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Hypervalent Bismuth Alkoxide Dimer Complexes: Syntheses, Structures, and Thermal Decompositions of [Bi(OCH(CF$_3$)$_2$)$_2$(μ-OCH(CF$_3$)$_2$)(THF)]$_2$ and [Bi(OC$_6$F$_5$)$_2$(μ-OC$_6$F$_5$)X$_n$]$_2$·zY (X = Y = C$_7$H$_8$, *n* = 1, *z* = 1 or 2; X = THF, Y = C$_6$H$_{14}$, *n* = 2, *z* = 0 or 1)

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The reaction of BiCl$_3$ with *in situ* generated NaOCH(CF$_3$)$_2$ in THF cleanly affords [Bi(OCH(CF$_3$)$_2$)$_2$(μ-OCH(CF$_3$)$_2$)(THF)]$_2$, **I**, a dimer containing a planar Bi$_2$(OR)$_2$ core. A THF ligand is coordinated to each bismuth center creating hypervalent 22 electron centers. Compound **I** has been characterized spectroscopically and by single crystal X-ray diffraction (monoclinic space group $P2_1/n$ (No. 14); a = 13.738(7) Å, b = 10.936(7) Å, c = 14.389(8) Å, β = 94.528(4)°, V = 2155(2) Å^3, Z = 2). A similar dimer, [Bi(OC$_6$F$_5$)$_2$(μ-OC$_6$F$_5$)(C$_7$H$_8$)]$_2$·2C$_7$H$_8$, **IIa**, is obtained via the reaction of BiPh$_3$ with HOC$_6$F$_5$ in toluene. Compound **IIa** has been characterized spectroscopically and by single-crystal X-ray diffraction (triclinic space group $P\bar{1}$ (No. 2); a = 11.086(6) Å, b = 13.378(8) Å, c = 10.771(9) Å, α = 98.58(7)°, β = 95.22(5)°, γ = 95.20(5)°, V = 1564(4) Å^3, Z = 1). A second, related crystal form of this compound which does not contain the lattice toluene molecules was also structurally characterized (**IIb**: monoclinic space group $P2_1/n$ (No. 14); a = 12.266(3) Å, b = 16.299(6) Å, c = 12.672(2) Å, β = 96.32(2)°, V = 2518(1) Å^3, Z = 2). Compounds **IIa,b** contain weakly bound η^6-toluene ligands with bismuth to ring centroid distances of 2.958(2) Å and 2.968(5) Å, respectively. Compounds **IIa,b** contain 26 electron bismuth centers. A detailed variable-temperature study of **II** is consistent with a monomer–dimer equilibrium. Recrystallization of compounds **IIa,b** from THF/hexane yields [Bi(OC$_6$F$_5$)$_2$(μ-OC$_6$F$_5$)(THF)$_2$]$_2$·C$_6$H$_{14}$, **IIIa** (triclinic space group $P\bar{1}$ (No. 2); a = 11.526(7) Å, b = 14.12(1) Å, c = 10.995(8) Å, α = 109.36(6)°, β = 101.63(6)°, γ = 105.20(6)°, V = 1545(2) Å^3, Z = 1), or [Bi(OC$_6$F$_5$)$_2$(μ-OC$_6$F$_5$)(THF)$_2$]$_2$, **IIIb** (triclinic space group $P\bar{1}$ (No. 2); a = 12.019(7) Å, b = 13.382(9) Å, c = 10.818(9) Å, α = 113.3(6)°, β = 91.36(6)°, γ = 111.7(5)°, V = 1454(2) Å^3, Z = 1). Compounds **IIIa,b** contain 24 electron bismuth centers. Compounds **I** and **IIb** decompose in H$_2$O-saturated oxygen atmospheres upon heating to 400 °C to give BiOF. Prehydrolysis of **IIb** followed by heating at 400 °C in air affords α-Bi$_2$O$_3$.

Introduction

Volatile and/or soluble metal alkoxide complexes are desirable for use as sol–gel or vapor-deposition reagents in the syntheses of metal oxide ceramics including high-T_C superconductors. Although much emphasis has recently been placed on creating mixed-metal alkoxide compounds which contain the stoichiometry of the target material,[1] very little is known about the chemistry of unimetallic alkoxide species. For instance, bismuth is an important component in many high-T_c superconductors such as Bi$_2$Sr$_2$CaCu$_2$O$_8$ as well as the non-copper-containing Ba$_{0.65}$K$_{0.35}$-BiO$_3$ however, bismuth alkoxide chemistry has not been extensively studied.[2] A more thorough understanding of the unimetallic alkoxide compounds is essential in order to design better mixed-metal alkoxide precursors.

In the 1960's Mehrotra and co-workers prepared the first examples of bismuth alkoxide compounds using nonsterically demanding alkoxide ligands. For R = Me, Et, or Pr the tris(alkoxide) species, Bi(OR)$_3$, were found to be insoluble. Although no structural information is available, they are thought to be polymeric.[3] More recently, in 1989, Evans and co-workers reported bismuth tris(alkoxide) compounds arising from the anion exchange reactions of bismuth trichloride with more bulky sodium alkoxide salts (R = ^{t}Bu, C$_6$H$_3$Me$_2$-2,6).[4a] The compound for which R = C$_6$H$_3$Me$_2$-2,6 was structurally characterized and shown to be monomeric. For R = ^{t}Bu the compound is also believed to be monomeric, but crystal disorder prevented a definitive solution. At about the same time a series of new bismuth alkoxide compounds was prepared by Buhro's research group via alcoholysis of Bi{N(SiMe$_3$)$_2$}$_3$.[4b] They structurally characterized Bi(OCH$_2$CH$_2$OMe)$_3$, which is polymeric with ether bridges. In 1991 Hubert-Pfalzgraf and co-workers used the same method to form Bi(OSiPh$_3$)$_3$, which has low solubility. The THF adduct Bi(OSiPh$_3$)$_3$(THF)$_3$ is, however, very soluble and has been shown by X-ray crystallography studies to be monomeric.[4c] Additionally, dimeric monoalkoxide complexes of the type [Bi(NO$_3$)$_2$(triethylene glycolate)]$_2$ have been synthesized by Rogers and co-workers. Higher order oligomerization is hindered via chelation by the triethylene glycolate ligand.[4d]

It appears that unless very sterically demanding ligands are used bismuth alkoxide species will oligomerize. The tris(alkoxide) compound, for which R = C$_6$H$_3$Me$_2$-2,6, contains an 18 electron bismuth center. However, the bismuth center is Lewis acidic and will become "hypervalent" through oligomerization when the OR functionality is small enough. We have recently communicated the syntheses and structures of two bismuth alkoxide dimer complexes[5] which contain intermediate-sized fluorinated ligands and act as Lewis acceptors to solvent molecules to create hypervalent bismuth centers. In many cases, bulky fluorinated ligands have allowed more volatile alkoxides of other

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Table I. Crystallographic Data Collection Parameters for **I**–**III**

	I	**IIa**	**IIb**	**IIIa**	**IIIb**
formula	$C_{26}H_{22}Bi_2F_{36}O_8$	$C_{64}H_{32}Bi_2F_{30}O_6$	$C_{50}H_{16}Bi_2F_{30}O_6$	$C_{58}H_{46}Bi_2F_{30}O_{10}$	$C_{52}H_{32}Bi_2F_{30}O_{10}$
cryst system	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
unit cell					
a (Å)	13.738(7)	11.0858(6)	12.266(3)	11.526(7)	12.019(7)
b (Å)	10.937(7)	13.3782(8)	16.299(6)	14.16(1)	13.382(9)
c (Å)	14.389(8)	10.771(9)	12.672(2)	10.995(8)	10.818(9)
α (deg)		98.576(7)		109.36(6)	113.3(6)
β (deg)	94.53(4)	95.224(5)	96.32(2)	101.63(6)	91.36(6)
γ (deg)		95.195(5)		105.20(6)	111.7(5)
V (Å^3)	2155(2)	1564(4)	2518(1)	1545(2)	1454(2)
Z	2	1	2	1	1
MW	1564.4	1998.9	1700.6	1890.9	1788.6
r(calc) (g/cm^3)	2.410	2.001	2.243	2.032	2.042
μ(Mo Kα) (mm^{-1})	8.32	5.74	7.12	5.81	6.17
R_w, R (%, obsd data)	4.7, 4.3	5.8, 5.9	5.6, 4.8	6.0, 4.7	3.2, 2.7
transm coeff		1.000–0.792	1.000–0.825	1.000–0.892	1.000–0.664

metals to be synthesized.[6] Here we extend these studies and investigate the hydrolytic and thermal decomposition of these bismuth compounds to give solid-state materials.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen atmosphere using glovebox, Schlenk, or vacuum-line techniques. Hydrocarbon solvents were freshly distilled from $LiAlH_4$. Tetrahydrofuran (THF) was dried over $LiAlH_4$ and freshly distilled from sodium/benzophenone ketyl. NMR solvents (benzene-d_6, toluene-d_8, THF-d_8) were dried over freshly cut sodium. $HOCH(CF_3)_2$ (Aldrich) was used as received. HOC_6F_5 (Strem) was dried via distillation from activated 4-Å molecular sieves at ~60 °C (10^{-3} Torr). Sodium hydride (Aldrich) was purchased as a mineral oil suspension, washed with THF, and stored in the glovebox. Commercial $BiCl_3$ (Matheson) was refluxed with $SOCl_2$ for several hours, after which the $SOCl_2$ was removed by distillation and the solid $BiCl_3$ dried under vacuum in a hot water bath. The solid was then dissolved in diethyl ether, the solution filtered, and the ether removed under vacuum in a hot water bath. $BiPh_3$ (Alfa) was used as received.

