Pergamon

0277-5387(94)00323-8

Polyhedron Vol. 14, No. 7, pp. 881–888, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277-5387/95 $9.50+0.00

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF VOLATILE YTTRIUM–SODIUM FLUOROISOPROPOXIDE DERIVATIVES. RETENTION OF SODIUM AS A GENERAL FEATURE

FLORENCE LABRIZE and LILIANE G. HUBERT-PFALZGRAF*

Laboratoire de Chimie Moléculaire, Université de Nice-Sophia-Antipolis,
Faculté des Sciences, BP 71, 06108 Nice Cédex, France

(*Received* 5 *August* 1994; *accepted* 18 *August* 1994)

Abstract—Metathesis involving YCl_3 and sodium 1,1,1,3,3,3-hexafluoro-2-propoxide offered a mixed-metal species, $YNa_3[OCH(CF_3)_2]_6(THF)_3$ (**1**). The reaction between **1** and yttrium and copper derivatives, *β*-diketonates and halides, gave access to $YNa_2[OCH(CF_3)_2]_4(thd)(THF)_4$ (**2**) and the Na—Cu species, $Na_2Cu[OCH(CF_3)_2]_4(THF)_4$ and $[NaCu[OCH(CF_3)_2]_2(thd)]_m$ (**5**), respectively (thdH = 2,2,6,6-tetramethylheptane-3,5-dione). Alcohol interchange reactions between $Y_5O(OPr^i)_{13}$ and fluoroisopropanol led to the isolation of $Y[OCH(CF_3)_2]_3L_3$ [L = THF (**3a**) or Pr^iOH (**3b**)] depending on the solvent, THF or hexane. The various compounds have been characterized by FT-IR, NMR (^1H, ^{13}C, ^{19}F) and mass spectrometry and thermogravimetric analysis. All compounds are volatile; sublimation of the Y—Na or Na—Cu species occurs with retention of the stoichiometry between the metals. The Lewis bases are readily lost during sublimation of compounds **1**, **2** and **3a** or **3b**.

Metal alkoxides are popular MOCVD precursors to metal oxides, since they are reasonably volatile, easy to modify and generally undergo clean thermal decomposition.[1,2] 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 hetero-metallic fluorinated alkoxides. Fluorinated ligands generally enhance the volatility of metallic compounds.[3,4] Metal–fluorine interactions have often been detected in the solid state,[5,6] resulting in the formation of either oxides or fluorides[7,8] by thermal decomposition, although the features governing these pathways remain to be determined. Fluorinated alkoxides might therefore find applications as precursors to fluorides which are attractive as optical materials.[9]

Fluorinated alkoxide ligands were expected to enhance volatility and to act as efficient assembling ligands between different metallic centres, the possible $M \cdots F$ interactions being a means to prevent the dissociation in the vapour phase. Tailoring of the most relevant properties for the MOCVD purposes, volatility and stability, can *a priori* be achieved by further substitution reactions. This strategy has given us access to the first volatile Y—Ba species $Y_2Ba[OCH(CF_3)_2]_4(thd)_4$.[10] We have investigated various synthetic routes, namely Lewis acid–base reactions and metathesis reactions, for building up mixed-metal Ba—Cu, Y—Ba and Y—Cu fluoroalkoxides[11] and the synthesis of some synthons was thus a prerequisite. A pentanuclear barium fluoroisopropoxide was obtained by direct reaction between the alcohol and the metal or by alcoholysis of classical alkoxides.[7] Reactions between YCl_3 and sodium 1,1,1,3,3,3-hexafluoro-2-propoxide were investigated as a possible access to $Y[OCH(CF_3)_2]_3$ derivatives. Reactions between yttrium or lanthanide chlorides and alkali metal alkoxides have been reported to lead to the isolation of a variety of polynuclear chloroalkoxides,[12] the stability of such compounds also being illustrated

---

* Author to whom correspondence should be addressed.

by their formation as side products when halides are used as catalysts to activate lanthanide metals in the course of reactions with alcohols.[13] The retention of the alkali metal, and thus the formation of "ate" complexes, has often been observed for organometallic lanthanide derivatives making the isolation of homoleptic compounds tedious.[14] Although retention of the alkali metal has been noticed in metal alkoxide chemistry, this is generally favoured by a poor control of the stoichiometry, the presence of a bulky OR ligand and/or by the small size of the alkali metal. However, yttrium and lanthanides appear to be more prone than transition metals to the formation of alkoxide aggregates incorporating alkali metal, and the isolation of compounds as different as $Li_5Sm(OBu^t)_8$, $LnNa_8(OBu^t)_{10}Cl$ (Ln = Y, Eu) or $La_2Na_3(OC_6H_4Me\text{-}4)_9(THF)_5$ illustrates these features.[15]

