Synthesis and Structures of $[((Me_3Si)_3CAlF_2)_2(\mu\text{-}O)Li_2(THF)_4]$ and $[\{Li(Me_3Si)_3CAlF_3(THF)\}_3LiF(THF)]$

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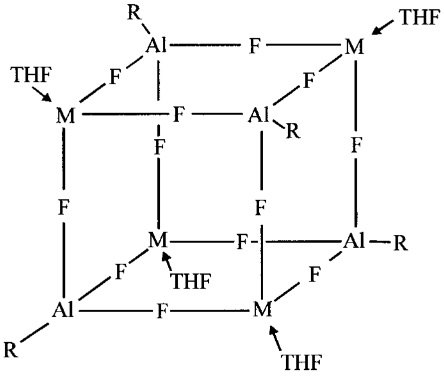
Received February 7, 2001

Summary: The synthesis of $[((Me_3Si)_3CAlF_2)_2(\mu\text{-}O)Li_2(THF)_4]$ *(**1**) and* $[\{Li(Me_3Si)_3CAlF_3(THF)\}_3LiF(THF)]$ *(**2**) is reported. Compound **1** was obtained either by the reaction of* $(Me_3Si)_3CAlMe_2{\cdot}THF$ *and* Me_3SnF *in the presence of* Li_2O *or by the reaction of* $[(Me_3Si)_3CAlF_2]_3$ *and* Li_2O*. **1** is an interesting example of an oxygen- and fluorine-containing alkyl aluminum compound. Complex **2** was prepared by the reaction of* $(Me_3Si)_3CAlF_2{\cdot}THF$ *with* $LiOCH(CF_3)_2$ *as an unexpected result that illustrates the variety of possible structures obtainable by the combination of* $[(Me_3Si)_3CAlF_2]_3$ *and LiF.*

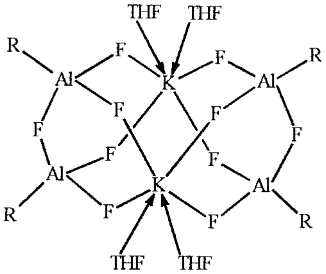
Introduction

Recently we reported the synthesis of soluble aluminum fluorides containing alkali metals such as $[Na(Me_3Si)_3CAlF_3(THF)]_4$ (**3**) and $[((Me_3Si)_3C)_4Al_4K_2(\mu\text{-}F)_2F_8(THF)_4]$ (**4**), as well as a silver derivative of composition $[Ag(toluene)_3]^+[\{((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4\}_2Li]^-$ (**5**) (THF = tetrahydrofuran).[1a−c] $[Li(Me_3Si)_3CAlF_3(THF)]_4$[1d] (**6**) and $[Na(Me_3Si)_3CAlF_3(THF)]_4$ are isostructural. These compounds contain the chelating $[(Me_3Si)_3CAlF_3]^-$ (**3** and **6**) or $[(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3]^-$ (**4** and **5**) anion, and the cations are structure directing to yield cubic arrays or unusual aggregates. The $[(Me_3Si)_3CAlF_2(\mu\text{-}O)F_2AlC(SiMe_3)_3]$ species in **1** is comparable to the $[(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3]$ part in $[((Me_3Si)_3C)_4Al_4K_2(\mu\text{-}F)_2F_8(THF)_4]$ and in $[Ag(toluene)_3]^+[\{((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4\}_2Li]^-$, where two of these units coordinate to a metal center. The reaction of $(Me_3Si)_3CAlF_2{\cdot}THF$ with $LiOCH(CF_3)_2$ afforded the unexpected compound $[\{Li(Me_3Si)_3CAlF_3(THF)\}_3LiF(THF)]$ (**2**). We were not able to isolate an adduct of $(Me_3Si)_3CAlF_2{\cdot}THF$ and $LiOCH(CF_3)_2$. However, **1**, **2**, and **6** indicate the variety of products obtained in reactions of $[(Me_3Si)_3CAlF_2]_3$ with various lithium derivatives.

