Synthesis and Characterization of Volatile Sodium Yttrium Fluoroalkoxides. Structure of Na$_3$Y(OCH(CF$_3$)$_2$)$_6$(THF)$_3$ and Na$_2$Y(OCMe(CF$_3$)$_2$)$_5$(THF)$_3$

Francois Laurent, John C. Huffman, Kirsten Folting, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, University of Indiana, Bloomington, Indiana 47405-4001

Received February 15, 1995[⊗]

Metathesis reactions between YCl$_3$ and various sodium fluoroalkoxides offered mixed-metal species such as Na$_3$Y-[OCH(CF$_3$)$_2$]$_6$(THF)$_3$ (**1**), Na$_2$Y[OCMe(CF$_3$)$_2$]$_5$(THF)$_3$ (**2**), and Na$_2$Y[OCMe$_2$(CF$_3$)]$_5$(THF) (**3**). The various compounds have been characterized by NMR, mass spectrometry, and thermogravimetric analysis, in addition to X-ray diffraction investigations for **1** and **2**. Compound **1** crystallizes in the space group $P\bar{1}$ with $a = 14.479(2)$ Å, $b = 17.155(2)$ Å, $c = 11.209(1)$ Å, $\alpha = 104.75(1)°$, $\beta = 109.48(1)°$, $\gamma = 85.23(1)°$, and $Z = 2$ while **2** crystallizes in the space group $P2_1/n$ with $a = 13.484(3)$ Å, $b = 15.762(4)$ Å, $c = 22.305(6)$ Å, $\beta = 102.42(1)°$, and $Z = 4$. The yttrium centers display a distorted octahedral geometry; the surrounding of the Na atoms is composed of bridging fluoroalkoxide oxygens, THF molecules, and secondary Na$\cdots$F interactions (2.246(8)−3.323(8) Å) giving rise to coordination numbers of up to 11. Sublimation of Y−Na species proceeds with retention of the stoichiometry between the metals but with loss of the THF ligands.

Introduction

The design of single-source precursors for the metal-organic chemical vapor deposition (MOCVD) of mixed-metal oxides is a challenge that many research groups have taken up. In this approach, the stoichiometry of the metallic elements in the precursor is the same as that in the desired mixed oxide. Thus, a great homogeneity of the final film may be obtained which is beneficial for its properties. However, this advantage can be lost if disproportionation (or dissociation) reactions occur during the transport of the starting heterometallic compound to the decomposition zone.[1] Use of functionalized (e.g., ether or amino) alkoxides can be a successful way to avoid this problem.[2] Mixed-metal derivatives based on alkoxides and β-diketonates represent another strategy for volatile single-source precursors.[3] Fluorinated ligands generally enhance the volatility of metallic compounds.[4,5] Metal−fluorine interactions have often been detected in the solid state,[6] this resulting in the formation of either oxides or fluorides[7] by thermal decomposition, although the features governing these pathways remain to be determined.

As part of a project aimed at obtaining metal precursors for the MOCVD of high-T_c superconductors, we have chosen to investigate homo- as well as heterometallic fluorinated alkox-ides. Fluorinated alkoxide ligands were expected to enhance volatility and to act as efficient assembling ligands between different metallic centers, the possible M...F interactions being a means to prevent the dissociation in the vapor phase. Finally, tailoring of the most relevant properties for MOCVD purposes, volatility and stability, can *a priori* be achieved by further substitution reactions. This strategy has offered access to the first volatile Y−Ba species Y$_2$Ba[OCH(CF$_3$)$_2$]$_4$(thd)$_4$.[8]

We report herein the synthesis and characterization of Na$_3$Y-(hfip)$_6$(THF)$_3$ (**1**), Na$_2$Y(hftb)$_5$(THF)$_3$ (**2**), and [Na$_2$Y(tftb)$_5$-(THF)] (**3**) where hfip = OCH(CF$_3$)$_2$, hftb = OCMe(CF$_3$)$_2$, and tftb = OCMe$_2$(CF$_3$). We also report the solid-state structures of **1** and **2**.

Experimental Section

All manipulations were routinely performed under argon or nitrogen using Schlenk tubes and vacuum-line techniques with solvents purified by standard methods. YCl$_3$ (Aldrich) was used as received. Fluorinated alcohols (PCR or Aldrich) were stored under nitrogen on molecular sieves and used without further purification. Infrared spectra were run on a Nicolet 510P FT-IR spectrometer as KBr pellets. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Nicolet NT-360 or a Varian 300 spectrometer. Samples were run in C$_6$D$_6$ and/or C$_6$F$_6$ with internal or external references (^{1}H, residual protons in C$_6$D$_6$; ^{19}F, CF$_3$COOH (neat, $\delta = -77$ ppm), CFCl$_3$ ($\delta = 0$ ppm), or C$_6$F$_6$ ($\delta = -162$ ppm)). Thermogravimetric analyses were achieved under helium on a Du Pont instrument at a heating rate of 5 °C/min. Elemental analyses were obtained from Oneida Research Services.

Na$_3$Y(hfip)$_6$(THF)$_3$ (1). A solution of Na(hfip) (6.06 g, 31.92 mmol) in 80 mL of toluene was added to a suspension of YCl$_3$ (1.04 g, 5.32 mmol) in 60 mL of THF. The reaction mixture was stirred for 12 h at room temperature and refluxed for an additional hour. After decantation, NaCl was eliminated by filtration. The filtrate was concentrated and left to crystallize at −20 °C. Several crops of crystals of **1**, soluble in hydrocarbons and ethers, were obtained (yield = 79%). ^{1}H NMR (C$_6$D$_6$): δ 5.08 (br heptet, 6H), 3.36 (m, 12H), 1.24 (m, 12H). ^{13}C-{^{1}H} NMR (C$_6$D$_6$): δ 125 (q, $^1J_{CF} = 287$ Hz), 74.0 (heptet, $^2J_{CF} = 30$ Hz), 68.2 (s), 25.2 (s). ^{19}F NMR (C$_6$D$_6$): δ −78.4 (br d, $J = 5.9$ Hz).