We report herein the synthesis of $Na_3Y(hfip)_6(THF)_3$ (**1**), $Na_2Y(hfip)_4(thd)(THF)_4$ (**2**), the $Y(hfip)_3$ adducts $Y(hfip)_3(THF)_3$ (**3a**) and $Y(hfip)_3(Pr^iOH)_3$ (**3b**) as well as of $[Y(hfip)(thd)_2]_m$ (**4**), where hfip = $OCH(CF_3)_2$ and thd = $t\text{-}BuCOCHCOBu^t$. The reactivity of the Na—Y fluoroisopropoxide derivative **1** toward various yttrium and copper derivatives illustrates that the Y—Na species are resilient in the loss of sodium, giving Na—Cu species, namely $Na_2Cu(hfip)_4(THF)_4$ and $[NaCu(hfip)_2(thd)]_m$. The various species were characterized by FT-IR, NMR (^1H, ^{13}C, ^{19}F) and mass spectrometry. Their thermal behaviour and stability are compared. Sodium-free yttrium fluoroisopropoxide adducts, $[Y(hfip)_3(NH_3)_{0.5}]_2$ and $Y(fip)_3(THF)_3$, have been reported, together with hexafluoro-tert-butoxide derivatives, during the progress of this work; they were obtained by alcoholysis of $Y[N(SiMe_3)_2]_3$.[16]

EXPERIMENTAL

All manipulations were routinely performed under nitrogen using Schlenk tubes and vacuum line techniques with solvents purified by standard methods. YCl_3 (Aldrich) was used as received. Fluoroisopropanol (Aldrich) was stored under nitrogen on molecular sieves and used without further purification. $Y_5O(OPr^i)_{13}$ was obtained as reported in the literature.[17] IR spectra were run on an IR-FTS 45 Bruker spectrometer as Nujol mulls. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer. Samples were run in C_6D_6 and/or C_6F_6 (references: ^1H, residual protons in C_6D_6; ^{19}F, $CFCl_3$). Mass spectra were obtained on a Ribermag R10 spectrometer. Thermogravimetric analyses were achieved under nitrogen on a Shimadzu system at a heating rate of 5°C min^{-1}; volatiles were analysed by FT-IR. Elemental analysis were obtained from the Centre de Microanalyses du CNRS. NMR data are collected in Tables 1 and 2.

Synthesis of $Na_3Y(hfip)_6(THF)_3$ (**1**)

A solution of Na(hfip) (6.06 g, 31.92 mmol) in 80 cm^3 of toluene was added to a suspension of YCl_3 (1.04 g, 5.32 mmol) in 60 cm^3 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** were obtained (79%), m.p. 73°C. Found: C, 27.0; H, 2.0; F, 45.0; Na, 4.7; Y, 6.4. Calc. for $C_{30}H_{30}F_{36}O_9Na_3Y$: C, 26.2; H, 2.2; F, 49.7; Na, 5.0; Y, 6.4%. IR (Nujol, cm^{-1}): 1277 s, 1247 s, 1221 vs, 1211 vs, 1184 vs, 1170 vs, ν(C—O), ν(C—F); 1088 s, 1049 m, 883 m, 845 s, ν(C—C); 742 m, 685 s; 530 w, 519 w, 504 w, 416 m, 372 s, ν(M—O). MS (*m/z*, %): $YNa_3F(hfip)_4$ (4%), $YNa_2(hfip)_4$ (11%), $YNa_2F(hfip)_3$ (1%), $Y(hfip)_3$ (5%), $Y(hfip)_2F$ (3%), $Na_2(hfip)$ (100%).

Compound **1** crystallizes in the space group *P*-1 with the unit cell parameters (297 K) $a = 14.476(3)$, $b = 17.154(3)$, $c = 11.210(2)$ Å, $\alpha = 104.76(2)$, $\beta = 109.48(2)$, $\gamma = 85.24(2)°$, $Z = 2$. The structure could not be solved due to disorder problems.

TGA (1 atmosphere, N_2): 50–120°C (−2 THF), 120–300°C sublimation, residue 7%.

$Na_3Y(hfip)_6$ (**1a**)

Sublimation of compound **1** at 110°C under 10^{-3} Torr offered **1a** (78%), m.p. 132°C. Found: C, 18.7; H, 0.5; F, 56.3. Calc. for $C_{18}H_6F_{36}O_6Na_3Y$: C, 18.5; H, 0.5; F, 58.9%.

Synthesis of $Na_2Y(hfip)_4(thd)(THF)_4$ (**2**)

A solution of 1.02 g (1.6 mmol) of $Y(thd)_3$ in 40 cm^3 of hexane was added dropwise to a solution of 4.4 g (3.2 mmol) of **1** in 60 cm^3 of a mixture of hexane–THF (1 : 2). The reaction medium was stirred for 4 h at room temperature, concentrated and cooled at −20°C offering 4.4 g (92%) of needle-like crystals. IR (cm^{-1}): 1597 m, 1580 s, 1561 m, 1544 m, 1507 s, ν(C=O), ν(C=C); 1282 s, 1250 s, 1222 vs, 1211 vs, 1179 vs, 1152 s, ν(C—O), ν(C—F); 1091 vs, 1053 s, 963 w, 935 w, 917 m, 884 s, 872 s, 848, ν(C—C); 797 m, 767 w, 742 s, 686 vs; 634 w, 609 w, 582 w, 531 w, 521 m, 493 w, 474 w, 409 m, 375 m, ν(M—O).