Results and Discussion



3: M = Li
6: M = Na



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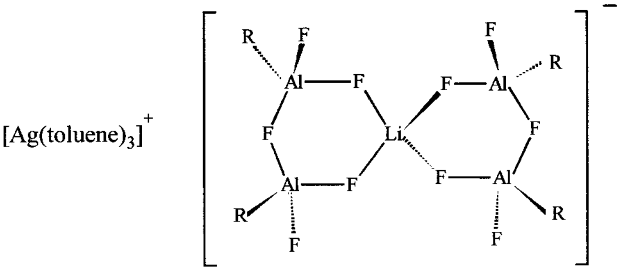

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Compound **1** is prepared by the reaction of $(Me_3Si)_3CAlF_2{\cdot}THF$ and Li_2O in THF (Scheme 1). A more convenient route to **1** is the in situ generation of $(Me_3Si)_3CAlF_2{\cdot}THF$ by the action of Me_3SnF on $(Me_3Si)_3CAlMe_2{\cdot}THF$ in the presence of Li_2O. The structure of **1** consists of an eight-membered $(Al{-}F{-}Li{-}F)_2$ ring with a transannular Al−O−Al bridge. The Li−F bond lengths are in the range 1.835(5)−1.854(4) Å and comparable to the mean Li−F distances (1.852 Å) in $[Li(Me_3Si)_3CAlF_3(THF)]_4$. The average Al−F bond length (1.733 Å) in **1** is slightly shorter than those in

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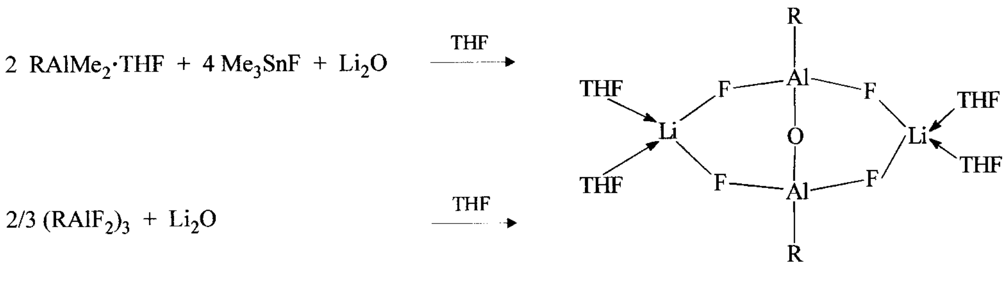
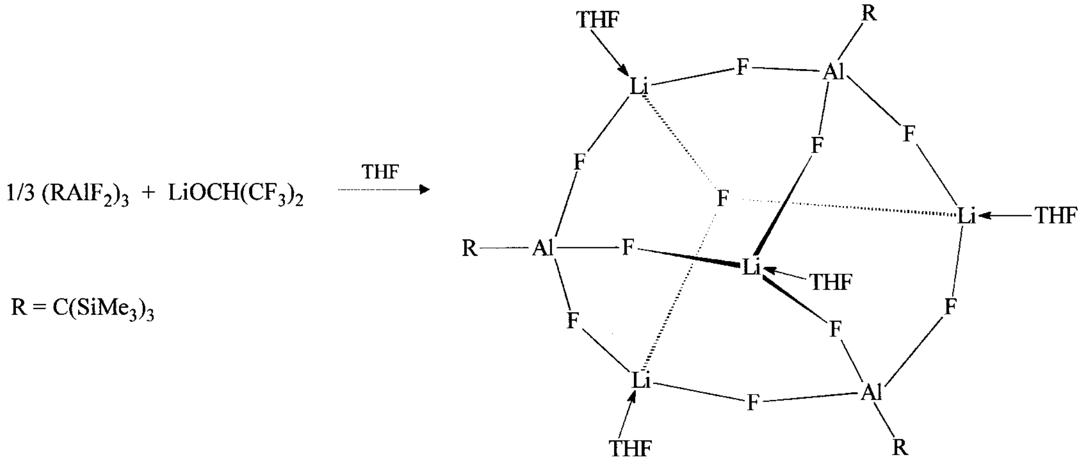
10.1021/om0100941 CCC: $20.00