⊗ Abstract published in *Advance ACS Abstracts*, June 15, 1995.

(1) Disproportionation upon volatilization might occur, yet LiNbO$_3$ films could be successfully obtained from LiNb(OEt)$_6$ (Wernberg, A. A., Gysling, H. J. *Chem. Mater.* **1993**, *5*, 1056); LiNb(O^{t}Bu)$_6$, by contrast, undergoes some disproportionation upon volatilization (Bradley, D. C.; Faktor, M. M.; Thompson, J. Unpublished results).

(2) The volatile mixed-metal alkoxides MNb(OCHRCH$_2$OMe)$_6$, where M = Li, Na, or K and R = H or Me, have been used as single-source precursors for deposition of MNbO$_3$ films: Goel, S. C.; Matchett, M. A.; Buhro, W. E. *Abstr. Pap.—Am. Chem. Soc.* **1993**, *205*, INOR 81.

(3) Sirio, C.; Poncelet, O.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Vaissermann, J. *Polyhedron* **1992**, *11*, 177.

(4) Willis, J. C. *Chem. Rev.* **1989**, *89*, 133.

(5) Hubert-Pfalzgraf, L. G. *Appl. Organomet. Chem.* **1992**, *6*, 627.

(6) (a) Samuels, J. A.; Lobkovsky, E. B.; Streib, W. E.; Folting, K.; Huffman, J. C.; Zwanziger, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 5093. (b) Purdy, A. P.; George, C. F.; Callahan, J. H. *Inorg. Chem.* **1991**, *30*, 2812. (c) Purdy, A. P.; George, C. F. *Inorg. Chem.* **1991**, *30*, 1969. (d) Vincent, H.; Labrize, F.; Hubert-Pfalzgraf, L. G. Submitted for publication.

(7) Lingg, L. J.; Berry, A. D.; Purdy, A. P.; Ewing, K. J. *Thin Solid Films* **1992**, *209*, 9.

(8) Labrize, F.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Halut, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1588. Labrize, F.; Hubert-Pfalzgraf, L. G. Paper presented at Comptes-rendus MRT-CNRS, Paris, June 1992; *Abstr. Pap.—Am. Chem. Soc.* **1993**, *206*, INOR 162.

Anal. Found (calc) for $C_{30}H_{30}F_{36}O_9Na_3Y$: C, 26.87 (26.18); H, 1.88 (2.20); F, 44.98 (49.69); Na, 4.73 (5.01); Y, 6.45 (6.46). IR (Nujol, cm^{-1}): 1277, 1247, 1221, 1211, 1184, 1170 (ν(C−F), ν(C−O)), 1088, 1049 (ν(C−O), ν(C−C)), 883, 845; 530, 519, 504, 416, 372 (ν(Y−O), ν(Na−O)). MS: YNa$_3$F(hfip)$_4$ (4%), YNa$_2$(hfip)$_4$ (11%), YNa$_2$F-(hfip)$_3$ (1%), Y(hfip)$_3$ (5%), Y(hfip)$_2$F (3%), Na$_2$(hfip) (100%).

Na$_3$Y(hfip)$_6$ (1b). Sublimation of compound **1** at 110 °C under 10^{-3} Torr offers **1b** (yield 78%): mp 132 °C; soluble in diethyl ether or C_6F_6. Anal. Found (calcd) for $C_{18}H_6F_{36}O_6Na_3Y$: C, 18.73 (18.53); H, 0.54 (0.54); F, 56.33 (58.97). ^{1}H NMR (C_6D_6/C_6F_6): δ 4.82 (m). $^{13}C\{^1H\}$ NMR (C_6D_6/C_6F_6, 1:2): δ 124 (q, $^1J_{CF}$ = 287 Hz), 73.2 (m, br). ^{19}F NMR (C_6D_6/C_6F_6): δ −79.7 (d, J = 5.4 Hz).

Na$_2$Y(hftb)$_5$(THF)$_3$ (2). The alcohol (hftb)H (1.2 g, 6.53 mmol) was deprotonated by NaH (0.2 g, 8.33 mmol) in THF (10 mL). The solution of Na(hftb) was filtered, and the filtrate was added to a stirred suspension of YCl$_3$ (0.4 g, 1.28 mmol) in THF (10 mL). The mixture was stirred for 30 min before the THF was removed under vacuum, and 40 mL of toluene was added. The colorless solution was then refluxed for 12 h and filtered through Celite. The filtrate was concentrated to 5−10 mL and cooled to −30 °C overnight to give 1.09 g of colorless solid **2** (yield 68%). ^{1}H NMR (C_6D_6): δ 3.66 (t, J = 6 Hz, 12H), 1.70 (br s, 15H), 1.38 (m, 12H). $^{13}C\{^1H\}$ NMR (C_6D_6): 126.2 (q, $^1J_{CF}$ = 288 Hz), 77.9 (heptet, $^2J_{CF}$ = 26 Hz), 68.9 (s), 25.2 (s), 19.5 (s). Anal. Found (calcd) for $C_{32}H_{33}F_{30}O_8Na_2Y$: C, 30.45 (30.59); H, 3.08 (3.13); F, 50.48 (45.36). IR (KBr, cm^{-1}): 3000, 2966, 2895 (ν(CH)), 1457, 1385, 1306, 1222, 1183 (ν(C−F), ν(C−O)), 1109, 1078, 1050 (ν(C−O), ν(C−C)), 966, 885, 858, 803, 760, 700, 663, 653, 617, 528, 498 (ν(Y−O), ν(Na−O)).

