# Preparation of New Lithium Organotrihydroaluminates: Crystal Structure of $\{(C_4H_8O)_2Li(\mu\text{-}H)_2AlH[C(SiMe_2Ph)_3]\}_2$

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*Received July 8, 1994*[⊗]

*Summary: Reaction of RLi (R = $(Me_3Si)_3C$ or $(Me_2PhSi)_3C$) with $Li[AlH_4]$ in tetrahydrofuran (THF) gives the new, stable alkyltrihydroaluminates $Li[AlRH_3]\cdot 2THF$, which are dimeric both in the solid state and in solution and are important starting materials for the synthesis of a range of organoaluminum compounds bearing bulky substituents.*

Previous attempts to obtain well-characterized trihydroaluminates, i.e. salts containing the anion $[AlRH_3]^-$, have failed owing to the facile rearrangement described in eq 1 (e.g. R = Me, Et).[1] Only limited evidence, from

$$2[AlRH_3]^- \rightarrow [AlH_4]^- + [AlR_2H_2]^- \qquad (1)$$

aluminum analyses and infrared spectra, has been used to identify $Li[AlEtH_3]$,[2] $Na[AlBu^iH_3]$,[3] and $HMg[AlRH_3]$ (R = Et[4,5] or $Bu^n$ [5]) in the solid state, and no structure of a crystalline compound has been determined. In contrast, alkali metal trihydroborates are well-known[6] and are used as selective reducing agents in organic synthesis[7] and ligand-transfer reagents in transition metal chemistry.[8]

We now describe the first well-defined organotrihydroaluminates, which are stabilized by the attachment of a bulky silyl-substituted alkyl group, R (R = $(Me_3Si)_3C$ or $(Me_2PhSi)_3C$), to the aluminum center.

The reaction of RLi with an excess of $Li[AlH_4]$ in THF at 60 °C, followed by removal of solvent and extraction with toluene, gave $Li[AlRH_3]\cdot 2THF$.[9,10] Crystals of compound **1** (R = $(Me_3Si)_3C$) were unsuitable for X-ray analysis, but those of the $(Me_2PhSi)_3C$ derivative, **2**, obtained from a toluene solution at −30 °C, were found to consist of dimers, as shown in Figure 1. The X-ray data were collected at −100 °C so that loss of THF was inhibited and hydrogen atoms could be located. The structure[11] of **2** is based on an eight-membered ring, in contrast to the analogous boron compound,[12] which has the monomeric structure $(THF)_3Li(\mu\text{-}H)_3BC(SiMe_2Ph)_3$, and to an indium compound,[13] $(Me_3Si)_3CIn(H)(\mu\text{-}H)Li(THF)_2(\mu\text{-}H)In(\mu\text{-}H)(H)C(SiMe_3)_3$, which was obtained by reduction of $Li[(Me_3Si)_3CInCl_3]\cdot 3THF$ with $Li[AlH_4]$ and has a six-membered-ring structure. Each dimer in **2** comprises two $[AlRH_3]^-$ anions and two $[(THF)_2Li]^+$ cations. The steric requirements of the alkyl group

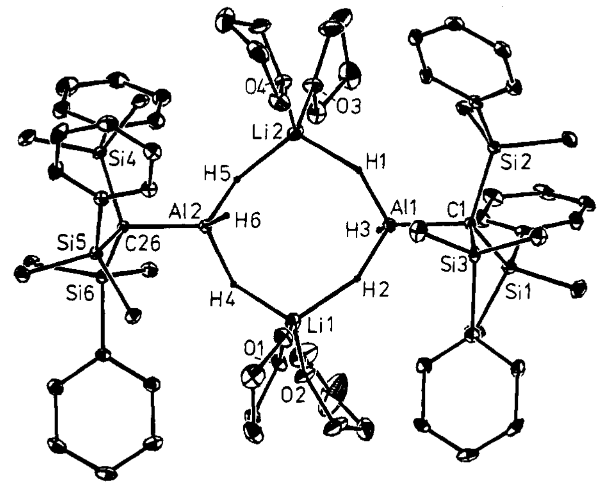

**Figure 1.**

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1994.

