The First Structurally Characterized Diorganoaluminate

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Dedicated to the memory of our friend and colleague Ron Snaith

Keywords: Aluminum / Silicon / Hydride ligands / Lithium

The first structurally characterized dialkylaluminate $[\{Li(THF)\}(AltBu\{C(SiMe_3)_3\}H_2)]_2$ (**3**) is dimeric in the solid state with $[Li(THF)]^+$ and $[AltBu\{C(SiMe_3)_3\}H_2]^-$ fragments linked by Li···H–Al bridges.

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Introduction

Dialkylaluminates − compounds containing the $[AlR_2H_2]^-$ fragment − have been known as useful intermediates in syntheses for nearly 50 years.[1] The $NaAlEt_4$-$NaAlH_4$ phase diagram shows that sodium diethylaluminate is a thermodynamically stable species,[2] and both this and sodium dimethylaluminate are commercially available reducing agents.[3] Several routes to dialkylaluminates have been reported but evidence for individual species has been confined to elemental analysis (R = Me,[4−6] Et,[2,4,5,7,8] *n*Pr,[4] *i*Bu [4,5,9]), IR spectroscopy[6,8,10] and ^{27}Al NMR spectroscopy.[11] Dialkylaluminates are sometimes obtained from reaction mixtures that might be expected to yield monoalkylaluminates. For example, attempts to make sodium ethylaluminate $Na[AlEtH_3]$ give $Na[AlEt_2H_2]$ and $Na[AlH_4]$, suggesting that any initially formed $Na[AlEtH_3]$ rearranges as shown in Equation (1) (R = Et).

$$2Na[AlH_3R] \rightarrow Na[AlH_2R_2] + Na[AlH_4] \qquad (1)$$

Diorganoaluminates are much less well characterized than the corresponding dialkoxo- and diaryloxoaluminates, which contain the ions $[Al(OR)_2H_2]^-$,[12,13] or aluminates containing the ions $[Al(ER_2)_2H_2]^-$ (E = N, P or As).[14,15] As far as we are aware, no diorganoaluminate has previously been structurally characterized, though the $[AlR_2H_2]^-$ fragment has been identified in titanium[16] and rhenium[17] hydride complexes and an aluminacarborane.[18]

In a footnote to a paper describing the alkylaluminate $[\{Li(THF)_2\}\{Al\{C(SiMe_2Ph)_3\}H_3\}]_2$ (**1a**), we mentioned briefly the di-*tert*-butylaluminate $Li[AltBu_2H_2]\cdot 2THF$ (**2**).[19] This was obtained from the reaction of $LiAlH_4$ with one equivalent of Li*t*Bu, indicating that any initially formed $Li[AltBuH_3]$ either reacted more rapidly than $LiAlH_4$ with Li*t*Bu, or rearranged according to Equation (1) (R = *t*Bu). Treatment of $LiAlH_4$ with LiR (R = $C_6H_2iPr_3$-2,4,6) followed by $SiMe_3Cl$ gave AlR_2H, again suggesting that a diarylaluminate intermediate was formed from the monoaryl species.[20]

We have not been able to obtain crystals of **2** suitable for an X-ray structure determination, but we report the synthesis of the related compound $[\{Li(THF)\}(AltBu\{C(SiMe_3)_3\}H_2)]_2$ (**3**) and its crystal structure. The iodide $AltBu_2I\cdot THF$ (**4**) and the compounds $Li(TMEN)_n$-$[AltBu_2H_2]$ (n = 2, **5**; n = 1, **6**; TMEN = tetramethylethylenediamine), are also described.

Results and Discussion

Treatment of $Li[AlH_4]$ with $LiC(SiMe_3)_3(THF)_2$ or $LiC(SiMe_2Ph)_3(THF)$ gave the alkylaluminates **1b** and **1a**, in each of which one of the four hydride ligands has been replaced by a bulky organic group. Treatment of $Li[AlH_4]$ with the smaller Li*t*Bu led to the replacement of two hydride ligands and the formation of a dialkylaluminate **2**. The formation of a di- rather than a mono-substituted aluminate appears, therefore, to depend on the size of the attacking lithium derivative. We surmised that the reaction between **1b** and Li*t*Bu might yield the dialkylaluminate **3**, and this proved to be the case. Compound **3** was isolated in good yield as an air- and moisture-sensitive solid.

