

Synthesis and Characterization of Sterically Encumbered Derivatives of Aluminum Hydrides and Halides: Assessment of Steric Properties of Bulky Terphenyl Ligands

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The synthesis and characterization of several sterically encumbered monoterphenyl derivatives of aluminum halides and aluminum hydrides are described. These compounds are [2,6-Mes₂C₆H₃AlH₃LiOEt₂]_n (**1**), (Mes = 2,4,6-Me₃C₆H₂–), 2,6-Mes₂C₆H₃AlH₂OEt₂ (**2**), [2,6-Mes₂C₆H₃AlH₂]₂ (**3**), 2,6-Mes₂C₆H₃AlCl₂OEt₂ (**4**), [2,6-Mes₂C₆H₃AlCl₃LiOEt₂]_n (**5**), [2,6-Mes₂C₆H₃AlCl₂]₂ (**6**), TriphAlBr₂OEt₂ (**7**), (Triph = 2,4,6-Ph₃C₆H₂–), [2,6-Trip₂C₆H₃AlH₃LiOEt₂]₂ (**8**) (Trip = 2,4,6-*i*-Pr₃C₆H₂–), 2,6-Trip₂C₆H₃AlH₂OEt₂ (**9**), [2,6-Trip₂C₆H₃AlH₂]₂ (**10**), 2,6-Trip₂C₆H₃AlCl₂OEt₂ (**11**), and the partially hydrolyzed derivative [2,6-Trip₂C₆H₃Al(Cl)_{0.68}(H)_{0.32}(μ-OH)]₂·2C₆H₆ (**12**). The structures of **2**, **3a**, **4**, **6**, **7**, **9a**, **10a**, **10b**, **11**, and **12** were determined by X-ray crystallography. The structures of **3a**, **9a**, **10a**, and **10b**, are related to **3**, **9**, and **10**, respectively, by partial occupation of chloride or hydride by hydroxide. The compounds were also characterized by ¹H, ¹³C, ⁷Li, and ²⁷Al NMR and IR spectroscopy. The major conclusions from the experimental data are that a single ortho terphenyl substituent of the kind reported here are not as effective as the ligand Mes* (Mes* = 2,4,6-*t*-Bu₃C₆H₂–) in preventing further coordination and/or aggregation involving the aluminum centers. In effect, one terphenyl ligand is not as successful as a Mes* substituent in masking the metal through agostic and/or steric effects.

Introduction

There is growing interest in the chemistry of the heavier main group 13 hydrides.^{1,2} For the neutral hydrido derivatives of these elements, the two major types of compound are their Lewis base adducts³ and the uncomplexed hydrides themselves. In the case of the latter only two binary compounds, [AlH₃]_n⁴ and [GaH₃]_n⁵ have been well-characterized, whereas the structures of a number of other derivatives are known in which either one or two hydrogens have been replaced by organic or related substituents.⁶ These compounds, like the binary derivatives, are characterized by strong hydride bridging unless other strongly bridging substituents such as –NR₂ or –OR are also present.^{6e,f} A recent focus of research in this area, however, has involved the use of very crowding organic groups to reduce the degree of aggregation in these compounds. The Mes* (Mes* = 2,4,6-*t*-Bu₃C₆H₂–) substituent has featured prominently in these investigations, and the synthesis and characterization of several new compounds such as [H₂MMes*]_n (M = Al,⁷ n = 2; M = Ga,⁸ n = 1) or HMMes*₂ (M = Al⁹ or Ga¹⁰), which have unusually low degrees of aggregation, have been reported.

The aluminum derivative [H₂AlMes*]₂ has already been shown to be extremely useful for the synthesis of novel unsaturated inorganic ring systems^{11,12} as well as providing a superior route to pure aluminum halide derivatives of the Mes* ligand.¹³ These results have suggested that other bulky aryls based upon the *o*-terphenyl configuration would also prove effective in the stabilization of low aggregation species. Prior work has shown that in Fe(SC₆H₃-2,6-Mes₂)₂¹⁴ (Mes = 2,4,6-Me₃C₆H₂–) the bulky *o*-dimesitylphenyl substituent produces a monomeric complex whereas the corresponding –SMes* derivative {Fe(SMes*)₂}₂ is a dimer.¹⁵ Similarly, ClGaMes*₂¹⁶ has a C–Ga–C angle of 135.6(2)° whereas in ClGa(C₆H₃-2,6-Mes₂)₂¹⁷ the corresponding angle is 153.3(5)°. These data tend to indicate that the –C₆H₃-2,6-Mes₂ ligand is more sterically demanding than the Mes* group. In this paper, the synthesis and characterization of several aluminum hydride and halide derivatives of the 2,6-Mes₂C₆H₃– and 2,6-Trip₂C₆H₃– (Trip = 2,4,6-*i*-Pr₃C₆H₂–) ligands and related species are reported. The results suggest that, when just one *o*-terphenyl ligand is attached to the aluminum center, the ligand is, in effect, not as sterically crowding as a Mes* substituent owing to the two dimensional configuration of the *o*-aryl substituents and to the presence of close metal···H–C interactions¹⁸ in –Mes* com-

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plexes which more effectively block the vacant coordination site at aluminum.

Experimental Section

General Procedures. All reactions were performed under N₂ by using either modified Schlenk techniques or a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled from sodium-potassium alloys and degassed twice before use. 2,6-Mes₂C₆H₃Li,¹⁹ 2,6-Trip₂C₆H₃Li,²⁰ [2,6-Mes₂C₆H₃Li]₂,²¹ 2,6-Trip₂C₆H₃LiOEt₂,²⁰ AlH₃NMe₃,²² [TriphLiOEt₂]₂,²³ and TriphLi(OEt₂)₂²⁴ (Triph = 2,4,6-Ph₃C₆H₂-) were prepared as previously described. Aluminum halides were freshly sublimed under reduced pressure. LiAlH₄ was purified by crystallization from Et₂O. Infrared spectra were recorded in the range 4000–200 cm⁻¹ as a Nujol mull between CsI plates using a Perkin-Elmer PE-1430 spectrometer. NMR spectra were recorded on a General Electric QE-300 spectrometer.

