspension was immediately obtained. The mixture was stirred overnight at room temperature. The insoluble material was removed by centrifugation, and a colorless solution was obtained. The filtrate was dried under vacuum to afford **1** as a white powder which was recrystallized from THF-pentane to give colorless crystals (0.54 g, 78% yield). ^{1}H NMR (THF-d_8): δ 7.15 (*s*, 4H, Ar*H*), 7.14 (*s*, 4H, Ar*H*), 4.41 (*d*, J = 15.4 Hz, 4H, ArC*H*$_2$Ar), 3.53 (*d*, J = 15.4 Hz, 4H, ArC*H*$_2$Ar), 1.34 (*s*, 18H, C(C*H*$_3$)$_3$), 1.26 (*s*, 18H, C(C*H*$_3$)$_3$). No ^{13}C NMR data is available because of the poor solubility in THF. IR (nujol, cm^{-1}): 2724w, 2672w, 1588w, 1553w, 1537w, 1463vs, 1411w, 1377s, 1364m, 1311w, 1286w, 1260m, 1205m, 1189s, 1106m, 1025m, 979w, 925w, 913w, 880m, 866w, 831m, 823s, 804s, 757s, 745w, 723m, 684w. Anal. Calcd for

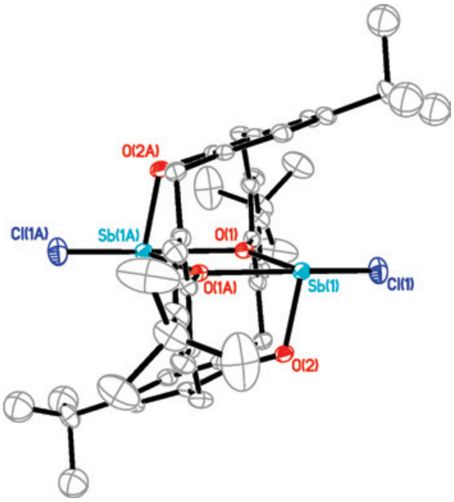

Figure 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram of **1**·4THF. The ellipsoids are shown at 30% probability, and the H atoms and noncoordinated solvent molecules are not shown for clarity.

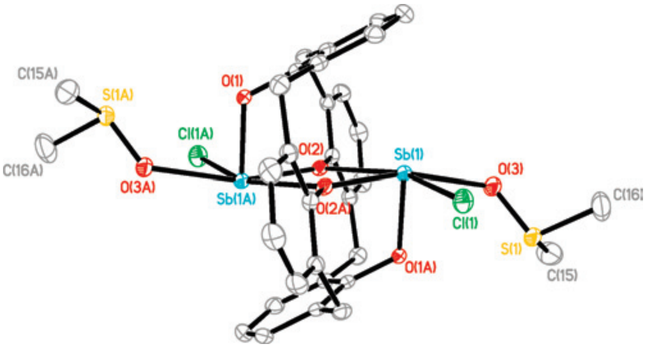

Figure 2. ORTEP diagram of **2**·2DMSO. The ellipsoids are shown at 30% probability, and the H atoms are not shown for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**·4THF and **2**·2DMSO

1·4THF		**2**·2DMSO	
Sb(1)−O(2)	1.9839(18)	Sb(1)−O(1A)	1.991(2)
Sb(1)−O(1)	2.0345(17)	Sb(1)−O(2A)	2.027(2)
Sb(1)−O(3)	2.569(2)	Sb(1)−O(3)	2.405(2)
Sb(1)−O(1A)	2.4363(17)	Sb(1)−O(2)	2.447(2)
Sb(1)−Cl(1)	2.4197(8)	Sb(1)−Cl(1)	2.4446(8)
O(2)−Sb(1)−O(1)	88.15(7)	O(1A)−Sb(1)−O(2A)	86.92(8)
O(2)−Sb(1)−O(1A)	81.24(6)	O(1A)−Sb(1)−O(3)	78.29(8)
O(1)−Sb(1)−O(1A)	65.98(5)	O(2A)−Sb(1)−O(3)	164.33(8)
Sb(1)−O(2)−Sb(1A)	114.02(8)	O(1A)−Sb(1)−O(2)	81.08(7)
C_{aryl}−O−Sb	114.64(14)−131.26(15)	O(2A)−Sb(1)−O(2)	65.79(8)
		O(3)−Sb(1)−O(2)	116.19(8)
		Sb(1)−O(2)−Sb(1A)	114.21(8)
		C_{aryl}−O−Sb	115.09(16)−130.66(17)

$C_{44}H_{52}Cl_2O_4Sb_2$·2THF: C, 55.09; H, 5.78. Found: C, 55.40; H, 5.78. mp: >190 °C (dec.). UV/vis λ_{max}/nm (THF) (ε/dm^3 mol^{-1} cm^{-1}): 267 (1.2 × 10^4), 272 (1.1 × 10^4), 287 (8.6 × 10^3).

Synthesis of HC4(SbCl)$_2$ (2). To a solution of **HC4** (0.21 g, 0.50 mmol) in THF (6.0 mL) was added a solution of LiOBu^t (0.17 g, 2.0 mmol) in THF (4.0 mL), and a light yellow suspension was obtained after 20 min. The reaction mixture was stirred overnight at room temperature, and a solution of $SbCl_3$ (0.23 g, 1.0 mmol) in THF (3.0 mL) was added. A white suspension was obtained, which was stirred overnight at room temperature. The insoluble material was collected on a medium pore frit, and a light yellow solution remained. The solid was extracted with DMSO, and the DMSO mixture was centrifuged to remove black insoluble material. The resulting DMSO solution was combined with the THF mother liquor. The combined solution was left untouched for 4 h at room temperature and colorless crystals (0.30 g, 61% yield) formed. ^{1}H NMR (DMSO-d_6): δ 7.00 (*m*, 8H, Ar*H*), 6.73 (*m*, 4H, Ar*H*), 4.34 (*d*, *J* = 15.0 Hz, 4H, ArC*H*$_2$Ar),3.43 (*d*, *J* = 15.0 Hz, 4H, ArC*H*$_2$Ar). No ^{13}C NMR data is available because of the poor solubility in DMSO. IR (nujol, cm^{-1}): 1589w, 1455vs, 1377s, 1305w, 1252s, 1235m, 1205s, 1196s, 1166w, 1083m, 1075m, 1050m, 968w, 908w, 883m, 854s, 778s, 773s, 765s, 743w, 715m, 617s. Anal. Calcd for $C_{28}H_{20}Cl_2O_4Sb_2$·DMSO: C, 44.32; H, 3.22. Found: C, 44.46; H, 3.52. mp: > 360 °C. UV/vis λ_{max}/nm (THF) (ε/dm^3 mol^{-1} cm^{-1}): 252 (6.0 × 10^3), 266 (5.8 × 10^3), 272 (5.3 × 10^3), 281 (3.9 × 10^3).

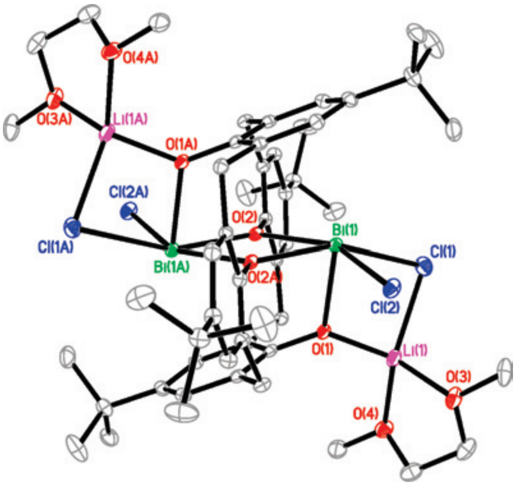

Figure 3. ORTEP diagram of **4a**. The ellipsoids are shown at 50% probability, and the H atoms are not shown for clarity.

