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Organotrialkoxy- and Organotrifluoroaluminates: Crystal Structures of Li[(Me$_3$Si)$_3$CAlX$_3$]·OC$_4$H$_8$ (X = ^{t}BuO, F)

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Summary: Reactions of the organotrihydroaluminate Li[(Me$_3$Si)$_3$CAlH$_3$]·2THF, (THF = tetrahydrofuran) with the protic reagents ^{t}BuOH or HF in toluene yield the novel compounds Li[(Me$_3$Si)$_3$CAlX$_3$]·THF, X = ^{t}BuO or F, which crystallize as a monomer and a tetramer, respectively. Multinuclear NMR measurements on the latter show that the tetrameric structure is broken down in THF but preserved in benzene; the [(Me$_3$Si)$_3$CAlF$_3$] fragments rotate on the NMR time scale about the body diagonal of the Al$_4$Li$_4$ cube.

Lithium aluminum hydrides, e.g. LiAlH$_4$ or LiAl(O-^{t}Bu)$_3$H, are widely used as reducing agents or hydride transfer reagents in organic and organometallic chemistry.[1] However, there is still much to learn about the structures of such reagents, the intermediates they form with organic substrates, or the aluminum-containing products, which are often insoluble in the reaction media or are destroyed during workup. The syntheses and structures of the first organotrihydroaluminates, Li[RAlH$_3$]·2THF (R = C(SiMe$_3$)$_3$ (**1**),[2] C(SiMe$_2$Ph)$_3$ (**2**),[2] 2,4,6-^{t}Bu$_3$C$_6$H$_2$ (**3**)[3]) and Li[2,4,6-Ph$_3$C$_6$H$_2$AlH$_3$]·1.5Et$_2$O (**4**)[3] were reported only recently. These compounds could be isolated because the bulky organic groups prevent the rearrangement of the organotrihydroaluminates to tetra- and di-hydroaluminates. Reactions of compound **3** with MeI or Me$_3$SiCl to give arylaluminum hydrides and halides have also been described.[4] We have now found that compound **1** reacts with a range of protic reagents, XH (e.g. X = F, ^{i}PrO, ^{t}BuO, PhO), to give well-defined species, Li[(Me$_3$Si)$_3$CAlX$_3$]·nTHF. As far as we are aware, the structure of only one compound of this type, Li[MeAl(BHT)$_2$(OCMePh$_2$)]·OEt$_2$ (BHT = OC$_6$H$_2$-2,6-^{t}Bu$_2$-4-Me), has previously been determined by X-ray crystallography.[5] The structures of our compounds, both in the solid state and in solution, depend on the nature of the group X, and we illustrate this by reporting the compounds in which X = ^{t}BuO or F and n = 1.

Reaction of **1** with ^{t}BuOH in toluene at room temperature gave the alkoxide-bridged complex (THF)Li(μ-O-^{t}Bu)$_2$Al(O^{t}Bu)C(SiMe$_3$)$_3$, **5**, in good yield.[6] The structure,[7] shown in Figure 1, contains an almost planar LiO$_2$Al ring (sum of internal angles, 357.6°). The lithium atom is in a three-coordinate planar environment, but the bond lengths to the alkoxy oxygen atoms (ca. 1.95(2) Å) are exceptionally long; Li−O(alkoxy) bond lengths involving three-coordinate planar lithium are usually *ca.* 1.85(1) Å.[8] The Li−O(THF) distance is normal. There is a short contact (2.596 Å) between the lithium atom and C(21) of the alkyl group, like those observed previously in compounds containing three-coordinate lithium (e.g. 2.280−2.295 Å in [^{n}BuLi]$_6$,[9a] 2.275−2.566 Å in [^{t}BuLi]$_4$,[9a] 2.34−2.36 Å in [^{n}BuLi·LiO-^{t}Bu]$_4$,[9b] and 2.75 Å in [Me$_2$Si(O^{t}Bu)(N^{t}Bu)Li]$_2$·THF[9c]). The Al−O(terminal) distance, 1.698(7) Å, is similar to that, 1.690(3) Å, in Al$_2$(O^{t}Bu)$_6$, **6**, but the mean Al−O(bridging) bond length, 1.788(7) Å, is shorter than is usual in alkoxides (*cf.* 1.828(3) Å in **6**).[10] The small difference between the Al−O(terminal) and Al−O(bridging) bond lengths (0.09 Å) and the long Li−O bond