Product of Sublimation of Na$_2$Y(hftb)$_5$(THF)$_3$. ^{1}H NMR (C_6D_6/C_6F_6): δ 3.96 (t, J = 6 Hz, 4H), 1.63, 1.60, 1.54, 1.51 (overlapped signals, 23H). Anal. Found (calcd) for $C_{24}H_{23}F_{30}O_6Na_2Y$: C, 23.58 (25.93); H, 1.57 (2.08); F, 46.56 (51.24).

Na$_2$Y(tftb)$_5$(THF) (3). A solution of Na(tftb), prepared by deprotonation of the alcohol (hftb)H (1.2 g, 6.53 mmol) by NaH (0.2 g, 8.33 mmol) in THF (10 mL), was filtered, and the filtrate was added to a stirred suspension of YCl$_3$ (0.4 g, 1.28 mmol) in THF (10 mL). After a 24-h reflux, the THF was removed under vacuum and replaced by toluene (20 mL). The solution was then filtered through Celite and the filtrate concentrated. Cooling at −30 °C offered 1.07 g of colorless solid **3** (yield 99%). ^{1}H NMR (C_6D_6/C_6F_6): δ 3.65 (t, J = 6 Hz, 4H), 1.59 (m, 4H), 1.52 (s, 30H). $^{13}C\{^1H\}$ NMR (C_6D_6/C_6F_6): δ 131.1 (q, $^1J_{CF}$ = 288 Hz), 73.5 (q, $^2J_{CF}$ = 24 Hz), 68.7 (s), 26.1 (s), 25.7 (s). Anal. Found (calcd) for $C_{24}H_{38}F_{15}O_6Na_2Y$: C, 34.18 (34.22); H, 4.53 (4.56); F, 25.85 (33.83). IR (KBr, cm^{-1}): 2990, 2943, 2884 (ν(CH)), 1472, 1385, 1364, 1314, 1215, 1166, 1137, 1127, 1104 (ν(C−F), ν(C−O)), 1048, 1013, 1005 (ν(C−O), ν(C−C)), 874, 801, 752, 608, 596, 486 (ν(Y−O), ν(Na−O)).

Compound **3** crystallized in space group $C2$, Cm, or $C2/m$ with a = 29.843(6) Å, b = 17.656(3) Å, c = 10.284(2), β = 95.60(1)°, and Z = 4, but the data set could not be solved.

Sublimation of Na$_2$Y(tftb)$_5$(THF). ^{1}H NMR (C_6D_6/C_6F_6): δ 1.61, 1.48, 1.45, 1.40, 1.33. Anal. Found (calcd) for $C_{20}H_{30}F_{15}O_5Na_2Y$: C, 31.07 (31.18); H, 3.94 (3.93).

X-ray Structure Determination of Na$_3$Y(hfip)$_6$(THF)$_3$. A small, colorless, nearly equidimensional crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −85 °C for characterization and data collection (6° < 2θ < 45°; see Table 1). Corrections were applied for Lorentz and polarization but not for absorption effects. The structure was readily solved by direct methods (SHELXS-86) and standard Fourier techniques. All hydrogen atoms were placed in fixed, idealized positions for the final cycles of refinement. The results are summarized in Table 2 and Figure 1.

X-ray Structure Determination of Na$_2$Y(hftb)$_5$(THF)$_3$. A small, colorless, well-formed crystal was cleaved from a large sample and affixed to the end of a glass fiber using silicone grease. The mounted sample was transferred to the goniostat where it was cooled to −115 °C for characterization and data collection (6° < 2θ < 45°, see Table 1). Corrections were applied for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86) and standard Fourier techniques. Although not located, hydrogen atoms were placed

Table 1. Crystallographic Data for Na$_3$Y[OCH(CF$_3$)$_2$]$_6$(THF)$_3$ (**1**) and Na$_2$Y[OCMe(CF$_3$)$_2$]$_5$(THF)$_3$ (**2**)

	1	2
formula	$C_{30}H_{30}F_{36}O_9Na_3Y$	$C_{32}H_{39}F_{30}O_8Na_2Y$
a, Å	14.479(2)	13.484(3)
b, Å	17.155(2)	15.762(4)
c, Å	11.209(1)	22.305(6)
α, deg	104.75(1)	
β, deg	109.48(1)	102.42(1)
λ, deg	85.23(1)	
V, Å^3	2538.29	4629.45
Z	2	4
MW	1376.38	1256.49
space group	$P\bar{1}$	$P2_1/n$
T, °C	−85	−115
λ, Å	0.710 69	0.710 69
ϱ_{calc}, g cm^{-3}	1.801	1.803
μ(Mo Kα), cm^{-1}	13.51	14.46
R	0.066	0.049
R_w	0.062	0.046

Table 2. Selected Bond Distances (Å) and Angles (deg) for Na$_3$Y(hfip)$_6$(THF)$_3$^{a}