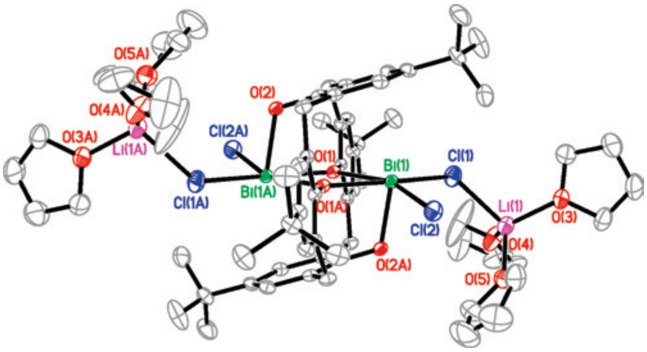

Figure 4. ORTEP diagram of **4b**. The ellipsoids are shown at 30% probability, and the H atoms are not shown for clarity.

Synthesis of AC4(SbCl)$_2$ (3). The procedure is the same as that for **2**, but using **AC4** (0.29 g, 0.50 mmol), LiOBu^t (0.17 g, 2.0 mmol), and $SbCl_3$ (0.23 g, 1.0 mmol). The product was recrystallized from DMSO-toluene (1:10). The yield is 0.32 g (71%).^{1}H NMR (THF-d_8): δ 6.90 (s, 4H, Ar*H*), 6.85 (s, 4H, Ar*H*), 6.03−5.87 (m, 4H, $CH_2-CH = CH_2$), 5.12−4.89 (m, 8H, $CH_2-CH=CH_2$), 4.43 (d, *J* = 15.4 Hz, 4H, ArC*H*$_2$Ar), 3.40 (d, *J* = 15.4 Hz, 4H, ArC*H*$_2$Ar), 3.32 (d, *J* = 6.2 Hz, 4H, C*H*$_2$-CH=CH$_2$), 3.23 (d, *J* = 6.6 Hz, 4H, C*H*$_2$-CH=CH$_2$). ^{13}C NMR (THF-d_8): δ 154.88, 151.14, 139.43, 135.55, 134.57, 133.92, 133.84, 129.24, 128.80, 115.45 (aromatic carbons and carbons from *C*H$_2$=*C*H of allyl groups), 40.83, 35.66 (methylene carbons from calix[4]arene and allyl

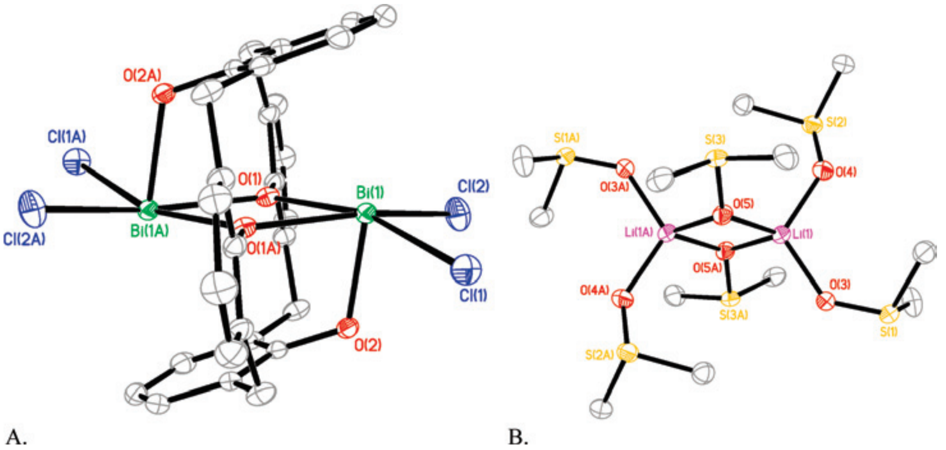

Figure 5. ORTEP diagram of **5**; anion (A) and cation (B). The ellipsoids are shown at 30% probability, and the H atoms are omitted for clarity.

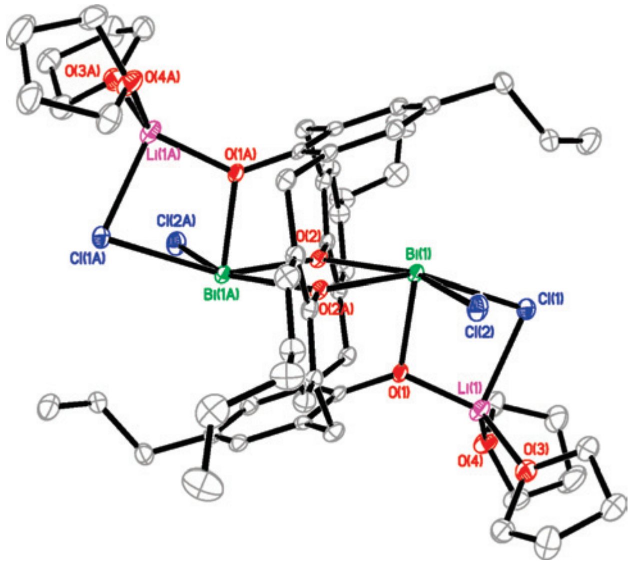

Figure 6. ORTEP diagram of **6**. The ellipsoids are shown at 30% probability, and the H atoms are omitted for clarity.

groups). IR (nujol, cm^{-1}): 2724w, 1637m, 1593w, 1575w, 1463vs, 1424m, 1377s, 1312m, 1287w, 1274w, 1260m, 1243m, 1204s, 1138s, 1133s, 1097m, 1016w, 1002w, 994m, 967w, 913s, 879m, 864w, 813s, 780s, 743m, 705m, 682w, 666w, 605s. Anal. Calcd for $C_{40}H_{36}Cl_2O_4Sb_2\cdot 2DMSO$: C, 53.26; H, 4.60. Found: C, 53.15; H, 4.95. mp: 279 °C (dec.). UV/vis λ_{max}/nm (THF) (ε/dm^3 mol^{-1} cm^{-1}): 266 (9.3×10^3), 276 (8.0×10^3), 288 (6.3×10^3).

Synthesis of $\mathrm{Bu^tC4(BiCl_2)_2Li_2}$ (4). Method A. To a suspension of **Bu^{t}C4** (0.32 g, 0.50 mmol) in THF (5.0 mL) was added a solution of LiOBu^t (0.16 g, 2.0 mmol) or Bu^{n}Li (1.0 mL, 2.0 M) at room temperature. The reaction mixture was stirred for 4 h, and then a solution of $BiCl_3$ (0.32 g, 1.0 mmol) in THF (3.0 mL) was added; immediately a yellow suspension was obtained. The resulting mixture was stirred overnight. Removal of the insoluble material by centrifugation gave a yellow solution. The filtrate was pumped dry to give **4** as yellow powder, which was recrystallized by pentane diffusion into its THF solution to afford yellow crystals (0.46 g, 69%). ^{1}H NMR (DMSO-d_6): δ 7.07 (*s*, 4H, Ar*H*), 6.99 (*s*, 4H, Ar*H*), 4.33 (*d*, J = 15.0 Hz, 4H, ArC*H*$_2$Ar), 3.63 (*d*, J = 15.0 Hz, 4H, ArC*H*$_2$Ar), 1.30 (*s*, 18H, (C*H*$_3$)$_3$C), 1.25 (*s*, 18H, (C*H*$_3$)$_3$C). ^{1}H NMR (THF-d_8): δ 7.20 (*s*, 4H, Ar*H*), 7.07 (*s*, 4H, Ar*H*), 4.44 (*d*, J = 15.0 Hz, 4H, ArC*H*$_2$Ar), 3.71 (*d*, J = 15.0 Hz, 4H, ArC*H*$_2$Ar), 1.30 (*s*, 18H, (C*H*$_3$)$_3$C), 1.27 (*s*, 18H, (C*H*$_3$)$_3$C). ^{13}C NMR (THF-d_8): δ 154.81, 152.04, 145.02, 144.41, 136.58, 135.60, 130.98, 125.77 (aromatic carbons), 35.18 (Ar*C*H$_2$Ar), 35.01, 34.66 (*C*(CH$_3$)$_3$), 32.90, 32.67 (C(*C*H$_3$)$_3$). IR (nujol, cm^{-1}): 2724w, 1764w, 1588w, 1553w, 1537w, 1462vs, 1410m, 1393m, 1377s, 1363s, 1306s, 1280s, 1250vs, 1200vs, 1115m, 1104m, 1048s, 991w, 913s, 894s, 878s, 868m, 830s, 824s, 805s, 752s, 723w, 701w, 682w. Anal. Calcd for $C_{44}H_{52}Bi_2Cl_2O_4\cdot 2THF\cdot 2LiCl$: C, 45.83; H, 5.07. Found: C, 45.98; H, 5.10. mp: 335 °C (dec.). UV/vis λ_{max}/nm (DMSO) (ε/dm^3 mol^{-1} cm^{-1}): 259 (3.9×10^3), 295 (2.9×10^3), 308 (2.8×10^3).