NMR spectra were recorded on a Bruker AC300 (299.95 MHz ^{1}H, 75.43 MHz ^{13}C) or a Bruker AC250 (250.13 MHz ^{1}H, 62.90 MHz ^{13}C, 235.34 MHz ^{19}F) spectrometer at ambient temperatures unless otherwise noted; chemical shifts are reported in ppm on a scale relative to $SiMe_4$ (^{1}H and ^{13}C NMR) or CF_3CO_2H (^{19}F NMR) as $\delta = 0$ ppm. Infrared spectra were taken as Nujol mulls on NaCl plates with a Perkin-Elmer 1600 series spectrometer. Thermogravimetric analyses were carried out on a Dupont 9900 thermal analysis system in an oxygen or argon atmosphere with a flow rate of 30 mL/min. The oxygen was passed through a water bubbler prior to entering the chamber. The heating program used was (1) isotherm for 10 min at room temperature, (2) heat at 5 °C/min to 400 °C, and (3) isotherm for 10 min at 400 °C. Powder X-ray diffraction patterns of the decomposition products were recorded at room temperature on a Phillips PW 1840 diffractometer with Cu Kα radiation and a Ni filter. NIST (National Institute of Standards and Technology) silicon was mixed with the samples and used as an internal standard. The X-ray diffraction powder patterns were collected for $10° \leq 2\theta \leq 60°$.

Synthesis of $[Bi(OCH(CF_3)_2)_2(\mu\text{–}OCH(CF_3)_2)(THF)]_2$, I. A THF solution of $HOCH(CF_3)_2$ (10.4 g, 61.9 mmol, in 50 mL) was added dropwise to a slurry of NaH in THF (1.92 g, 80 mmol, in 50 mL). Gas evolution occurred immediately. After being stirred for approximately 30 min, the solution was filtered through Celite. To the filtrate was added a THF solution of $BiCl_3$ (6.60 g, 20.1 mmol, in 100 mL) via canula resulting in the immediate formation of a white precipitate and a pale yellow solution. After the mixture was stirred for 12 h, the THF was removed in vacuo resulting in a white oily solid which was extracted with 250 mL of toluene with the extract filtered through Celite. The filtrate volume was reduced to approximately 100 mL and the solution allowed to crystallize at room temperature for 2 days. Large, colorless crystals (2.88 g, 18%) were collected by filtration. Removal of the toluene in vacuo from the filtrate followed by redissolution of the resulting white powder in THF produced a pale yellow solution. Removal of the THF in vacuo resulted in an oily yellow solid, which upon trituration with hexane resulted in a white powder and pale yellow solution. The white powder was collected on a frit as a second crop of **I** (3.83 g, 21%). Spectroscopic data: ^{1}H NMR (benzene-d_6) 5.58 (s), 3.39 (m), 1.26 (m) ppm; ^{19}F NMR (benzene-d_6, 297 K) 0.34 (d, $J_{FH} = 4$ Hz), (toluene-d_8, 242 K) 0.172 (d, $J = 4$ Hz); infrared spectrum 1294 (s), 1284 (s), 1258 (s), 1188 (s), 1165 (m), 1138 (s), 1095 (s), 1022 (m), 926 (w), 889 (m), 859 (s), 850 (m), 831 (w), 744 (s), 690 (s), 684 (s) cm^{-1}. Repeated attempts to obtain analytical data were unsuccessful due to fractional loss of tetrahydrofuran from analytical samples.

Synthesis of $[Bi(OC_6F_5)_2(\mu\text{–}OC_6F_5)(C_7H_8)]_2 \cdot nC_7H_8$ (IIa, $n = 2$; IIb, $n = 0$). Solid $BiPh_3$ (5.4 g, 12.3 mmol) and HOC_6F_5 (6.9 g, 37.5 mmol) were mixed in a Schlenk flask to which toluene was added resulting in a colorless solution and a white solid. The mixture was refluxed overnight resulting in a clear yellow solution. The solution was allowed to cool to room temperature and the solvent volume reduced in vacuo resulting in small yellow crystals. Crystallization was continued overnight at room temperature. The crystals were collected on a frit (5.95 g, 51%), and a single-crystal X-ray diffraction study showed these to be the compound labeled as **IIa**. Spectroscopic data: ^{19}F NMR (toluene-d_8, 297 K) –81.91 (d, $J_{FF} = 19$), –88.27 (t, $J_{FF} = 19$), –90.92 (m), (toluene-d_8, 213 K) –87.35 (d, $J_{FF} = 20$), –88.47 (t, $J_{FF} = 20$), –93.70 (m); infrared spectrum 2653 (w), 2450 (w), 1649 (w), 1635 (w), 1377 (m), 1366 (m), 1317 (w), 1310 (m), 1307 (m), 1260 (w), 1162 (m), 1140 (m), 1027 (s), 997 (s), 751 (m), 731 (w), 695 (w), 641 (w), 627 (w) cm^{-1}. A sample of **IIa** was dissolved in toluene was cooled to –20 °C and after a period of 12 h large yellow crystals had formed which were shown by single crystal X-ray analysis to be **IIb**.

Synthesis of $[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)(THF)_2]_2 \cdot nC_6H_{14}$ (IIIa, $n = 2$; IIIb, $n = 0$). A sample of **IIa** was redissolved in THF, and the solution was stirred for 24 h. The solvent was removed in vacuo resulting in a yellow oil, which was dissolved in hexane. Partial removal of the solvent in vacuo resulted in large yellow columns of **IIIa**.

Compound **IIIb** was obtained by recrystallization from THF as follows. A sample of **IIa** was redissolved in hexane. After being stirred for 2 h, the solution was filtered and the solvent was removed in vacuo. The resulting yellow oil was dissolved in THF and stirred for 2 h. Reduction of solvent in vacuo resulted in clear, colorless crystals of **IIIb**. Infrared spectrum: 2660 (m), 2454 (m), 2279 (w), 2142 (w), 2077 (w), 1770 (m) 1650 (m) 1632 (m), 1368 (s), 1310 (s), 1263 (s), 1155 (s), 991 (vs), 865 (vs).

Single Crystal Structure Determinations of I–III. All crystals were mounted with epoxy on the tip of a glass fiber. All data were collected at 193 K using the Rigaku TEXSAN Automatic Data Collection Series (Molecular Structure Corp., The Woodlands, TX) on a Rigaku AFC5S diffractometer using Mo Kα radiation (λ = 0.710 69 Å). The crystal-

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Table II. Positional Parameters and *B*(eq) Values for **I**

atom	*x*	*y*	*z*	*B*(eq)^a (Å^2)
Bi(1)	0.13988(3)	0.04558(4)	0.02608(3)	1.79(2)
O(1)	0.0486(5)	−0.1141(6)	−0.0098(5)	1.9(3)
O(2)	0.1368(5)	0.0945(7)	−0.1127(5)	2.4(3)
O(3)	0.2528(5)	−0.0817(7)	0.0080(5)	2.6(3)
O(4)	0.2748(5)	0.2094(7)	0.0400(5)	2.6(3)
C(11)	0.036(1)	−0.311(1)	−0.079(1)	4.0(7)
C(12)	0.0857(8)	−0.234(1)	−0.0012(8)	2.5(5)
C(13)	0.075(1)	−0.286(1)	0.094(1)	3.7(7)
C(21)	0.066(1)	0.008(1)	−0.254(1)	4.0(7)
C(22)	0.1580(8)	0.018(1)	−0.1840(8)	2.6(5)
C(23)	0.244(1)	0.066(1)	−0.231(1)	3.9(7)
C(31)	0.405(1)	−0.166(1)	−0.009(1)	4.7(8)
C(32)	0.3488(8)	−0.074(1)	0.042(1)	2.6(5)
C(33)	0.360(1)	−0.093(2)	0.145(1)	4.8(8)
C(41)	0.284(1)	0.304(1)	−0.0313(8)	3.3(6)
C(42)	0.326(1)	0.412(1)	0.023(1)	4.4(7)
C(43)	0.299(1)	0.395(1)	0.119(1)	4.0(7)
C(44)	0.304(1)	0.260(1)	0.1315(8)	3.2(6)
F(11A)	0.0612(6)	−0.2734(8)	−0.1622(6)	5.2(4)
F(11C)	0.0599(6)	−0.4282(6)	−0.0708(7)	5.4(5)
F(13A)	0.1064(6)	−0.2046(7)	0.1584(5)	5.1(4)
F(13B)	0.1269(7)	−0.3868(8)	0.1090(6)	6.3(5)
F(13C)	−0.0170(6)	−0.3131(7)	0.1089(6)	5.3(4)
F(21A)	−0.0117(5)	−0.0273(7)	−0.2107(5)	4.0(4)
F(21B)	0.0426(6)	0.1137(9)	−0.2953(6)	5.6(4)
F(21C)	0.0783(6)	−0.074(1)	−0.3197(6)	6.3(5)
F(23A)	0.2675(6)	−0.003(1)	−0.3015(6)	7.4(5)
F(23B)	0.2314(6)	0.1799(9)	−0.2635(6)	6.1(5)
F(23C)	0.3209(5)	0.0730(7)	−0.1703(5)	4.6(4)
F(31A)	0.5001(6)	−0.1713(8)	0.0257(8)	8.0(6)
F(31B)	0.4068(8)	−0.1415(9)	−0.0984(7)	7.6(6)
F(31C)	0.3701(6)	−0.2797(7)	−0.0019(7)	6.5(5)
F(33A)	0.3422(7)	−0.2036(8)	0.1740(7)	6.9(5)
F(33B)	0.2975(7)	−0.0171(8)	0.1868(6)	5.5(5)
F(33C)	0.4491(7)	−0.060(1)	0.1838(7)	8.4(6)

^{a} $B(\mathrm{eq}) = (8\pi^2/3)(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{22}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

lographic data collection parameters are listed in Table I. The monoclinic space groups were determined unambiguously from systematic absences. For the triclinic cells, the more common centrosymmetric settings were chosen and shown to be correct by subsequent structure solution and refinement. The data were corrected for Lorentz and polarization factors and for absorption using ψ-scans except for **I**. For **I** icing problems at the end of data collection prohibited ψ-scan data collection. The structures were solved by Patterson methods using SHELXS-86,[7] which identified the positions of the bismuth atoms. The remaining non-hydrogen atoms were found by using successive least-squares refinement cycles and electron density difference maps. Refinement was performed using the TEXSAN (5.0) structure solution and refinement package (Molecular Structure Corp.). The analytical form of the scattering factors for the appropriate neutral atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[8] For all structures, the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions where appropriate but not refined.