(a) Distances

Y−O(1)	2.231(6)	Y−O(2)	2.226(6)
Y−O(3)	2.234(6)	Y−O(5)	2.240(6)
Y−O(6)	2.243(6)	Y−O(4)	2.234(6)
Y−Na(1)	3.483(4)	Y−Na(2)	3.466(4)
Y−Na(3)	3.492(4)	Na(1)−Na(2)	6.617(5)
Na(1)−Na(3)	5.794(5)	Na(2)−Na(3)	5.448(5)
Na(1)−O(1)	2.298(7)	Na(1)−O(2)	2.308(7)
Na(1)−O(7)	2.251(8)	Na(1)−F(3)	2.566(8)
Na(1)−F(9)	2.621(8)	Na(1)−F(36)	2.503(8)
Na(1)−F(11)	3.027(8)	Na(2)−O(3)	2.269(7)
Na(2)−O(4)	2.316(7)	Na(2)−O(5)	2.238(9)
Na(2)−F(15)	2.751(8)	Na(2)−F(30)	2.514(8)
Na(2)−F(19)	2.486(11)	Na(2)−F(16)	3.095(11)
Na(2)−F(23)	3.207(11)	Na(3)−O(5)	2.301(8)
Na(3)−O(6)	2.306(8)	Na(3)−O(9)	2.286(8)
Na(3)−F(18)	2.883(9)	Na(3)−F(26)	2.736(8)
Na(3)−F(33)	2.805(8)	Na(3)−F(29)	3.153(8)
Na(3)−F(10)'	3.178(8)	Na(3)−F(35)	3.323(8)

(b) Angles

O(1)−Y−O(2)	78.7(2)	O(1)−Y−O(5)	166.8(2)
O(1)−Y−O(4)	101.4(2)	O(1)−Y−O(6)	88.7(2)
O(2)−Y−O(5)	94.8(2)	O(2)−Y−O(3)	167.9(2)
O(2)−Y−O(4)	94.7(2)	O(2)−Y−O(6)	97.4(2)
O(3)−Y−O(6)	91.5(2)	O(3)−Y−O(5)	94.8(2)
O(5)−Y−O(6)	80.7(2)	O(3)−Y−O(4)	77.8(2)
O(6)−Y−O(4)	165.6(2)	O(5)−Y−O(4)	90.6(2)
O(1)−Na(1)−O(7)	134.8(3)	O(1)−Na(1)−O(2)	75.7(2)
O(3)−Na(2)−O(4)	75.4(2)	O(2)−Na(1)−O(7)	148.2(3)
O(4)−Na(2)−O(8)	145.4(3)	O(3)−Na(2)−O(8)	139.1(3)
O(5)−Na(3)−O(9)	127.5(3)	O(5)−Na(3)−O(6)	78.1(2)
Y−O(1)−Na(1)	100.5(3)	O(6)−Na(3)−O(9)	144.0(3)
Na(1)−O(1)−C(1)	122.1(5)	Y−O(1)−C(1)	134.1(6)
Y−O(2)−C(4)	142.3(6)	Y−O(2)−Na(1)	100.4(3)
Y−O(3)−Na(2)	100.6(3)	Na(1)−O(2)−C(4)	116.6(5)
Na(2)−O(3)−C(7)	120.5(5)	Y−O(3)−C(7)	137.3(6)
Y−O(5)−C(13)	138.5(6)	Y−O(5)−Na(2)	100.5(3)
Y−O(6)−Na(3)	100.3(3)	Na(2)−O(5)−C(13)	120.8(5)
Na(3)−O(6)−C(16)	123.5(5)	Y−O(6)−C(16)	136.0(6)
Y−O(4)−C(10)	142.9(6)	Y−O(4)−Na(3)	99.2(3)
O(1)−Y−O(3)	93.3(2)	Na(3)−O(4)−C(10)	117.4(5)

^{a} Atoms labeled with a prime are related by the symmetry operation $(-x, 2 - y, 2 - z)$.

in fixed, idealized positions for the final cycles of refinement. The results are summarized in Table 3 and Figure 2.