Method B. To a suspension of **Bu^{t}C4** (0.32 g, 0.50 mmol) in THF (8.0 mL) a yellow solution of $ClBi(NCy_2)_2$ (0.60 g, 1.0 mmol) in THF (5.0 mL) was added. The resulting mixture was stirred for 4 days. Removal of insoluble material by centrifugation gave a yellow solution. The filtrate was dried under vacuum to give **4**, which was recrystallized with THF/pentane or DME/hexane to provide yellow crystals (0.57 g, 84% yield).

Synthesis of $\mathrm{HC4(BiCl_2)_2Li_2\cdot 6DMSO}$ (5). To a solution of **HC4** (0.21 g, 0.50 mmol) in THF (6.0 mL) was slowly added a solution of 2.0 M Bu^{n}Li in pentane (1.0 mL, 2.0 mmol) to obtain a light yellow suspension. The reaction mixture was stirred for 4 h at room temperature. A solution of $BiCl_3$ (0.32 g, 1.0 mmol) in THF (3.0 mL) was added to the resulting suspension of calix[4]arene lithium salt,[68] and a dark suspension was obtained. The mixture was stirred overnight at room temperature. The insoluble material was collected by filtration, and a yellow solution remained. The solid was extracted with anhydrous DMSO (3.0 mL); then the mixture was centrifuged to remove the black insoluble material. The DMSO solution was combined with the mother liquor, and then an additional 10 mL of THF was added to the combined solutions. The resulting solution was allowed to settle for 2 h, and X-ray quality light yellow crystals (0.45 g, 62% yield) were formed. ^{1}H NMR (DMSO-d_6): δ 7.01 (*d*, J = 7.5 Hz, 4H, Ar*H*), 6.95 (*d*, J = 7.5 Hz, 4H, Ar*H*), 6.59 (*t*, J = 7.5 Hz, 2H, Ar*H*), 6.48 (*t*, J = 7.5 Hz, 2H, Ar*H*), 4.32 (*d*, J = 15.0 Hz, 4H, ArC*H*$_2$Ar), 3.63 (*d*, J = 15.0 Hz, 4H, ArC*H*$_2$Ar). No ^{13}C NMR data is available because of the poor solubility in DMSO. IR (nujol, cm^{-1}): 2723w, 1668w, 1579m, 1455vs, 1422s, 1377s, 1312w, 1298m, 1259s, 1212s, 1171w, 1158w, 1099w, 1072m, 1039vs, 1025vs, 1000vs, 959s, 938m, 913w, 900m, 878m, 850s, 807s, 767s, 757s, 748m, 720m, 709m, 676w, 609m. Anal. Calcd for ($C_{28}H_{20}Bi_2Cl_2O_4\cdot 6DMSO\cdot 2LiCl$): C, 32.75; H, 3.97. Found: C, 33.11; H, 4.08. mp: > 350 °C (165−167 °C appears to lose DMSO). UV/vis λ_{max}/nm (THF): 283, 303 (absorption coefficient ε is not available because of the limited solubility).

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(68) Guillemot, G.; Solari, E.; Rizzoli, C.; Floriani, C. *Chem.—Eur. J.* **2002**, *8*, 2072–2080.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **4a** and **4b**

4a		**4b**	
Bi(1)−O(1)	2.1698(12)	Bi(1)−O(2A)	2.125(2)
Bi(1)−O(2A)	2.2256(12)	Bi(1)−O(1A)	2.245(2)
Bi(1)−O(2)	2.3891(12)	Bi(1)−O(1)	2.364(2)
Bi(1)−Cl(2)	2.5616(5)	Bi(1)−Cl(2)	2.6106(10)
Bi(1)−Cl(1)	2.7715(5)	Bi(1)−Cl(1)	2.7847(11)
Cl(1)−Li(1)	2.367(4)	Cl(1)−Li(1)	2.328(8)
O−Li(1)	1.905(4)−2.003(4)	O−Li(1)	1.913(9)−1.940(9)
O(1)−Bi(1)−O(2A)	81.85(4)	O(2A)−Bi(1)−O(1A)	84.30(9)
O(1)−Bi(1)−O(2)	80.10(4)	O(2A)−Bi(1)−O(1)	81.68(8)
O(2)−Bi(1)−O(2A)	65.26(5)	O(1A)−Bi(1)−O(1)	65.83(9)
Cl(2)−Bi(1)−Cl(1)	92.112(16)	Cl(2)−Bi(1)−Cl(1)	107.17(4)
C_{aryl}−O−Bi	118.47(10)−126.78(11)	C_{aryl}−O−Bi	117.17(19)−123.0(2)
Bi(1)−O(2)−Bi(1A)	114.74(5)	Bi(1A)−O(1)−Bi(1)	114.17(9)

Table 4. Selected Bond Lengths (Å) and Angles (deg) of **5** and **6**

5		**6**	
Bi(1)−O(2)	2.124(3)	Bi(1)−O(1)	2.167(2)
Bi(1)−O(1)	2.300(3)	Bi(1)−O(2A)	2.227(2)
Bi(1)−O(1A)	2.362(3)	Bi(1)−O(2)	2.441(2)
Bi(1)−Cl(2)	2.6067(13)	Bi(1)−Cl(2)	2.5386(8)
Bi(1)−Cl(1)	2.7239(15)	Bi(1)−Cl(1)	2.7907(8)
O−Li(1)	1.890(9)−1.958(10)	O−Li(1)	1.921(6)−1.957(6)
O(2)−Bi(1)−O(1)	83.02(11)	O(1)−Bi(1)−O(2A)	82.56(7)
O(2)−Bi(1)−O(1A)	81.79(11)	O(1)−Bi(1)−O(2)	80.85(7)
O(1)−Bi(1)−O(1A)	65.47(13)	O(2A)−Bi(1)−O(2)	63.93(8)
Cl(2)−Bi(1)−Cl(1)	98.50(4)	Cl(2)−Bi(1)−Cl(1)	87.54(3)
C_{aryl}−O−Bi	118.2(2)−125.1(3)	C_{aryl}−O−Bi	118.23(17)−125.69(17)
Bi(1)−O(2)−Bi(1A)	114.53(13)	Bi(1A)−O(1)−Bi(1)	116.07(8)

Table 5. Selected Structural Parameters for **4**−**6** and **11**

	Bi−C(aryl)/Å	Bi···centroid (aryl)/Å	Bi···Bi/Å
4a	3.343−3.468	3.098	3.887
4b	3.362−3.432	3.103	3.870
5	3.432−3.478	3.157	3.922
6	3.399−3.481	3.146	3.962
11	3.243−3.474, 3.303−4.573	3.060, 3.736	