For **I**, the crystal selected for the X-ray diffraction study was a colorless block cut to dimensions 0.5 × 0.5 × 0.5 mm. Final unit cell parameters are based upon a least-squares analysis of the angular setting of 24 reflections (7.0° ≤ 2θ ≤ 12.1°). The CF_3 groups were found to be ordered. The final residuals were obtained by inclusion of those 2786 reflections with $I > 3\sigma(I)$. Final positional and thermal parameters are listed in Table II, and selected bond distances and angles, in Table VIII.

A yellow block-shaped crystal of **IIa**, cut to dimensions 0.3 × 0.3 × 0.3 mm, was selected for X-ray analysis. The data were corrected for absorption using ψ-scans. The final unit cell parameters were derived from a least-squares analysis of the angular setting of 25 reflections (7.8° ≤ 2θ ≤ 15.1°). The tabulated residuals were obtained for refinement using those 6823 reflections with $I > 3\sigma(I)$. Final positional and thermal parameters are listed in Table III, and selected bond distances and angles, in Table IX.

Table III. Positional Parameters and *B*(eq) Values for **IIa**

atom	*x*	*y*	*z*	*B*(eq)^a (Å^2)
Bi(1)	0.48332(5)	0.12530(4)	0.11915(5)	2.28(2)
O(1)	0.6406(8)	0.2310(6)	0.1897(8)	3.4(4)
O(2)	0.5937(7)	0.0604(6)	−0.0275(7)	2.5(3)
O(3)	0.5579(7)	0.0427(6)	0.2516(8)	2.7(3)
F(12)	0.5163(7)	0.3307(6)	0.0174(8)	4.7(4)
F(13)	0.629(1)	0.4944(6)	−0.061(1)	6.7(5)
F(14)	0.865(1)	0.5641(6)	0.029(10	7.5(5)
F(15)	0.9853(9)	0.4657(7)	0.200(1)	7.3(5)
F(16)	0.8732(8)	0.3028(7)	0.2754(9)	5.8(4)
F(22)	0.8440(7)	0.0917(6)	0.0311(8)	4.4(4)
F(23)	0.9817(7)	0.2299(6)	−0.0654(8)	5.0(4)
F(24)	0.8788(8)	0.3413(6)	−0.2296(8)	5.4(4)
F(25)	0.6340(8)	0.3073(6)	−0.3027(8)	5.2(4)
F(26)	0.4940(7)	0.1726(6)	−0.2035(7)	4.2(4)
F(32)	0.7239(7)	−0.0768(6)	0.1377(7)	4.2(3)
F(33)	0.9581(7)	−0.0560(6)	0.2320(9)	5.1(4)
F(34)	1.0411(7)	0.0844(7)	0.4397(8)	5.5(4)
F(35)	0.8839(7)	0.2033(7)	0.5504(8)	5.8(4)
F(36)	0.6448(7)	0.1843(6)	0.4571(8)	4.9(4)
C(1)	0.313(1)	0.149(1)	0.342(1)	3.9(7)
C(2)	0.360(1)	0.249(1)	0.338(1)	4.5(7)
C(3)	0.319(2)	0.299(1)	0.241(2)	5.0(8)
C(4)	0.234(2)	0.249(1)	0.145(2)	5.1(8)
C(5)	0.190(1)	0.153(1)	0.147(1)	4.1(7)
C(6)	0.229(1)	0.104(1)	0.244(2)	4.2(7)
C(7)	0.350(1)	0.098(1)	0.451(2)	6.1(9)
C(11)	0.693(1)	0.313(1)	0.150(1)	3.4(6)
C(12)	0.633(1)	0.367(1)	0.065(1)	3.4(6)
C(13)	0.691(2)	0.449(1)	0.023(1)	4.5(7)
C(14)	0.811(2)	0.482(1)	0.071(2)	5.1(8)
C(15)	0.870(2)	0.432(1)	0.154(2)	4.8(7)
C(16)	0.812(1)	0.351(1)	0.195(1)	3.9(7)
C(21)	0.664(1)	0.1268(9)	−0.084(1)	2.2(5)
C(22)	0.790(1)	0.142(1)	−0.052(1)	3.1(6)
C(23)	0.860(1)	0.214(1)	−0.101(1)	3.3(6)
C(24)	0.811(1)	0.268(1)	−0.187(1)	3.7(6)
C(25)	0.686(1)	0.253(1)	−0.223(1)	3.3(6)
C(26)	0.616(1)	0.181(1)	−0.172(1)	3.1(6)
C(31)	0.677(1)	0.053(1)	0.295(1)	2.4(5)
C(32)	0.759(1)	−0.006(1)	0.244(1)	3.0(5)
C(33)	0.880(1)	0.005(1)	0.289(1)	3.4(6)
C(34)	0.922(1)	0.075(1)	0.392(1)	3.2(6)
C(35)	0.842(1)	0.134(1)	0.448(1)	3.3(6)
C(36)	0.723(1)	0.124(1)	0.403(1)	3.5(6)
C(41)	0.236(1)	0.3606(8)	0.641(1)	10.8(7)
C(42)	0.152(1)	0.390(1)	0.553(1)	7.2(5)
C(43)	0.184(1)	0.472(1)	0.491(1)	12.2(8)
C(44)	0.301(2)	0.524(1)	0.518(2)	14(1)
C(45)	0.385(1)	0.494(1)	0.606(2)	11.5(7)
C(46)	0.353(1)	0.413(1)	0.667(1)	8.1(5)
C(47)	0.201(2)	0.271(1)	0.708(2)	14(1)

^{a} $B(\mathrm{eq}) = (8\pi^2/3)(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{22}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

Crystals of **IIb** were also yellow. The block-shaped crystal selected for X-ray analysis was cut to dimensions 0.5 × 0.5 × 0.5 mm. The final unit cell parameters were derived from a least-squares analysis of the angular setting of 25 reflections (21.7° ≤ 2θ ≤ 29.9°). Refinement of those 4725 reflections with $I > 3\sigma(I)$ gave the residuals listed in the table. Final positional and thermal parameters are listed in Table IV, and selected bond distances and angles, in Table X.

Yellow crystals of **IIIa,b** were also cut to a suitable size for X-ray analysis. For **IIIa** the final crystal dimensions were 0.2 × 0.2 × 0.2 mm. The final unit cell parameters were derived from a least-squares analysis of the angular setting of 24 reflections (7.5° ≤ 2θ ≤ 13.1°). The residuals listed were based on 4467 reflections with $I > 3\sigma(I)$. Final positional and thermal parameters are listed in Table V, and selected bond distances and angles, in Table XI. For **IIIb**, the final crystal dimensions were 0.3 × 0.3 × 0.5 mm. The final unit cell parameters were derived from a least-squares analysis of the angular setting of 25 reflections (6.6° ≤ 2θ ≤ 12.3°). The tabulated values are based on those 5117 reflections with $I > 3\sigma(I)$. Final positional and thermal parameters are listed in Table VI, and selected bond distances and angles, in Table XII.

Thermogravimetric Analysis of I in an O_2/H_2O Atmosphere. A 20-mg sample of **I** was subjected to thermogravimetric analysis in an oxygen/ H_2O atmosphere. The total decomposition to BiOF (identified by powder

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(7) Sheldrick, G. M. SHELXS86, Program for Crystal Structure Solution. University of Göttingen, FRG, 1986.

(8) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–101 and 149–150.