Results

Synthesis and Characterization. The reaction between YCl$_3$ and sodium hexafluoroisopropoxide, Na(hfip), was envisioned as a route to produce a homoleptic yttrium derivative Y(hfip)$_3$.
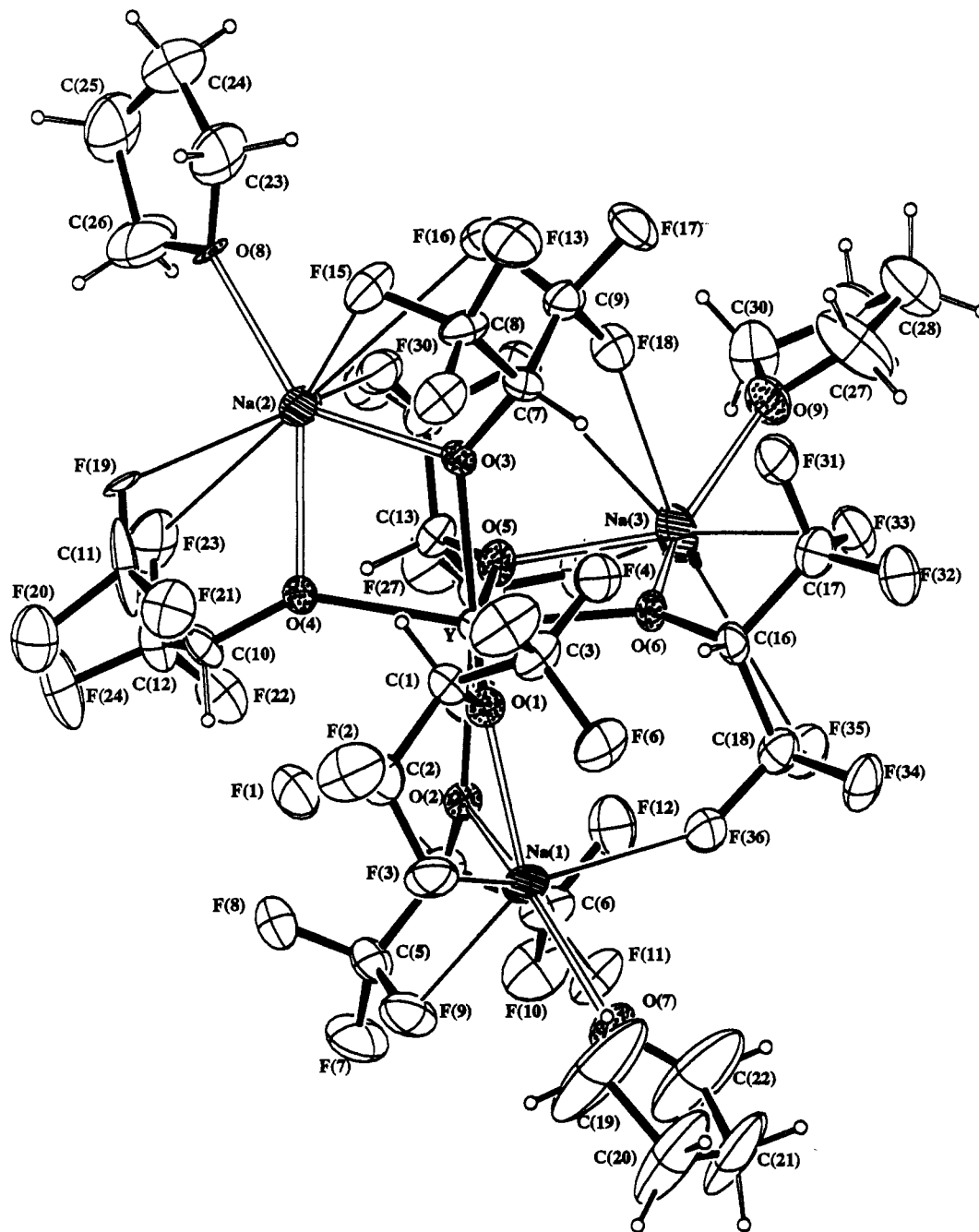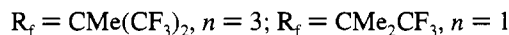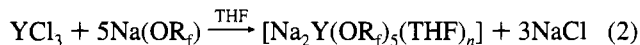
Figure 1. ORTEP drawing of Na₃Y[OCH(CF₃)₂]₆(THF)₃. Oxygens are stippled, and Na/O bonds are drawn as open lines. Na/F interactions are single lines.

Surprisingly, the reaction between YCl₃ and Na(hfip) (1:3 stoichiometry) in THF produced a sodium-containing material of the type Na₃Y(hfip)₆ as the only volatile derivative (5% yield). A THF adduct Na₃Y(hfip)₆(THF)₃ (**1**) is obtained by crystallization from toluene/THF. When the reaction is conducted in the appropriate 1:6 stoichiometry (eq 1), compound **1** is isolated in high yield (79%) by crystallization from the reaction medium.

$$YCl_3 + 6Na(hfip) \xrightarrow{THF} Na_3Y(hfip)_6(THF)_3 + 3NaCl \quad (1)$$
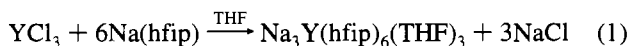
A comparable retention of sodium with formation of mixed-metal Y−Na species is observed with other fluorinated alkoxide ligands. However, the Na:Y stoichiometry of the final compounds is a function of the nature of the OR_f groups. Thus, the reaction between YCl₃ and Na(hftb) or Na(tftb) leads to Na₂Y(hftb)₅(THF)₃ (**2**) and Na₂Y(tftb)₅(THF) (**3**), respectively (eq 2), even if the reaction is conducted in the 1:6 stoichiometry.

$$YCl_3 + 5Na(OR_f) \xrightarrow{THF} [Na_2Y(OR_f)_5(THF)_n] + 3NaCl \quad (2)$$

$$R_f = CMe(CF_3)_2, \; n = 3; \; R_f = CMe_2CF_3, \; n = 1$$

The various compounds have been characterized by elemental analysis, FT-IR, mass spectrometry, ¹H, ¹³C{¹H}, and ¹⁹F NMR, and **1** and **2**, by single-crystal X-ray diffraction.

The ¹H NMR spectra of **1** in C₆H₆ or C₆H₆/C₆D₆ confirm the presence of THF molecules in the metal coordination sphere. No ligand dissociation reactions are detected. However, since all OR_f and THF ligands appear magnetically equivalent, NMR spectra (¹H, ¹³C, or ¹⁹F) are quite uninformative of structure. Similar observations are valid for compounds **2** and **3**, and characterization was achieved in the solid state by single-crystal X-ray diffraction.