Synthesis of $AC4(BiCl_2)_2Li_2\cdot 4THF$ (6). To a solution of **AC4** (0.29 g, 0.50 mmol) in THF (5.0 mL) was added a solution of $LiOBu^t$ (0.17 g, 2.0 mmol) in THF (3.0 mL), and the reaction mixture was stirred for 4 h at room temperature. A solution of $BiCl_3$ (0.32 g, 1.0 mmol) in THF (3.0 mL) was added to the resulting lithium salt suspension, and a yellow suspension was obtained. The resulting suspension was stirred overnight at room temperature. Removal of insoluble material by centrifugation gave a yellow solution. The solvent was slowly reduced to one-fifth under vacuum, and yellow crystals were obtained (0.43 g, 60% yield). ^1H NMR (DMSO-d_6): δ 6.95 (s, 4H, Ar*H*), 6.90 (s, 4H, Ar*H*), 6.05−5.81 (m, 4H, CH_2−C*H*=CH_2), 5.16−4.96 (m, 8H, CH_2−CH=CH_2), 4.26 (d, J = 15.0 Hz, 4H, ArCH_2Ar), 3.75 (d, J = 15.0 Hz, 4H, ArCH_2Ar), 3.42 (d, J = 6.6 Hz, 4H, CH_2-CH=CH_2), 3.34 (d, J = 7.0 Hz, 4H, CH_2-CH=CH_2). IR (nujol, cm^{-1}): 1638m, 1593w, 1567w, 1505w, 1464vs, 1451vs, 1429s, 1377m, 1330w, 1306s, 1268s, 1247s, 1233vs, 1222vs, 1182w, 1144m, 1132m, 1085m, 1044s, 998m, 928s, 915vs, 874s, 810s, 801vs, 749m, 711m, 667w. Anal. Calcd for $C_{40}H_{36}Bi_2Cl_2O_4\cdot 4THF\cdot 2LiCl$: C, 46.62; H, 4.75. Found: C, 46.57; H, 4.95. mp: 310 °C (110 °C lost THF). UV/vis λ_{max}/nm (DMSO) (ε/dm^3 mol^{-1} cm^{-1}): 257 (6.0×10^3), 296 (4.2×10^3), 306 (4.0×10^3).

Reactions of 1,3-Dimethyl Ethers of Calix[4]arenes (7 and 8) with $Bi[N(SiMe_3)_2]_3$. To a solution of 1,3-dimethyl ether of calix[4]arene (0.50 mmol, 0.34 g for **7** and 0.23 g for **8**) in toluene (10 mL) was added a solution of $Bi[N(SiMe_3)_2]_3$ (0.35 g, 0.50 mmol) in toluene (6 mL), and immediately a yellow solution was formed. The reaction mixture was transferred to a 50 mL solvent bomb and heated for 6 h at 95 °C. An orange yellow suspension was obtained. While the suspension was hot, removal of the black precipitate by centrifugation gave an orange yellow solution which was left untouched for 3 h to give orange red crystals. ^1H NMR and X-ray characterization were unsuccessful.

Synthesis of Bismuth Complex of 1,2-Dibenzyl Ether of Calix[4]arene (11). To a solution of **9** (0.30 g, 0.50 mmol) in THF (8.0 mL) was added a solution of $Bi(OBu^t)_3$ (0.21 g, 0.50 mmol) in THF (3.0 mL), and the reaction mixture was stirred overnight at room temperature. The solvent was evaporated under vacuum, and a yellow residue was obtained. The residue was triturated with pentane to give a light yellow solid. The crude product was recrystallized by pentane diffusion into its THF solution, and needle crystals (0.29 g, 66% yield) were obtained. ^1H NMR (C_6D_6): δ 7.33 (d, J = 7.5 Hz, 2H, Ar*H*), 7.01 (two triplets partially overlap at 7.02 ppm and 7.00 ppm, J = 7.5 and 6.6 Hz, 8H, Ar*H*), 6.87 (d, J = 7.0 Hz, 2H, Ar*H*), 6.77 (two triplets partially overlap at 6.77 ppm, J = 7.5 and 6.6 Hz, 4H, Ar*H*), 6.59 (t, J = 7.5 Hz, 4H, Ar*H*), 6.40 (d, J = 7.0 Hz, 2H, Ar*H*), 5.57 (d, J = 12.3 Hz, 1H, ArCH_2Ar), 4.40 (d, J = 16.3 Hz, 2H, ArCH_2Ar), 4.14 (d, J = 11.9 Hz, 2H, CH_2 from Bn, AB pattern), 3.94 (d, J = 11.9 Hz, 2H, CH_2 from Bn, AB pattern), 3.84 (d, J = 12.3 Hz, 1H, ArCH_2Ar), 3.58 (two doublets partially overlap at 3.56 ppm, J = 16.3 and 12.8 Hz, 3H, ArCH_2Ar), 2.67 (d, J = 12.8 Hz, 1H, ArCH_2Ar), 1.50 (s, 9H, OC(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 155.9, 155.0, 138.7, 138.2, 136.9, 136.5, 131.7, 131.2, 129.4, 128.6, 128.5, 128.2, 127.8, 127.5, 125.3, 121.0 (aromatic carbons), 75.6 (O$CH_2C_6H_5$), 38.8 (CH_2), 36.0 (OC(CH_3)$_3$), 31.0, 29.9 (CH_2) (one carbon from O*C*(CH_3)$_3$ missing). IR (nujol, cm^{-1}): 2724w, 2671w, 1584w, 1495m, 1459vs, 1377vs, 1305w, 1260m, 1214w, 1169w, 1158w, 1093s, 1017s, 969w, 915w, 901w, 805s, 770w, 751m, 723s, 699m. Anal. Calcd for $C_{46}H_{43}Bi_1O_5$: C, 62.44; H, 4.90. Found:

C, 62.11; H, 4.87. mp: 189−191 °C. UV/vis λ_{max}/nm (DMSO) (ε/dm^3 mol^{-1} cm^{-1}): 267 (2.7 × 10^3), 282 (2.3 × 10^3), 294 (2.1 × 10^3), 313 (1.4 × 10^3).

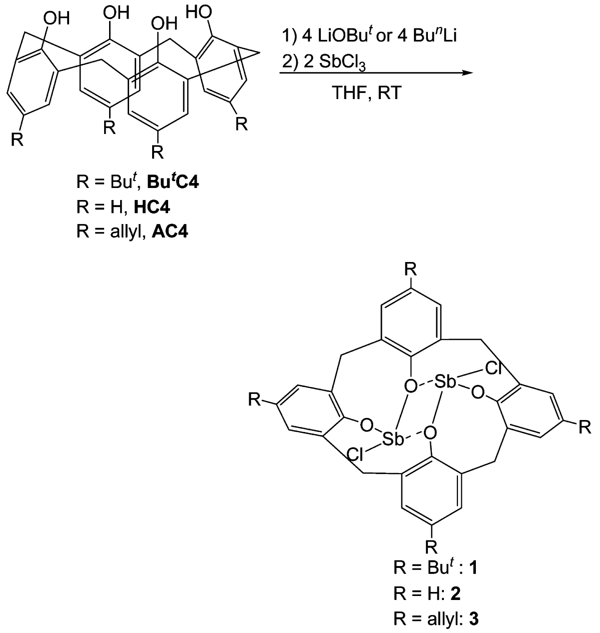
Synthesis of [Bu^{t}C8(BiCl$_2$)$_4$(μ-Cl)$_2$Li$_6$][4THF·7DME] (12). To a suspension of **Bu^{t}C8** (0.32 g, 0.25 mmol) in THF (8 mL) was slowly added a solution of 2.0 M Bu^{n}Li (2.0 mL), and an orange yellow solution was obtained. The mixture was stirred for 4 h, and then a solution of BiCl$_3$ (0.63 g, 1.00 mmol) in THF (4 mL) was added. Immediately a black suspension was formed. The resulting mixture was stirred overnight. The insoluble material was removed by centrifugation to give a yellow solution. The volume of the solution was reduced to one-fifth under vacuum, and yellow crystals precipitated at room temperature (0.59 g, 78% yield). No NMR data is available because of extremely poor solubility in organic solvents after recrystallization. Single crystals suitable for X-ray crystal structure analysis were obtained by hexane diffusion into its THF/DME (1:3) solution at room temperature. IR (nujol, cm^{-1}): ν 1627w, 1481s, 1462vs, 1392m, 1378s, 1363s, 1293m, 1260m, 1202s, 1154w, 1118m, 1086w, 1042m, 944w, 912w, 875m, 817m, 801m, 728m. Anal. Calcd (%) for C$_{88}$H$_{104}$Bi$_4$Cl$_{10}$Li$_6$O$_8$·7THF: C, 46.03; H, 5.33. Found (%): C 45.84, H, 5.65; mp: > 360 °C. UV/vis λ_{max}/nm (THF) (ε/dm^3 mol^{-1} cm^{-1}): 263 (2.6 × 10^4), 288 (2.7 × 10^4), 332 (1.6 × 10^4).