Table IV. Positional Parameters and *B*(eq) Values for **IIb**

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Bi(1)	0.00892(4)	0.11833(3)	0.03131(3)	1.91(2)
O(1)	0.0079(6)	0.0292(4)	−0.0958(6)	2.2(3)
O(2)	0.0663(7)	0.1959(5)	−0.0867(6)	2.6(4)
O(3)	0.1708(7)	0.0898(5)	0.0886(6)	2.5(4)
F(12)	−0.2043(6)	0.0699(4)	−0.1815(5)	3.5(3)
F(13)	−0.2529(6)	0.0959(5)	−0.3899(6)	3.9(4)
F(14)	−0.0912(6)	0.0970(5)	−0.5210(5)	3.7(3)
F(15)	0.1183(6)	0.0748(5)	−0.4393(5)	3.6(4)
F(16)	0.1684(6)	0.0430(5)	−0.2311(5)	3.7(4)
F(22)	0.2191(6)	0.3134(5)	−0.0909(6)	3.9(4)
F(23)	0.1654(8)	0.4739(5)	−0.1248(7)	5.6(5)
F(24)	−0.0479(8)	0.5170(5)	−0.1579(8)	6.5(5)
F(25)	−0.2088(7)	0.4002(5)	−0.1533(9)	6.6(5)
F(26)	−0.1528(6)	0.2438(5)	−0.1177(7)	4.7(4)
F(32)	0.2994(6)	0.2246(4)	0.1072(6)	4.2(4)
F(33)	0.4855(7)	0.2343(5)	0.0103(7)	5.5(5)
F(34)	0.5436(6)	0.1057(5)	−0.1114(7)	5.2(4)
F(35)	0.4150(7)	−0.0287(5)	−0.1341(6)	4.4(4)
F(36)	0.2356(6)	−0.0383(4)	−0.0362(5)	3.3(3)
C(11)	−0.016(1)	0.0507(7)	−0.2019(9)	2.4(5)
C(12)	−0.122(1)	0.0665(7)	−0.245(1)	2.4(5)
C(13)	−0.146(1)	0.0812(7)	−0.353(1)	2.5(5)
C(14)	−0.067(1)	0.0821(7)	−0.4165(8)	2.3(5)
C(15)	0.038(1)	0.0711(7)	−0.376(1)	2.3(5)
C(16)	0.063(1)	0.0556(7)	−0.2690(9)	1.9(5)
C(21)	0.036(1)	0.2725(7)	−0.104(1)	2.6(6)
C(22)	0.113(1)	0.3346(8)	−0.107(1)	2.5(6)
C(23)	0.082(1)	0.4158(8)	−0.125(1)	3.4(6)
C(24)	−0.024(1)	0.4371(9)	−0.142(1)	4.0(7)
C(25)	−0.103(1)	0.3789(8)	−0.140(1)	3.4(6)
C(26)	−0.075(1)	0.3007(8)	−0.121(1)	2.8(6)
C(31)	0.259(1)	0.0946(7)	0.033(1)	2.2(5)
C(32)	0.325(1)	0.1625(8)	0.045(1)	3.0(6)
C(33)	0.420(1)	0.1663(8)	−0.001(1)	3.9(7)
C(34)	0.451(1)	0.102(1)	−0.066(1)	3.7(7)
C(35)	0.386(1)	0.0331(9)	−0.077(1)	3.1(6)
C(36)	0.293(1)	0.0316(8)	−0.024(1)	2.4(5)
C(41)	−0.152(1)	0.2340(9)	0.180(1)	3.4(6)
C(42)	−0.107(1)	0.1680(8)	0.245(1)	3.3(6)
C(43)	0.007(1)	0.1646(9)	0.274(1)	3.4(6)
C(44)	0.073(1)	0.221(1)	0.238(1)	3.8(7)
C(45)	0.023(1)	0.2842(8)	0.171(1)	4.4(8)
C(46)	−0.088(1)	0.2876(8)	0.144(1)	3.6(7)
C(47)	−0.275(1)	0.233(1)	0.153(1)	6(1)

[a] $B(\mathrm{eq}) = (8\pi^2/3)(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{22}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma$ $2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

Table V. Positional Parameters and *B*(eq) Values for **IIIa**

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Bi(1)	0.48898(5)	0.15031(5)	0.03325(6)	2.39(2)
O(1)	0.6421(8)	0.2968(7)	0.157(1)	3.1(3)
O(2)	0.6228(8)	0.0698(8)	0.072(1)	3.3(3)
O(3)	0.4525(8)	0.1735(8)	0.222(1)	3.4(3)
O(4)	0.351(1)	0.2613(9)	−0.007(1)	4.1(4)
O(5)	0.580(1)	0.1957(8)	−0.148(1)	3.8(4)
F(12)	0.6974(7)	0.3010(7)	0.4176(9)	3.9(3)
F(13)	0.6953(8)	0.4659(7)	0.6278(9)	4.4(3)
F(14)	0.6460(8)	0.6332(7)	0.5911(9)	4.4(3)
F(15)	0.5970(9)	0.6341(7)	0.339(1)	4.8(4)
F(16)	0.5911(8)	0.4674(7)	0.126(1)	4.4(3)
F(22)	0.6552(8)	0.0533(8)	0.319(1)	5.3(4)
F(23)	0.8859(9)	0.1411(8)	0.508(1)	5.6(4)
F(24)	1.0926(8)	0.2457(8)	0.457(1)	5.0(3)
F(25)	1.0641(7)	0.2620(8)	0.215(1)	5.5(4)
F(26)	0.8333(8)	0.1794(7)	0.0269(8)	4.3(3)
F(32)	0.2164(7)	0.0585(7)	0.0337(8)	3.8(3)
F(33)	0.0189(8)	−0.0355(8)	0.106(1)	5.6(4)
F(34)	0.0507(9)	−0.0048(9)	0.369(1)	5.9(4)
F(35)	0.284(1)	0.1077(8)	0.555(1)	5.8(4)
F(36)	0.4813(9)	0.1960(8)	0.4828(9)	5.5(4)
C(11)	0.640(1)	0.377(1)	0.262(2)	2.7(5)
C(12)	0.667(1)	0.381(1)	0.394(2)	2.8(5)
C(13)	0.668(1	0.465(1)	0.503(2)	3.0(5)
C(14)	0.643(1)	0.551(1)	0.486(2)	3.5(5)
C(15)	0.618(1)	0.549(1)	0.358(2)	3.7(6)
C(16)	0.616(1)	0.463(1)	0.249(2)	3.4(5)
C(21)	0.738(1)	0.116(1)	0.169(2)	3.1(5)
C(22)	0.754(1)	0.105(1)	0.291(2)	3.4(5)
C(23)	0.872(2)	0.150(1)	0.388(2)	4.4(6)
C(24)	0.977(1)	0.202(1)	0.363(2)	4.1(6)
C(25)	0.962(1)	0.211(1)	0.239(2)	3.8(6)
C(26)	0.845(1)	0.169(1)	0.145(1)	3.3(5)
C(31)	0.355(1)	0.128(1)	0.254(1)	2.9(5)
C(32)	0.236(1)	0.072(1)	0.164(1)	3.0(5)
C(33)	0.133(1)	0.025(1)	0.202(2)	3.5(6)
C(34)	0.150(1)	0.037(1)	0.333(2)	3.8(6)
C(35)	0.267(2)	0.096(1)	0.428(2)	4.3(6)
C(36)	0.366(1)	0.140(1)	0.389(2)	3.7(5)
C(41)	0.286(2)	0.231(2)	−0.145(2)	8(1)
C(42)	0.188(2)	0.281(2)	−0.150(2)	6.5(9)
C(43)	0.187(3)	0.325(2)	−0.018(3)	10(1)
C(44)	0.287(2)	0.315(1)	0.075(2)	5.0(7)
C(51)	0.606(2)	0.125(1)	−0.250(2)	4.6(6)
C(52)	0.718(2)	0.183(2)	−0.277(2)	6.2(8)
C(53)	0.741(2)	0.293(2)	−0.205(3)	8(1)
C(54)	0.640(2)	0.306(1)	−0.141(2)	6.1(8)
C(100)	0.992(1)	0.471(1)	0.424(2)	4.3(6)
C(101)	0.980(1)	0.541(2)	0.348(2)	5.3(7)
C(102)	0.960(2)	0.487(2)	0.200(2)	6.6(8)

[a] $B(\mathrm{eq}) = (8\pi^2/3)(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{22}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

X-ray diffraction[9a]) occurred in multiple steps with a total weight loss of 49.1% (vs 68.8% theoretical). Compound **I** is very hygroscopic, and substantial decomposition had occurred from brief exposure to air prior to analysis.

Thermogravimetric Analysis of I in an Ar Atmosphere. A 20-mg sample of **I** was subjected to thermogravimetric analysis in an argon atmosphere. The total decomposition to BiOF (identified by powder X-ray diffraction)[9a] occurred in multiple steps with a weight loss of 56.6% (vs 68.8% theoretical). A small amount of hexagonal bismuth[9b] may also be present in the decomposition product. Substantial decomposition had occurred from brief exposure to air prior to analysis.

Hydrolysis and Thermal Decomposition of IIb. A 40-mg sample of **IIb** was heated in air at 400 °C for 6 h resulting in a tan colored solid. Powder X-ray diffraction identified the resulting solid as BiOF. A second sample was placed in an H_2O-saturated N_2 atmosphere for 24 h and then heated overnight in air at 400 °C resulting in a bright yellow powder which was identified as α-Bi_2O_3.[9c] No other phases were detected in these analyses.

Thermogravimetric Analysis of IIb in an O_2/H_2O Atmosphere. A 20-mg sample of **IIb** was subjected to thermogravimetric analysis in an oxygen/H_2O atmosphere. The total decomposition to BiOF (identified by powder X-ray diffraction) occurred in multiple steps with a weight loss of 69.8% (vs 71.3% theoretical).

Thermogravimetric Analysis of IIb in an Ar Atmosphere. A 20 mg sample of **IIb** was subjected to thermogravimetric analysis in an argon atmosphere. The total decomposition to BiOF and hexagonal Bi (identified by powder X-ray diffraction)[9b] occurred in multiple steps with a weight loss of 70.2% (vs 71.3% theoretical for decomposition to BiOF only).

Results

Syntheses of I–III. Bismuth trichloride reacts with 3 equiv of *in situ* generated sodium 1,1,1,3,3,3-hexafluoro-2-propoxide in THF to afford a colorless tris(alkoxide) dimer **I** in moderate yield (eq 1).

$$\mathrm{BiCl_3 + 3NaOCH(CF_3)_2 \xrightarrow[-3NaCl]{THF} [Bi(OCH(CF_3)_2)_2(\mu\text{-}OCH(CF_3)_2)(THF)]_2} \quad (1)$$

I

Compound **I** is very soluble in THF, sparingly soluble in aromatic solvents, and insoluble in aliphatic hydrocarbon solvents

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(9) Joint Committee on Powder Diffraction Standards, Swarthmore, PA, No. 22-114 (one of the reflections is missing; see note 9d). (b) *Ibid.*, No. 5-519. (c) *Ibid*, No. 14-669. (d) The X-ray powder diffraction pattern of BiOF was calculated using the LAZY PULVERIX computer program (Yvon, Jeitschko, Parthe, 1977) and the atomic coordinates from B. Aurivillius (*Acta Chem. Scand.* **1964**, *18*, 8).