Preparations. [2,6-Mes₂C₆H₃AlH₃LiOEt₂]_n (1). A solution of [2,6-Mes₂C₆H₃Li]₂ (2.11 g, 3.3 mmol) in Et₂O (50 mL) was added to a slurry of AlH₃NMe₃ (0.58 g, 6.6 mmol) in Et₂O (30 mL) at -78 °C. The mixture was warmed slowly to room temperature and was stirred for an additional 14 h. All volatile compounds were removed under reduced pressure from the resultant pale yellow solution to give a pale yellow solid residue. It appears to be essential to remove completely the donor NMe₃ by prolonged pumping (ca. 2 h at room temperature); otherwise, the isolated yield is dramatically decreased to <50%. The residue was dissolved in Et₂O/hexane (50/20 mL), and the solution filtered. The filtrate was concentrated to ca. 50 mL, and cooling to -20 °C for 5 days yielded 2.31 g of the product as colorless long needles (>5 mm). Yield: 82% (based on [2,6-Mes₂C₆H₃Li]₂). The compound **1** loses Et₂O of solvation when isolated. Mp: softens at 235 °C; melts with slow gas evolution at 260–280 °C. NMR (C₆D₆; ca. 1.5 equiv of THF was added to dissolve the otherwise insoluble sample): [2,6-Mes₂C₆H₃AlH₃Li(OEt₂)_{0.6}]_n·1.5THF. ¹H NMR (t, *p*-H, 1H), ³J_{HH} = 7.2 Hz, 7.08 (d, *m*-H(Ph), 2H), 6.88 (s, *m*-H(Mes), 4H), 3.40 (m, OCH₂(THF), 11.5H), 3.25 (q, OCH₂(Et₂O), 2.5H), ³J_{HH} = 7.5 Hz, 2.30 (s, *o*-Me, 12H), 2.25 (s, *p*-Me, 6H), 1.36 (m, CH₂(THF), 11.5H), 1.09 (t, CH₂(Et₂O), 3.75H). ¹³C {¹H} NMR: 151.3 (*o*-C(Ph)), 144.9 (*i*-C(Mes)), 136.6 (*o*-C(Mes)), 134.5 (*p*-C(Mes)), 127.9 (*m*-C(Mes)), 127.5 (*p*-C(Ph)), 125.9 (*m*-C(Ph)), 68.2 (OCH₂(THF)), 65.8 (OCH₂(Et₂O)), 25.4 (CH₂(THF)), 21.6 (*o*-CH₃), 21.3 (*p*-CH₃), 15.5 (CH₃(Et₂O)). ⁷Li NMR: -1.33 (s). IR: ν_{Al-H} 1815 cm⁻¹ (st, broad), 1725 cm⁻¹ (vst, broad).

2,6-Mes₂C₆H₃AlH₂OEt₂ (2). Me₃SiCl (0.90 mL, 0.77 g, 7.1 mmol) was added slowly, via syringe, to a slurry of 2,6-Mes₂C₆H₃AlH₃Li·OEt₂ (**1**) (3.01 g, 7.1 mmol) in Et₂O/hexane (40/20 mL) with cooling in a dry ice/acetone bath. The reaction mixture was warmed to room temperature and stirred overnight (ca. 16 h), and the precipitate (LiCl) was allowed to settle. The colorless, clear supernatant liquid was removed by a double-tipped needle and was concentrated to ca. 30 mL. Cooling in a -20 °C freezer for 3 days gave 1.86 g of **2** as colorless crystals. Concentration of the mother liquor to ca. 2 mL and cooling overnight to -20 °C afforded a further 0.48 g of **2**. Yield: 79%. Mp: turns opaque at 70 °C; desolvation at 105 °C; melts at 219–221 °C. ¹H NMR (ca. 50 mg in 0.4 mL C₆D₆, 20 °C): mixture of ca. 74% **2** and 26% **3** (vide infra). ¹H NMR data for **2**: 7.36 (t, *p*-H(Ph)), ³J_{HH} = 7.5 Hz, 7.03 (d, *m*-H(Ph)), 6.87 (s, *m*-H(Mes)), 3.75 (s, broad, *w*_{1/2} ≈ 60 Hz, Al-H), 3.06 (q, OCH₂), ³J_{HH} = 6.3 Hz, 2.26 (s, *o*-CH₃), 2.21 (s, *p*-CH₃), 0.74 (s, broad, *w*_{1/2} ≈ 30 Hz, CH₃(Et₂O)). ¹³C {¹H} NMR: 150.9 (*o*-C(Ph)), 143.0 (*i*-C(Mes)), 136.4 (*o*-C(Mes)), 135.7 (*p*-C(Mes)), 128.5 (*p*-C(Ph)), 128.3 (*m*-C(Mes)), 126.8 (*m*-C(Ph)), 68.0 (OCH₂), 21.5 (*o*-CH₃), 21.2 (*p*-CH₃), 14.0 (CH₃(Et₂O)). IR: ν_{Al-H}: 1875 cm⁻¹ (st, sharp), 1785 cm⁻¹ (st, broad), relative intensity ca. 1:2.

[2,6-Mes₂C₆H₃AlH₂]₂ (3). Finely ground **2** (0.2 g, 0.48 mmol) was heated to 110–120 °C under reduced pressure for ca. 10 min to give **3** as a colorless solid in essentially quantitative yield. The compound **3** is sparingly soluble in hexane but readily dissolves in benzene or toluene. Crystals suitable for X-ray diffraction were grown in an NMR tube from C₆D₆ solution (ca. 50 mg in 0.4 mL) over 6 days at 6 °C. ¹H NMR (C₆D₆): 7.21 (t, *p*-H(Ph), 2H), ³J_{HH} = 7.2 Hz, 6.89 (d, *m*-H(Ph), 4H), 6.86 (s, *m*-H(Mes), 8H), 3.5 (s, broad, *w*_{1/2} ≈ 30 Hz, Al-H, 2H), 2.28 (s, *p*-CH₃, 12H), 1.99 (s, *o*-CH₃, 24H). ¹³C NMR (C₆D₆): 151.0 (*o*-C(Ph)), 141.3 (*i*-C(Mes)), 136.6 (*p*-C(Mes)), 136.0 (*o*-C(Mes)), 130.2 (*p*-C(Ph)), 128.8 (*m*-C(Mes)), 126.3 (*m*-C(Ph)), 21.3 (*p*-CH₃), 20.9 (*o*-CH₃). IR: ν_{Al-H(term)} = 1872 cm⁻¹ (st).