TGA (N_2, 1 atmosphere): 60–130°C (−2THF),

Table 1. ^1H and ^{19}F NMR data in C_6D_6 for yttrium and Y—Na fluoroisopropoxide derivatives

	^1H chemical shifts (ppm)									^{19}F chemical shifts (ppm)	
	(hfip)		(thd)		L	(L)				(hfip)	
Compound	CH	$^3J_{HF}$ (Hz)	CH	Bu^t						CF$_3$	$^3J_{FH}$ (Hz)
NaORf	4.23 h (1H)	6								−79.5 d	6.2
1	5.08 h (6H)	6			THF	CH$_2$ α		CH$_2$ β		−78.4 d	5.9
						3.36 m		1.24 m	(24H)		
1a	4.88 m									−78.2 d	5.5
2	5.02 h (4H)	5.1	5.97 s (1H)	1.25 s (18H)	THF	3.5 m		1.37 m	(32H)	−77.9 d	5.9
3a	4.31 m (3H)				THF	3.6 m		1.3 m	(12H)	−76.6 d	6.1
3b	4.9 m (3H)				Pr^{i}OH	OH	CH	CH$_3$	(24H)	−75.8 s	$\Delta\nu_{1/2} = 43$ Hz
						2.6 s	3.9 m	0.9 d			
4	5.2 m (1H)		5.97 s (2H)	1.22 s (36H)						−75.6 d	6.2

h = heptuplet, m = multiplet.

130–200°C (−hfipH−THF), 200–250°C (−thdH), residue 7%.

$Na_2Y(hfip)_4(thd)$ (**2a**)

Sublimation of **2** at 130°C under 10^{-3} Torr gave **2a** (yield 70%). Found: Na, 4.2; Y, 8.2. Calc. for $C_{23}H_{23}F_{24}O_6Na_2Y$: Na, 4.6; Y, 9.0%.

Synthesis of $Y(hfip)_3L_3$ [L = THF (**3a**), Pr^{i}OH (**3b**)]

Perfluoroisopropanol (1.97 cm^3, 18.75 mmol) was added to a solution of $Y_5O(OPr^i)_{13}$ (1.53 g, 1.25 mmol) in 40 cm^3 of THF. Agitation was maintained for 3 h at room temperature. Cooling at −20°C gave 3.25 g (90%) of **3a**. Found: C, 29.7; H, 3.3; Y, 11.0. Calc. for $C_{21}H_{27}F_{18}O_6Y$: C, 31.3; H, 3.35; Y, 11.0%. IR (cm^{-1}): 1291 s, 1261 s, 1224 sh, 1215 vs, 1186 vs, ν(C—O), ν(C—F); 1103 m, 1091 sh, 1029 m, 919 w, 890 m, 844 m, ν(C—C); 742 m, 682 m; 530 w, 520 w, 464 sh, ν(Y—OR).

If the reaction was carried out in toluene or hexane, $Y(hfip)_3(Pr^iOH)_3$ (**3b**) was obtained (85%). Found: C, 26.4; H, 2.9; Y, 11.1. Calc for $C_{18}H_{27}F_{18}O_6Y$: C, 28; H, 3.5; Y, 11.5%. IR (cm^{-1}): 3672 w, 3634 w, 3440 w, 3188 w, ν(OH); 1294 s, 1261 s, 1215 vs, 1184 vs, ν(C—O), ν(C—F); 1094 s, 933 m, 887 m, 847 m, 814 m, ν(C—C); 743 m, 687 m, 534 sh, 522 w, 464 sh, 441 sh, 424 sh, 405 sh, 379 sh, ν(Y—OR).

Both compounds sublimed at 150°C (10^{-3} Torr) with extensive decomposition, especially for **3b**, and with loss of the neutral ligand, giving $[Y(hfip)_3]_m$.

Synthesis of $Y(hfip)(thd)_2$ (**4**)

A solution of thdH (1.4 ml, 6.7 mmol) in 10 cm^3 of hexane was added to a suspension of **3** (2.7 g, 3.35 mmol) in 60 cm^3 of hexane. Dissolution occurred while a microcrystalline product precipitated at the end of the addition. A second crop of crystals was obtained from the filtrate. Sublimation of these crystals at 140°C and 10^{-3} Torr gave **4**, yield 89%, m.p. 286°C. Found: C, 48.8; H, 6.5; Y, 13.9. Calc. for $C_{25}H_{39}F_6O_5Y$: C, 48.2; H, 6.3; Y, 14.3%. IR (cm^{-1}): 1603 m, 1580 s, 1554 s, 1508 s, ν(C═O), ν(C═C); 1289 s, 1254 s, 1227 vs, 1184 vs, 1134 vs, ν(C—O), ν(C—F); 1101 vs, 1028 w, 962 w, 935 w, 891 m, 872 s, 858 s, 800 m, ν(C—C); 765 w, 741 m, 687 s; 631 sh, 613 m, 523 w, 494 m, 474 m, 405 s, 363 s, ν(Y—O).