Compound **1** sublimes at 110 °C under 10⁻³ Torr. The analytical data for the sublimate indicate the conservation of

Table 3. Selected Bond Distances (Å) and Angles (deg) for
$Na_2Y(hftb)_5(THF)_3$

(a) Distances			
Y−O(1)	2.221(4)	Y−O(3)	2.208(4)
Y−O(2)	2.223(4)	Y−O(5)	2.150(4)
Y−O(4)	2.295(4)	Y−O(6)	2.425(4)
Y−Na(2)	3.309(5)	Y−Na(1)	3.355(5)
Na(1)−Na(2)	4.315(5)		
Na(1)−O(7)	2.320(6)	Na(1)−O(1)	2.385(6)
Na(1)−O(2)	2.478(6)	Na(1)−O(4)	3.028(6)
Na(2)−O(8)	2.356(6)	Na(2)−O(3)	2.389(6)
Na(2)−O(4)	2.496(6)	Na(2)−O(2)	2.815(6)
Na(1)−F(22)	2.408(6)	Na(1)−F(9)	2.521(6)
Na(1)−F(3)	2.621(6)	Na(1)−F(12)	2.633(6)
Na(1)−F(6)	2.658(6)	Na(2)−F(19)	2.489(6)
Na(2)−F(10)	2.520(6)	Na(2)−F(15)	2.589(6)
Na(2)−F(24)	2.598(6)	Na(2)−F(16)	2.857(6)

(b) Angles			
O(1)−Y−O(3)	168.0(2)	O(3)−Y−O(6)	92.1(2)
O(1)−Y−O(5)	97.6(2)	O(2)−Y−O(4)	78.9(2)
O(1)−Y−O(6)	88.8(1)	O(5)−Y−O(4)	177.3(2)
O(3)−Y−O(5)	94.4(2)	O(4)−Y−O(6)	89.8(2)
O(7)−Na(1)−O(2)	138.7(3)	O(2)−Y−O(5)	102.6(2)
O(8)−Na(2)−O(3)	137.0(3)	O(2)−Y−O(6)	168.4(2)
O(3)−Na(2)−O(4)	75.6(3)	O(5)−Y−O(6)	88.8(2)
Y−O(1)−C(1)	152.4(4)	O(7)−Na(1)−O(1)	138.2(3)
Y−O(2)−Na(1)	90.9(3)	O(1)−Na(1)−O(2)	78.4(3)
Na(1)−O(2)−C(5)	110.0(5)	O(8)−Na(2)−O(4)	139.5(3)
Y−O(3)−C(9)	152.9(4)	Y−O(1)−Na(1)	93.4(3)
Y−O(4)−Na(2)	87.3(3)	Na(1)−O(1)−C(1)	112.4(5)
Na(2)−O(4)−C(13)	108.5(5)	Y−O(2)−C(5)	152.1(4)
Y−O(6)−C(21)	127.5(4)	Y−O(3)−Na(2)	92.0(3)
O(1)−Y−O(2)	87.5(2)	Na(2)−O(3)−C(9)	115.1(5)
O(1)−Y−O(4)	84.6(2)	Y−O(4)−C(13)	163.2(4)
O(3)−Y−O(2)	89.2(2)	Y−O(5)−C(17)	169.6(4)
O(3)−Y−O(4)	83.4(2)	Y−O(6)−C(24)	128.1(4)

the $Na_3Y(hfip)_6$ stoichiometry and loss of THF. The elimination
of the Lewis base probably leads to an oligomerization of the
$Na_3Y(hfip)_6$ moiety as suggested by the decrease of the solubility
properties compared to the original THF adduct (**1**). However,
depolymerization of this THF-free material (**1b**) is easily
achieved by dissolution in THF, to re-form **1**. Mass spectro-
scopic data confirm the retention of the Na−Y moiety in the
vapor phase, $Na_3YF(hfip)_4^+$ being the heaviest fragment detected
with $m/z = 845$. The thermal behavior of compound **1** has been
analyzed by thermogravimetric analysis (TGA) up to 1000 °C.
The data show the elimination of only two THF molecules in
a first step (9.6%, between 80 and 120 °C) followed by a large
weight loss (85.5%, 120−210 °C) in a second step.

Compounds **2** and **3** are also volatile but sublime to leave
appreciable residue. Sublimation of **2** at 80−120 °C under 10^{-4}
Torr gave a white, less-soluble compound (yield 80%). The
^1H NMR spectrum shows that some THF remains in this
material, which is assigned the formula $Na_2Y(hftb)_5(THF)$.
Several NMR signals are observed for the methyl groups. The
elemental analysis confirms that some decomposition occurred
upon sublimation. The loss of THF results in the aggregation
of the $Na_2Y(hftb)_5$ units. However, ^1H NMR shows that
compound **2** may be partially recovered by dissolution in THF.
By contrast, the TGA study shows a large weight loss (97%,
50−205 °C) which can be assigned to the vaporization of the
intact molecule. However, several overlapped steps are ob-
served which suggest that dissociation might also occur.

Sublimation of **3** at 90 to 130 °C under 10^{-4} Torr gave a
white, less-soluble compound (yield 67%). The ^1H NMR shows
several small signals in addition to one strong sharp line at 1.40
ppm for the methyl groups. Redissolution of this material in
THF failed to return **3**. The total loss of THF certainly took
place with oligomerization of the $Na_2Y(tftb)_5$ moiety. More

over, the dissociation of these units may also occur upon
sublimation. The lack of volatility of **3** has been confirmed by
thermal analysis. The thermogram shows a first step (9.4%,
40−105 °C) which is consistent with the loss of the THF
molecule and two poorly-resolved steps between 125 and 255
°C. The weight loss after these steps (82.9%) suggests that
decomposition and vaporization took place.

Molecular Structures. The molecular structures of Na_3Y-
$(hfip)_6(THF)_3$ and $Na_2Y(hftb)_5(THF)_3$ are represented in Figures
1 and 2, respectively. Selected bond lengths and angles are
collected in Tables 2 and 3.