Scheme 1



1

Scheme 2



2

(Cp$_2$ZrMe)(μ-F)[(Me$_3$Si)$_3$CAlF$_2$] (bridging 1.779(2) Å). The Al−O distance (av 1.709 Å) is shorter than those in [{(Me$_3$Si)$_3$CAl}$_4$(μ-O)$_2$(μ-OH)$_4$] (1.79 Å).[2] The C−Al−F angle (109.17(9)−111.06(10)°) is narrower than those in [Li(Me$_3$Si)$_3$CAlF$_3$(THF)]$_4$ (111.9−115.2°). Obviously, due to a lesser steric influence in **1**, the angles at fluorine are in the range 120.60(15)−128.51(17)° and much narrower than those at fluorine in [Li(Me$_3$Si)$_3$CAlF$_3$(THF)]$_4$ (140.0−162.9°). The O−Al−F angles in **1** (105.08(8)−107.10(8)°) differ significantly from those in [(C(CH$_2$COOEt)$_2$(COOEt))OAlFMe]$_2$ (127.7° and 90.7−96.8°).[3]

Compound **2** is obtained by reacting [(Me$_3$Si)$_3$CAlF$_2$]$_3$ with LiOCH(CF$_3$)$_2$ (Scheme 2). The X-ray structural analysis reveals that **2** consists of three (Me$_3$Si)$_3$CAlF$_3$$^-$ anions interconnected with three Li cations to form a 12-membered ring. In the center on one side of this ring is a fluorine atom that is coordinated to three lithiums of the 12-membered ring. The opposite side of the ring is occupied by a lithium atom that is coordinated to three fluorine atoms, each of which is coordinated to an aluminum atom of the ring. The fourth coordination site of each of the Li atoms is occupied by an oxygen atom of a THF molecule. There is a 3-fold axis (Figure 2) going through Li(2) and F giving a molecule of high symmetry.

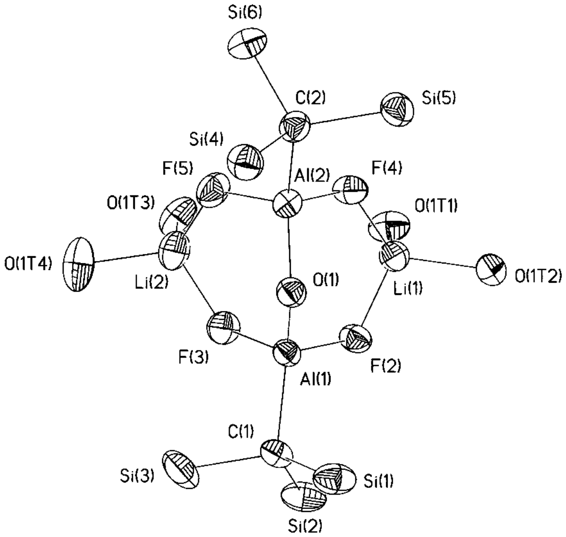


Figure 1. Structure of **1**. 50% probability of thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Al(1)−O(1) = 1.7083(18), Al(2)−O(1) = 1.7097(17), Al(1)−F(2) = 1.7373(15), Al(2)−F(5) = 1.7294(16), Li(1)−F(2) = 1.854(4), Li(2)−F(5) = 1.835(5); F(2)−Al(1)−C(1) = 111.06(10), F(3)−Al(1)−C(1) = 109.17(9), Al(1)−F(2)−Li(1) = 120.60(15), Al(1)−F(3)−Li(2) = 128.51(17), O(1)−Al(1)−F(3) = 107.10(8), O(1)−Al(2)−F(4) = 105.08(8).