Table VI. Positional Parameters and B(eq) Values for **IIIb**

atom	x	y	z	$B(\mathrm{eq})^a$ (Å^2)
Bi(1)	0.13213(2)	0.15951(2)	0.01671(2)	1.839(8)
O(1)	0.3164(3)	0.1915(3)	0.0690(3)	2.4(1)
O(2)	0.1444(3)	0.2399(3)	0.2354(4)	3.1(1)
O(3)	0.0973(3)	−0.0259(3)	−0.0123(4)	2.5(1)
O(4)	0.1991(3)	0.1395(3)	−0.2171(4)	3.4(1)
O(5)	0.2155(4)	0.3730(3)	0.0383(4)	3.5(1)
F(12)	0.4908(3)	0.3939(3)	0.0714(3)	3.9(1)
F(13)	0.6704(3)	0.5521(3)	0.2906(4)	5.2(1)
F(14)	0.6806(3)	0.5183(3)	0.5209(3)	4.7(1)
F(15)	0.5075(3)	0.3217(3)	0.5274(3)	4.5(1)
F(16)	0.3270(3)	0.1622(3)	0.3091(3)	3.7(1)
F(22)	0.1312(3)	0.2330(3)	0.4816(3)	4.4(1)
F(23)	−0.0203(4)	0.3066(4)	0.6355(4)	6.5(2)
F(24)	−0.1720(4)	0.3821(4)	0.5437(5)	7.0(2)
F(25)	−0.1646(3)	0.3879(3)	0.2957(4)	5.2(1)
F(26)	−0.0113(3)	0.3170(3)	0.1422(3)	3.5(1)
F(32)	0.2599(3)	−0.0553(3)	−0.1846(4)	4.2(1)
F(33)	0.4268(4)	−0.1329(4)	−0.1400(5)	6.1(2)
F(34)	0.4422(4)	−0.1779(4)	0.0823(6)	7.3(2)
F(35)	0.2859(4)	−0.1448(4)	0.2588(4)	6.2(2)
F(36)	0.1145(3)	−0.0738(3)	0.2084(3)	4.1(1)
C(11)	0.4008(4)	0.2736(4)	0.1831(5)	2.4(2)
C(12)	0.4917(5)	0.3744(5)	0.1836(5)	2.8(2)
C(13)	0.5849(5)	0.4552(5)	0.2948(6)	3.2(2)
C(14)	0.5904(5)	0.4381(5)	0.4107(6)	3.2(2)
C(15)	0.5018(5)	0.3388(5)	0.4136(5)	2.9(2)
C(16)	0.4099(4)	0.2592(4)	0.3024(5)	2.4(2)
C(21)	0.0649(5)	0.2718(4)	0.3064(5)	2.5(2)
C(22)	0.0582(5)	0.2712(5)	0.4332(6)	3.1(2)
C(23)	−0.0185(6)	0.3096(6)	0.5135(6)	4.3(2)
C(24)	−0.0948(6)	0.3469(6)	0.4686(7)	4.4(2)
C(25)	−0.0917(5)	0.3500(5)	0.3425(6)	3.6(2)
C(26)	−0.0130(5)	0.3135(5)	0.2655(5)	2.9(2)
C(31)	0.1848(4)	−0.0593(4)	0.0103(5)	2.2(2)
C(32)	0.2656(5)	−0.0769(5)	−0.0749(6)	2.8(2)
C(33)	0.3501(5)	−0.1168(5)	−0.0520(7)	3.7(2)
C(34)	0.3583(6)	−0.1402(5)	0.0577(8)	4.5(2)
C(35)	0.2793(6)	−0.1238(5)	0.1476(7)	3.8(2)
C(36)	0.1937(5)	−0.0859(4)	0.1220(6)	2.7(2)
C(41)	0.1191(6)	0.0481(7)	−0.3429(6)	4.8(2)
C(42)	0.1991(8)	0.0175(8)	−0.4402(8)	6.9(3)
C(43)	0.3205(9)	0.108(1)	−0.3804(9)	9.1(4)
C(44)	0.3211(6)	0.1859(6)	−0.2404(7)	4.4(2)
C(51)	0.1586(8)	0.3915(7)	−0.0644(7)	5.5(3)
C(52)	0.189(1)	0.5229(8)	−0.003(1)	7.2(4)
C(53)	0.229(2)	0.5660(8)	0.139(1)	12.1(7)
C(54)	0.2699(6)	0.4840(5)	0.1653(8)	4.9(2)

[a] $B(\mathrm{eq}) = (8\pi^2/_3)(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{22}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

and diethyl ether. The NMR spectra of compound I in benzene-d_6 or toluene-d_8 exhibit a single signal in both the ^{1}H and ^{19}F NMR spectra for the 1,1,1,3,3,3-hexafluoro-2-propoxide ligands at room temperature. This situation will arise if the ligands are equivalent by symmetry or if they are fluctional. One set of THF signals appears in the ^{1}H NMR spectrum, and rapid exchange is observed with free additional THF. A second signal appears in the ^{19}F NMR spectrum (toluene-d_8)as the temperature is lowered and is the predominant signal at 208 K. The low temperature form also has only a single signal for the 1,1,1,3,3,3-hexafluoro-2-propoxide ligands. The infrared spectrum of I is consistent with the presence of 1,1,1,3,3,3-hexafluoro-2-propoxide and THF ligands.

Samples of I easily lose THF. It is volatile and readily sublimes at 100 °C (10^{-3} Torr) losing approximately 30% of the bound THF (by ^{1}H NMR) after one sublimation. It decomposes in an H_2O-saturated oxygen atmosphere in multiple steps upon heating to 400 °C giving BiOF. When the decomposition is carried out in an argon atmosphere, the predominant product is also BiOF with hexagonal bismuth as a possible minor product.

The analogous anion-exchange reaction of bismuth trichloride with sodium penta-fluorophenoxide does not yield a tris(alkoxide) complex. Instead, complex (aryloxy)bismuthoxide clusters are obtained.[10] However, refluxing triphenylbismuth with 3 equiv of pentafluorophenol in toluene for 24 h cleanly affords $[\mathrm{Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)(C_7H_8)}]\cdot n\mathrm{C_7H_8}$, **II** (**a**, $n = 2$; **b**, $n = 0$) (eq 2).

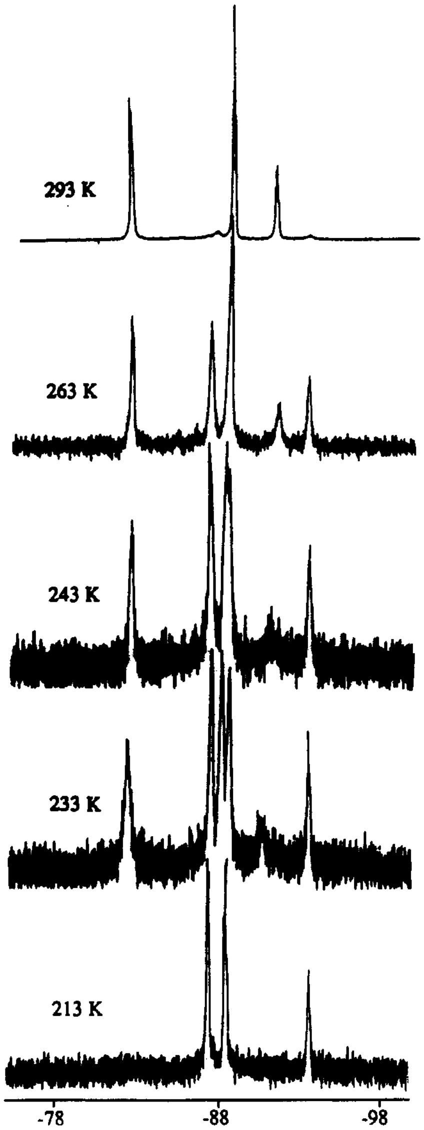

Figure 1. Variable-temperature ^{19}F NMR spectra for **II** in toluene-d_8.

$$\mathrm{BiPh_3 + 3HOC_6F_5 \xrightarrow[-3C_6H_6]{Tol} [Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)(C_7H_8)]_2} \quad (2)$$

II

Compound **II** is soluble in THF with displacement of the ligated toluene (*vide infra*), sparingly soluble in aromatic solvents, and insoluble in aliphatic hydrocarbon solvents and diethyl ether. The ^{19}F NMR spectrum of solutions of **II** in benzene-d_6 (which have been freshly heated to dissolve the compound) again shows only a single environment for the ligand. When the measurements were repeated in freshly heated toluene-d_8 solutions, the room temperature spectrum of **II** was identical to that in benzene. As the temperature was lowered, these signals disappeared and a weak set of three new signals slowly grew in. The changes as a function of temperature are shown in Figure 1. At 213 K only

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(10) (a) Jones, C. M.; Whitmire K. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1638. (b) Whitmire, K. H.; Jones, C. M.; Burkart, M. D., Hutchison, J. C.; McKnight, A. L. Better Ceramics Through Chemistry. *Materials Research Society Symposium Proceedings*; eds. Hampden-Smith, M. J., Klemperer, W. G., Brinker, C. J., Eds.; Elsevier: New York, 1992; Vol. 271, pp 149–154.