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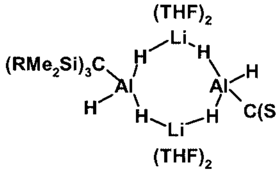
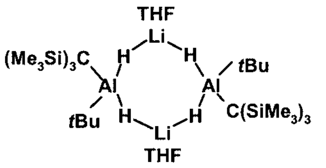


1a R = Ph, **1b** R = Me
1c R = NMe$_2$

Li[AltBu$_2$H$_2$].2THF

2



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The molecular structure is shown in Figure 1 and selected bond lengths and angles in Table 1. The molecules of **3** are dimeric with a twofold axis through O2Li2···Li1O1. As in the organoaluminates **1a**[19] and **1c**,[21] the arylaluminates Li[Al{$C_6H_2R_3$-2,4,6}H_3] with R = Ph (**1d**) or tBu (**1e**),[22] the aryloxyaluminate [Li(Et_2O)$_2$][Al{OC_6H_3tBu$_2$-2,6}H_3],[12] the bis(trimethylsilyl)amido derivatives [Li(Et_2O)$_2$][Al{N($SiMe_3$)$_2$}H_3][15] and [Li(Et_2O)$_2$]-[Al{PhNN($SiMe_3$)$_2$}H_3],[23] and the tetrahydoaluminates [LiL{AlH_4}]$_2$ {L = HN(tBu)CH(tBu)CH=NtBu,[24] HN(tBu)CH(tBu)CH_2N(H)tBu,[25] or TMEN[26]}, the cationic lithium and anionic aluminum fragments are held together by hydride bridges to give an eight-membered puckered $Li_2Al_2H_4$ ring. However, the conformation of this ring differs from those in the previously described compounds. In these the rings are in a chair conformation **I** with the aluminum atoms bent away from the almost planar Li_2H_4 array so that the large organic groups R on the periphery of the molecule point outwards. In **3** the $Li_2Al_2H_4$ ring adopts a skew-boat configuration **II** in which the atoms H1a′ and H1b lie above and H1a and H1b′ lie below the plane containing the Li, Al and O atoms; the larger ligands R are *trans* with respect to the ring. We cannot at present say whether the conformation is determined by other than crystal packing forces. In contrast to **1a**, there are no problems with crystallographic disorder.

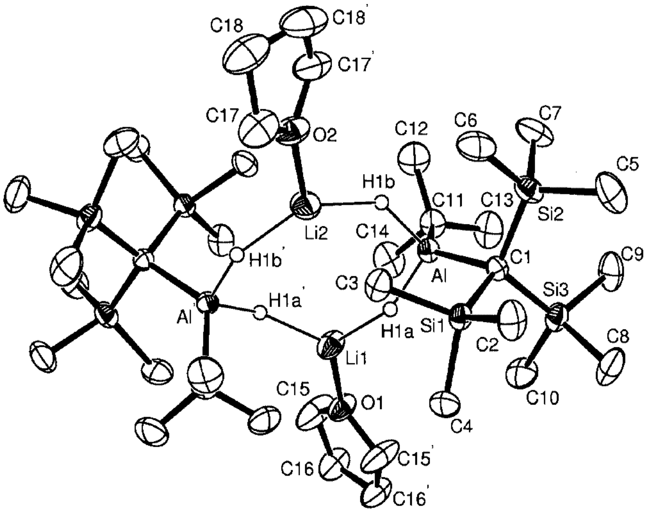
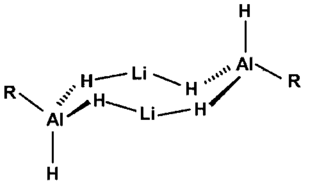


Figure 1. The molecular structure of **3** with thermal ellipsoids 50% probability

Table 1. Selected bond lengths [Å] and angles [°] in [{Li(THF)}(AltBu{C($SiMe_3$)$_3$}H_2)]$_2$ (**3**)

Al−CSi$_3$	2.041(2)	Li−H1a	1.79(3)
Al−CC$_3$	2.043(2)	Li−H1b	1.82(3)
Al−H1a	1.55(3)	Li−O1	1.862(6)
Al−H1b	1.59(3)	Li−O2	1.891(6)
Si−C1[a]	1.878(2)	Si−Me[a]	1.881(3)
C−Al−C	130.23(10)	Al−C−Si	105.11(10) −110.26(11)
H−Al−H	101(1)	Si−C1−Si	109.37(11) −112.64(11)
H−Li1−H	114(2)	Me−Si−Me	102.42(13) −106.36(14)
H−Li2−H	141(2)	C1−Si−Me	112.07(11) −115.24(12)
O1−Li1−H1a	123(1)	C−Al−H	103(1) −109(1)
O2−Li2−H1b	110(1)		

[a] Average value, with esd's of individual measurements in parentheses. None differs significantly from the mean.