X-ray Crystallography. X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer at 100 K (**4a**, **6**, **11**) and 213 K (**1**, **2**, **4b**, **5**, **12**) using Mo Kα radiation. Data were integrated and corrected for Lorentz and polarization effects using SAINT.[69] Absorption corrections in all cases were applied by SADABS.[70] Structures were solved using direct methods or the Patterson function, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. Some molecules were refined with restrictions on the bond distances; in the refinement, typical average values were used as targets for corresponding bond distances. All non-hydrogen atoms were refined with anisotropic displacement coefficients, except atoms of disordered fragments which were refined with isotropic thermal parameters. The H atoms in **2** and **4a** were found from the residual density and refined with isotropic thermal parameters. H atoms in other structures were refined in a rigid group model. Highly disordered pentane and hexane solvent molecules sharing the same positions in **4a** and disordered THF solvent molecules in **12** were treated by SQUEEZE.[71] Corrections of the X-ray data by SQUEEZE, 210 and 366 electron/cell, were close to the required values of 184 and 320 electron/cell, respectively, for two pentane and two hexane molecules in the full unit cell of **4a** and eight THF molecules in the full unit cell of **12**. All calculations were performed using the SHELXTL suite of programs.[69] A summary of X-ray collection parameters is given in Table 1.

Results and Discussion

Synthesis. We have communicated the synthesis of the first antimony calixarene complex, **1**.[48] For this compound, the calix[4]arene tetraanion (**Bu^{t}C4**·Li$_4$)[68] is a more reliable precursor than the monoanion (**Bu^{t}C4**·Na).[65] The reaction of the monoanion and SbCl$_3$ always produced a mixture of parent calix[4]arene (**Bu^{t}C4**) and the product **1**.[48] As might be expected, the product yield is highest (>60%) if 2−4 equiv of SbCl$_3$ is used; a 1:1 ratio gave only a 29% yield. The reaction of the de-*tert*-butylated monoanion, **HC4**·Na, with SbCl$_3$ could not form **2** and only **HC4** was recovered.

In contrast, the reactions of SbCl$_3$ with **RC4**·Na$_4$ (R = H, Bu^t, or allyl) gave the corresponding products **1**, **2**, and **3** in >60% yield (eq 1). Complexes **1**−**3** were purified by recrystallization from THF/DMSO, THF, and THF/hexane, respectively. All complexes have limited solubility in organic solvents, but the solubility of **3** is much better than that of **1** and **2**.



(1)

The analogous reaction of **RC4**·M monoanion (R = H or Bu^t; M = Li, Na, or K) with BiCl$_3$ yielded an intractable yellow solid that was insoluble in organic solvents. Again the tetraanion **RC4**·Li$_4$ (R = H, Bu^t, or allyl) was more reliable, but the reaction stoichiometry was important. The molar ratio of 1 **RC4**·Li$_4$ to 2 BiCl$_3$ in THF gave a single air-sensitive product (**4**−**6**) (eq 2). When other ratios were used, a soluble yellow solid was formed, that decomposed to calix[4]arene and an unidentified black solid at room temperature. Products **4**−**6** were purified by recrystallization from THF-hexane (1:3). Their solubility depends on the substituents at the *para* position of calix[4]arene, and the order of their solubility is **6** > **4** > **5**.

Lattman et al.[55] compared phosphorus and arsenic calixarene complexes; whereas solely monophosphorus derivatives were observed, arsenic led to either mono- or diarsenic derivatives depending on reaction stoichiometry. As we continue down the periodic table, we find that both Sb and Bi form solely the dimetal derivatives irrespective of reaction stoichiometry. This is similar to other metals such as zinc and postulated to occur via an unstable monometallic intermediate.[47] Presumably the starting calixanion is protonated to form the side product calixarene, forming the unstable anionic monometallocalixarene intermediate that is

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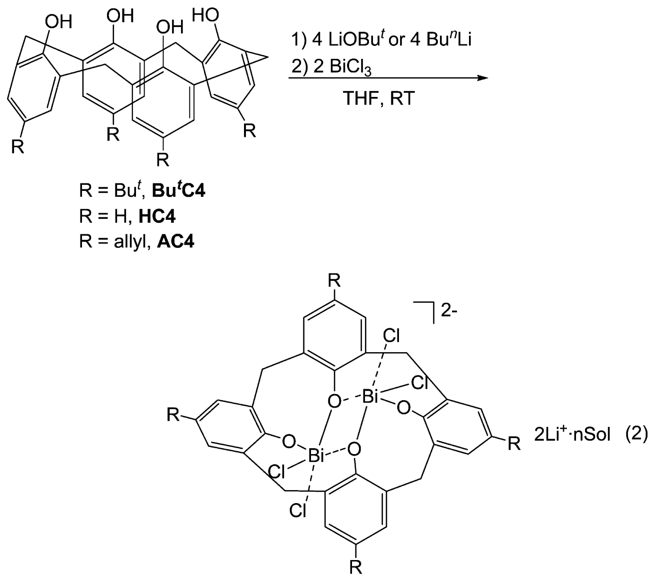


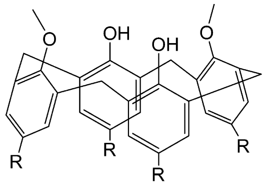
R = Bu^t, **Bu^{t}C4**
R = H, **HC4**
R = allyl, **AC4**

(2)

R = Bu^t, n = 2, Sol = DME: **4a** R = Bu^t, n = 6, Sol = THF:**4b**
R = H, n = 6, Sol = DMSO: **5** R = allyl, n = 4, Sol = THF: **6**

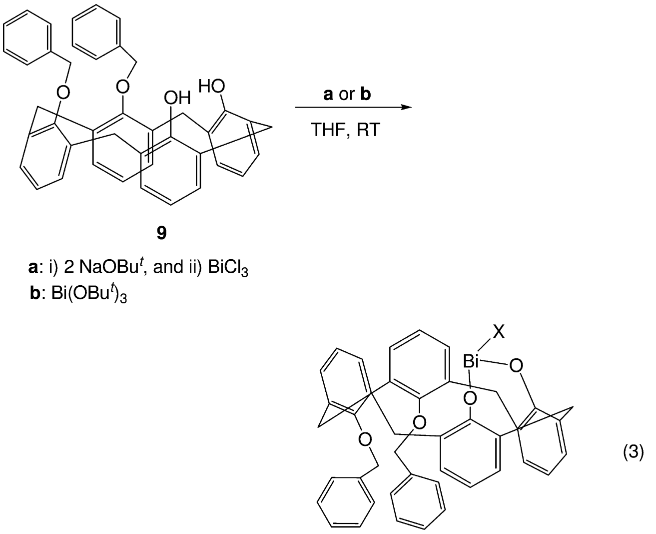
trapped with a second equivalent of metal. Monobismuth derivatives were obtained only by blocking two of the calixarene phenol groups, below.

To obtain calix[4]arene monobismuth complexes, we explored the reactions of the dialkyl ethers as dianionic macrocyclic ligands with suitable bismuth and antimony precursors (similar to the strategy used by Atwood et al. to make monoaluminum calixarene complexes[53]). The reactions of $BiCl_3$ with the salts of 1,3-dimethyl ethers of calixarenes (**7** and **8**) yielded orange yellow powders that were both unstable and insoluble in most organic solvents. There was no reaction at room temperature when **7** and **8** were treated with $Bi[N(SiMe_3)_2]_3$. Heating to 90−100 °C in toluene provided orange red crystals with complex NMR spectra. Although this compound appeared to contain bismuth, the orange red crystals decomposed to parent calixarene and unidentified insoluble material after 3 days. Demethylation was observed when **7** and **8** were treated with $Sb[N(SiMe_3)_2]_3$ in toluene at 90−100 °C.