The consequence of this symmetrical arrangement is that the three Li atoms of the 12-membered ring form a perfect triangle of Li$_3$ (Li−Li−Li 60°). The Al−F bond distances are in a narrow range (1.694(2)−1.701(2) Å).

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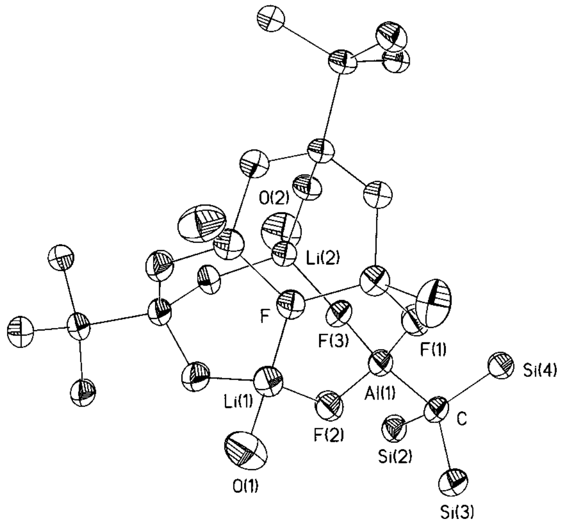

Figure 2. Structure of **2**. 50% probability of thermal ellipsoids. Selected bond lengths (Å) and angles (deg): F(1)−Al(1) = 1.694(2), F(3)−Al(1) = 1.701(2), F(1)−Li(1)#1 = 1.873(6), F−Li(1) = 1.801(6); Al(1)−F(1)−Li(1)#1 = 125.3(2), Al(1)−F(3)−Li(2) = 149.6(3), F(1)−Al(1)−C = 113.36(11), F(3)−Al(1)−C = 115.74(13), Li(1)#1−Li(1)−Li(1)#2 = 60. Symmetry transformations used to generate equivalent atoms: #1 $-y, x-y-1, z$; #2 $-x+y+1, -x, z$.

They are comparable to those in $[Li(Me_3Si)_3CAlF_3(THF)]_4$ (av 1.688 Å) but are considerably shorter than the Al−F(bridging) distances in $[(Me_3Si)_3CAlF_2]_3$ (1.795−1.815 Å).[1b] The Li−F bond lengths are in the range 1.801(6)−1.873(6) Å and close to the Li−F distances in **1** (1.835(5)−1.854(4) Å). The C−Al−F angles cover a range of 113.36(11)−115.74(13)° and are wider than those in **1** (109.17(9)−111.06(10)°). The Al−F−Li angles range from 125.3(2)° to 149.6(3)° (**1** 120.60(15)−128.51(17)°).

We assume that the four LiF molecules necessary for the formation of **2** are formed by an exchange reaction of $LiOCH(CF_3)_2$ with $(Me_3Si)_3CAlF_2{\cdot}THF$, where the $(CF_3)_2HCO^-$ is replacing a F^-. The easy generation of **2** is due to its insolubility in toluene. However, we were not able to isolate a compound of composition $[(Me_3Si)_3CAlF(OCH(CF_3)_2)]{\cdot}THF$ in proof of this assumption. Compound **2** shows good stability in the gas phase, which is demonstrated by a FAB experiment that gives an anion of **2** minus a lithium and a THF molecule.

The known examples of aluminum compounds containing unsubstituted oxygen and fluorine atoms that are soluble in organic solvents are rare.[4] In the series of the alkali metals the lithium derivative **2** has a different structural arrangement compared to those of the analogous compounds of the heavier alkali metals.