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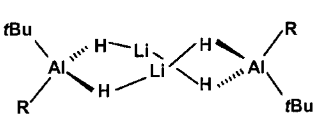

II

The distances from aluminum to the central carbon atoms of the tBu [2.043(2) Å] and C($SiMe_3$)$_3$ groups [2.041(2) Å] are the same within the experimental uncertainty and identical to those in **1a** [2.046(4) Å]. Similar distances [2.001(2) to 2.081(4) Å] are found in the *tert*-butylaluminium compounds (AltBu$_2$H)$_3$ (**7**) and Li[AltBu$_3$H] (**8**).[27] The Li−H bond lengths are greater than the Al−H bond lengths and cover a wider range, indicating that the ionic formulation [Li(THF)][AltBu{C($SiMe_3$)$_3$}H_2] accurately describes the structure. The experimental uncertainties in the mean Al−H and Li−H distances are considerably greater than those in the exocyclic Al−C bonds, but the endocyclic bonds in **3** [Al−H 1.57(3) and Li−H 1.80(3) Å] are not significantly different from the bridging bonds in **1a** [1.62(4) and 1.93(4) Å, respectively], other compounds containing $Li_2Al_2H_4$rings,[12,15,22−26] or **8** [1.68(3) and 1.92(3) Å].[27] The increased crowding from the replacement of an exocyclic hydrogen in **1b** by a *tert*-butyl group to give **3** results in the displacement of one molecule of coordinated THF. The conformations of the bulky groups attached to aluminum are such that the crowding at Li1 is different from that at Li2; the mean planes of the attached THF molecules are orthogonal and the H−Li−H angles [114(2)° at Li1 and 141(2) at Li2] are significantly different. The C−Al−C angle [130.23(10)°] in **3** is considerably wider and

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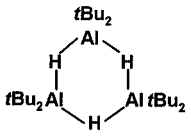

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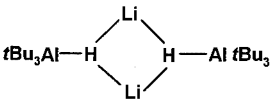

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the H−Al−H angle within the ring [101(1)°] narrower than the tetrahedral value.

The NMR spectra of **3** at 298 K are consistent with the structure found in the solid state but, as we have not collected data over a range of temperatures, we cannot comment on whether isomeric species are obtained under different conditions. The ^{27}Al resonance (δ = 137 ppm) is at higher frequencies than those in **1a** and **1b** (δ = 113−115); similar shifts (δ = 132−141) have been reported in **2**[19] and other diorganoaluminates.[11]

The organoaluminates **1a−1e** are versatile starting materials for the synthesis of a range of organoaluminum derivatives bearing bulky groups,[20,28,29] since the Al−H bonds are considerably more reactive than the more protected Al−C bonds towards a variety of reagents. The reactions of the diorganoaluminates **2** and **3** can be expected to lead to a similar range of products containing AlR_2 or $AlRR'$ fragments, in which R and R′ are bulky or fairly bulky organic groups. We report two preliminary results here.

Treatment of **2** with iodomethane gave a good yield of $AltBu_2I$·THF (**4**) as an air- and moisture-sensitive solid [Equation (2)]. Although di-*tert*-butylaluminum fluoride, chloride,[30] bromide[31] and hydride[27] have been described we cannot find any previous report of the iodide.

$$\underset{\mathbf{2}}{\mathrm{Li[Al}t\mathrm{Bu_2H_2].2THF}} + \mathrm{MeI} \longrightarrow \underset{\mathbf{4}}{\mathrm{Al}t\mathrm{Bu_2I.THF}} + \mathrm{CH_4} + \mathrm{LiH} \qquad (2)$$

$$\underset{\mathbf{1e}}{\mathrm{[\{Li(THF)_2\}\{AlRH_3\}]_2}} + 2\mathrm{MeI} \longrightarrow \mathrm{(AlRH_2)_2} + 2\mathrm{CH_4} + 2\mathrm{LiI} + 4\mathrm{THF}$$