R = Bu^t: **7** R = H: **8**

On the basis of the 1,2-disubstitution pattern observed in calix[4]arene bismuth and antimony complexes, we considered 1,2-dialkyl ethers of calix[4]arenes as potential supporting ligands. The dibenzylated calix[4]arene **9** was chosen as a ligand for bismuth complexes because of its ease of synthesis.[64] Treatment of **9** with NaOBu^t and $BiCl_3$ in THF gave the product **10** (eq 3, condition **a**). However, **10** decomposed to **9** and black solid during recrystallization. Complex **10** was therefore treated with 1 equiv of NaOBu^t at −78 °C to afford a stable compound **11**, which can also be directly prepared by the reaction of **9** with $Bi(OBu^t)_3$ (eq 3, condition **b**).



9

a: i) 2 NaOBu^t, and ii) $BiCl_3$
b: $Bi(OBu^t)_3$

(3)

X = Cl: **10**
X = OBu^t: **11**

As mentioned above, the molar ratio of calixarene to $BiCl_3$ is a key factor for forming stable bismuth complexes. We have found that the best molar ratio of oxygen atoms to bismuth atom is 2:1 for making calix[4]arene bismuth complexes. We then tried to apply this strategy to calix[8]arenes. The desired calix[8]arene bismuth complex was successfully synthesized by the reaction of octalithium salt of **Bu^{t}C8** with $BiCl_3$ in a 1:4 ratio in THF at room temperature. After recrystallization by hexane diffusion into its THF/DME (1:2) solution, [**Bu^{t}C8**$(BiCl_2)_4(\mu\text{-}Cl)_2$][6Li·4THF·7DME] (**12**) was obtained. This complex was extremely air-sensitive and had very limited solubility in organic solvents.

Spectral Data. The calix[4]arene antimony complexes **1**·3THF and **1**·4THF, prepared from the mono- or tetraanions, display different ^{1}H NMR spectra. The calix[4]arene antimony complex **1**·3THF prepared by the reaction of **Bu^{t}C4**Na with $SbCl_3$ exhibits two pairs of doublets for the methylene groups at 4.45, 4.36, 3.74, and 3.39 ppm, two doublets for aromatic protons at 7.21 and 7.12 ppm, and two singlets for *tert*-butyl groups at 1.35 and 1.26 ppm in THF-d_8. The calix[4]arene antimony complex **1**·4THF prepared by the reaction of **Bu^{t}C4**Li_4 with $SbCl_3$ shows only one pair of doublets for methylene groups at 4.41 and 3.53 ppm, two singlets for the aromatic protons at 7.15 and 7.14 ppm, and two singlets for *tert*-butyl groups at 1.34 and 1.26 ppm. However, both of the calix[4]arene antimony complexes show the same core crystal structures; just different THF coordination. We do not have an explanation for this observation.

The ^{1}H NMR spectra of bismuth complexes **4**−**6** (R = H, Bu^t, and allyl) show one pair of doublets for the methylene groups and two kinds of aromatic protons, which is typical for the flattened partial cone conformation of calix[4]arene complexes.[49,51−54] The ^{1}H NMR spectrum of **11** displays one singlet for OBu^t at 1.50 ppm (in comparison to that of $Bi(OBu^t)_3$ at 1.43 ppm) and three pairs of doublets at 5.57,

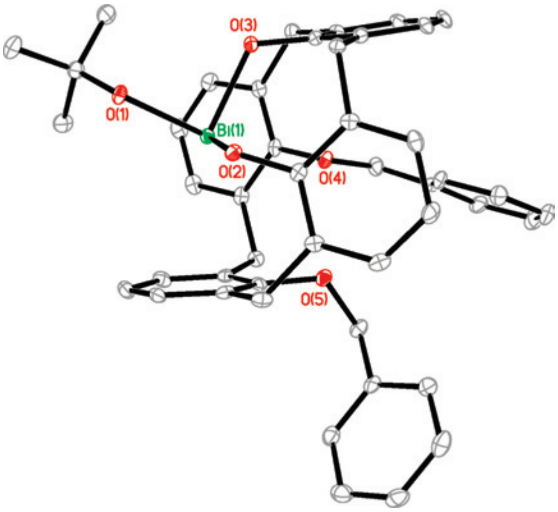
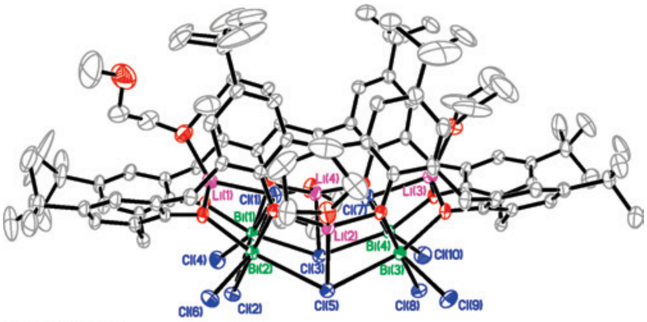


Figure 7. ORTEP diagram of **11**. The ellipsoids are shown at 30% probability, and the H atoms are not shown for clarity.

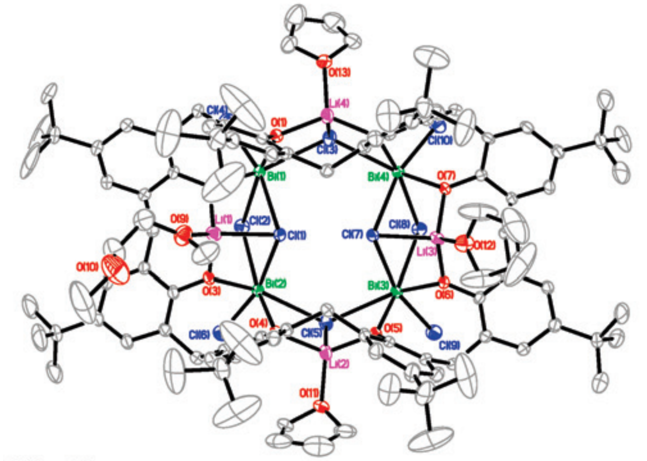
4.39, 3.84, 3.59, 3.58, and 2.45 ppm for methylene groups of calix[4]arene, which is a typical pattern of methylene groups in the 1,2-alternate conformation. The benzyl methylene groups give one pair of doublets at 4.14 and 3.94 ppm because of the diastereostopic protons.[64] The ^{13}C NMR spectrum of **11** shows three peaks for methylene carbons of calix[4]arene at 38.8, 31.0, and 29.9 ppm, which indicates that calix[4]arene has proximal substituents on the lower rim. A total of 16 peaks for aromatic carbons were observed in its ^{13}C NMR spectrum (only 12 peaks should theoretically be observed) because of the bismuth-arene π interaction in the molecule (this has been confirmed by its X-ray crystal structure, see next section). For **12** no NMR data is available because of poor solubility.

All calixarene bismuth and antimony complexes are air-sensitive and readily decompose to the corresponding calixarenes and other insoluble materials when exposed to air in solution for ~15 min. Treatment of complexes **1**−**6** with strong bases led to decomposition.

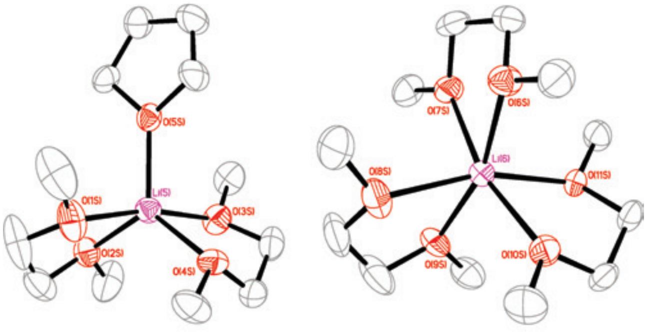
Crystal and Molecular Structures. Calixarene Antimony Complexes. The crystal structures of **1** and **2** are shown in Figures 1 and 2, and selected bond lengths and angles are listed in Table 2. The compounds are isostructural with their arsenic analogues,[55] displaying the flattened partial cone conformation and $M_2(\mu\text{-O})_2$ cores typical of main group metallocalixarenes,[49,51−54] and similar to compounds **4**−**6** (see next section). The $Sb_2(\mu\text{-O})_2$ cycles in **1** and **2** are asymmetric; the Sb−O bond lengths are 2.027(2) and 2.447(2) Å for **2**·2DMSO and 2.0345(17) and 2.4363(17) Å for **1**·4THF. The coordination of the Sb atom in **1**·4THF and **2**·2DMSO can be described as a distorted square pyramid. The apical Sb−O lengths (1.9839(18) and 1.991(2) Å, respectively, in **1** and **2**) are close to the short Sb−O length in the central $Sb_2(\mu\text{-O})_2$ cycles, and a little longer than the Sb−O bonds in $Sb(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ (1.967−1.976 Å).[28]



A. Side View



B. Top View



Cations Li(5) and Li(6)

Figure 8. ORTEP diagram of **12** (anion and cations). The ellipsoids are shown at 30% probability, and the H atoms and noncoordinated solvents are omitted for clarity.