2,6-Mes₂C₆H₃AlCl₂OEt₂ (4). Me₃SiCl (2.4 mL, 2.10 g, 19.3 mmol, 20% excess) was added via syringe to a slurry of **1** (2.27 g, 5.3 mmol) in Et₂O/hexane (40/40 mL) at -78 °C. (The excess of Me₃SiCl appears to be essential for the completion of the reaction within ca. 20 h. A reaction employing the stoichiometric amount of Me₃SiCl under the same conditions led to a 3:1 mixture of **4** and probably 2,6-Mes₂C₆H₃Al-(H)₂Cl_{2-x}·OEt₂ according to NMR and IR spectroscopy. Subsequent addition of the required amount of Me₃SiCl to this mixture followed by standard workup gave pure **4**.) The mixture was warmed to room temperature and stirred for 16 h. The colorless clear supernatant was decanted from the LiCl, concentrated to ca. 50 mL under reduced pressure, and allowed to stand at room temperature for 2 h. Small amounts of colorless amorphous precipitate were separated from the supernatant liquid, and concentration of the solution to ca. 15 mL resulted in further amounts of precipitate, which was separated from the supernatant liquid by decanting. Subsequent cooling of the clear solution to -20 °C for 4 days gave 1.95 g of **4** as small colorless crystals that were of sufficient quality for X-ray crystallography. Yield: 75%. Mp: 120–122 °C with gas evolution (desolvation). ¹H NMR (C₆D₆): 7.28 (t, *p*-H(Ph), 1H), ³J_{HH} = 7.5 Hz, 6.92 (d, *m*-H(Ph), 2H), 6.86 (s, *m*-H(Mes), 4H), 3.28 (q, OCH₂, 4H), ³J_{HH} = 7.1 Hz, 2.24 (s, *o*-CH₃, 12H), 2.18 (s, *p*-CH₃, 6H), 0.73 (t, CH₃, 6H). ¹³C NMR (C₆D₆): 151.3 (*o*-C(Ph)), 142.3 (*i*-C(Mes)), 136.8 (*o*-C(Mes)), 136.4 (*p*-C(Mes)), 129.7 (*p*-C(Ph)), 128.6 (*m*-C(Mes)), 128.1 (*m*-C(Ph)), 71.1 (OCH₂), 21.8 (*o*-CH₃), 21.2 (*p*-CH₃), 14.3 (CH₃). ²⁷Al NMR: 115 (s, broad, *w*_{1/2} ≈ 5600 Hz at 78.340 MHz).

[2,6-Mes₂C₆H₃AlCl₃LiOEt₂] (5). With stirring, [2,6-Mes₂C₆H₃Li]₂ (1.56 g, 2.4 mmol), dissolved in toluene (30 mL), was slowly added to a solution of AlCl₃ (1.20 g, 5.8 mmol) in toluene (20 mL), which was cooled in a dry ice/acetone bath. After warming to room temperature, the solution was stirred for a further 12 h. All volatile materials were removed under reduced pressure and the resulting white solid was extracted with hexane/diethyl ether (8:1, 75 mL). The pale yellow solution was concentrated to ca. 40 mL and cooled to -20 °C overnight yielding colorless crystals of 2,6-Mes₂C₆H₃AlCl₃LiOEt₂ (0.30 g, 0.6 mmol, 11% based on lithium). Mp: 190 °C dec. ¹H NMR (C₆D₆): 7.08 (t, *J* = 7.8 Hz, 1H, *p*-H), 6.87 (s, 4H, *m*-H, Mes), 6.84 (d, *J* = 8.1 Hz, 2H, *m*-H), 3.41 (q, *J* = 7.2 Hz, 4H, OCH₂CH₃), 2.20 (s, 6H, *p*-Me), 2.06 (s, 12H, *o*-Me), 0.63 (t, *J* = 7.2 Hz, 6H, OCH₂CH₃). ²⁷Al NMR (C₆D₆): 101.8. The lattice parameters of a crystal of **5** (*a* = 8.746-(11) Å, *b* = 13.019(24) Å, *c* = 48.962(46) Å, α = 89.52(12)°, β = 92.15(9)°, γ = 89.98(13)° and V = 5571(13) Å³) further support the formulation of **5** as [2,6-Mes₂C₆H₃AlCl₃LiOEt₂].

[2,6-Mes₂C₆H₃AlCl₂]₂ (6). Finely ground 2,6-Mes₂C₆H₃AlCl₂OEt₂, **4** (0.60 g, 1.2 mmol), was heated to 120–130 °C for 2.5 h to give **6** in nearly quantitative yield. (Care has to be taken not to exceed 140 °C while desolvating **4** to avoid decomposition into AlCl₃ and other unidentified species.) The product **6** is only sparingly soluble in hexane but dissolves readily in benzene and toluene. X-ray quality crystals were grown from a saturated solution in benzene at room temperature overnight. (ca. 0.4 g in 5 mL). Mp: turns opaque at 95 °C; melts at 242–254 °C. ¹H NMR (C₆D₆): 7.19 (t-*p*-H, 2H), ³J_{HH} = 7.5 Hz, 6.83, (d, *m*-H(Ph), 4H), 6.85 (*m*-H(Mes), 8H), 2.34 (s, *p*-CH₃, 12H), 2.08 (s, *o*-CH₃, 24H). ¹³C NMR (C₆D₆): 150.8 (*o*-C(Ph)), 139.8 (*i*-C(Mes)), 137.2 (*p*-C(Mes)), 137.0 (*o*-C(Mes)), 131.2 (*p*-C(Ph)), 128.8 (*m*-C(Mes)), 127.4 (*m*-C(Ph)), 21.5 (*p*-CH₃), 21.2 (*o*-CH₃).

TriphAlBr₂OEt₂ (7). TriphLi(OEt₂)₂ (7.70 g, 16.7 mmol) in Et₂O (100 mL) was added dropwise to a solution of AlBr₃ (4.40 g, 16.5 mmol) in Et₂O (100 mL) at 0 °C. The pale yellow mixture was warmed to room temperature and stirred for 21 h. Solvents were removed under

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reduced pressure, and the remaining colorless solid was extracted with *n*-hexane (200 mL) and then Et₂O (100 mL) for 12 h at room temperature and 5 h at reflux. The resultant, almost clear, ether solution was filtered through Celite while warm and was allowed to stand at room temperature for 15 h during which time some well-formed colorless crystals were observed to grow. Cooling to -20°C for 10 days afforded **7** (3.42 g, 6.04 mmol) as X-ray quality crystals. Yield: 36%. Mp: softens at 140°C ; melts at $167\text{--}168^{\circ}\text{C}$. ¹H NMR: 7.88 (dd, 4H), ³J_{HH} = 7.7 Hz, J_{HH} = 1.3 Hz, 7.70 (s, 2H), 7.55 (dd, 2H), ³J_{HH} = 7.9 Hz, J_{HH} = 1.3 Hz, 7.32 (t, 4H), ³J_{HH} = 7.6 Hz, 7.23 (t, 2H), ³J_{HH} = 7.0 Hz, J_{HH} = 1.3 Hz, 7.17 (tt, 2H), ³J_{HH} = 7.5 Hz, J_{HH} = 1.3 Hz, 3.16 (q, OCH₂, 4H) ³J_{HH} = 6.6 Hz, 0.50 (t, CH₃, 6H), ³J_{HH} = 6.6 Hz.