$$\mathrm{R} = \mathrm{C_6H_2}\,t\mathrm{Bu_3\text{-}2,4,6} \qquad (3)$$

The reaction of **3** with iodomethane gave a complex mixture but reaction of the compound $[\{Li(THF)_2\}\{AlH_3\{C_6H_2tBu_3\text{-}2,4,6\}\}]_2$ (**1e**) gave $[AlH_2C_6H_2\text{-}tBu_3\text{-}2,4,6]_2$ and LiI cleanly [Equation (3)].[29] These results can be attributed to effects of steric hindrance to attack at bonds in the eight-membered $Li_2Al_2H_4$ rings. In **2** the two *t*Bu groups attached to aluminum are not large enough to prevent coordination of the iodine of MeI and consequent reaction at Al−H bonds. In **1d**, however, coordination of iodine at aluminum is inhibited by the bulky aryl group so that the iodomethane attacks at Li−H rather than Al−H bonds. In **3** the rates of attack by MeI at Al−H and Li−H bonds appear to be similar so that a complex mixture of products is formed. The fact that the aluminum iodide rather than the hydride is isolated in reaction (2) indicates that under the conditions that we employed LiH is an ineffective reagent for reduction of $AltBu_2I$.

Reaction of **2** with an excess of TMEN gave a colorless solid that was shown by chemical analysis and NMR spectroscopy to be $[Li(TMEN)_2][AltBu_2H_2]$ (**5**). One equivalent of TMEN was lost when the compound was sublimed at 120 °C in a way that is reminiscent of the behavior of $[Li(TMEN)_2][AlH_4]$. This was shown to crystallize in an extended ionic lattice, but the species obtained after loss of one mol of TMEN was $[\{Li(TMEN)\}\{(\mu\text{-}H)_2AlH_2\}]_2$, which formed a lattice of dimeric ion pairs having Li···H−Al bridges like those in **3**.[26] With the elucidation of the structure of **3**, examples of compounds containing each of the species $[AlR_nH_{4-n}]^-$ with $n = 0-4$ (R = alkyl or aryl) are now known. However, when $n = 1-3$, the group R varies from compound to compound[19,21,22,27,31,32] so that it is not possible at this stage to draw meaningful conclusions about trends in bond lengths and angles.

Experimental Section

Air and moisture were excluded by Schlenk-tube techniques with Ar as blanket gas. All glassware was flame-dried immediately before use and solvents were carefully dried by standard methods. NMR spectra were recorded at 300.13 (^{1}H), 75.43 (^{13}C), 194.5 (^{7}Li), 130.4 (^{27}Al) or 99.36 MHz (^{29}Si) and chemical shifts are given relative to $SiMe_4$, aqueous LiCl or $Al(NO_3)_3$. IR spectra are for Nujol mulls.

The compound $[Li(THF)_2][AlH_2tBu_2]$ (**2**) has been made previously.[19]

$[\{Li(THF)\}(AltBu\{C(SiMe_3)_3\}H_2)]_2$ (3): A solution of Li*t*Bu (0.97 mmol) in pentane (0.6 mL) was added dropwise to a stirred solution of **1b** (0.40 g, 0.97 mmol) in toluene (20 mL) at room temperature. The mixture was stirred for 15 h, then the white precipitate was filtered off, solvent was removed from the filtrate and the residue was recrystallised from benzene to give **3** as a white air- and moisture-sensitive solid (0.28 g, yield 74%), m.p. 160 °C. $C_{18}H_{46}AlLiOSi_3$ (396.7): calcd. C 54.4, H 11.7; found C 53.3, H 11.4. IR: $\tilde{\nu}_{max}$ = 1731m, 1612br, (Al−H), 1253s, 1205w, 1168w, 1043m, 1008w, 855s, 782w, 670m cm^{-1}. ^{1}H NMR (C_6D_6, 298 K): δ = 0.48 (s, 27 H, $SiMe_3$), 1.23 (m, 4 H, THF), 1.39 (s, 9 H, *t*Bu), ca. 2.9 (br. s, 2 H, AlH), 3.42 (m, 4 H, THF) ppm. ^{7}Li NMR: δ = −0.37 ppm. ^{13}C NMR: δ = −2.9 (CSi_3), 5.8 ($^1J_{SiC}$ = 50 Hz, $SiMe_3$), 25.1 (THF), 34.6 (*t*Bu), 68.9 (THF) ppm. ^{27}Al NMR: δ = 137 ppm ($\Delta\nu_{1/2}$ = 3 kHz). ^{29}Si NMR: δ = −3.9 ppm.