Experimental Section

General Data. All experiments were carried out using standard Schlenk techniques under a dry nitrogen atmosphere due to the sensitivity of the reactants and products toward air and moisture. A Braun MB 150-GI box was used to store the compounds and to prepare the samples for spectroscopic characterization. All solvents were distilled from sodium/benzophenone and degassed prior to use. $[(Me_3Si)_3CAlF_2]_3$,[1b] Me_3SnF,[5] and $(Me_3Si)_3CAlMe_2{\cdot}THF$[2] were prepared as described in the literature. Elemental analyses were performed at the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. NMR spectra were recorded on a Bruker Avance 200 or Bruker AC 250 and were referenced to Me_4Si, C_6F_6, and LiCl, respectively. FT-IR spectra were measured on a Bio-Rad FTS-7 as KBr plates in the range 4000−400 cm^{-1}. Mass spectra were obtained on a Finnigan MAT 95. Melting points were measured in sealed glass tubes on a Büchi 540 instrument and are reported uncorrected.

Crystal structure solutions and refinements for compounds **1** and **2** are shown in Table 1. Data for compound **1** were collected on a Stoe-Siemens-Huber four-circle diffractometer

Table 1. Crystal Data and Structure Refinement for 1 and 2

	1	**2**
empirical formula	$C_{36}H_{86}Al_2F_4Li_2O_5Si_6$	$C_{50}H_{121}Al_3F_{10}Li_4O_5Si_9$
fw	911.43	1353.98
temp (K)	133(2)	133(2)
cryst syst	triclinic	rhombohedral
cryst group	$P\bar{1}$	$R3$
a (Å)	12.953(2)	14.899(2)
b (Å)	13.442(2)	14.899(2)
c (Å)	16.391(2)	30.472(6)
α (deg)	89.33(2)	90
β (deg)	88.04(2)	90
γ (deg)	70.02(2)	120
cell vol (Å^3)	2680.6(7)	5857.9(16)
Z	2	3
ρ_c (g cm^{-3})	1.129	1.151
μ (mm^{-1})	0.236	0.247
$F(000)$	988	2184
cryst size (mm)	0.70 × 0.70 × 0.60	0.60 × 0.60 × 0.60
2θ range (deg)	4−50	3.5−50
index ranges	$-15 < h < 15$, $-16 < k < 11$, $-19 < l < 19$	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-35 \leq l \leq 35$
no. of data measd	33 521	37 248
no. of unique reflens	9477	4425
R(int)	0.0409	0.0490
R,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0490, 0.1171	0.0323, 0.0841
R, $wR2$ (all data)	0.0730, 0.1313	0.0336, 0.0873
goodness-of-fit on F^2	1.049	1.086
no. of data/restraints/params	9477/924/706	4425/822/410
largest diff peak/hole (e Å^{-3})	0.316 and −0.313	0.268 and −0.125

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$.

with a Siemens SMART CCD area detector. Data for compound **2** were collected on a Stoe IPDS II system. Mo Kα radiation ($\lambda = 0.71073$ Å) was used in all cases. A semiempirical absorption correction for **1** was performed using the program SADABS.[6] All structures were solved by direct methods[7] and refined anisotropically with SHELXTL. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atom.

In both structures one $C(SiMe_3)_3$ and some of the THF groups are disordered. They were refined with distance restraints and restraints for the anisotropic displacement parameters. The uncoordinated THF in **2** was refined as a disordered C_5H_{10} ring. Again restraints were used. The data of **2** are severely twinned by a combination of obverse/reverse twinning and merohedral twinning. The twinning was taken into account and the fractional contributions refined to 0.004(2) (operation −1 0 0, 0−1 0, 0 0 1), 0.135(1) (operation 0 1 0, 1 0 0, 0 0−1), and 0.339(3) (operation 0−1 0, −1 0 0, 0 0 1). Because of the twinning the absolute structure could not be reliably determined. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC-160782−160783.