In compound **1**, $Na_3Y(\mu\text{-hfip})_6(THF)_3$, the yttrium atom is
surrounded by six oxygen atoms from the hfip ligand in a
distorted octahedral geometry (cis O−Y−O bond angles from
78.7(2) to 101.4(2)°). The Y−O distances observed in **1** (from
2.226(6) to 2.243(6) Å) are comparable to the values observed
in the mixed-metal Y−Ba species $Y_2Ba(\mu\text{-hfip})_4(thd)_4$ where
the fluoroisopropoxide ligands have the same structural func-
tionality.[8] Each sodium binds to two OR_f groups (yielding
intrabridge O−Y−O angles which are smaller than 90°) and to
one THF oxygen atom (these Na−O bond lengths range from
2.238(9) to 2.308(7) Å) in a quasi-planar geometry (sums of
the three angles around Na(1), Na(2), and Na(3) are respectively
358.7(9), 359.9(9), and 349.6(9)°). Na−O distances are shorter
(by 0.05 Å) to the THF oxygen than to the μ-OR_f oxygen,
indicating the weak donor power of the μ-OR_f oxygen when it
is attached to the strongly electrophilic Y^{III}. The overall
structure of **1** is comparable to that of the homometallic Al-
$[(\mu\text{-O}^iPr)_2Al(O^iPr)_2]_3$ alkoxide[9] or to the Y−Al species $Y[(\mu\text{-}
O^tBu)(\mu\text{-Me})AlMe_2]_3$.[10] The environment of each sodium is
completed by contacts with the fluorine atoms, six for Na(1)
and Na(2) and eight for Na(3). In the cases of Na(1) and Na(2),
all the fluorines describe a plane (sum of angles to Na(1) =
359(1) and to Na(2) = 358(2)°), while the Na(3) lacks such
planarity. Moreover, the Na(3)..F distances, ranging from
2.736(8) to 3.323(8) Å, are weaker than those to Na(1) or Na(2)
[2.486(11)−3.207(11) Å]. Curiously, Na(3) shows a weak
interaction (Na(3)···F(10)′ = 3.178(8) Å) with a fluorine atom
of a neighboring molecule, in spite of the presence of the THF
ligand. The increase of the Na···F secondary bonds for Na(3)
and the presence of an intermolecular interaction may explain
the distortion of its environment, as well as the weaker character
of the interactions.

In compound **2**, $Na_2Y(\mu\text{-hftb})_4(tftb)(THF)_3$, the yttrium atom
is in a distorted octahedral geometry (Figure 2) formed by five
oxygen atoms from the hftb ligands and one oxygen atom from
a THF molecule. Y−O bond lengths range from 2.150(4) to
2.425(4) Å and the cis O−Y−O bond angles from 87.5(2) to
102.6(2)°. This structure thus has some similarity to that of
$Y(O^tBu)[(\mu\text{-O}^tBu)(\mu\text{-Me})AlMe_2]_2(THF)$,[10] **A**, except that mol-

A
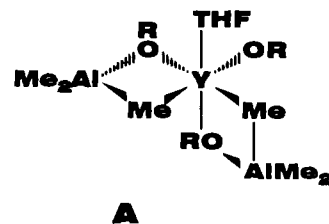
ecule has no additional Al/O contacts which increase the
aluminum coordination number above 4. In **2**, each sodium

(9) Folting, K.; Streib, W. E.; Poncelet, O.; Hubert-Pfalzgraf, L. G.;
Caulton, K. G. *Polyhedron* **1991**, *10*, 1639.

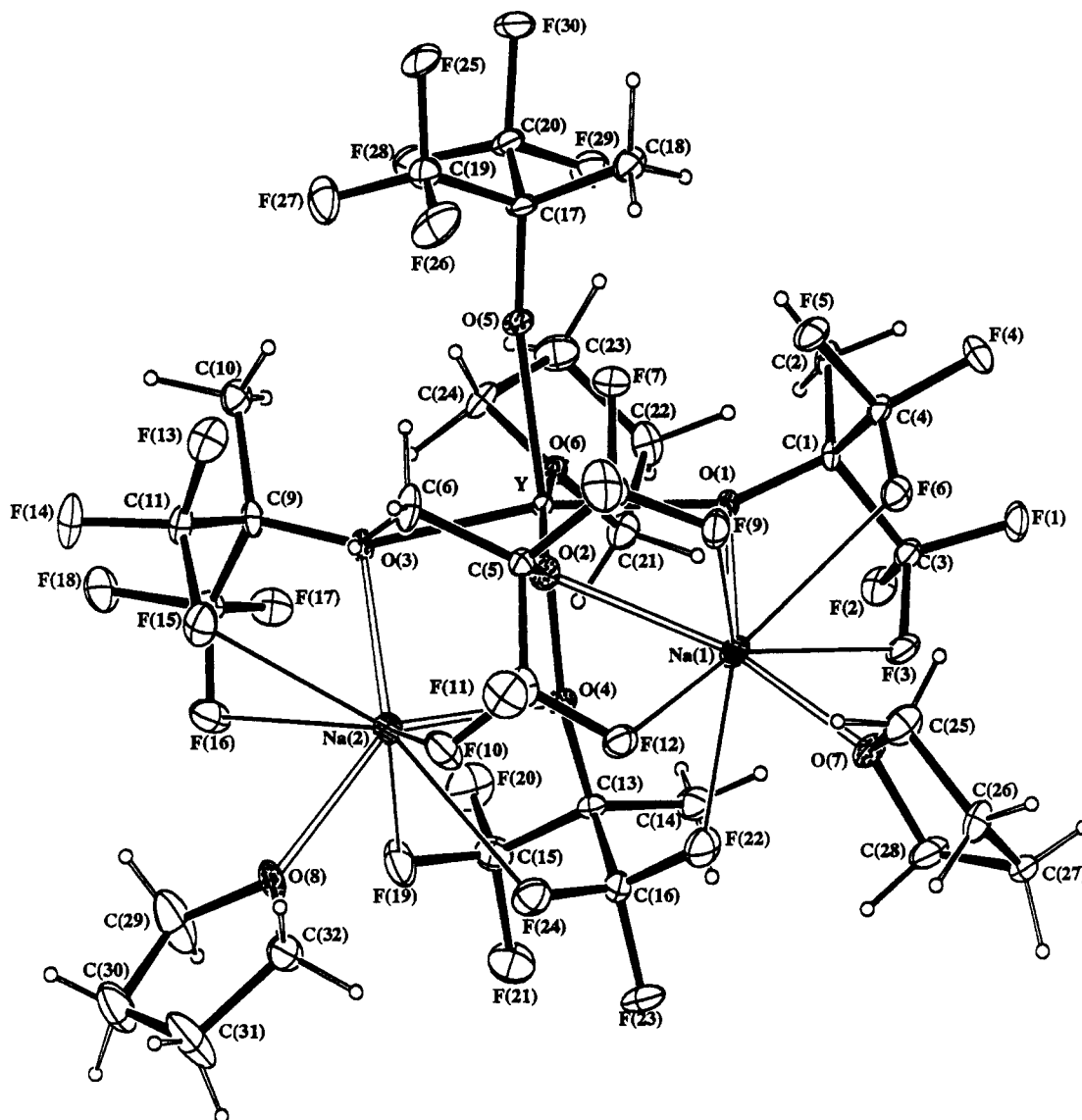(10) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*,
5084.