Reaction of 2 with MeI: Iodomethane (0.20 g, 3.2 mmol) was added dropwise to a stirred solution of **2** (0.70 g, 2.4 mmol) in toluene (25 mL) at room temperature. After 15 h the solvent was pumped from the white suspension and the residue was extracted with heptane (25 mL). The extract was filtered and the filtrate reduced to ca. 10 mL in volume to give $AltBu_2I$.THF (**4**) as a white crystalline solid, m.p. 46 °C, which was filtered off and dried (0.64 g, 79%). $C_{12}H_{26}AlIO$ (340.2): calcd. C 42.4, H 7.6; found C 42.4, H 7.7. IR: $\tilde{\nu}$ = 1359s, 1301w, 1252m, 1177m, 1044s, 1004s, 923m, 854m, 812s, 683m cm^{-1}. ^{1}H NMR (C_6D_6, 298 K): δ = 0.94 (m, 4 H, THF), 1.20 (s, 18 H, CMe_3), 3.63 (m, 4 H, THF) ppm. ^{13}C NMR: δ = 17.4 (CMe_3), 24.8 (THF), 30.5 (CMe_3), 74.8 (THF) ppm. ^{27}Al NMR: δ = 158 ppm ($\Delta\nu_{1/2}$ = 3.4 kHz). MS: *m*/*z* = 268 (69) [M − THF], 211 (100) [M − THF − *t*Bu], 169 (90), 154 (70).

$[Li(TMEN)_2][AltBu_2H_2]$ (5) and $[Li(TMEN)][AltBu_2H_2]$ (6): TMEN (4.5 mL, 29.8 mmol) was added to a stirred solution of **2** (2.20 g, 7.5 mmol) in toluene (30 mL) at room temperature. After 30 min the solvent was removed until the solution became cloudy, then the mixture was cooled to give colorless air-sensitive crystals of **5** (2.40 g, 84%). $C_{20}H_{52}AlLiN_4$ (382.6): calcd. C 62.8, H 13.7, N 14.6; found C 62.2, H 13.3, N 13.5. IR: $\tilde{\nu}_{max}$ = 1651vs, br (Al−H), 1361s, 1291s, 1251m, 1187m, 1166m, 1132s, 1103m, 1070m, 1036s, 1018s, 1003sh, 948s, 811m, 788m, 750m cm^{-1}. ^1H NMR (C_6D_6, 298 K): δ = 1.48 (s, 18 H, *t*Bu), 1.95 (s, 8 H) and 1.99(s, 24 H) (TMEN) ppm. ^7Li NMR: δ = 0.37 ppm. ^{13}C NMR: δ = 15.0 (CMe_3), 32.3 (CMe_3), 45.9 and 75.4 (TMEN) ppm. ^{27}Al NMR: δ = 152 ppm ($\Delta\nu_{1/2}$ 1.37 kHz).

With the same experimental procedure, the reaction between **2** (1.65 g, 5.6 mmol) and TMEN (0.85 mL, 5.6 mmol) gave colorless crystals of **6** (1.32 g, 89%), m.p. 140 °C. $C_{14}H_{36}AlLiN_4$ (294.4): calcd. C 63.1, H 13.6, N 10.5; found C 62.5, H 13.0, N, 10.5. IR: $\tilde{\nu}_{max}$ 1740s, 1633s, br (Al−H), 1358s, 1291s, 1250m, 1208w, 1180sh, 1160s, 1130s, 1101m, 1069m, 1035s, 1021s, 1002m, 974s, 811w cm^{-1}. ^1H NMR: δ = 1.44 (s, 18 H, *t*Bu), 1.66 (s, 4 H) and 1.94 (s, 12 H, TMEN) ca. 2.7 (vb s, 2 H, AlH) ppm. ^7Li NMR: δ = 0.26 ppm. ^{13}C NMR: δ = 15.8 and 32.3 (*t*Bu), 45.9 and 56.8 (TMEN) ppm. ^{27}Al NMR: δ = 151 ppm ($\Delta\nu_{1/2}$ 1.57 kHz). Compound **6** was also obtained by sublimation of **5** at 120 °C/0.01 Torr.

Crystal Data for Compound 3: $C_{36}H_{92}Al_2Li_2O_2Si_6$: M = 793.5; T = 173(2) K; orthorhombic, $C222_1$ (no. 20); a = 15.705(4), b = 19.977(6), c = 17.089(5) Å; U = 5361(3) $Å^3$; Z = 4; μ = 0.21 mm^{-1}. Data from 9405 reflections, 4721 unique [R(int) = 0.038], were collected on an Enraf−Nonius CAD4 diffractometer by use of Mo-K_α radiation and full-matrix least-squares refinement was by use of SHELXL-97 programs. All non-H atoms were isotropic, the hydrogen atoms attached to Al were refined freely, and the others were refined in riding mode to give $R1$ = 0.034, $wR2$ = 0.080 [$I > 2\sigma(I)$] and $R1$ = 0.041, $wR2$ = 0.083 (all data). CCDC-208982 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: Fax +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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