Attempted Synthesis of TripAlH₂OEt₂. [TripLiOEt₂]₂ (2.65 g 4.65 mmol) was added via a solids-addition funnel in several portions to a slurry of LiAlH₄ (0.38 g, 10.0 mmol) in Et₂O/hexane (40/60 mL) at -50°C . The cloudy reaction mixture was warmed to room temperature and stirred overnight (18 h). The very fine, greyish precipitate was allowed to settle for 3 d. Then the slightly cloudy supernatant liquid was concentrated to ca. 30 mL and cooled to -20°C overnight. Small amounts of a colorless, amorphous solid were separated, and the resulting clear solution was concentrated to ca. 20 mL and cooled to -20°C for 3 d. As no crystals had formed, the solution was further concentrated to ca. 5 mL, whereupon it solidified after a few minutes at room temperature. This was redissolved in Et₂O (10 mL) and cooled to -20°C for 6 d to afford small amounts of an amorphous colorless solid, which was separated. Finally, concentration to ca. 3–4 mL and subsequent cooling to -20°C for 2 days gave 1.30 g of very fine colorless needles. NMR and IR spectroscopic investigations were consistent with the formulation of [TripAlH₃LiOEt₂]_n, which was contaminated with small amounts (<15%) of an unknown Trip-containing species. Yield: $\approx 35\%$. Mp: $250\text{--}255^{\circ}\text{C}$ (melts with gas evolution and turns into a gray solid). ¹H NMR: 7.21 (s *m*-H, 2H), 3.77 (sept, *o*-CH, 2H), ³J_{HH} = 6.9 Hz, 3.55 (s, broad, *w*_{1/2} ≈ 55 Hz, Al-H, ≈ 2 H), 3.22 (q, OCH₂, 4.5H), ³J_{HH} = 7.2 Hz, 2.92 (sept, *p*-CH, 1H), ³J_{HH} = 6.9 Hz, 1.49 (s, *o*-CH₃, 12H), 1.33 (s, *p*-CH₃, 6H), 0.92 (t, CH₃, 6.7H). ¹³C {¹H} NMR: 158.2 (*o*-C), 148.4 (*p*-C), 141.6 (*i*-C, broad), 119.6 (*m*-C), 65.9 (OCH₂), 36.9 (*o*-CH), 35.1 (*p*-CH), 25.5 (*o*-CH₃), 24.5 (*p*-CH₃), 14.5 (CH₃). ⁷Li NMR: 0.27 (s). ²⁷Al NMR: 106 (s, broad, *w*_{1/2} ≈ 5200 Hz at 78.34 MHz). IR: $\nu_{\text{Al-H}} = 1775$ (st, broad).

A solution of [TripAlH₃LiOEt₂]₂ (1.13 g, 3.6 mmol) in Et₂O/hexane (20/30 mL) was reacted with Me₃SiCl (0.46 mL, 3.6 mmol, 0.39 g) at -78°C . The mixture was warmed to room temperature and stirred for 16 h. The colorless solid was separated by decanting and the colorless, clear supernatant was concentrated to ca. 15 mL and cooled to -20°C overnight. As no crystals had formed, the solution was concentrated further to ca. 5 mL and cooled to -20°C for 1 week to give 0.61 g of small colorless crystals and some amorphous solid. NMR spectrum of the mixture, which did not dissolve completely (LiH), showed the presence of [Trip₂AlH]₂ as the main product. Recrystallization from *n*-hexane (10–15 mL, -20°C) for one week gave 0.23 g of pure [Trip₂AlH]₂.

[2,6-Trip₂C₆H₃AlH₃LiOEt₂]₂ (8**).** A solution of 2,6-Trip₂C₆H₃-LiOEt₂ (1.62 g, 2.9 mmol) in Et₂O (25 mL) was added dropwise to a solution of 0.26 g (2.9 mmol) AlH₃NMe₃ (Et₂O, 20 mL) at -78°C . The colorless, clear reaction mixture was warmed to room temperature and stirred for 19 h. Removal of the solvent afforded **8** as a colorless solid in almost quantitative yield. ¹H NMR (C₆D₆): 7.23 (t, *p*-H(Ph), 1H), ³J_{HH} = 7.8 Hz, 7.20 (s, *m*-H, 4H), 7.07 (d, *m*-H(Ph), 2H), 3.11 (m, *o*-CH, OCH₂(Et₂O), 8H), 2.91 (sept, *p*-CH, 2H), ³J_{HH} = 6.9 Hz, 2.49 (s, broad, *w*_{1/2} ≈ 60 Hz, Al-H, ≈ 2 H), 1.36 (d, *o*-CH₃, 12H), ³J_{HH} = 6.6 Hz, 1.29 (d, *p*-CH₃, 12H), 1.14 (d, *o*, 12H), ³J_{HH} = 6.6 Hz, 0.94 (t, CH₃(Et₂O)), ³J_{HH} = 6.9 Hz. ¹³C {¹H} NMR (C₆D₆): 149.2, 148.3, 142.7 (quaternary carbons), 148.0 (*o*-C(Trip)), 127.6 (*m*-C(Ph)), 126.6 (*p*-C(Ph)), 120.7 (*m*-C(Trip)), 65.9 (OCH₂), 34.3 (*p*-CH), 30.9 (*o*-CH), 25.1, 24.1, 23.4 (*o*- and *p*-CH₃), 15.1 (CH₃(Et₂O)). ⁷Li NMR (C₆D₆): -2.9 (s). IR: $\nu_{\text{Al-H}} = 1800$ cm⁻¹ (st), 1650 cm⁻¹ (st, broad).