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(9) $Li[(Me_3Si)_3CAlH_3]\cdot 2THF$, **1**: A solution of $(Me_3Si)_3CLi\cdot 2THF$ made[19] from $(Me_3Si)_3CH$ (3 g, 12.9 mmol) in THF (20 $cm^3$) was added to a stirred suspension of $Li[AlH_4]$ (0.6 g, 15.8 mmol) in THF (10 $cm^3$), and the mixture was stirred at 60 °C for 2 h and then allowed to cool to room temperature. The solvent was removed and the residue extracted with toluene (40 $cm^3$) at 60 °C. Filtration through Celite and concentration of the filtrate to *ca.* 10 $cm^3$, followed by storage at −30 °C, gave colorless, air-sensitive crystals of **1**. Yield: 3.4 g, 64.2%. Mp: 207−213 °C. Anal. Found: C, 49.2; H, 9.2; Al, 6.6. Calcd for $C_{36}H_{92}Al_2Li_2O_4Si_6$: C, 52.4; H, 11.2; Al, 6.5. IR: $\nu$(Al−H) ($cm^{-1}$) 1729 s, br. $^1H$ NMR (360 MHz, $C_7D_8$): $\delta$ 0.40 (27H, s, $CH_3$), 1.44 (8H, m, $CH_2$), 3.67 (8H, m, $OCH_2$). $^{13}C$ NMR (62.88 MHz, $C_7D_8$): $\delta$ 5.0 ($CH_3$), 25.5 ($CH_2$), 68.9 ($OCH_2$). $^7Li$ NMR (97.263 MHz, $C_7D_8$, relative to aqueous LiCl): $\delta$ −0.57. $^{29}Si$ NMR (99.36 MHz, $C_7D_8$): $\delta$ −2.2. $^{27}Al$ NMR (65.223 MHz, $C_7D_8$, relative to aqueous $Al(NO_3)_3$): $\delta$ 113.0 ppm.

(10) $Li[(Me_2PhSi)_3CAlH_3]\cdot 2THF$, **2**: A solution of $(Me_2PhSi)_3CLi\cdot THF$ made[20] from $(Me_2PhSi)_3CH$ (3 g, 7.16 mmol) in THF (15$cm^3$) was added to a stirred suspension of $Li[AlH_4]$ (0.38 g, 10 mmol) in THF (10$cm^3$), and the mixture was stirred at 60 °C for 4 h and then allowed to cool to room temperature. The solvent was removed, and the residue was extracted with toluene (40 $cm^3$) at 60 °C. Filtration through Celite and concentration of the filtrate to *ca.* 10 $cm^3$ gave colorless, air-sensitive crystals of **2**. Yield: 2.4 g, 56%. Mp: *ca.* 131 °C. Anal. Found: C, 62.1; H, 8.7; Al, 4.5. Calcd for $C_{66}H_{104}Al_2Li_2O_4Si_6$: C, 66.2; H, 8.7; Al, 4.5. IR: $\nu$(Al−H) ($cm^{-1}$) 1721 br. $^1H$ NMR (360 MHz, $C_7D_8$): $\delta$ 0.65 (18H, s, $CH_3$), 1.42 (8H, m, $CH_2$), 3.68 (8H, m, $OCH_2$), 6.93−7.15, 7.47−7.58 (15H, m, $C_6H_5$). $^{13}C$ NMR (62.88MHz, $C_7D_8$): $\delta$ 4.3 ($CH_3$), 25.5 ($CH_2$), 69.1 ($OCH_2$), 128.6 (*m*), 129.1 (*p*), 137.5 (*o*), 144.5 (*ipso* C). $^7Li$ NMR (97.253 MHz, $C_7D_8$): $\delta$ −0.76. $^{29}Si$ NMR (99.36 MHz, $C_7D_8$): $\delta$ −8.44. $^{27}Al$ NMR (MHz, $C_7D_8$): $\delta$ 115.0 ppm.

