Preparation and Crystal Structures of Aluminium Hydride Adducts with Tetrahydrofuran $[AlH_3{\cdot}OC_4H_8]_2$ and $AlH_3{\cdot}2OC_4H_8$

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Crystalline adducts $[AlH_3{\cdot}OC_4H_8]_2$ and $AlH_3{\cdot}2OC_4H_8$ [OC_4H_8 = tetrahydrofuran (THF)] can be obtained from solutions of alane in THF and from the reaction of $[Me_3N{\cdot}AlH_3]_2$ with THF.

Amine adducts of alane, $AlH_3{\cdot}L$ are well known[1] and several have been structurally characterised including those with L = Me_3N (monomeric in gas phase,[2] dimeric in solid state[3]), Bu_3N[4] (monomeric), TMEDA,†[5] (polymeric), $Me_2(PhCH_2)N$,[3] $\overline{\mathrm{NMeCH_2CH_2CH{=}CHCH_2}}$,[3] Me_2PhN[6] (dimeric), TMTZ,†[7] (monomeric or polymeric depending on stoichiometry) and TMPDA,†[7] (polymeric). The compound $AlH_3{\cdot}2Me_3N$ has long been known to be monomeric.[8] Several phosphine adducts have also been reported recently.[9] In contrast, ether adducts of alane, containing Et_2O, THF or dioxane, although known for many years, have not been structurally characterized. A material of composition $AlH_3{\cdot}$ *ca.* $0.3Et_2O$ can be isolated from diethyl ether solutions of alane.[1,10] The species $AlH_3{\cdot}THF$[11–16] and $AlH_3{\cdot}2THF$,[12–16] with four- and five-coordinate aluminium, respectively, have been postulated to explain the IR and NMR spectroscopic results, but structural evidence is incomplete. Molecular weight measurements[17] gave a degree of association of 1.55 for $AlH_3{\cdot}THF$ in benzene and it has also been reported to be polymeric in the solid state.[14] Dioxane[1,18] and dibutyl ether[19] also form both 1 : 1 and 1 : 2 adducts.

We now report the preparation and crystal structures‡ of the mono-, **1**, and bis-THF, **2**, adducts of alane, which are very

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† *Abbreviations*: THF = tetrahydrofuran; TMEDA = *N,N,N′,N′*-tetramethylethylenediamine; TMTZ = 1,3,5-trimethylhexahydro-1,3,5-triazine; TMPDA = *N,N,N′,N′*-tetramethylpropylenediamine.

‡ *Crystal Data* for **1**: $C_8H_{22}Al_2O_2$, $M = 204.2$, triclinic, space group $P\bar{1}$, $a = 6.509(5)$, $b = 6.676(7)$, $c = 8.337(11)$ Å, $\alpha = 68.63(10)$, $\beta = 73.52(9)$, $\gamma = 74.56(8)°$, $U = 318.1$ Å^3, Mo-Kα radiation, $\lambda = 0.71069$ Å, $Z = 1$, $D_c = 1.07\ \mathrm{g\,cm^{-3}}$, $F(000) = 112$. μ(Mo-Kα) $1.9\ \mathrm{cm^{-1}}$. $T = 173$ K, 1535 reflections measured and 1251 with $|F^2| > 2\sigma(F^2)$ used, no absorption or decay correction. Structure analysis by direct methods using SHELXS-86. Full-matrix least-squares refinement using Enraf-Nonius MOLEN programs with non-H atoms anisotropic. Al(H) atoms refined isotropically; THF(H) fixed, calculated with $U_{iso} = 1.3U_{eq}$ for parent atom. Final R 0.066 and R' 0.085.

Crystal Data for **2**: $C_8H_{19}AlO_2$, $M = 174.2$, monoclinic, space group $P2_1/m$, $a = 7.265(5)$, $b = 10.317(9)$, $c = 7.422(10)$ Å, $\beta = 111.67(8)°$, $U = 517.0$ Å^3, Mo-Kα radiation, $\lambda = 0.71069$ Å, $Z = 2$, $D_c = 1.12\ \mathrm{g\,cm^{-3}}$, $F(000) = 192$. μ(Mo-Kα), $1.5\ \mathrm{cm^{-1}}$, $T = 173$ K. Data collection as for **1**. 967 Unique reflections measured and 693 with $|F^2| > 2\sigma(F^2)$ used. Structure analysis and refinements as for **1**. H atoms from difference map, refined isotropically. $R = 0.045$, $R' = 0.055$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

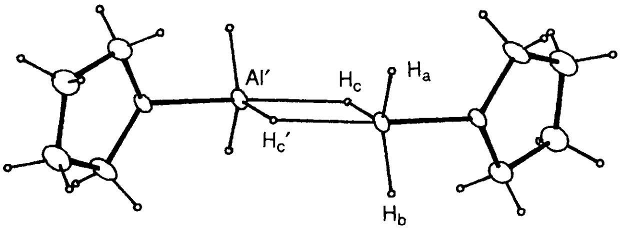

Fig. 1 The molecular structure of **1**. Selected bond lengths (Å) and angles (°): Al–O 1.967(2), Al–H_a 1.39(4), Al–H_b 1.38(4), Al–H_c 1.54(3), Al–H_c' 2.05(3); O–Al–H_a 99(1), O–Al–H_b 90(1), O–Al–H_c 89(1), O–Al–H_c' 167.5(9), H_a–Al–H_b 119(2), H_a–Al–H_c 121(2), H_a–Al–H_c' 87(2), H_b–Al–H_c 119(2), H_b–Al–H_c' 96(2), H_c–Al–H_c' 79(1), Al–H_c–Al′ 101(2).