2,6-Trip₂C₆H₃AlH₂OEt₂ (9**).** A slurry of 2,6-Trip₂C₆H₃AlH₃LiOEt₂, **8**, (2.8 mmol) in Et₂O/hexane (10/40 mL) was treated with Me₃SiCl (0.34 mL, 2.7 mmol, 0.29 g) at -78°C . After ca. 30 min the mixture was allowed to warm to room temperature (ca. 2 h) and stirred for 2 h. The colorless precipitate (LiCl) was separated, and the supernatant

liquid was concentrated to ca. 20 mL and cooled to -20°C overnight. The small amount of microcrystalline solid was redissolved by addition of ca. 30 mL Et₂O. Concentration to ca. 5 mL gave a slightly viscous solution from which colorless crystals began to form (ca. 2 h). Cooling overnight in a -20°C freezer gave 0.95 g of **9** as colorless crystals. Yield: 60%. Mp: becomes opaque at 85°C (with desolvation); does not melt below 300°C . ¹H NMR (C₆D₆) (mixture of **9**, **10**, and Et₂O in solution): 7.19 (s, *m*-H(Trip), **9**), 7.13 (s, *m*-H(Trip), **10**), 6.99 (d, *m*-H(Ph), **10**), ³J_{HH} = 7.2 Hz, 3.75 (s, broad, *w*_{1/2} ≈ 83 Hz, Al-H), 3.20 (sept, *o*-CH, **9**), ³J_{HH} = 6.9 Hz, 2.97 (sept, *p*-CH, **10**), ³J_{HH} = 6.9 Hz, 2.87, 2.84 (sept, *o*-CH, **10**, *p*-CH, **9**), ³J_{HH} = 6.9 Hz, 2.71 (s, broad, *w*_{1/2} ≈ 13 Hz, Al-H), 1.41 (**9**), 1.37 (**10**), 1.26 (**9**), 1.18 (**9**), 1.15 (**10**), 1.05 (**10**) (d, *o*- and *p*-CH₃), 0.68 (s, broad, *w*_{1/2} ≈ 40 Hz, CH₃(Et₂O)). IR: $\nu_{\text{Al-H}} = 1913$ (st), 1798 (sh), 1782 (st). Crystals of composition 2,6-Trip₂C₆H₃Al(H)_{1.76}(Cl)_{0.24}(OEt₂)_{0.58}(THF)_{0.42}, **9a**, were obtained in a first attempt to synthesize **9** without isolating 2,6-Trip₂C₆H₃LiOEt₂ and **8**. The presence of THF is probably due to contamination with THF solutions from adjacent work on the same Schlenk line. The presence of Cl may be explained by the use of an excess of Me₃SiCl.

[2,6-Trip₂C₆H₃AlH₂]₂ (10**).** Crystals of **9** (0.90 g, 1.5 mmol) were heated to 95°C for 30 min under reduced pressure (0.5 mm Hg) to afford **10** as a colorless powder. Impurities (<10%) were removed by recrystallization from benzene (ca. 0.73 g in 40 mL) at $+6^{\circ}\text{C}$ for 2 weeks. Crystals of **10a**, of sufficient quality for X-ray diffraction studies, were obtained from the concentrated mother liquor. Yield: 78%. Mp: melts with gas evolution at $310\text{--}320^{\circ}\text{C}$ and turns gray (decomposes). ¹H NMR (C₆D₆): 7.13 (s, *m*-H(Trip)), 7.08 (t, *p*-H(Ph)), ³J_{HH} = 7.2 Hz, 6.98 (d, *m*-H(Ph)), 3.30 (s, broad, *w*_{1/2} ≈ 66 Hz, Al-H), 2.96 (sept, *p*-CH), ³J_{HH} = 6.9 Hz, 2.84 (sept, *o*-CH), ³J_{HH} = 6.9 Hz, 2.72 (s, *w*_{1/2} ≈ 10 Hz, Al-H), 1.37 (d), 1.14 (d), 1.05 (d) (*o*-*p*-CH₃). ¹³C NMR (C₆D₆): 150.1, 148.3, 141.7, 139.4 (quaternary carbons), 146.5 (*o*-C(Trip)), 121.2 (*m*-C(Trip)), 34.5 (*p*-CH), 30.7 (*o*-CH), 25.8, 24.2, 23.6 (*o*-, *p*-CH₃). ²⁷Al NMR (C₆D₆, 80°C): 142 (s, broad, *w*_{1/2} ≈ 8500 Hz at 78.340 MHz). IR: $\nu_{\text{Al-H}} = 1920$ cm⁻¹ (st.). Crystals of the composition [2,6-Trip₂C₆H₃Al(H)_{0.72}(OH)_{0.28}(μ -H)_{0.48}(μ -OH)_{0.52}]₂C₆H₆, **10b**, were obtained in an attempt to synthesize **10** without isolation of the intermediate compounds **8** and **9**. Repeated crystallizations of the resulting mixture finally yielded a small amount of the partially hydrolyzed **10b** as large (>1 mm) colorless crystals of sufficient quality for an X-ray structure determination.

2,6-Trip₂C₆H₃AlCl₂OEt₂ (11**).** 2,6-Trip₂C₆H₃LiOEt₂ (0.97 g, 1.73 mmol) was dissolved in toluene (30 mL) and cooled in a dry ice/acetone bath. AlCl₃ (0.46 g, 3.46 mmol) was added via a solids-addition funnel. With stirring, the solution was allowed to warm to room temperature and stirred for a further 16 h. All volatile materials were removed under reduced pressure. The resulting yellow oil was extracted into hexane–diethyl ether (10:1, 80 mL) and the solution concentrated to ca. 30 mL. Slow cooling to -20°C overnight yielded colorless crystals of 2,6-Trip₂C₆H₃AlCl₂OEt₂ (0.20 g, 0.3 mmol, 18% based on aluminum). Further concentration of the supernatant yielded additional crystals of 2,6-Trip₂C₆H₃AlCl₂OEt₂ (0.30 g). Mp: $151\text{--}153^{\circ}\text{C}$. ¹H NMR (C₆D₆): 7.21 (m, 7H, ArH), 3.41 (m, 4H, OCH₂CH₃), 3.14 (sept, *J* = 6.9 Hz, 4H, *o*-CH(CH₃)₂), 2.87 (sept, *J* = 6.9 Hz, 2H, *p*-CH(CH₃)₂), 1.45 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.27 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.12 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 0.74 (m, 6H, OCH₂CH₃). ¹³C NMR (C₆D₆): 149.7 (s, ipso-C, Trip), 148.6 (s, *p*-C, Trip), 147.6 (s, *o*-C, Trip), 140.9 (s, *o*-C), 130.2 (d, *m*-C), 127.3 (d, *p*-C), 121.0 (d, *m*-C, Trip), 70.9 (t, OCH₂CH₃), 35.0 (d, *p*-CH(CH₃)₂), 31.2 (d, *o*-CH(CH₃)₂), 26.6 (q, CH(CH₃)₂), 24.6 (q, CH(CH₃)₂), 23.2 (q, CH(CH₃)₂), 13.9 (q, OCH₂CH₃). ²⁷Al NMR (C₆D₆): 101.0 (*w*_{1/2} = 192 Hz). IR (Nujol): ν 1630 (m), 1590 (w), 1410 (mw), 1330 (w), 1260 (s), 1190 (w), 1100 (vs, br), 1015 (vs, br), 880 (ms), 800 (vs), 760 (ms), 535 (s, br), 400 (mw) cm⁻¹.