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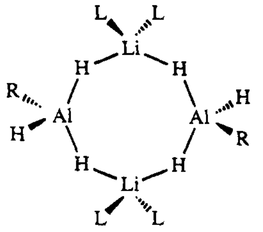
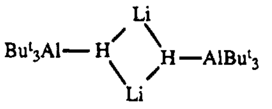


1 R = $(Me_3Si)_3C$, L = THF

2 R = $(Me_2PhSi)_3C$, L = THF



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inhibit the approach of cation and anion and cause the eight-membered ring to buckle, with the two aluminum atoms *ca.* 0.9 Å above and below and the two lithium atoms *ca.* 0.16 Å above the mean ring plane, giving a distorted chair arrangement. The O—Li—H angles involving H(4) (95, 119°) and H(5) (96, 125°) are distorted from the tetrahedral value. The mean Al—H distance, 1.61(2) Å, is shorter than that in the trialkylaluminate, **3** (1.75(3) Å),[14] and the mean Li—H distance, 1.93(4) Å, is similar to that of the longer bond of the asymmetrical $Li_2H_2$ ring (1.92(3) Å) in **3**. The Al—C and Li—O bond lengths are normal. An eight-membered ring was recently shown to be present in the (amido)aluminum compound $[(Et_2O)_2Li(\mu\text{-}H)_2AlHN(SiMe_3)_2]_2$,[15] but the lower steric requirements of the $(Me_3Si)_2N$ group compared with those of the $(Me_2PhSi)_3C$ group in **2** give a planar ring, with shorter Li—H bonds, 1.78(4) Å, and smaller H—Li—H angles, 107(2)° (cf. 117(1)° in **2**). Interestingly, the carbene adduct 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene·$AlH_3$ which can be represented as $R^+{-}AlH_3^-$ is monomeric.[16]

It seems likely that compounds containing the $[AlRH_3]^-$ anion can be isolated only when R is so large that formation of $[AlR_2H_2]^-$ is inhibited. When we treated Bu$^t$Li with 1 molar equiv of $Li[AlH_4]$ in THF, we isolated only $Li[AlBu^t_2H_2]{\cdot}2THF$.[17] Crystals suitable for an X-ray diffraction study have so far not been obtained.

The new organotrihydroaluminates **1** and **2** are highly soluble in diethyl ether, THF, and toluene and sparingly soluble in light petroleum. Cryoscopic molecular weight measurements suggest that the structure of **1** is preserved in benzene (RMM, 825; found 915).

Compounds **1** and **2** are valuable starting materials for the synthesis of a wide range of new compounds of aluminum containing bulky alkyl groups. Previous attempts to make various tris(trimethylsilyl)methylaluminum derivatives directly from $(Me_3Si)_3CLi{\cdot}2THF$ in THF were frustrated by ring opening reactions of THF,[18] but the reactions of **1** in toluene with HCl, HBr, $Br_2$, or $I_2$ have given the new compounds $(Me_3Si)_3CAlX_2{\cdot}THF$ (X = Cl, Br, I, respectively), opening the way to much new aluminum chemistry. We have also found that HF—pyridine reacts with **1** in toluene to give a compound of composition $Li[(Me_3Si)_3CAlF_3]{\cdot}THF$, which contains, as far as we are aware, the first alkyltrifluoroaluminate anion.

**Acknowledgment.** We thank the SERC for financial support.

**Supplementary Material Available:** Tables listing crystal structure details, complete fractional atomic coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and least squares planes and ORTEP figures (18 pages). Ordering information is given on any current masthead page.

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(11) Crystal data for **2**: $C_{66}H_{104}Al_2Li_2O_4Si_6$, $M = 1197.9$, monoclinic, $a = 22.625(8)$ Å, $b = 12.206(3)$ Å, $c = 27.217(5)$ Å, $\beta = 111.30(2)°$, $V = 7003.0$ Å$^3$, space group $P2_1/n$, Mo K$\alpha$ radiation, $\lambda = 0.710\ 69$ Å, $Z = 4$, $D_c = 1.14$ g cm$^{-3}$, $F(000) = 2592$, crystal dimensions 0.5 × 0.4 × 0.4 mm, $\mu = 1.8$ cm$^{-1}$, CAD4 diffractometer, $\theta-2\theta$ mode, $T = 173$ K, $2 < \theta < 25°$, 12931 unique reflections measured and 8087 with $|F^2| > 2\sigma(F^2)$ used, no decay or absorption correction. Structure analysis was by direct methods using SHELXS-86. Full-matrix least-squares refinement proceeded using Enraf-Nonius MOLEN programs with non-H atoms anisotropic, hydride H atoms refined isotropically, and the rest fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. Final $R = 0.063$ and $R' = 0.067$. $S = 1.7$. The alkyl group on Al(1) is disordered in a way commonly found for $(Me_3Si)_3C$ derivatives[21] but not previously observed for a $(Me_2PhSi)_3C$ compound.

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