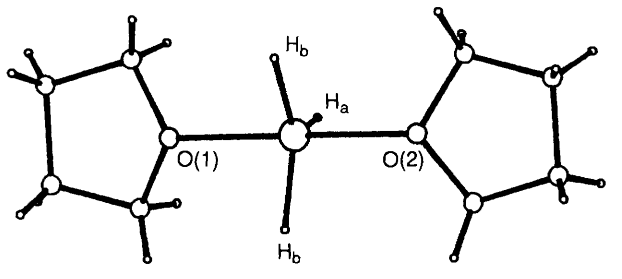

Fig. 2 The molecular structure of **2**. Selected bond lengths (Å) and angles (°): Al–O(1) 2.070(3), Al–O(2) 2.063(3), Al–H_a 1.50(3), Al–H_b 1.51(2); O(1)–Al–O(2) 176.09(8), O(1)–Al–H_a 89(2), O(1)–Al–H_b 88(1), O(2)–Al–H_a 95(2), O(2)–Al–H_b 90(1), H_a–Al–H_b 117.8(8), H_b–Al–H_b' 124(1).

similar to the mono- and bis-trimethylamine adducts.[2,3,8] Compound **1** is dimeric as shown in Fig. 1. The coordination around each aluminium is trigonal bipyramidal with hydrogen atoms equatorial [Σ(H–Al–H) = 359°] and an oxygen atom and a more distant bridging hydrogen atom in apical positions. The Al–H(terminal) distances are slightly shorter than those to the nearest bridging hydrogen atom. Although THF adducts of aluminium species have not been structurally characterized, the structures of a series of adducts[20] of AlR_3 (R = Me, Et, or CH_2Ph) with oxygen donors show Al–O distances in the range 1.901(4)–2.03(4) Å. Other distances and angles in **1** are similar to those reported for $[L{\cdot}AlH_3]_2$ [L = $Me_2(PhCH_2)N$, $\overline{NMeCH_2CH_2CH{=}CHC}H_2$].[3] The Al···Al distance is 2.79 Å.

The aluminium atom in **2**, the structure of which is shown in Fig. 2, again lies at the centre of a trigonal bipyramid [Σ(H–Al–H) = 359.6°], similar to that in $L_2{\cdot}AlH_3$ (L = Me_3N,[8] or TMTZ[7]). The Al–O distance [mean 2.066(3) Å] is longer than that in **1** [1.967(2) Å], reflecting the lower electron density at aluminium in compound **1**. This effect has been observed previously in amine adducts.[7]

Both **1** and **2** can be prepared by the reaction of either (*i*) $[Me_3N{\cdot}AlH_3]_2$ with THF or (*ii*) $LiAlH_4$ with concentrated sulfuric acid in THF,[21] and are crystallised from light petroleum–THF. Compound **1**§ is obtained when light petroleum is in excess and **2**,¶ which is in equilibrium with **1**, is obtained when THF is in excess. Solutions from reaction (*ii*) have been used to effect a wide range of organic transformations.[21,22]

Compound **1** loses THF under dynamic vacuum at 60 °C to give alane. Compound **2** is converted into **1** when it is left to stand under argon, and is only stable, both in the solid state and in solution, in the presence of an excess of THF.

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§ *Compound* **1**: The solvent was removed from a solution of alane in THF (10 cm^3), prepared from $LiAlH_4$ (1.30 g, 34.2 mmol) and conc. H_2SO_4 (98%, 0.9 cm^3, 16.5 mmol) in THF (60 cm^3), and a mixture of light petroleum (b.p. 60–80 °C) (20 cm^3) and THF (10 cm^3) added to the residue to give a cloudy solution. This was filtered and the filtrate kept at −30 °C overnight to give colourless, air-sensitive crystals of **1** (0.46 g, 82%). Loss of solvent prevented satisfactory C and H analyses. ν_{max}/cm^{-1} 1807br (AlH); δ_H (C_6D_6) 1.15 (4H, m, CH_2), 3.60 (4H, m, OCH_2), 4.17 (3H, s, Al*H*); δ_C (C_6D_6) 25.2 (s, CH_2) δ 70.1 (s, OCH_2); δ_{Al} (C_6D_6) 109.3 (br).

¶ *Compound* **2**: Light petroleum (b.p. 60–80 °C) (1 cm^3) was added to a solution of alane in THF (10 cm^3), prepared as described above, and the mixture stored at −30 °C overnight to give colourless, air-sensitive crystals of **2** (0.19 g, 40%). ν_{max}/cm^{-1} 1727w, br (AlH); δ_H (C_6D_6) 1.15 (8H, m, CH_2), 3.54 (8H, m, OCH_2), 4.32 (3H, s, Al*H*); δ_C (C_6D_6) 25.4 (s, CH_2), 69.2 (s, OCH_2); δ_{Al} (C_6D_6) 104.6 (br).