Crystals of 2,6-Trip₂C₆H₃AlCl₂OEt₂ were contaminated with an AlCl₃·OEt₂ impurity. The sample of 2,6-Trip₂C₆H₃AlCl₂OEt₂ could not be obtained pure, free of AlCl₃OEt₂, even after several recrystallizations.

[2,6-Trip₂C₆H₃Al(Cl)_{0.68}(H)_{0.32}(μ -OH)]₂C₆H₆ (12**).** Me₃SiCl (0.18 mL, 1.4 mmol, 0.15 g) was added to a solution of **10** (0.41 g, 0.7 mmol) in Et₂O/hexane (20/30 mL) at -78°C . The reaction mixture was warmed to room temperature and stirred for additional 16 h. It was concentrated to ca. 5 mL and cooled to -20°C for 3 days to afford

Table 1. Selected Crystallographic Data for **2**, **3a**, **4**, **6**, **7**, **9a**, **10a**, **10b**, **11**, and **12**

	2	3a	4	6	7
formula	C ₂₈ H ₃₇ AlO	C ₄₈ H ₅₄ Al ₂ O _{0.52}	C ₂₈ H ₃₅ AlCl ₂ O	C ₄₈ H ₅₀ Al ₂ Cl ₄	C ₂₈ H ₂₇ AlBr ₂ O
fw	416.56	693.24	485.44	822.64	566.30
color and habit	colorless block	colorless plate	colorless block	colorless block	colorless plate
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> ₂ / <i>c</i>	<i>C</i> ₂ / <i>m</i>	<i>P</i> ₂ / <i>c</i>	<i>P</i> <i>bca</i>	<i>P</i> ₂
<i>a</i> , Å	12.816(4)	10.188(4)	9.196(2)	18.093(4)	10.686(3)
<i>b</i> , Å	14.080(4)	22.629(6)	14.454(3)	20.183(4)	9.351(3)
<i>c</i> , Å	28.004(7)	8.746(2)	19.913(4)	23.995(5)	12.930(3)
α, deg					
β, deg	90.63(2)	99.21(3)	97.89(3)		90.45(2)
γ, deg					
<i>V</i> , Å ³	5053(3)	1990.3(10)	2621.9(9)	8763(3)	1292.0(6)
<i>Z</i>	8	2	4	8	2
cryst dimens, mm	0.80 × 0.80 × 0.60	1.24 × 0.84 × 0.36	0.55 × 0.45 × 0.38	0.30 × 0.25 × 0.20	0.68 × 0.52 × 0.16
<i>d</i> _{calc} , g cm ⁻³	1.095	1.156	1.230	1.247	1.456
<i>μ</i> , mm ⁻¹	0.802	0.899	2.677	3.081	3.189
no. of obsd rflcns	5056 (<i>I</i> > 2σ(<i>I</i>))	1300 (<i>I</i> > 2σ(<i>I</i>))	3234 (<i>I</i> > 2σ(<i>I</i>))	3128 (<i>I</i> > 2σ(<i>I</i>))	2459 (<i>I</i> > 2σ(<i>I</i>))
<i>R</i> , wR2	0.075, 0.184	0.045, 0.120	0.040, 0.101	0.124, 0.292	0.067, 0.164

	9a	10a	10b	11	12
formula	C ₄₀ H _{59.93} AlCl _{0.24} O	C ₉₆ H ₁₂₆ Al ₂ O _{0.52}	C ₈₄ H ₁₁₄ Al ₂ O _{1.62}	C ₄₀ H ₅₉ AlCl ₂ O	C ₈₄ H _{112.64} Al ₂ Cl _{1.36} O ₂
fw	592.38	1341.42	1204.12	653.75	1256.20
color and habit	colorless block	colorless parallelepiped	colorless plate	colorless prism	colorless block
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₁	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ ₁ ₂ ₁	<i>P</i> ₂ / <i>c</i>
<i>a</i> , Å	12.733(9)	13.075(7)	13.849(3)	16.324(3)	13.936(2)
<i>b</i> , Å	17.852(5)	13.337(7)	15.957(5)	18.145(3)	15.850(2)
<i>c</i> , Å	16.913(3)	13.400(6)	17.689(5)	12.968(2)	17.823(3)
α, deg		93.66(4)			
β, deg	105.86(4)	97.58(4)	108.55(2)		108.54(1)
γ, deg		115.41(4)			
<i>V</i> , Å ³	3698(3)	2073(2)	3706(2)	3841.0(11)	3732.5(9)
<i>Z</i>	4	1	2	4	2
cryst dimens, mm	0.60 × 0.60 × 0.50	0.62 × 0.50 × 0.42	0.56 × 0.49 × 0.26	0.30 × 0.10 × 0.08	0.49 × 0.25 × 0.25
<i>d</i> _{calc} , g cm ⁻³	1.064	1.074	1.079	1.131	1.118
<i>μ</i> , mm ⁻¹	0.830	0.642	0.678	1.941	1.130
no. of obsd rflcns	3385 (<i>I</i> > 2σ(<i>I</i>))	4156 (<i>I</i> > 2σ(<i>I</i>))	4328 (<i>I</i> > 2σ(<i>I</i>))	2809 (<i>I</i> > 2σ(<i>I</i>))	3841 (<i>I</i> > 2σ(<i>I</i>))
<i>R</i> , wR2	0.098, 0.224	0.080, 0.206	0.043, 0.103	0.097, 0.220	0.059, 0.132