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[1] See, for example: Trost, B. M., Fleming, I., Eds. *Comprehensive Organic Synthesis*; Pergamon: Oxford, U.K., 1991; Vol. 8, Reduction. Barron, A. R.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1897−1915. Bulychev, B. M. *Polyhedron* **1990**, *9*, 387−408 and references therein.

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[6] Li[(Me$_3$Si)$_3$CAl(O^{t}Bu)$_3$]·THF, **5**: Addition of dry *tert*-butyl alcohol (0.28 cm^3, 2.93 mmol) to a stirred solution of **1** (0.40 g, 0.97 mmol) in toluene (25 cm^3) at room temperature caused immediate evolution of hydrogen. The solution was stirred for 3 h, the solvent removed, and the residue extracted with heptane (10 cm^3). The extract was filtered, concentrated, and cooled to −30 °C to give air-sensitive, colorless crystals of **5**. Yield: 0.27 g, 50%. Mp: >395 °C. Anal. Found: C, 53.9; H, 11.1. Calcd for C$_{26}$H$_{62}$AlLiO$_4$Si$_3$: C, 56.1; H, 11.2. IR: 1254 s, 1227 m, 1208 m, 1149 w, 1118 m, 1090 m, 1067 m, 1029 m, 963 s, 860 m, 665 m cm^{-1}. ^{1}H NMR (360 MHz, C$_6$D$_6$): δ 0.59 (27H, s, Me$_3$Si), 1.10 (4H, m, CH$_2$), 1.48 (27H, s, O^{t}Bu), 3.24 (4H, m, OCH$_2$). ^{13}C NMR (62.88 MHz, C$_6$D$_6$): δ 7.4 (Me$_3$Si), 25.1 (CH$_2$), 34.3 ((*C*H$_3$)$_3$CO), 69.1 (OCH$_2$), 70.1 ((CH$_3$)$_3$*C*O). ^{7}Li NMR (97.263 MHz, C$_6$D$_6$, relative to aqueous LiCl): δ −0.29. ^{27}Al NMR (65.223 MHz, C$_6$D$_6$, relative to aqueous Al(NO$_3$)$_3$): δ 63.5 ($\Delta\nu_{1/2}$ = 572 Hz). ^{29}Si NMR (99.36 MHz, C$_6$D$_6$): δ −2.32 ppm.

[7] Crystal data for **5**: C$_{26}$H$_{62}$AlLiO$_4$Si$_3$, M = 556.95, orthorhombic, a = 11.299(2) Å, b = 16.535(8) Å, c = 36.827(10) Å, V = 6880(4) Å^3, space group $P2_12_12_1$, Mo Kα radiation, λ = 0.710 73 Å, Z = 8, D_c = 1.075 Mg m^{-3}, $F(000)$ = 2464, crystal dimensions 0.4 × 0.3 × 0.2 mm, μ = 0.189 mm^{-1}, CAD4 diffractometer, θ−2θ mode, T = 293 K, $2 < \theta < 22°$, 4715 unique reflections measured and 2936 with $I > 2\sigma(I)$, no decay or absorption correction, structure analysis by direct methods (SHELXS-86), full-matrix least-squares refinement on F^2 (SHELXL-93) with non-H atoms anisotropic, H atoms refined in riding mode with U_{iso}(H) = 1.2U_{eq}(C) for CH$_2$ and 1.5Ueq(C) for CH$_3$. Final R ($I > 2\sigma(I)$): $R1$ = 0.0677, w$R2$ = 0.1305. R (all data): $R1$ = 0.1296, w$R2$ = 0.1733. S = 1.025. There are two independent molecules with essentially the same geometry. The quoted structural parameters are for molecule 1.