Synthesis of $NaCu(hfip)_2(thd)$ (**5**)

A solution of $Cu(thd)_2$ (1.1 g, 2.55 mmol) in 40 cm^3 of hexane was added dropwise to a solution of **1** (1.17 g, 0.85 mmol) in 40 cm^3 of hexane; the

Table 2. $^{13}C\{^1H\}$ NMR data in C_6D_6 for yttrium and Y—Na fluoroisopropoxide derivatives

	$^{13}C\{^1H\}$ chemical shifts (ppm)									
	(hfip)				(thd)				(THF)	
Compound	CF_3	$J_{CF\,gem}$ (Hz)	CH	$^2J_{CF}$ (Hz)	C=O	CH	C quat	CH_3	$CH_2\alpha$	$CH_2\beta$
1	125 q	287	74 h	30					68.2 s	25.2 s
1a	124 q	287	73.2 m							
2	125 q	288	74.1 h	30	201.8	92.4	41	28.3	68 s	25.5 s
4	122.4 q	287	73.2 h	30	203.8	92.6	40.9	28.3		

q = quadruplet, h = heptuplet, m = multiplet.

colour changed from blue to purple. After 2 h, the reaction medium was filtered; cooling of the filtrate offered a first crop (60%) of **5**. The mother liquor was stripped to dryness giving an inhomogeneous solid. Its sublimation at 110°C and 10^{-3} Torr gave **5**, leaving $Y(thd)_3$. Total yield: 70%. Found: C, 33.8; H, 3.8; F, 32.1; Na, 3.7; Cu, 10. Calc. for $C_{17}H_{21}F_{12}O_4NaCu$: C, 33.8; H, 3.5; F, 37.8; Na, 3.8; Cu, 10.5%. IR (cm^{-1}): 1610 m, 1577 s, 1558 vs, 1547 sh, 1507 s, ν(C=C), ν(C=O); 1283 s, 1259 s, 1222 s, 1206 s, 1181 s, 1145 s, ν(C—O), ν(C—F); 1084 s, 964 m, 938 w, 891 s, 875 s, 853 s, 823 w, 804 m, ν(C—C); 771 m, 743 s, 686 vs; 640 m, 606 w, 534 sh, 526 sh, 521 s, 494 s, 437 sh, 432 m, 421 m, ν(M—O). MS (*m*/*z*, %): $Na_2Cu_2(hfip)_2(thd)_2$ (6%), $Na_2Cu_2(hfip)_3(thd)$ (4%), $NaCu_2(hfip)_2(thd)_2$ (2%), $NaCu_2(thd)_3$ (2%), $NaCu_2(hfip)(thd)_2$ (2%), $NaCu_2(hfip)_2(thd)$ (1%), $Na_2Cu(hfip)_2(thd)$ (23%), $NaCu(thd)_2$ (15%), NaCu(hfip)(thd) (6%), $Cu(thd)_2$ (2%), NaCu(thd) (7%), Na(thd) (12%), Na(hfip) (6%), Na(thd) – Bu (100%), Bu (51%).

Compound **5** was obtained quantitatively by reacting $Na_2Cu(hfip)_4(THF)_4$ (prepared from the reaction of **1** with $CuCl_2$) and $Cu(thd)_2$ (1 : 1 stoichiometry) in hexane over 15 h. Compound **5** was also obtained by reacting **2** (1 g, 0.78 mmol) in 50 cm^3 of toluene and $CuCl_2$ (0.1 g, 0.78 mmol) in 20 cm^3 of THF for 12 h. After filtration, the solution was cooled at -20°C, leaving purple crystals of **5**, purified by sublimation. Yield 50%.

The various compounds are sparingly soluble in hydrocarbons (pentane, toluene), more in C_6F_6 or in ethers. The tetramethylheptanedionato-fluoroisopropoxides are more soluble than the homoleptic fluoroisopropoxides. The Na—Cu derivatives are the least soluble.