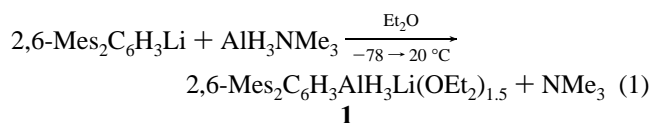
0.24 g of small colorless crystals which were nearly pure unreacted **10**. The crystals and the supernatant liquid were recombined, the solvent was changed to THF/*n*-hexane (30/5 mL), and Me₃SiCl (0.15 mL, 1.2 mmol, 0.13 g) was added at room temperature. After 2 days the solvent was removed from the clear colorless solution to give a colorless solid which was a mixture of several 2,6-Trip₂C₆H₃-containing compounds. Recrystallization from benzene (*ca.* 5–10 mL) at +6 °C for 1 week yielded 0.18 g of well-shaped colorless crystals of **12**. Mp: turns opaque at 110 °C; melts with some gas evolution at 290–305 °C. ¹H NMR (C₆D₆): mixture of compounds: 7.21, 7.19, 7.16, 7.14, 7.08, 7.05, 7.03, 6.98, 6.96 (Ar-H), 3.18 (sept, *p*-CH(CH₃)₂), ³J_{HH} = 6.6 Hz, 2.98 (sept, *o*-CH(CH₃)₂), ³J_{HH} = 6.6 Hz, 2.48, 2.03 (s, OH), 1.45 (d), 1.19 (d), 1.16 (d), 1.03 (d), 1.01 (d) (*o*-, *p*-CH₃). IR: ν_{OH} = 3630 cm⁻¹ (st), ν_{AlH} = 1853⁻¹ (st).

X-ray Crystallographic Studies. The crystals were removed from the Schlenk tube (NMR tube in the case of **3a**) under a stream of N₂ and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream as described in ref 25. All data were collected near 130 K with either a Syntex P₂₁ instrument in the case of **2–4**, **6**, **9a**, **10a**, and **12** or a Siemens P4-RA in the case of **10b** and **11** (using Cu Kα, λ = 1.541 78 Å radiation) or a Siemens R3m/v instrument (using Mo Kα, λ = 0.710 73 Å radiation) in the case of **7**. All diffractometers were equipped with a locally modified Enraf-Nonius universal low-temperature device for low temperature work. Crystallographic programs used for the structure solutions and refinements were those of the SHELXTL-Vers. 5.03 program package installed on IBM compatible 486 or Pentium PC clones. Scattering factors were obtained from ref 26a. An absorption correction was

applied by using the method described in ref 26b (XABS2). Some details of the data collection and refinement are given in Table 1. Selected bond distances and angles are given in Table 2. Further details are provided in the Supporting Information. The crystal structures were solved by direct methods, and they were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically except those involved in a disorder which were maintained isotropic. Hydrogen atoms attached to the carbons were included in the refinement at calculated positions using a riding model included in the SHELXTL program. Hydrogen atoms bound to aluminum or oxygen in the case of **10b** and **12** were located on Fourier difference maps and were allowed to refine freely with fixed isotropic parameters. The structures of **2**, **3a**, and **9a–12** were subject to disorder problems which could be modeled successfully using partial occupancies for the disordered atoms and groups as described in the Supporting Information and as indicated in the discussion of the structures.

Discussion

[2,6-Mes₂C₆H₃AlH₃Li(OEt₂)_{1.5}]_{*n*}, **1**, was easily prepared by the reaction of [2,6-Mes₂C₆H₃Li]₂²¹ with AlH₃NMe₃²² in Et₂O (eq 1) in good yield (up to 82%). The reaction of [2,6-



Mes₂C₆H₃Li]₂ with LiAlH₄ (eq 2) also gives **1**, but in somewhat

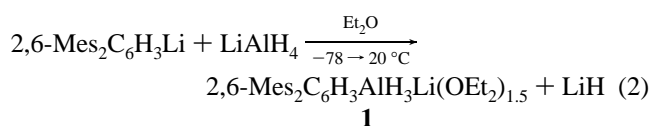
(25) This method is described by: Hope, H. A Practicum in Synthesis and Characterization. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington DC, 1987; Chapter 10.

(26) (a) *International Tables for Crystallography*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1993; Vol. C. (b) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**, **3a**, **4**, **6**, **7**, **9a**, **10a**, **10b**, **11**, and **12**

