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Synthesis and Characterization of $[Mes^*AlH_2]_2$ ($Mes^* = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$): A Base-Free Arylalane

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Neutral aluminum hydride compounds that are free of donor ligands (i.e. no base complexation) are rare.[1,2] The few structurally characterized examples include the hydrogen bridged species $[(t\text{-}Bu)_2AlH]_3$,[3] $[(TMP)_2AlH]_2$[4] (TMP = 2,2,6,6-tetramethylpiperidinyl), $(Me_2AlH)_2$[5] and the amide bridged compound $(Me_2NAlH_2)_3$.[6] It is clear that even when two crowding substituents are present, as in $[(t\text{-}Bu)_2AlH]_3$[3] and $[(TMP)_2AlH]_2$[4], association through hydrogen bridging is observed. Nonetheless it has been shown that when the vapor of $[(TMP)_2AlH]_2$ is condensed with argon to form a matrix the IR spectrum shows a single sharp band at 1858 cm^{-1}, which corresponds to a terminal Al−H stretch for monomeric $(TMP)_2AlH$.[4] In addition to these data, recent reports have shown that the extremely bulky Mes*[7-10] ($Mes^* = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$) and Trip[7] ($Trip = 2,4,6\text{-}(i\text{-}Pr)_3C_6H_2$) groups can prevent association in mono- or diarylhalide derivatives such as Mes^*MX_2 or Mes^*_2MX (M = Al, Ga or In; X = Cl or Br) or complex formation when donor molecules such as Et_2O or THF are present. This leads to the expectation that other derivatives such as amides, phosphides, thiolates or hydrides, which are normally associated[1], might also be found to have monomeric structures. Some recent reports dealing with aluminum and gallium amide derivatives,[11] aluminum phosphides[12] and the monomeric gallium hydrides[13] Mes^*GaH_2 and $Mes^*(3,5\text{-}(t\text{-}Bu)_2C_6H_3CMe_2CH_2)GaH$ have demonstrated that this view is well-founded. The appearance of the latter publication prompts this group to describe some of its recent work on aluminum compounds that has resulted in the synthesis and characterization of the unique species $[Mes^*AlH_2]_2$ (**1**) which is dimeric in the solid and the solution phases.

The compound (**1**) was synthesized in *ca.* 70% yield as in eq 1 by the reaction of $[Mes^*AlH_3Li(THF)_2]_2$[14] with 2 equiv

$$[Mes^*AlH_3Li(THF)_2]_2 + 2MeI \xrightarrow[25\ °C]{PhMe} \underset{\mathbf{1}}{[Mes^*AlH_2]_2} + 2LiI + 2CH_4 + 4THF \quad (1)$$

of MeI.[15] An X-ray diffraction study[16] of **1** indicated a dimeric

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(15) The synthesis of $[Mes^*AlH_2]_2$ was carried out under anaerobic and anhydrous conditions. (**1**) A 0.15 mL sample (0.35 g, 2.5 mmol, 40% excess) of MeI was added via syringe to a stirred solution of 0.75 g (0.88 mmol) of $[Mes^*AlH_3Li(THF)_2]_2$[14] in toluene (40 mL) with cooling in a dry-ice bath. As no reaction was observed to occur at this temperature, the solution was slowly warmed to room temperature, during which a smooth gas evolution (CH_4) occurred. After stirring for ca. 14 h at room temperature, all volatile materials were removed from the slightly cloudy solution and the remaining colorless solid was extracted with 80 mL of *n*-hexane. After filtration, concentration to 50 mL and cooling in a −20 °C freezer for 20 h, 0.34 g of large (ca. 2 mm × 2 mm) colorless plates of **1** were isolated (71% yield). ^1H NMR (C_6D_6), 80 °C: 7.42 (s, *m*-H, 2H), 4.78 (s, br, Al−H, 2H), 1.48 (s, *o*-CH_3, 18H), 1.33 ppm (s, *p*-CH_3, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6), 80 °C: 159.2 (*o*-C), 150.9 (*p*-C), 131.2 (br, *i*-C), 120.7 (*m*-C), 38.6 (*o*-*C*(CH_3)$_3$), 34.9 (*p*-*C*(CH_3)$_3$), 32.6 (*o*-CH_3), 31.5 ppm (*p*-CH_3). ^{27}Al NMR (C_7D_8), 90 °C: 122 ppm ($\Delta\nu_{1/2} = 7.2$ kHz). Mp: turns opaque at ca. 130 °C, melts with gas evolution at 173−176 °C and turns gray (dec). IR (Nujol): ν_{Al-H} 1888 (st, br, $\Delta\nu_{1/2} \approx 60\ cm^{-1}$), 1345−1390 cm^{-1} (st, very broad, partially obscured by δ_{CH_3} of **1** and Nujol).