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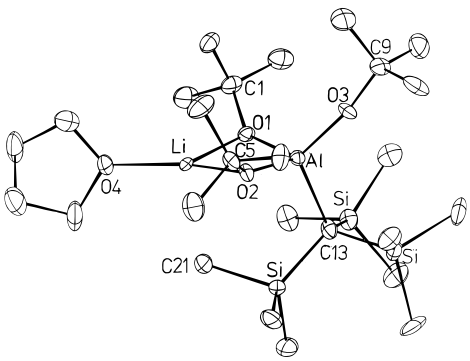

Figure 1. Molecular structure of (THF)Li(μ-O^{t}Bu)Al(O^{t}Bu)C(SiMe$_3$)$_3$, **5** (50% thermal ellipsoids). Selected distances (Å) and angles (deg): Al1−O1 1.789(7), Al1−O2 1.788(7), Al1−O3 1.698(7), Li1−O1 1.94(2), Li1−O2 1.97(2), Li1−O4 1.95(2), Al1−C13 2.031(11), mean C13−Si 1.887(11), mean Si−Me 1.879(11); O1−Li1−O2 82.2(7), Lil−O2−Al 92.1(7), O1−Al−O2 92.0(3), Li−O1−Al 91.3(6), Al−O3−C9 167.4(8), O−Al−C13 112.5(4), C1−O1−Al 138.8(5), Cl−O1−Li 112.5(8) C5−O2−Al 142.4(6), C5−O2−Li 114.7(8), mean Si−C13−Si 108.2(5), mean Al−C13−Si 110.7(5), mean Me−Si−Me 104.2(5).

lengths suggest that compound **5** is best regarded as a cation−anion pair. Similar long Li−O and short Al−O(bridging) bonds are found in Li[Al(OCEt$_3$)$_3$Cl]·2THF,[11] in which the lithium atom is four-coordinate and the configuration at the bridging oxygen atoms is planar, and in Li[MeAl(BHT)$_2$(OCMePh$_2$)]·OEt$_2$,[5] which contains a three-coordinate lithium atom and one planar (BHT) and one pyramidal (OCMePh$_2$) bridging oxygen atom. The pyramidal configuration at O$_1$ (sum of angles = 343.4°) and O$_2$ (348.4°) in **5** is a consequence of the bulk of the alkyl group attached to aluminum. Large C−O(terminal)−Al angles (167.4(8)° in **5**) and short Al−O(terminal) bond lengths have been explained in terms of both Al−O π-bonding and ionic effects, but it is difficult to separate these interactions.[10,12,13]

Treatment[14] of a toluene solution of **1** with a 70% solution of HF in pyridine gave a compound of empirical formula Li[(Me$_3$Si)$_3$CAlF$_3$]·THF, **7**, which was found to adopt a tetrameric structure in the solid state.[15] The core (Figure 2) can be considered as a distorted cube derived from an [Al$_8$F$_{12}$]$^{12+}$ fragment of the AlF$_3$ structure[16] by replacement of alternate Al^{3+} ions with [Li(THF)]$^+$ units and attachment of [C(SiMe$_3$)$_3$]$^-$ anions at the remaining aluminums. Eight-membered rings with near-linear fluorine bridges (as found on the cube faces in **7**) are also observed in [Me$_2$AlF]$_4$.[17] The mean Al−F bond length in **7**, 1.687(8) Å, is similar to that in [Me$_4$N][AlF$_4$], 1.658(3) Å[18] (*cf.* 1.797(3) Å in AlF$_3$[16]). The mean Li−F distance (1.85(2) Å) is similar to that in P(Si^{t}Bu$_2$F)$_2$Li·2THF (1.861(2) Å)[19] and [Pt(Ph$_3$P)$_2$(μ-O)]$_2$·LiBF$_4$ (1.89(2)Å).[20] These distances show that compound **7** may be described as a lithium alkyltrifluoroaluminate, with four anions and four cations in each tetramer. The mean angle at aluminum (109.3°) is close to that expected for a tetrahedral geometry, but the C−Al−F angles (111.9−115.2°) are wider and the FAlF angles (102.1−106.3°) narrower. The mean angle at lithium (109.5°) is again close to the tetrahedral value, but the individual angles are much more variable (F−Li−F, 102.9−119°; F−Li−O, 103.2−124°). The angles at fluorine are in the range 140.0−162.9° (*cf.* 146° in [Me$_2$AlF]$_4$[17]). The ^{7}Li NMR signal of **7** in benzene solution is a decet with a binomial distribution of intensities (Figure 3) indicating that each lithium is coupled to nine equivalent ^{19}F nuclei ($I = {}^1/_2$). The corresponding ^{19}F signal, a 1:3:6:10:12:12:10:6:3:1 decet (Figure 3), shows that that each fluorine is coupled to three equivalent ^{7}Li nuclei ($I = {}^3/_2$). Therefore, within each tetramer the [(Me$_3$Si)$_3$CAlF$_3$]$^-$ anions rotate about the 3-fold axis along the body diagonal of the cube core, breaking the weaker Li−F but maintaining the stronger Al−F bonds. The fact that the Li−F coupling is retained shows that the tetramers are preserved in benzene