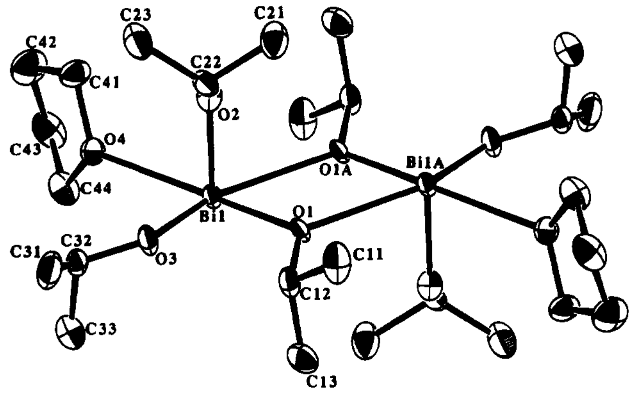

Figure 2. ORTEP diagram of the molecular structure (40% probability ellipsoids) and labeling scheme for I. Fluorine and hydrogen atoms were omitted for clarity.

one set of signals consistent with a single ligand environment is observed. If the sample is allowed to sit for several hours at room temperature, small yellow crystals form and the spectrum shows the presence of signals due to both high-temperature and low-temperature forms. In contrast, when the ^{19}F NMR is measured in THF-d_8, the spectrum remains constant from room temperature to 183 K. The ^1H NMR spectrum shows the presence of free toluene but no other aromatic signals that can be attributed to coordinated toluene. The infrared spectrum is consistent with the presence of the pentafluorophenoxide groups.

Compound **IIa** is nonvolatile and decomposes at temperatures above 170 °C (10^{-3} Torr). It decomposes in an H_2O-saturated oxygen atmosphere in multiple steps upon heating to 400 °C giving BiOF. When the decomposition is carried out in an argon atmosphere, a mixture of BiOF and hexagonal bismuth is obtained. Hydrolysis of **IIb** in a water saturated nitrogen atmosphere for 24 h followed by heating at 400 °C in air produced only α-Bi_2O_3.

Recrystallization of **II** from hexane after dissolution in THF resulted in crystals of $[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)(THF)_2]_2{\cdot}C_6H_{14}$, **IIIa**. Alternatively, recrystallization of **II** directly from THF afforded single crystals of $[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)(THF)_2]_2$, **IIIb**. The infrared spectrum is consistent with the presence of both pentafluorophenoxide and THF groups. Compounds **III a,b** were *not* formed upon refluxing triphenylbismuth with pentafluorophenol in THF; instead complex alkoxide–oxo clusters resulted.[10b]

Structures of I–III. ORTEP diagrams and labeling schemes for the alkoxide compounds **I**, **IIa**, and **IIIa** are provided in Figures 2–4. Diagrams for **IIb** and **IIIb** are very similar to those for **IIa** and **IIIa** and are included in the supplementary material. Bond distances and angles are given in Tables VIII–XII. All are loose dimers which sit about crystallographically-imposed inversion centers. The core $Bi_2(\mu\text{-}OR)_2$ ring structures are thus rigorously planar in all cases.

For **I** the bismuth centers are in a square-pyramidal coordination geometry in which two of the sites are occupied by asymmetrically bridging alkoxide ligands. A THF molecule is coordinated in the site *trans* to the shorter bismuth–oxygen bond of the $Bi_2(\mu\text{-}OR)_2$ unit. Two additional terminal alkoxide ligands complete the square-pyramid. A stereoactive lone pair of electrons occupies one of the sites *cis* to the bridging alkoxide ligands and is arranged *trans* to the lone pair of electrons on the other bismuth center of the dimer (see Table VIII and Figure 2). The square-pyramid is only slightly distorted (O(2)–Bi(1)–O(basal) = 86(4)° average[11]) to accommodate the lone pair of electrons. The O(1)–Bi(1)–O(1A) angle is acute (70.9(3)°). Additionally, two long contacts are made with fluorines on the alkoxides to bismuth. These contacts are 3.141(8) Å (Bi1–F11B) and 3.307(7) Å (Bi1–F21A).

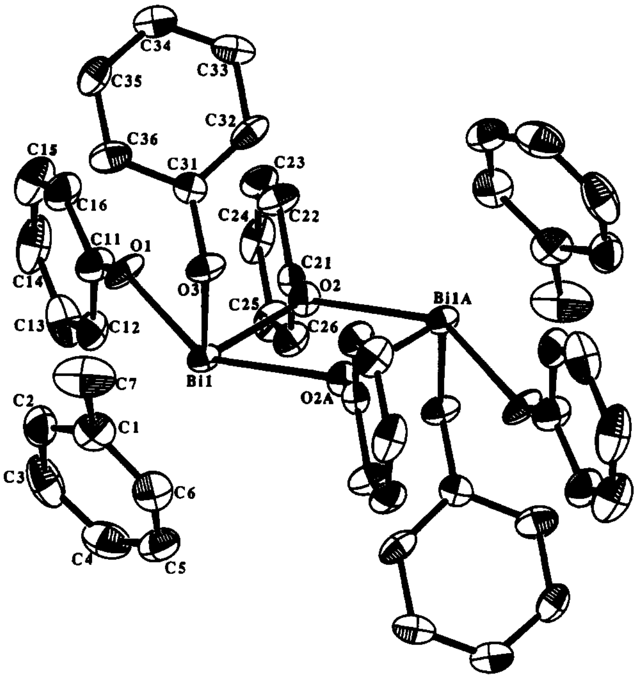

Figure 3. ORTEP diagram of the molecular structure (40% probability ellipsoids) and labeling scheme for **IIa**. Fluorine atoms, hydrogen atoms, and lattice toluene have been omitted for clarity. The carbons of the pentafluorophenoxide rings are numbered sequentially from the ipso carbon.

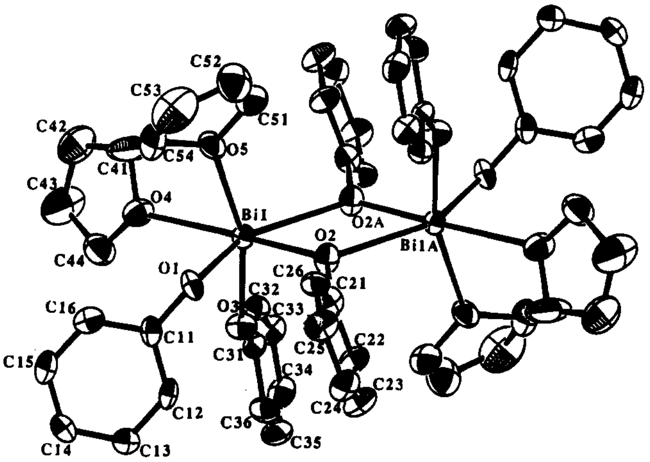

Figure 4. ORTEP diagram of the molecular structure (40% probability ellipsoids) and labeling scheme for **IIIa**. The fluorine atoms, hydrogen atoms, and lattice hexane have been omitted for clarity. The carbons of the pentafluorphenoxide rings are numbered sequentially from the ipso carbon.

Table VII. Bismuth–Oxygen Bond Distance (Å) Comparison for I–III

	I	IIa	IIb	IIIa	IIIb
$Bi\text{–}(\mu\text{-}OR)_{short}$	2.188(7)	2.210(8)	2.168(7)	2.198(9)	2.245(4)
$Bi\text{–}(\mu\text{-}OR)_{long}$	2.688(7)	2.571(7)	2.5553(9)	2.75(1)	2.661(4)
$Bi\text{–}OR_{terminal}$	2.116(7)	2.147(8)	2.136(8)	2.21(1)	2.151(4)
	2.064(7)	2.088(9)	2.089(8)	2.132(9)	2.111(3)

Compounds **IIa,b** are two crystalline morphologies of the same molecule differing by the presence of a nonbonded lattice toluene in **IIa**. The bond metricals of **IIa,b** are essentially the same and are similar to that found in compound **I** except that a toluene molecule is coordinated in place of the THF ligand. The bismuth to toluene ring centroid distances are 2.96(4) Å for **IIa** and 2.958-

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[11] Esd's of average values are calculated with the scatter formula:

$$\sigma = [\sum_{i=1}^{i=N}(d_i - d)^2/(N-1)]^{1/2}$$

Table VIII. Selected Bond Distances (Å) and Angles (deg) for I

(A) Distances

Bi(1)–O(1)	2.188(7)	Bi(1)–O(3)	2.116(7)
Bi(1)–O(1A)	2.688(7)	Bi(1)–O(4)	2.575(8)
Bi(1)–O(2)	2.064(7)	Bi(1)–Bi(1A)	3.984(2)

(B) Angles

O(1)–Bi(1)–O(1A)	70.9(3)	O(1A)–Bi(1)–O(4)	119.7(2)
O(1)–Bi(1)–O(2)	90.6(3)	O(2)–Bi(1)–O(3)	90.6(3)
O(1)–Bi(1)–O(3)	81.8(3)	O(2)–Bi(1)–O(4)	81.6(3)
O(1)–Bi(1)–O(4)	165.8(2)	O(3)–Bi(1)–O(4)	86.4(3)
O(1A)–Bi(1)–O(2)	84.1(3)	Bi(1)–O(1)–Bi(1A)	109.1(3)
O(1A)–Bi(1)–O(3)	152.1(2)		

Table IX. Selected Bond Distances (Å) and Angles (deg) for **IIa**

(A) Distances

Bi(1)–O(1)	2.147(8)	Bi(1)–C(2)	3.16(2)
Bi(1)–O(2)	2.210(8)	Bi(1)–C(3)	3.28(2)
Bi(1)–O(2A)	2.571(7)	Bi(1)–C(4)	3.36(2)
Bi(1)–O(3)	2.088(9)	Bi(1)–C(5)	3.34(1)
Bi(1)–Bi(1A)	3.974(4)	Bi(1)–C(6)	3.24(2)
Bi(1)–C(1)	3.19(2)	Bi(1)–centroid	2.958(2)