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structure with a crystallographically required inversion center as shown in Figure 1. The terminal Al−C bond has a normal length of 1.966(3) Å.[1,17] The bridging and terminal Al−H bonds have the lengths 1.687(35), 1.702(36), and 1.498(37) Å and the Al--Al separation is 2.652(2) Å. The bridging distances are essentially the same as those observed in [(TMP)$_2$AlH][4] and [Me$_2$AlH]$_2$[5] although there is an extremely wide H(1)−Al(1)−C(1) angle of 135.5(1.3)° in **1** which is suggestive of some strain in the molecule. A feature of the structure is the bending (by 21.3°) of the Al(1)−C(1) bond from the line of the C(1)- -C(4) vector and the parallel, intra- and intermolecular, orientation of the aromatic ring planes. An IR spectrum (Nujol mull) indicated strong Al−H bands at 1888 and 1345−1390 cm^{-1}. The ^{1}H NMR spectrum in benzene-d_6 or toluene-d_8 at room temperature shows one broad Al−H resonance at δ 4.64 which has an intensity corresponding to two aluminum hydrogens per Mes* group. Heating the solution to *ca.* 80 °C results in a sharpening of all resonances and a small shift of the Al−H resonance to δ 4.79. Cooling the solution to −60 °C results in a broadening of the Al−H and ortho H resonances. The ^{27}Al NMR spectrum at 90 °C displays a broad peak ($\Delta\nu_{1/2}$ = 7.2 kHz) at 122 ppm which is indicative of a 4-coordinate organoaluminum compound.[18]

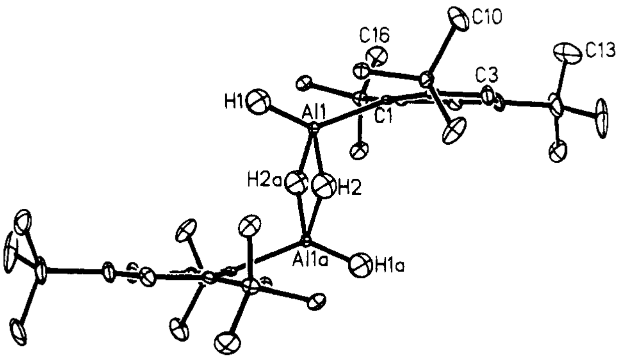

Figure 1. Computer generated drawing of **1**. Hydrogen atoms not attached to aluminum are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−C(1) = 1.966(3), Al(1)−H(1) = 1.498(37), Al(1)−H(2) = 1.687(35), Al(1−H(2a) = 1.702(36), H(1)−Al(1)−C(1) = 135.5(1.3), H(2)−Al(1)−H(2a) = 77.0(2.0), Al(1)−H(2)−Al(1a) = 103.0(2.0). The Al- -Al separation is 2.652(2) Å.

The synthetic route to **1** differs from the preparation of Mes*GaH$_2$ (from LiGaH$_4$ and Mes*GaCl$_2$)[13] or Mes*$_2$GaH (alkene elimination from Mes*$_2$GaCl and t-BuLi)[14] and represents a previously unreported route to neutral molecular aluminum hydrides. The dimeric structure is not known in the solid state for any other uncomplexed aluminum hydride except [(TMP)$_2$AlH]$_2$.[4] It may be compared to the monomeric structure of the gallium analogue Mes*GaH$_2$ (**2**).[13] The difference between the solid state structure of **1** and **2** is undoubtedly a result of the lower tendency of many gallium compounds to associate (cf. dimeric Al$_2$Me$_6$ and monomeric GaMe$_3$) owing to the smaller size and lower electropositive character of gallium.[19] It is notable that **1** does not form a strong THF adduct even though the synthesis was carried out in the presence of THF. The unique properties of both **1** and **2** are directly attributable to the steric characteristics of the Mes* substituents. The chemistry of **1** is currently under intensive investigation.

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Supplementary Material Available: Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (6 pages). Ordering information is given on any current masthead page.

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(16) Crystal data at 130 K with Cu Kα (λ = 1.514 78 Å) a = 10.838(2) Å, b = 11.377(2) Å, c = 29.709(6) Å, orthorhombic, space group *Pbca*, Z = 4, R = 0.058, for 2142 ($I > 2\sigma(I)$) data.

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(18) (a) Akitt, J. W. In *Multinuclear NMR*; Mason, J., Ed; Plenum: New York, 1987. (b) Ongoing attempts to confirm the molecular weight of **1** in solution are marred by its reactivity toward many solvents and its relatively low solubility in hydrocarbons. The lack of solubility (probably a result of the efficient parallel packing of the Mes* groups in the solid) also affects low temperature NMR work and the broadening of the resonances observed at low temperatures is, most probably, a result of the precipitation of solid **1**.

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