RESULTS AND DISCUSSION

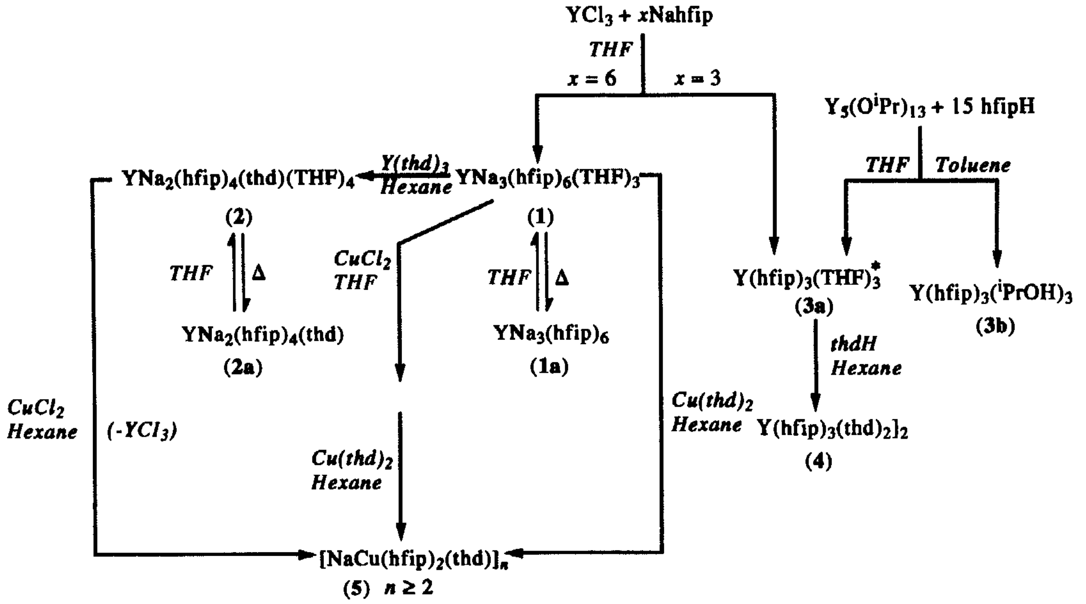
Synthesis

Several routes to yttrium fluoroalkoxides have been investigated (Scheme 1). The reaction between YCl_3 and sodium hexafluoroisopropoxide, Na (hfip), was envisioned as a means to acceed to a homoleptic yttrium derivative which could be used further as a synthon for the building up of Y—M species by metathesis reaction with halides. Surprisingly, the reaction between YCl_3 and Na(hfip) (1 : 3 stoichiometry) in THF offered a sodium-containing material of the type $Na_3Y(hfip)_6$ as the most volatile derivative (15%). A THF adduct, $Na_3Y(hfip)_6(THF)_3$ (**1**), is obtained by crystallization in toluene–THF. ^{19}F NMR of the reaction medium evaporated to dryness shows the presence of essentially two species, **1** as well as a species whose chemical shift is in agreement with that of $Y(hfip)_3(THF)_3$. When the reaction is conducted in the appropriate 1 : 6 stoichiometry, compound **1** is isolated in high yield (79%) by crystallization from the reaction medium. The facile formation of **1** is consistent with the observation that the reaction between $ZrCl_4$ and Nahfip (1 : 4 stoichiometry) offered $Na_2Zr(hfip)_6$.[5]

Sodium-free yttrium fluoroisopropoxide was formed selectively by ligand exchange reaction between $Y_5O(OPr^i)_{13}$ and fluoroisopropanol. The high acidity of $(CF_3)_2CHOH$ (pK_a = 9.3) allows the reaction to proceed to completion even at room temperature and with the stoichiometric amount of fluoroalcohol. The lability of the Y—OPr^i bonds contrasts with the behaviour of $Zr(OR)_4$ (R = Pr^i, Bu^t), which failed to give $Zr(hfip)_4$ by alcoholysis.[5] The high Lewis acidity of the fluoralkoxides is illustrated by their isolation as adducts, $Y(hfip)_3L_3$ [L = THF (**3a**) or Pr^iOH (**3b**)], depending on the solvent, THF or toluene (or hexane), respectively.

Substitution reactions have also been investigated. The reaction between **1** and yttrium 2,2,6,6-tetramethylheptane-3,5-dionate $Y(thd)_3$ (2 : 1 molar ratio) proceeds quantitatively with the formation of $Na_2Y(hfip)_4(thd)(THF)_4$ (**2**) as the only product.

Heterometallic alkoxides based on classical OR groups and on alkali metals have found a large use



Scheme 1. Various synthetic routes to heterometallic yttrium–sodium fluoroisopropoxides and their reactivity.

as synthons for building up mixed-metal alkoxides with a controlled stoichiometry.[18] Comparable metathesis reactions involving **1** have thus been investigated. $Na_3Y(hfip)_6(THF)_3$ reacts readily with $CuCl_2$ in THF at room temperature, over several days, giving a volatile (sublimation at 150°C and 10^{-2} Torr) mixed-metal Na—Cu derivative $Na_2Cu(hfip)_4(THF)_4$ (as evidenced by its IR by comparison with an authentic sample).[19,20] Similar behaviour is observed using **2** as starting material, the $NaCu(hfip)_2(thd)$ (**5**) derivative then being isolated in about 50% yield. A more selective route to **5** is the reaction between **1** or **1a** and $Cu(thd)_2$ (1 : 3 stoichiometry) in hexane. The volatility of **5** allowed its separation from the yttrium by-product $Y(thd)_3$ by sublimation (110°C and 10^{-3} Torr). Although **5** could be obtained starting from Y—Na species, **1** or **2**, it is best obtained by reacting $Na_2Cu(hfip)_4(THF)_4$ and $Cu(thd)_2$ (1 : 1 stoichiometry), since this reaction proceeds without formation of any by-product.