[((Me$_3$Si)$_3$CAlF$_2$)$_2$(*μ*-O)Li$_2$(THF)$_4$] (1). First method: A mixture of $[(Me_3Si)_3CAlF_2]_3$ (0.66 mmol, 589 mg) and Li_2O (1.0 mmol, 30 mg) in THF (20 mL) was stirred for 2 days. The mixture was filtered. Crystallization at −20 °C resulted in a colorless crystalline solid **1** (0.62 g, 0.68 mmol, 68%), mp 178−179 °C. ^{1}H NMR (C_6D_6, 200 MHz, ppm): δ 0.43 (s, 54 H, Si−CH_3), 0.90 (m$_c$, 16 H, CH_2−CH$_2$−O), 3.79 (m$_c$, 16 H, CH$_2$−CH_2−O). ^{19}F NMR (C_6D_6, 188 MHz, ppm): δ 3.8 (s). ^{29}Si NMR (C_6D_6, 50 MHz, ppm): δ −3.37. ^{7}Li NMR (C_6D_6, 97 MHz, ppm): δ −0.82. IR (KBr, cm^{-1}): 2957 vs, 2903 vs, 1262 s, 1098 s, 1047 s, 1020 s, 855 vs, 718 vs, 674. Anal. Calcd for $C_{36}H_{86}Al_2F_4Li_2O_5Si_6$: C, 47.44; H, 9.51. Found: C, 46.8; H, 9.4.

Second method: A mixture of $(Me_3Si)_3CAlMe_2{\cdot}THF$ (2.0 mmol, 722 mg), Me_3SnF (4.0 mmol, 732 mg), and Li_2O (1.0 mmol, 30 mg) in THF (20 mL) was heated at reflux for 6 h. All solvents were removed in vacuo. The residue was dissolved in THF (20 mL) and filtered. Crystallization at −20 °C afforded **1** (0.73 g, 0.81 mmol, 81%) as a colorless crystalline solid, mp 177−179 °C.

[{Li(Me$_3$Si)$_3$CAlF$_3$(THF)}$_3$LiF(THF)] (2). MeLi (3.75 mL, 1.6 M in Et_2O, 6 mmol) was added to $(CF_3)_2CH(OH)$ (1.0 g, 6 mmol) in THF (30 mL), and the mixture was stirred for 3 h. This solution was added to $[(Me_3Si)_3CAlF_2]_3$ (1.79 g, 2.0 mmol) in THF (30 mL), and the resulting mixture was stirred for 3 days. The THF was removed in vacuo. The residue was dissolved in toluene/THF (30 mL, 20:1) and filtered. Crystallization at −20 °C afforded **2** (0.30 g, 0.22 mmol, 11%) after 2 weeks as a colorless crystalline solid, mp >300 °C. ^{1}H NMR (THF-d_8, 200 MHz, ppm): δ 0.15 (s, Si−CH_3), 1.77 (m$_c$, CH_2−CH$_2$−O), 3.61 (m$_c$, CH$_2$−CH_2−O). ^{19}F NMR (THF-d_8, 188 MHz, ppm): at δ −4.2 (s) the main resonance, with a very small resonance at −40.5 (s). ^{29}Si NMR (THF-d_8, 99 MHz, ppm): δ −1.83. ^{7}Li NMR (THF-d_8, 97 MHz, ppm): δ −0.5. FAB *m*/*z* (%): 1202 (M − Li − THF), 1057 (M − Li − 3 THF). IR (KBr, cm^{-1}): 2978 vs, 2956 vs, 2900 vs, 1463 w, 1292 s, 1212 w, 1054 vs, 874 vs, 837 vs, 755 s, 724 s, 708 s, 674 vs, 626 s. For the elemental analysis the crystals of composition **2** + THF were used. Anal. Calcd for $C_{50}H_{121}Al_3F_{10}Li_4O_5Si_9$: C, 44.35; H, 9.01. Found: C, 44.8; H, 9.0.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Tables giving positional and thermal parameters and estimated standard deviations for all atoms, bond distances and angles, and anisotropic thermal parameters of compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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