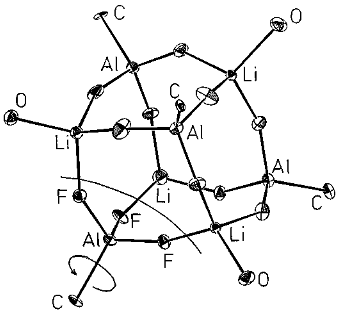

Figure 2. Al$_4$Li$_4$F$_{12}$ core of Li[(Me$_3$Si)$_3$CAlF$_3$]·THF, **7**, with Me$_3$Si groups and THF CH$_2$ groups omitted for clarity. See text for significant bond lengths and angles: Mean Si−C 1.88(1), Si−Me 1.88(2) Å; Si−C−Si 111.5(6), Me−Si−Me 105.8(6)°. The arrow shows the rotation of one [(Me$_3$Si)$_3$CAlF$_3$]$^-$ ion as observed by NMR measurements.

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(14) Li[(Me$_3$Si)$_3$CAlF$_3$]·THF, **7**: A solution of hydrofluoric acid (70%) (0.065 g, 2.25 mmol) in pyridine was added dropwise to a stirred solution of **1** (0.31 g, 0.75 mmol) in toluene (25 cm^3) at room temperature. Hydrogen gas was evolved immediately, and stirring was continued for 2 h. A small amount of solid was filtered off, and solvent was removed to give a white solid. This was stirred with THF (10 cm^3) to remove residual pyridine, and after the THF had been pumped away the residue was crystallized from heptane to give air-sensitive, colorless crystals of **7**. Yield: 0.15 g, 52%. Mp: >400 °C. Anal. Found: C, 42.7; H, 8.9. Calcd for C$_{14}$H$_{35}$AlF$_3$LiOSi$_3$: C, 42.6; H, 8.9. IR: 1292 m, 1260 s, 1082 sh, 1051 s, 916 sh, 864 s, 800 sh, 757 w, 729 m, 703 w, 666 m, 617 m cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.41 (27H, s, CH$_3$), 1.55 (4H, m, CH$_2$), 3.91 (4H, m, OCH$_2$). ^{13}C NMR (C$_6$D$_6$): δ 5.4 (CH$_3$, $J_{\text{Si-C}}$ 50 Hz), 25.3 (CH$_2$), 68.9 (OCH$_2$). ^{7}Li NMR (C$_6$D$_6$): δ −0.94 (decet, $J_{\text{Li-F}}$ 72 Hz). ^{7}Li NMR (THF-d_8): δ −1.18 (s). ^{19}F NMR (376.498 MHz, C$_6$D$_6$, relative to CFCl$_3$): δ −174.7 (decet, $J_{\text{Li-F}}$ 72 Hz). ^{19}F NMR (THF-d_8): δ −169.2 (s). ^{27}Al NMR (C$_6$D$_6$): δ 74 ($\Delta\nu_{1/2}$ = 2.4 kHz). ^{27}Al NMR (THF-d_8): δ 75 ($\Delta\nu_{1/2}$ = 2.16 kHz). ^{29}Si NMR (C$_6$D$_6$): δ −3.7 ppm.