Figure 2. ORTEP drawing of $Na_2Y[OCCH_3(CF_3)_2]_5(THF)_3$. See Figure 1 caption for symbols.

binds to two alkoxide oxygens and leans toward a *third* (Na(1)−O(1) = 2.385(6), Na(1)−O(2) = 2.478(6), Na(1)··O(4) = 3.028(6); Na(2)−O(3) = 2.389(6), Na(2)−O(4) = 2.496(6), Na(2)··O(2) = 2.815(6) Å). As for **1**, the environment of each sodium is completed by one oxygen of a THF ligand. The Y−μ_2-OR$_f$ bond lengths (values from 2.208(4) to 2.295(4) Å) are comparable to those in compound **1**, and the Y−O(5) (terminal alkoxide = 2.150(4) Å) and Y−O(6) (THF = 2.425(4) Å) distances are similar to those in Y(hftb)$_3$(THF)$_3$.[11] The terminal alkoxide is nearly linearly bound to Y (∠Y−O(5)−C(17) = 169.6(4)°). The metal−oxygen framework is of the type generally encountered for mixed-metal alkoxides with MM′$_2$ metallic units,[12] which can be visualized as a MM′$_2$ triangle where each face is triply bridged by an alkoxide and the two M··M′ edges are bridged by another alkoxide. The semi-μ_3-bridging nature of the hftb ligands in **2** can be explained by the electron-withdrawing effect of the CF$_3$ groups and by the presence of short sodium−fluorine contacts, five for each sodium with Na··F distances from 2.408(6) to 2.815(6) Å. These secondary Na··F bonds give sodium a coordination number of 8. The incorporation of only five hftb ligands in

the yttrium coordination sphere reveals the large steric bulk of the CMe(CF$_3$)$_2$ groups.

Discussion

Synthetic Aspects. The reactions between YCl$_3$ and sodium fluoroalkoxides lead to the formation of mixed-metal Na−Y species, even in the case where the amounts of the sodium reactant are less than those required by the stoichiometry. The control of product stoichiometry between the metals is apparently imposed by the steric demand of the alkoxide groups. Six of the larger OR$_f$ ligands cannot be accommodated around Y. The fluoroalkoxide products are generally obtained as THF adducts in which the ether binds to Na and to any empty coordination site on Y.

Structural Aspects. A common feature of the structurally-characterized Y−Na species is the distorted octahedral surrounding of the yttrium center, the sodium atoms being connected as Na(μ-OR$_f$)$_2$ units. The coordination sphere of the sodium atoms is complemented by neutral ligands such as THF but also by secondary Na··F bonds. These interactions allow sodium to attain high coordination numbers in small aggregates (i.e., without polymerization), ensuring volatility as well as stability in the vapor phase. By contrast, the THF ligands are labile, both in solution in the presence of polar solvents such

(11) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1993**, *12*, 1907.
(12) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969.

as dimethoxyethane or acetonitrile and in the vapor phase. In the latter case, the loss of THF results in oligomerization of the initial species, but the process can be reversed upon addition of the initial donor solvent.

Fluorinated alkoxides are versatile ligands since they can accommodate, via a variable number of M...F interactions (up to 8 for barium, up to 11 for sodium in the case of fluoroisopropoxides), the usual coordination numbers of these metals. In addition, the high Lewis acidity of fluorinated alkoxide metal complexes makes most polar solvents able to complement the metal coordination sphere. A variety of adducts, which can display quite different volatility and stability properties, thus become available.

Supporting Information Available: Tables of atomic coordinates with isotropic thermal parameters and of anisotropic displacement coefficients for compounds **1** and **2** (8 pages). Ordering information is given on any current masthead page.

IC950175N