Calixarene Bismuth Complexes. Crystal structures of **4**−**6** are illustrated in Figures 3−6, and selected bond lengths and angles are listed in Tables 3 and 4. The structures of **4**−**6** are again very similar to those of other main group metallocalixarenes, with a flattened partial cone conformation of the calixarene ring and a central planar $Bi_2(\mu\text{-O})_2$ core. In this case, though, the overall complex is dianionic because of coordination of another Cl^- on each bismuth atom. This difference may be due to the larger size and/or greater Lewis acidity of bismuth compared to its lighter congeners. Complexes **4**−**6** contain central planar $Bi_2(\mu\text{-O})_2$ four-membered rings bearing two *trans* terminal chlorine atoms and two *trans* bridging chlorine atoms. Each bismuth atom in these four structures is five-coordinate with a distorted square-based pyramidal geometry in which the apical site is occupied by an oxygen atom from a phenolate and the basal plane consists of two *cis* chlorine atoms and two *cis* oxygen atoms from phenolates. Each bismuth has one short (2.1698(12)−2.300(3) Å) and one long (2.245(2)−2.441(2) Å) $Bi{-}O_\mu$ bond distance.

Table 6. Selected Bond Lengths (Å) and Angles (deg) of **11** and **12**

11		**12**			
Bi(1)−O(1)	2.061(3)	Bi(1)−O(2)	2.151(3)	Bi(3)−Cl	2.5506(12)−3.0266(11)
Bi(1)−O(2)	2.098(3)	Bi(1)−O(1)	2.217(3)	Bi(4)−Cl	2.5595(13)−2.9747(12)
Bi(1)−O(3)	2.112(3)	Bi(2)−O(3)	2.158(3)	Li(1)−O	1.889(9)−1.918(9)
Bi(2)−O(1′)	2.069(3)	Bi(2)−O(4)	2.203(3)	Li(2)−O	1.938(9)−1.966(8)
Bi(2)−O(2′)	2.096(3)	Bi(3)−O(6)	2.161(3)	Li(3)−O	1.912(9)−1.955(8)
Bi(2)−O(3′)	2.100(3)	Bi(3)−O(5)	2.210(3)	Li(4)−O	1.923(9)−1.945(8)
		Bi(4)−O(7)	2.164(3)	Li(5)−O	1.975(11)−2.072(11)
O(1)−Bi(1)−O(2)	89.05(10)	Bi(4)−O(8)	2.202(3)	Li(6)−O	2..093(10)−2.180(10)
O(1)−Bi(1)−O(3)	91.15(10)	Bi(1)−Cl	2.5413(13)−2.9864(12)	Li(1)−C	2.722(9)−2.752(9)
O(2)−Bi(1)−O(3)	94.52(11)	Bi(2)−Cl	2.5580(12)−3.0079(11)	Li(3)−C	2.787(9)−2.790(8)
O(1′)−Bi(2)−O(2′)	87.83(11)				
O(1′)−Bi(2)−O(3′)	89.54(11)	O(2)−Bi(1)−O(1)	88.03(11)	Cl_{bridge}−Bi−Cl_{bridge}	103.46(3)−112.16(3)
O(2′)−Bi(2)−O(3′)	94.05(11)	O(3)−Bi(2)−O(4)	88.86(11)	Cl_{bridge}−Bi−Cl_{bridge}	82.54(3)−83.92(3)
C_{aryl}−O−Bi	121.2(2)−128.6(2)	O(5)−Bi(3)−O(6)	86.72(11)	Bi−Cl−Bi	94.90(4)−114.32(4)
		O(7)−Bi(4)−O(8)	87.32(11)	C_{aryl}−O−Bi	124.5(2)−134.3(3)

Table 7. Comparison of Bi−Cl_{bridge} Distances

	Bi−Cl_{bridge} /Å	ref
12	2.8421(11)−3.0266(12)	this work
$[TmBiCl(\mu\text{-}Cl)]_2$	2.807(5)−3.009(5)	85
$Bu_4N[PhBiCl_2Br][NMe_4]_2$	2.861(7)−3.020(7)	82
$[Bi_2(OC_6H_3Me_2\text{-}2,6)6(\mu\text{-}Cl)_2]$	2.9325(13)−3.0020(12)	72
$Mo(OMe)_5(CH_3CN)]Bi_2Cl_7$	2.859(1)−3.074(13)	86
$[Ph_2BiCl]_\infty$	2.746(4)−2.763(3)	87
$[\{(Me_3Si)_2CHBiCl_2\}_2\cdot Et_2O]_\infty$	2.729(4)−2.852(4)	83

The longer bond can be thought of as donation arising from one metal aryloxide to a second metal center.[30]

The addition of a halide anion source provides a facile method of preparing anionic bismuthate compounds because of the Lewis acidity of bismuth(III).[72] There are two kinds of chlorine atoms in **4**−**6**. One is the terminal chlorine atom with a short Bi−Cl bond; the other is the bridging chlorine atom between lithium and bismuth, which has a long Bi−Cl bond distance. The Bi−$Cl_{terminal}$ distances are in the range of 2.5386(8)−2.6106(10) Å, which are comparable to those in $[Bi_2Cl_4(THF)_2(\mu\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)_2]$ and $[Bi_2Cl_4(THF)_2(\mu\text{-}O\text{-}2,4,6\text{-}Me_3C_6H_2)_2]$.[72] The Bi−$Cl_{bridge}$ distances are in the range of 2.7239(15)−2.7907(8) Å, which are similar to those in oligomeric chlorobismuth(III) structures.[10] The Cl−Bi−Cl angles in **4**−**6** (87.54(3)−107.17(4) Å, Tables 1 and 2) vary greatly, most likely because of different coordination environments of the lithium cations connected to the bridging chlorine atoms. The Bi−O−Bi angles (114.17(9)−0 116.07(8)°, Tables 1 and 2) are close to each other, and similar to those in $[Bi[OCH(CF_3)_2]_3(THF)_2]$ (109.1(3)°),[30,31] $[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)X_n]_2\cdot zY$ ($X = Y = C_7H_8$, $n = 1$, $z = 1$ or 2; $X = THF$, $Y = C_6H_{14}$, $n = 2$, $z = 0$ or 1) (112.1(3)−112.8(3)°),[30] **1**, and **2** (114.21(7) and 114.02°). The average Bi−O−C (aryl) angles (121° for **4a**, **4b**, **5**, and **6**) are in good agreement with that in $Bi(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ (123.4°).[29]

The lithium cations in **4a**, **4b**, and **6** associate with the bismuth core by a chlorine bridge and additionally bind to solvent. Only in **5** are the lithium cations separated from the core structure, and their geometry can be described as distorted tetrahedral.