(15) Crystal data for **7**: C$_{56}$H$_{140}$Al$_4$F$_{12}$Li$_4$O$_4$Si$_{12}$, M = 1578.4, triclinic, a = 13.532(8) Å, b = 13.739(5) Å, c = 26.252(11) Å, α = 103.64(3)°, β = 90.90(4)°, γ = 104.39(4)°, V = 4580(4) Å^3, space group $P\bar{1}$, Mo Kα radiation, λ = 0.710 73 Å, Z = 2, D_c = 1.14 Mg m^{-3}, F(000) = 1696, crystal dimensions 0.3 × 0.3 × 0.2 mm, μ = 2.6 cm^{-1}, CAD4 diffractometer, θ−2θ mode, T = 173 K, $2 < \theta < 22°$, 11 195 unique reflections measured and 5371 with $I > 2\sigma(I)$, no decay or absorption correction, structure analysis by direct methods (SHELXS-86), full-matrix least-squares refinement on F (Enraf-Nonius MolEN programs) with non-H atoms anisotropic except for Li, H atoms in fixed positions with $U_{\text{iso}} = 1.2U_{\text{eq}}$ for parent atom, $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$, R = 0.091, R' = 0.086, S = 1.5. Two of the (Me$_3$Si)$_3$C groups were disordered with minor sites of occupancy 0.13 and 0.20.

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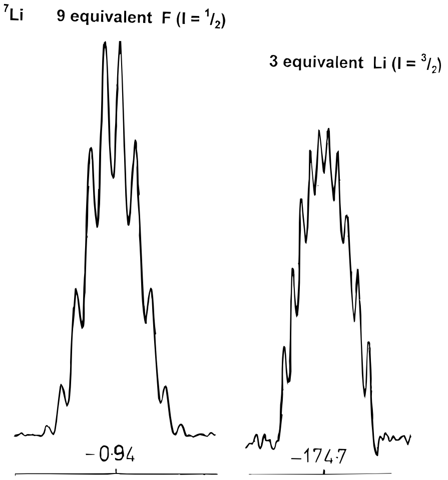

Figure 3. NMR spectra of **7** in benzene with chemical shifts in ppm.

solution. A splitting of 24 Hz was observed, but as each lithium is coupled to only three fluorines at any one time, the actual coupling constant is ca.72 Hz. This value was confirmed by cooling the sample to 253 K, at which temperature the anion rotation was slowed down and a quartet ($^1J_{\mathrm{Li-F}} = 74$ Hz) was observed. As far as we are aware, very few Li−F coupling constants have been published and these, from lithium {organo(fluoro)silyl}amides, range from 15 to 95 Hz.[21] Samples of **7** in THF-d_8 give singlets in both ^{7}Li and ^{19}F NMR spectra indicating that there is dissociation, probably to give discrete [Li(THF-d_8)$_4$]$^+$ and [(Me$_3$Si)$_3$CAlF$_3$]$^-$ ions. Proton spectra of a sample of **7** in benzene-d_6 were unchanged after 48 h at 110 °C indicating that there had been no detectable decomposition.

The fact that compound **5** is monomeric and compound **7** tetrameric may be related, at least in part, to the smaller size of the fluorine atom compared with that of the *tert*-butoxide group and to the tendency of fluorine to form linear, or near-linear, bridges between metal centers.

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Supporting Information Available: Tables of crystallographic parameters, positional and thermal parameters, and bond distances and angles and ORTEP diagrams (17 pages). Ordering information is given on any current masthead page.

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