(B) Angles

O(1)–Bi(1)–O(2)	86.5(2)	Bi(1)–O(2)–Bi(1A)	112.3(3)
O(1)–Bi(1)–O(2A)	145.4(3)	O(1)–Bi(1)–centroid	107.57(6)
O(1)–Bi(1)–O(3)	82.7(3)	O(1A)–B(1)–centroid	103.23(4)
O(2)–Bi(1)–O(2A)	67.7(3)	O(2)–Bi(1)–centroid	161.08(2)
O(2)–Bi(1)–O(3)	92.6(3)	O(3)–Bi(1)–centroid	101.46(5)
O(2A)–Bi(1)–O(3)	76.1(3)		

Table X. Selected Bond Distances (Å) and Angles (deg) for **IIb**

(A) Distances

Bi(1)–O(1)	2.168(7)	Bi(1)–C(42)	3.2976(5)
Bi(1)–O(1A)	2.5553(9)	Bi(1)–C(43)	3.1726(5)
Bi(1)–O(2)	2.136(8)	Bi(1)–C(44)	3.1343(5)
Bi(1)–O(3)	2.089(8)	Bi(1)–C(45)	3.2235(8)
Bi(1)–Bi(1A)	3.940(1)	Bi(1)–C(46)	3.3824(8)
Bi(1)–C(41)	3.4122(6)	Bi(1)–centroid	2.968(5)

(B) Angles

O(1)–Bi(1)–O(1A)	67.2(2)	Bi(1)–O(1)–Bi(1A)	112.8(3)
O(1)–Bi(1)–O(2)	81.5(3)	O(1)–Bi(1)–centroid	166.96(2)
O(1)–Bi(1)–O(3)	92.1(3)	O(1A)–Bi(1)–centroid	106.47(2)
O(1A)–Bi(1)–O(2)	145.6(2)	O(2)–Bi(1)–centroid	106.93(2)
O(1A)–Bi(1)–O(3)	77.7(2)	O(3)–Bi(1)–centroid	97.74(1)
O(2)–Bi(1)–O(3)	90.0(3)		

Table XI. Selected Bond Distances (Å) and Angles (deg) for **IIIa**

(A) Distances

Bi(1)–O(1)	2.12(1)	Bi(1)–O(3)	2.132(9)
Bi(1)–O(2)	2.198(9)	Bi(1)–O(4)	2.58(1)
Bi(1)–O(2A)	2.75(1)	Bi(1)–O(5)	2.62(1)
Bi(1)–Bi(1A)	4.146(4)		

(B) Angles

O(1)–Bi(1)–O(2)	86.5(4)	O(2)–Bi(1)–O(5)	92.2(3)
O(1)–Bi(1)–O(2A)	152.6(3)	O(2A)–Bi(1)–O(3)	94.0(3)
O(1)–Bi(1)–O(3)	81.9(4)	O(2A)–Bi(1)–O(4)	118.7(3)
O(1)–Bi(1)–O(4)	88.3(4)	O(2A)–Bi(1)–O(5)	106.5(4)
O(1)–Bi(1)–O(5)	78.5(4)	O(3)–Bi(1)–O(4)	88.0(4)
O(2)–Bi(1)–O(2A)	66.6(3)	O(3)–Bi(1)–O(5)	159.3(3)
O(2)–Bi(1)–O(3)	93.3(4)	O(4)–Bi(1)–O(5)	84.8(3)
O(2)–Bi(1)–O(4)	174.4(3)		

Table XII. Selected Bond Distances (Å) and Angles (deg) for **IIIb**

(A) Distances

Bi(1)–O(1)	2.111(3)	Bi(1)–O(3A)	2.661(4)
Bi(1)–O(2)	2.151(4)	Bi(1)–O(4)	2.615(4)
Bi(1)–O(3)	2.243(4)	Bi(1)–O(5)	2.562(4)
Bi(1)–Bi(1A)	4.140(2)		

(B) Angles

O(1)–Bi(1)–O(2)	84.3(2)	O(2)–Bi(1)–O(5)	86.0(2)
O(1)–Bi(1)–O(3)	83.2(1)	O(3)–Bi(1)–O(3A)	65.2(1)
O(1)–Bi(1)–O(3A)	144.1(1)	O(3)–Bi(1)–O(4)	97.1(1)
O(1)–Bi(1)–O(4)	80.2(1)	O(3)–Bi(1)–O(5)	168.8(1)
O(1)–Bi(1)–O(5)	86.1(1)	O(3A)–Bi(1)–O(4)	118.5(1)
O(2)–Bi(1)–O(3)	98.2(2)	O(3A)–Bi(1)–O(5)	126.6(1)
O(2)–Bi(1)–O(3A)	84.0(2)	O(4)–Bi(1)–O(5)	75.8(1)
O(2)–Bi(1)–O(4)	156.7(1)		

(2) Å for **IIb**. The angle between the ring normal and the metal to ring center vector in **IIa** is 5.7° and in **IIb** is 6.8°.

Compounds **IIIa,b** are two crystalline forms of the same molecule which differ by the presence of lattice hexane in **IIIa**. In **IIIa,b** each bismuth atom is ligated by two THF molecules. The geometry about each bismuth center is a very distorted octahedron. The lone pair appears to be stereochemically active. Surprisingly, the core Bi–(μ-O) bond lengths are significantly different in compounds **IIIa,b**. The central ring structure in compound **IIIa** is more asymmetric. The unique, shorter Bi–(μ-O) bond distance in **IIIa** is 0.047 Å shorter than that in **IIIb**, while the long Bi–(μ-O) bond is 0.089 Å longer.

Discussion

Syntheses of I–III. Anion exchange reactions between bismuth trichloride and sodium alkoxide salts (NaOR) have been used successfully to form bismuth alkoxide compounds.[3,4] When $HOCH(CF_3)_2$ is deprotonated with NaH and then treated with $BiCl_3$, I is formed. When R = C_6F_5, however, the anion-exchange reaction does not give clean metathesis. Instead, oxide ligands are formed and complex aryloxy/oxo clusters are obtained regardless of whether the starting pentafluorophenol has been dried prior to reaction.[10] Contamination of the NaH could be a source of this problem, but the same NaH was used for deprotonoation of $HOCH(CF_3)_2$ where no problems were encountered. Thus cluster formation appears to be peculiar to the pentafluorophenol reaction. It is possible that the sodium pentafluorophenolate forms tightly ion paired complexes with NaOH or Na_2O that give rise to cluster formation, but this has yet to be demonstrated. Complexes having 3, 4, 6, and 9 bismuth atoms have been obtained, and in several cases Na^+ ions are also present.[10]

The trisubstituted compound **II** can, however, be formed in high yield via an alternate methodology in which the NaH deprotonation step is avoided. The reaction employed treats triphenylbismuth directly with pentafluorophenol in refluxing toluene. It has been previously reported in the literature that trialkylbismuth compounds do not react with aliphatic alcohols.[12a] However, we have found this reaction to be facile for simple phenols; the reaction of triethylbismuth with HOC_6F_5 or HOC_6H_5 produces a monosubstituted phenoxy-bridged chain polymer.[13] BiR_3 complexes are generally more reactive than $BiAr_3$,[12b] and it is therefore somewhat surprising that the reaction of pentafluorophenol with triethylbismuth proceeds with the replacement of only one ethyl group whereas the reaction with triphenylbismuth leads to the trisubstituted complex. It is possible that the bulkier ethyl groups make it more difficult for the reaction to proceed, but this is surprising in light of the tendency of the bismuth atom to form hypervalent complexes as in the examples provided in this paper. It should be noted that no reaction occurs between 1,1,1,3,3,3-hexafluoro-2-propanol and triphenyl- or triethylbismuth probably because of the low acidity of the aliphatic alcohol.[14]

Compound **II** is not very soluble in toluene at room temperature but will redissolve in that solvent upon heating. Solid **II** slowly precipitates from cooled toluene solutions which are allowed to stand overnight. Compound **II** is stable in the solid state (except for solvent loss from the crystals) and solution so that inherent

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(12) (a) Gilman, H.; Nelson, J. F. *J. Am. Chem. Soc.* **1957**, *59*, 935. (b) Freedman, L. D.; Doack, G. O. *Chem. Rev.* **1982**, *82*, 15.

(13) Whitmire, K. H.; Hutchison, J. C.; McKnight, A. L.; Jones, C. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1021.

(14) Jones, C. M.; Hutchison, J. C.; Burkart, M. D.; Whitmire, K. H. Unpublished results.

thermodynamic instability does not appear to be the explanation for the formation of the cluster complexes via the salt metathesis method.

NMR Data. Compounds **I** and **II** both exhibit a single ligand environment at room temperature. For **I** a single resonance appears at 0.34 ppm, but upon cooling of the sample to 208 K a second signal 0.17 ppm grows in and becomes predominant. At room temperature, **II** shows three resonances in a 2:2:1 ratio consistent with a single or averaged C_6F_5 environment. As the temperature is lowered, these signals diminish and a new set of three signals, also in a 2:2:1 ratio, gradually appears. Careful integration of the signals in relation to an added standard shows that **II** has limited solubility in toluene at lower temperatures and precipitates as it forms. The product that forms as the temperature is lowered is also seen to have only one C_6F_5 environment which may be due to either ligand equivalence or fluctionality. The spectrum of **II** in THF is similar to that observed in toluene; however, no change takes place in this spectrum as the temperature is lowered to 183 K. Presumably when **II** is dissolved in THF, the toluene is displaced by THF ligands as indicated by the crystal structure analyses.