η^6-Bismuth-arene π interactions have been observed previously in mixed bismuth aryloxides, such as $[\{Bi(OC_6F_5)_3(C_7H_8)\}_2]\cdot 2C_7H_8$,[31] bismuth complexes of aminetris(phenoxide)s,[32] $[Bi_8O_4($**Bu^{t}C**$8)_2]\cdot 4C_7H_8$,[48] and $[Bi(OSiBu^t\text{-}Ph_2)_3]_2$.[73] Asymmetric intramolecular bismuth-arene π interactions have also been reported for the $Bi(OCPh_3)_3$ molecule.[57] The Bi−Ar centroid distances are generally determined by the acid−base properties of the donors and the acceptors. In **4**−**6** the bismuth atoms are each coordinated to the aromatic rings from their own ligands, which is facilitated by the doubly flattened partial cone conformation of the calixarene. The Bi−C distances and Bi···centroid (aryl) distances in **4**−**6** (Table 6) are comparable with those in the literature.[30−32,48,57,74−76] The Bi···Bi distances in **4**−**6** (3.8698(4)−3.917(5) Å) are much longer than those in the polymetallic bismuth oxo aryloxide $Bi_8O_4($**Bu^{t}C8**$)_2$ (3.6985(3), 3.6992(3), and 3.7670(3) Å)[48] and the dimeric units of $Bi(OCH_2CH_2OCH_3)_3$ (3.6426(4) Å)[77] because of the rigidity of the calix[4]arene backbone.

The crystal structure of **11** is shown in Figure 7, and selected bond lengths and angles are listed in Table 6. In the crystal structure of **11** the asymmetric unit has two independent molecules. Their bond distances and angles are similar. The calix[4]arene moiety in **11** adopts a 1,2-alternate conformation, and the *tert*-butoxide group faces away from the cavity of the calix[4]arene. The Bi−O bond lengths fall into the range of 2.061(3)−2.112(3) Å, typical for bismuth(III) aryloxides/alkoxides.[29,31,32,48,74,78] The $O(2)_{aryl}$−Bi−$O(3)_{aryl}$ bond angle (94.52(11)°) is slightly larger than the O_{aryl}−Bi−O_{alkyl} bond angles (89.01(11) and 91.15(11)°) because of the calix[4]arene backbone. The Bi−O−C (aryl) angles (121.2(2)−122.8(2)°) are in agreement with those in other bismuth aryloxides[29,33] and calix[4]arene main group element complexes.[55,79−81] Two of the calixarene aryl rings

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are puckered around the bismuth atom to enhance both η^6 and η^3 bismuth-arene π interactions. The ranges of Bi−C distances and Bi···centroid (aryl) distances (Table 5) are comparable with those in **4**−**6**.

The crystal structure of **12** is shown in Figure 8, and selected bond lengths and angles are listed in Table 6. The structure of **12** has a complex anion [**Bu^{t}C8**(Bi(μ_3-Cl)Cl)$_4$(μ-Cl)$_2$·4Li·3THF·DME]$^{2-}$. Its length is about 2 nm. The planar [Bi(1)Bi(2)Bi(3)Bi(4)] core bears the four terminal chlorine atoms Cl(4), Cl(6), Cl(9), and Cl(10). These chlorine atoms adopt a *syn* arrangement with respect to the plane defined by four bismuth atoms and orient away from each other. The Bi−Cl$_{terminal}$ distances are in the range of 2.5413(13)−2.5595(13) Å, similar to those in [Bi$_2$Cl$_4$(THF)$_2$(μ-O-2,6-Me$_2$C$_6$H$_3$)$_2$] (2.456(2)−2.585(2) Å) and [Bi$_2$Cl$_4$(THF)$_2$(μ-O-2,4,6-Me$_3$C$_6$H$_2$)$_2$] (2.4563(13)−2.5695(13) Å).[72]

Aryloxide groups can form strong bridging interactions in bismuth(III) aryloxide/alkoxide complexes,[72] and chlorine bridges are also well established in oligomeric chlorobismuth(III) structures.[82−84] In **12**, each pair of bismuth atoms is linked by chlorine bridges. Bi(1) and Bi(2) are linked together by Cl(1) and Cl(2), and Bi(3) and Bi(4) are fused together via Cl(7) and Cl(8). There is one chlorine bridge Cl(5) for Bi(3) and Bi(2), and one chlorine bridge Cl(3) for Bi(1) and Bi(4). Two bridging chlorine atoms Cl(1) and Cl(7) are located on the inside of the cavity of calix[8]arene, as well as their lithium cations Li(1) and Li(3). The rest of the bridging chlorine atoms are outside the cavity and located on the same side as the terminal chloride atoms. All bridging chlorine atoms are asymmetric. The Bi−Cl$_{bridge}$ distances are in the range of 2.8421(11)−3.0266(12) Å, comparable to those in the literature (Table 7).

The Cl$_{bridge}$−Bi−Cl$_{bridge}$ angles in **12** are of two types, larger angles with the range of 103.46(3)−112.16(3)° and smaller angles with the range of 82.54(3)−83.92(3)°. The smaller angles are the internal angles of two quadrangles [Bi(1)Cl(1)Bi(2)Cl(2)] and [Bi(3)Cl(7)Bi(4)Cl(8)]. The Bi−Cl$_{bridge}$−Bi angles (94.90(4)−114.32(4)) are consistent with those in [{(Me$_3$Si)$_2$CHBiCl$_2$}$_2$·Et$_2$O]$_\infty$ (98.88(16)°).[83] The O−Bi−O angles (88.03(3)−88.86(3)°) are close to the idealized 90° angles for the equatorial plane in a square-based bipyramid. The Bi−O−C (aryl) angles (126.0(2)−134.3(3)°) are somewhat larger than those in **4**−**6** (Tables 1 and 2) and Bi(O-2,6-Me$_2$C$_6$H$_3$)$_3$ (123(4)°).[29]

Each bismuth atom in **12** resides in a distorted square-based bipyramidal coordination environment being bonded to three bridging chlorines, one terminal chlorine, and two oxygen atoms of the phenolates. The apical sites are occupied by either a bridging or a terminal chlorine, and the equatorial plane consists of two *cis* oxygen atoms and two *cis* chlorine atoms. The Bi−O (aryl) distances are in the range of 2.151(3)−2.217(3) Å, typical for bismuth aryloxide complexes.[29,31,32,48] The conformation of **Bu^{t}C8** can be described as a slightly pinched cone, similar to that observed in our polymetallic bismuth oxo aryloxide Bi$_8$O$_4$(**Bu^{t}C8**)$_2$.[48]

Irregular coordination polyhedra are observed for the lithium cations. The lithium cations Li(5) and Li(6) are separate from the core structure of **12** (see Figure 8). Li(5) is five-coordinate with a distorted square-based pyramidal geometry and Li(6) is six-coordinate with a distorted square-based bipyramidal geometry. The lithium cations attached to the core structure are coordinated to two oxygen atoms from phenolates, one oxygen atom from solvent (THF or DME), and one chlorine atom, and their coordination geometry is distorted trigonal bipyramidal with the Cl atom in the apical position.

The Li−O bond lengths differ depending on the coordination environment of the lithium cations. The shorter Li−O bond lengths are observed for the lithium cations attached to the core structure [Li(1)−O 1.889(9)−1.918(9) Å, Li(2)−O 1.938(9)−1.966(8) Å, Li(3)−O 1.912(9)−1.955(8) Å, and Li(4)−O 1.923(9)−1.945(8) Å], similar to those found in calix[4]arene alkali metal/molybdenum dioxo complexes (1.860(11)−1.933(9) Å).[37] The longer Li−O bond lengths are found for the lithium cations that are away from the core structure [Li(5)−O 1.975(11)−2.072(11) Å, and Li(6)−O 2..093(10)−2.180(10) Å].

Conclusion

We have developed a systematic procedure to synthesize novel Bi(III) and Sb(III) calixarene complexes. Both antimony and bismuth favor a 2:1 metal/calixarene ratio, forming M$_2$(μ-O)$_2$ cores in partially flattened cone calixarenes, similar to several other main group elements.[49,51−55] To form 1:1 metal/calixarene complexes it is necessary to block two of the calixarene phenol groups, preferably in 1,2 orientation. The Lewis acidity of bismuth causes the association of chloride anion to form anionic bismuth calixarene complexes, as well as significant cation-π interactions with the calixarene ring. The 2:1 bismuth/phenol stoichiometry has allowed the controlled synthesis of the bismuth calix[8]arene complex, which is again anionic because of chloride association, but does not exhibit π-cation interactions.

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Supporting Information Available: X-ray crystallographic data in CIF format and sample NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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