It should be noticed that, in all cases, a change of the stoichiometry between the metals, namely a reduction of the sodium content, is observed for the Y—Na and Cu—Na species by substitution of fluoroisopropoxides by thd ligands. Reactions with $Y(thd)_3$ and $Cu(thd)_2$ respectively are thus more selective than with the β-diketone thdH.

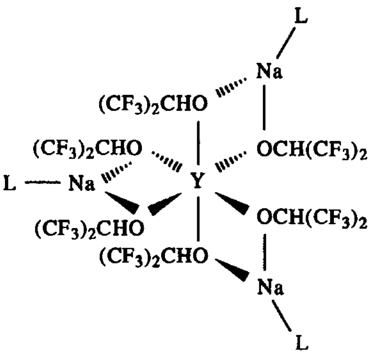
Characterization

The various compounds have been characterized by elemental analysis, FT-IR, mass spectrometry, thermal gravimetric analysis (TGA) and NMR (^1H, $^{13}C\{^1H\}$ and ^{19}F). NMR data are summarized in Tables 1 and 2.

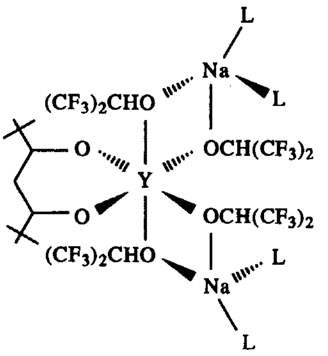
IR and ^1H NMR were used primarily as tools for the presence of additional neutral ligands in the metal coordination sphere. Thus, for instance, the formation of $Y(hfip)_3(Pr^iOH)_3$ is supported by $\nu(O—H)$ vibrations (3672—3188 cm^{-1}) in the FT-IR spectra. The presence of several absorption bands suggests that the hydroxyl groups are involved in different types of hydrogen bonds. The tetramethylheptanedionate derivatives **2**, **4** and **5** are characterized by $\nu(C=O)$ and $\nu(C=C)$ absorption bands around 1600–1500 cm^{-1}. All yttrium and Y—Na derivatives are soluble, although sparingly in non-polar solvents, the introduction of thd in the metal coordination sphere leading generally to an increase in solubility properties. The ^1H NMR spectra of **1** and **2** in C_6D_6 or C_6D_6–C_6F_6 confirm the presence of THF ligands. No dissociation reactions are observed. These ligands are, however, labile and can undergo exchange reactions with other donors such as acetonitrile or dimethoxyethane. All hfip and THF ligands appear magnetically equivalent by NMR (^1H, ^{13}C) for either **1**, **2**, **3** or **4**. ^{19}F NMR spectra are characterized by relatively sharp lines, the chemical shifts being slightly displaced to high field with respect to the free alcohol or to sodium fluoroisopropoxide.

Mixed-metal alkoxides with an M : M′ 1 : 3 stoichiometry are quite scarce. Representative examples include lanthanides derivatives such as $Ln[Al(\mu\text{-}OPr^i)_2(OPr^i)_2]_3$, $V(\mu\text{-}OPh)_6Li_3(DME)_3$[18] or

Y[(μ-OBu^t)(μ-Me)AlMe$_2$]$_3$.[21] Their structure is based on a central hexacoordinated metal. Although single crystals of **1** could be grown, its solid state structure could not be solved from a room temperature X-ray data collection due to disorder problems. The spectroscopic data of **1** are, however, compatible with a YNa$_3$(μ-hfip)$_6$(THF)$_3$ framework[22] (**I**), the environment of each sodium being completed by one oxygen of a THF ligand and eventually by fluorine interactions, as observed on other Na—M fluoroisopropoxides.[5,17] The YNa$_3$ stoichiometry of **1** also matches that of the double YNa hydroxide YNa$_3$(OH)$_6$ formed in aqueous media.[23] The structure of **2** is most probably related to that of Y(OBu^t)[(μ-OBu^t)[(μ-Me)AlMe$_2$]$_2$[21] with sodium centres linked to one THF ligand (**II**) and probably having secondary fluorine bonds.[5,17] The data of **4** are in agreement with a dimeric structure (**III**) which would ensure hexacoordination for the yttrium atoms.