One interpretation that is consistent with the results for **II** envisages a monomer–dimer equilibrium with the dimeric form being the most stable at lower temperatures. At elevated temperatures **II** most likely exists as a solvated monomer. Upon cooling, the dimeric form would be favored and would precipitate as it forms. This is consistent with the observation of crystals forming in the NMR tube of benzene and toluene solutions at lower temperatures. That a single, temperature-invariant NMR spectrum is obtained for the complex when dissolved in THF is consistent with the coordinating ability of THF. THF is more strongly Lewis basic than toluene and as a solvent is more likely to solvate the bismuth atoms and inhibit dimerization. The coordination of a third THF ligand in solution to form a monomeric $Bi(THF)_3(OR)_3$ complex is suggested by the reported structure of the R = $SiPh_3$ compound.

Structures of I–III. Several structurally characterized bismuth alkoxide complexes have been found to be polymeric.[3,4b,13] For R = OC_2H_4OMe the tris(alkoxide) compound is made up of alkoxide-bridged dimeric units which are linked together via ether bridges. Monomers occur only when the R group is very sterically demanding (i.e. ^{t}Bu, $C_6H_3Me_2$-2,6) thus preventing oligomerization. Solubility and/or volatility are limited by polymerization and the use of large alkoxide ligands. Compounds **I–III** contain intermediate-sized alkoxide or aryloxide ligands which allow dimerization but do not allow further oligomerization. The solubilities of compounds **I–III** are limited to aromatic and polar solvents such as THF. When R = $CH(CF_3)_2$ the tris(alkoxide) compound is fairly volatile although this is not the case for R = C_6F_5 which did not sublime under high vacuum.

The coordination geometries of compounds **I–III** are similar with respect to their alkoxide ligands. Compounds **I–III** form dimeric species with very asymmetric $Bi_2(\mu\text{-}OR)_2$ cores. Each bismuth center has one short (*ca.* 2.20 Å) and one long (*ca.* 2.6 Å) Bi-O(μ-alkoxide) bond distance. The longer bond can be thought of as arising from donation of a lone pair of electrons on an alkoxide oxygen of one metal center to a second metal center. This asymmetry is contrasted with monoalkoxide dimeric complexes like $[Bi(NO_3)_2(EO3^-)]_2$,[4d] which have a nearly symmetrical Bi_2O_2 core. Bi–O(alkoxide) bond lengths are compared in Table VII. Of the bridging alkoxide ligands the "short" distance is identical within experimental error for all except **IIIb** regardless of the identity of the alkoxide ligand or the coordination number. Differences are observed however in the "long" Bi–O(μ-alkoxide) bond. Compounds **IIa,b** have the shortest distances which are identical within experimental error. This is not surprising since they are essentially the same molecule. Compounds **IIIa,b** are quite different, however. The "long" Bi-O(μ-alkoxide) bond is nearly 0.1 Å longer in **IIIa** than in **IIIb**. Both are longer than in compounds **IIa,b**. These two molecules differ only in the presence of a lattice hexane in **IIIa**, and therefore, differences in their structures probably arise from packing considerations. The "long" Bi–O(μ-alkoxide) bond in **I** is longer than for compounds **IIa,b** and intermediate between **IIIa** and **IIIb**. In each compound the terminal Bi–O(alkoxide) bond distances are the shortest as is generally observed in alkoxide chemistry and compare well with those found in $Bi(OC_6H_3Me_2\text{-}2,6)_3$[4a] and $Bi(OCH_2CH_2OMe)_3$.[4c] The Bi–O(alkoxide) distances are comparable to the range of bismuth–oxygen distances (2.130–2.787 Å) found in α-Bi_2O_3.[15]

Each bismuth center in compounds **I–III** has one stereoactive lone pair of electrons which is located *trans* to the lone pair of electrons on the other bismuth center as required by the crystallographically-imposed inversion center symmetry. This is similar to the arrangement found in the dimeric units of $Bi(OCH_2CH_2OMe)_3$.[4c] In all cases the geometry at each metal center is distorted from ideal due to the presence of the lone pair of electrons.

An intriguing feature of this series of molecules is the variety of coordination geometries observed for added solvent molecules. Compound **I** contains pentacoordinate square-pyramidal bismuth centers that are similar to those found as a first approximation for the dimeric units of $Bi(OCH_2CH_2OMe)_3$[4c] in which a THF ligand has replaced the bridging OMe functionality. If, in compounds **IIa,b**, the toluene ligand is thought of as taking one coordination site with the centroid of the toluene ring being the focal point, the overall geometry is very similar to compound **I** with comparable distortions from an ideal square pyramid. Toluene ligands are, however, generally thought of as taking three coordination sites making each bismuth center seven-coordinate with an irregular geometry. Each bismuth center in compounds **IIIa,b** is six-coordinate and highly distorted from an octahedron.

Compounds **IIa,b** are particularly interesting in that they are rare examples of bismuth–arene π-complexes and the first such bismuth alkoxides. That antimony chloride forms adducts known as Menshutkin complexes[16] with aromatic solvents has been known for some time. The first examples of bismuth–arene complexes to be structurally characterized were the bismuth trichloride adducts, $[1,3,5\text{-}(CH_3)_3C_6H_3][BiCl_3]$ and $[(CH_3)_6C_6][BiCl_3]$, described by Schmidbaur.[17a] Even longer bismuth–arene interactions are observed in the solid state for $[PhBiX_2(thf)]$ (X = Cl, Br, I).[17b,c] Two aluminum trichloride/bismuth chloride arene complexes have also been structurally characterized.[17d] In compounds **IIa,b** the distances between the bismuth atom and the toluene ring centroid are slightly shorter than in the bismuth trichloride mesitylene complex (2.96(4) Å for **IIa** and 2.958(2) Å for **IIb** vs 3.07 (2) Å) and are close enough to be considered real (albeit weak) interactions. The bonding of the arene to bismuth is weak as evidenced by the facile exchange of the aromatic in the ^{1}H NMR spectrum. The angle between the ring normal and the metal to ring center vector is in the range observed for the bismuth trichloride adducts (5.7° for **IIa** and 6.8° for **IIb** vs 2.1–7.3°) indicating η^6-bound toluene molecules. It should be noted that the lone pair of electrons is not stereochemically active in the bismuth trichloride–arene complexes.

The toluene ligands in compounds **IIa,b** can be replaced by two THF ligands. THF is generally considered a better donor than toluene and thus replacement of the toluene ligand in the presence

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of THF is not surprising. The Bi–O–C angles for compounds **IIa,b** and **IIIa,b** average 125° with no clear difference observable between those found for **II** and those for **III**. Therefore it appears that one toluene molecule exerts the same steric influence as two THF molecules. It is also interesting to compare the coordination found in compounds **III** to that in compound **I**. Compound **I** has only a single THF ligand, while compounds **IIIa,b** have two THF ligands about each metal center. A steric argument can be made to explain this observation, but it is also possible that the pentafluorophenoxide ligands are more electron withdrawing than the 1,1,1,3,3,3-hexafluoro-2-propoxide ligands, making each bismuth center more Lewis acidic in compounds **IIIa,b**.

Compounds **I–III** can all be considered "hypervalent" having more than 18 electrons/metal center. A monomeric $Bi(OR)_3$ species would contain 18 electron bismuth centers. As mentioned earlier, only one unsolvated monomeric bismuth alkoxide compound, $Bi(OC_6H_3Me_2\text{-}2,6)_3$,[4a] has been structurally characterized. In all other cases the Lewis-acidic nature of the bismuth centers allows solvent coordination, as in $Bi(OSiPh_3)_3(THF)_3$,[4d] or oligomerization/polymerization. Compounds **I–III** not only dimerize but the bismuth atoms are a strong enough Lewis acids to coordinate THF or toluene. In **I** the bismuth atoms are formally 22 electron metal centers, while in **IIa,b** and **IIIa,b** the bismuth atoms are 26 and 24 electron bismuth centers, respectively.

Thermal and Hydrolytic Decomposition of I and IIa. Compounds **I** and **IIa** decompose cleanly in water-saturated oxygen atmospheres upon heating to give BiOF. The incorporation of fluoride is consistent with findings from the decomposition of $Bi(OR_f)_3$ ($R_f = C_6H_2(CF_3)_3\text{-}2,4,6$).[18] Decomposition in a dry argon atmosphere does not cleanly give a single product. Instead, a mixture of BiOF and hexagonal bismuth is obtained. The presence of fluoride in the product is a potential problem for use of fluorinated bismuth alkoxide ligands to high-T_C superconductors where incorporation of fluoride is detrimental to superconductivity. When compound **IIa** is allowed to prehydrolyze for 24 h in a water saturated nitrogen atmosphere, a strong odor of the phenol is noted and the decomposition product obtained is α-Bi_2O_3. Presumably no fluorine is incorporated because the alkoxide ligands have been totally removed through controlled hydrolysis prior to heating.

Conclusion

A series of dimeric bismuth tris(alkoxide) compounds have been synthesized via anion exchange ($R = CH(CF_3)_2$) or alcoholysis of a triarylbismuth compound ($R = C_6F_5$). Unfortunately, neither synthetic strategy is a general one; compound **I** cannot be formed via the alcoholysis reaction, and compounds **II** and **III** were not formed via anion exchange. The use of intermediate-sized ligands has allowed the formation of dimeric units instead of higher order polymeric structures usually obtained when the alkoxide ligand is small. Bismuth has a strong "desire" to become hypervalent, a tendency satisfied via dimerization and solvent coordination.

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Supplementary Material Available: Tables of hydrogen positional and thermal parameters, anisotropic thermal parameters, and bond metricals and ORTEP diagrams of **IIb** and **IIIb** (37 pages). Ordering information is given on any current masthead page.

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