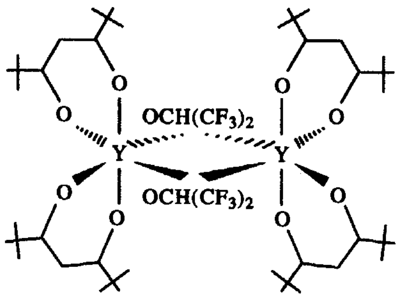


I



L = THF

II



III

Thermal behaviour

The homo- or hetero-metallic yttrium fluoroisopropoxides are all volatile. This allowed their separation from by-products and/or their purification from trace amounts of donor solvent molecules. The mixed-metal species YNa$_3$(hfip)$_6$(THF)$_3$ is more stable and more volatile than the homometallic derivative Y(hfip)$_3$(THF)$_3$. Compound **1** sublimes at 110°C under 10^{-3} Torr as compared to 150°C (10^{-3} Torr) for **3**. This behaviour, quite common in metal alkoxide chemistry,[1] allowed a facile isolation of **1** even if the reaction between YCl$_3$ and Na(hfip) was carried out in a 1 : 3 stoichiometry. The analytical data of the sublimate indicate the conservation of the Na$_3$Y(hfip)$_6$ stoichiometry and loss of THF. The elimination of the Lewis base probably leads to an oligomerization of the Na$_3$Y(hfip)$_6$ moiety as suggested by the decrease of the solubility properties compared to the THF adduct **1** and as also observed, for instance, for Na$_2$Cu(hfip)$_4$.[6] However, depolymerization of **1a** is easily achieved by dissolution in THF giving **1**. The mixed-metal β-diketonatoalkoxide (**2**) displays behaviour comparable to that of **1** : sublimation occurs at 130°C and 10^{-3} Torr, giving a THF-free derivative **2a** which can be converted into the original compound **2** by dissolution in THF. Mass spectroscopy data confirm the retention of the mixed-metal Y—Na and Na—Cu species in the vapour phase. Na$_3$YF(hfip)$_4^+$ corresponds to the heaviest fragment detected with m/z 845 for **1**. Mass spectrometry data of **5** account for a dimeric species in the vapour phase, the highest fragment corresponding to $Na_2Cu_2(hfip)_2(thd)_2^+$. For the yttrium derivatives, metal fluoride fragments are observed in appreciable amounts. The formation of such species implies the cleavage of C—F bonds with the loss of an OC_3F_5H molecule, probably pentafluoropropane-2-one. C—F bond cleavage reactions appear less favoured for the Na—Cu derivatives. The introduction of the thd ligand in the metal coordination sphere improves the stability and, as a result, **4** sublimes at 140°C and 10^{-3} Torr with almost no decomposition, by contrast with **3a** and **3b**.

The thermal behaviour of some yttrium–sodium compounds has been analysed by thermogravimetric analysis (TGA) under nitrogen (at 1 atmosphere) up to 500°C. The data of compound **1** show the elimination of two molecules of THF then sublimation. EDX (scanning electron microscopy) analysis of the residue left after the thermal treatment of **1** accounts for the formation of fluorides. A more complex behaviour is observed for **2**. It should be noticed that the nature of the ligand might affect the thermal behaviour of fluoroisopropoxides and thus the nature of the final material. Although slow to hydrolyse in solution at room temperature, fluoroalkoxide derivatives are generally quite hygroscopic solids[7] and water can act as a competive ligand with respect to THF, as evidenced by the presence in the IR spectra of absorptions due to hydroxyl stretching vibrations [ν(OH) 3680, 3391, 3187 cm^{-1}, for example when **1** is exposed to air for a few minutes]. Thermal decomposition of **1** was then observed to result in the formation of oxides. Similar transformations might occur quite easily during thermolysis in a hot-wall reactor, generally based on glass walls.

CONCLUSIONS

The reaction between YCl_3 and sodium fluorisopropoxide leads to the formation of a mixed-metal YNa_3 species, even in the case where the amount of the sodium reactant is less than that required by the stoichiometry. This might be due to the better stability of the mixed-metal species as compared to the homometallic homoleptic derivative or to the limited solubility and/or reactivity of yttrium chloride in the reaction medium, resulting in an excess of reactant. Solubility properties of the lanthanide halides have also been observed to govern the issue of the reactions with alkali metal aryloxides.[24] The reactions between the $Na_3Y(hfip)_6(THF)_3$ fluoroisopropoxide and yttrium or Cu^{II} derivatives, β-diketonates or halides respectively, also proceeds with retention of sodium and thus with formation of mixed-metal Y—Na or Na—Cu species. Although the Y—Na species are resilient to the loss of sodium, derivatization can be achieved using the lability of the fluoroisopropoxide ligands, an $Na(hfip)_2(THF)^-$ moiety being replaced by the thd$^-$ ligand. The steric demand of the anionic ligands, hexafluoroisopropoxide or 2,2,6,6-tetramethylheptane-3,5 dionate, actually achieves the control of the stoichiometry between the two metals, sodium and yttrium, and thus precursors for various materials such as composites or Nasicon become available.[25]

Mixed-metal Y—Ba and Y—Cu fluoroalkoxides and β-diketonatofluoroalkoxides are thermodynamically stable derivatives; they can be obtained in high yields by a variety of routes, but all excluding sodium reactants.[11] For building up these aggregates, compounds **3a** or **4** have been used, as well as $Y(thd)_3$, as the source of yttrium. The high Lewis acidity of fluorinated alkoxides makes most polar solvents able to complement the metal coordination spheres; these adducts can display quite different volatility and stability properties, allowing further tailoring.

Acknowledgements—We acknowledge the CNRS-PIRMAT for financial support and Prof. A. Albinati (U. Milano) for the X-ray data of **1**.

REFERENCES

1. D. C. Bradley, *Chem. Rev.* 1989, **89**, 1317.
2. L. G. Hubert-Pfalzgraf, *New J. Chem.* 1987, **11**, 663.
3. L. G. Hubert-Pfalzgraf, *Appl. Organomet. Chem.* 1992, **6**, 627.
4. J. C. Willis, *Coord. Chem. Rev.* 1988, **88**, 133.
5. J. A. Samuels, E. B. Lobkovsky, W. E. Streib, K. Folting, J. C. Huffman, J. W. Zwanziger and K. G. Caulton, *J. Am. Chem. Soc.* 1993, **115**, 5093.
6. A. P. Purdy, C. F. George and J. H. Callahan, *Inorg. Chem.* 1991, **30**, 2812. A. P. Purdy and C. F. George, *Inorg. Chem.* 1991, **30**, 1969.
7. H. Vincent, F. Labrize and L. G. Hubert-Pfalzgraf, *Polyhedron* 1994, **13**, 3323.
8. L. J. Lingg, A. D. Berry, A. P. Purdy and K. J. Ewing, *Thin Solid Films* 1992, **209**, 9.
9. K. Fujiura, Y. Nishida, K. Kobayashi and S. Takahashi, *Optical Wave Guide Materials, Material Research Society Symposium Proceedings* 1992, 244. H. J. Kormer, *Bull. Am. Phys. Soc.* 1988, **33**, 1091. M. Dejneka, R. E. Riman and E. Snitzer, *J. Am. Ceram. Soc.* 1994, **76**, 3147.
10. F. Labrize, L. G. Hubert-Pfalzgraf, J. C. Daran and S. Halut, *J. Chem. Soc., Chem. Commun.* 1993, 1588; F. Labrize and L. G. Hubert-Pfalzgraf,

Comptes-rendus MRT-CNRS, Paris, June 1992; ACS Meeting, Chicago, 1993, INOR 162.

11. L. G. Hubert-Pfalzgraf, F. Labrize, H. Guillon and P. Tobaly, *Better Ceramics Through Chemistry* VI. MRS (1994).
12. R. C. Mehrotra, A. Singh and U. M. Tripathi, *Chem. Rev.* 1991, **91**, 1287.
13. O. Poncelet and L. G. Hubert-Pfalzgraf, *Polyhedron* 1989, **8**, 2183.
14. H. Schumann, *Angew. Chem., Int. Edn Engl.* 1984, **23**, 474. R. D. Ernst and T. J. Marks, *J. Organomet. Chem.* 1987, **318**, 29.
15. W. J. Evans, R. E. Golden and J. W. Ziller, *Inorg. Chem.* 1993, **32**, 3041. W. J. Evans, M. S. Sollberger and J. W. Ziller, *J. Am. Chem. Soc.* 1993, **115**, 4120. F. T. Edelmann, A. Steiner, D. Stalke, J. W. Gilge, S. Jagner and M. Hakansson, *Polyhedron* 1994, **13**, 539.
16. D. C. Bradley, H. Chudzynska, M. B. Hursthouse and M. Motevalli, *Polyhedron* 1993, **12**, 1907.
17. O. Poncelet, W. Sartain, K. Folting, L. G. Hubert-Pfalzgraf and K. G. Caulton, *Inorg. Chem.* 1989, **28**, 263.
18. K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.* 1990, **90**, 969.
19. P. M. Jeffries, S. R. Wilson and G. S. Girolami, *Inorg. Chem.* 1992, **31**, 4503.
20. F. Laurent, J. C. Huffman and K. G. Caulton, submitted.
21. W. J. Evans, T. J. Boyle and J. W. Ziller, *J. Am. Chem. Soc.* 1993, **115**, 5084.
22. F. Laurent and K. G. Caulton, private communication.
23. *Gmelin Handbuch der Anorganische Chemie: Yttrium and Lanthanides*, teil Cl. Springer, Berlin (1974).
24. D. Clark, J. C. Huffman and J. G. Watkin, *Inorg. Chem.* 1992, **31**, 1554.
25. K. Yamashita, T. Nojiri, T. Umegaki and T. Kanazawa, *Chem. Lett.* 1989, 375.