Compound 2							
Al(1)–H(1)	1.62(4)	Al(2)–H(3)	1.60(5) av ^a	Al(1)–O(1)	1.922(3)	Al(2)–O(2)	1.924(15) av ^a
Al(1)–H(2)	1.45(4)	Al(2)–H(4)	1.51(5) av ^a	Al(1)–C(1)	2.002(3)	Al(2)–C(29)	2.01(2) av ^a
H(1)–Al(1)–H(2)	108(2)	H(1)–Al(1)–O(1)	98.6(14)	H(2)–Al(1)–O(1)	101(2)	C(1)–Al(1)–O(1)	103.60(14)
H(1)–Al(1)–C(1)	120.8(14)	H(2)–Al(1)–C(1)	120(2)				
H(3)–Al(2)–H(4)	106(2) av ^a	H(3)–Al(2)–O(2)	96(2) av ^a	H(4)–Al(2)–O(2)	98(3) av ^a	C(29)–Al(2)–O(2)	106.2(10) av ^a
H(3)–Al(2)–C(29)	121(2) av ^a	H(4)–Al(2)–C(29)	122(3) av ^a				
Compound 3a							
Al(1)–H(1)	1.65(5)	Al(1)–H(2)	1.44(4)	Al(1)–C(1)	1.956(3)	Al(1)–---Al(1A)	2.630(2)
H(1)–Al(1)–H(1A)	74.7	H(1)–Al(1)–H(2)	107.9(14)	H(1)–Al(1)–C(1)	108.9(5)	H(2)–Al(1)–C(1)	133(2)
Compound 4							
Al(1)–Cl(1)	2.1399(10)	Al(1)–Cl(2)	2.1317(10)	Al(1)–C(1)	1.992(3)	Al(1)–O(1)	1.877(2)
Cl(1)–Al(1)–Cl(2)	103.92(4)	Cl(1)–Al(1)–O(1)	103.22(6)	Cl(2)–Al(1)–O(1)	100.25(6)	C(1)–Al(1)–O(1)	106.88(9)
Cl(1)–Al(1)–C(1)	118.60(8)	Cl(2)–Al(1)–C(1)	121.09(8)				
Compound 6							
Al(1)–Cl(1)	2.118(5)	Al(1)–C(1)	1.922(12)	Al(2)–Cl(3)	2.171(5)	Al(2)–C(25)	1.952(12)
Al(1)–Cl(2)	2.191(5)	Al(2)–Cl(2)	2.176(5)	Al(2)–Cl(4)	2.101(5)	Al(1)–---Al(2)	3.084
Al(1)–Cl(3)	2.173(5)						
Cl(1)–Al(1)–Cl(2)	107.1(2)	Cl(2)–Al(1)–Cl(3)	89.6(2)	Cl(2)–Al(2)–Cl(3)	90.0(2)	Cl(3)–Al(2)–Cl(4)	106.5(2)
Cl(1)–Al(1)–Cl(3)	105.2(2)	Cl(2)–Al(1)–C(1)	113.5(3)	Cl(2)–Al(2)–Cl(4)	105.3(2)	Cl(3)–Al(2)–C(25)	113.7(4)
Cl(1)–Al(1)–C(1)	121.4(4)	Cl(3)–Al(1)–C(1)	115.1(3)	Cl(2)–Al(2)–C(25)	114.9(4)	Cl(4)–Al(2)–C(25)	121.5(4)
Compound 7							
Al(1)–Br(1)	2.302(3)	Al(1)–Br(2)	2.297(3)	Al(1)–C(1)	1.983(9)	Al(1)–O(1)	1.868(8)
Br(1)–Al(1)–Br(2)	109.41(12)	Br(1)–Al(1)–O(1)	105.4(2)	Br(2)–Al(1)–O(1)	100.5(3)	C(1)–Al(1)–O(1)	106.7(4)
Br(1)–Al(1)–C(1)	119.2(3)	Br(2)–Al(1)–C(1)	113.5(3)				
Compound 9a							
Al(1)–H(1)	1.66(3)	Al(1)–H(2)	1.72(3)	Al(1)–C(1)	1.983(5)	Al(1)–O(1)	1.903(5)
H(1)–Al(1)–H(2)	115(3)	H(1)–Al(1)–O(1)	101(2)	H(2)–Al(1)–O(1)	88(3)	C(1)–Al(1)–O(1)	112.4(2)
H(1)–Al(1)–C(1)	118(2)	H(2)–Al(1)–C(1)	116(2)				
Compound 10a							
Al(1)–H(1)	1.74(5)	Al(1)–H(2)	1.46(4)	Al(1)–C(1)	1.963(4)	Al(1)–---Al(1A)	2.635(3)
Al(1)–H(1A)	1.74(5)						
H(1)–Al(1)–H(2)	116(3)	H(1)–Al(1)–C(1)	104(3)	H(1A)–Al(1)–H(2)	102(3)	H(2)–Al(1)–C(1)	127(2)
H(1)–Al(1)–H(1A)	81(3)						
Compound 10b ^b							
Al(1)–H(1)	1.62(8)	Al(1)–H(2)	1.36(4)	Al(1)–---Al(1A)	2.7042(13)	Al(1)–O(1A)	1.812(4)
Al(1)–H(1B)	1.57(8)	Al(1)–C(1)	1.966(2)	Al(1)–O(1)	1.783(4)	Al(1)–O(2)	1.975(6)
H(1)–Al(1)–H(1B)	64(3)	H(1B)–Al(1)–H(2)	108(3)	O(1)–Al(1)–O(1A)	82.5(2)	O(1A)–Al(1)–O(2)	115.0(2)
H(1)–Al(1)–H(2)	130(2)	H(1B)–Al(1)–C(1)	122(3)	O(1)–Al(1)–O(2)	108.8(2)	O(1A)–Al(1)–C(1)	110.28(11)
H(1)–Al(1)–C(1)	107(3)	H(2)–Al(1)–C(1)	117(2)	O(1)–Al(1)–C(1)	111.76(13)	O(2)–Al(1)–C(1)	121.7(2)
Compound 11							
Al(1)–Cl(1)	2.141(4)	Al(1)–Cl(2)	2.138(4)	Al(1)–C(1)	1.954(11)	Al(1)–O(1)	1.887(9)
Cl(1)–Al(1)–Cl(2)	105.7(2)	Cl(1)–Al(1)–O(1)	100.3(3)	Cl(2)–Al(1)–O(1)	103.6(3)	C(1)–Al(1)–O(1)	113.8(4)
Cl(1)–Al(1)–C(1)	119.8(4)	Cl(2)–Al(1)–C(1)	112.0(4)				
Compound 12							
Al(1)–O(1)	1.817(2)	Al(1)–Cl(1)	2.103(2)	Al(1)–C(1)	1.949(3)	Al(1)–---Al(1A)	2.788(2)
Al(1)–O(1A)	1.817(2)						
O(1)–Al(1)–O(1A)	79.82(11)	O(1)–Al(1)–Cl(1)	110.90(9)	O(1A)–Al(1)–Cl(1)	107.88(9)	C(1)–Al(1)–Cl(1)	123.23(10)
O(1)–Al(1)–C(1)	113.19(12)	O(1A)–Al(1)–C(1)	113.48(12)				

^a Disordered second independent molecule. ^b Mixture of two compounds, see text.



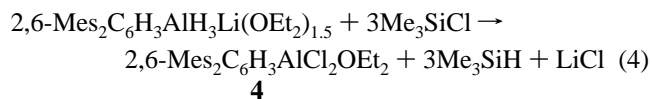
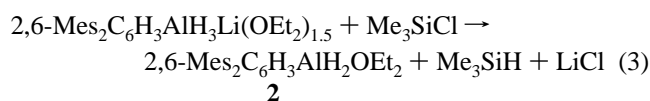
lower yield (ca. 60%), owing to the difficulty in separating the extremely fine precipitate of LiH from the product. Compound **1** crystallizes in the form of large colorless needles (> 5 mm in length) and readily loses Et₂O of solvation when it is isolated. NMR samples usually have a ca. 1:1 ratio of Et₂O: aryl ligand

but an NMR sample prepared from a large crystal showed 1.3 Et₂O per aryl group. Thus, **1** probably is a dimer with an eight-membered Li₂Al₂H₄ ring structure similar to those of the organo derivatives [TriphAlH₃Li(OEt₂)_{1.5}]₂,¹⁰ [Mes*AlH₃Li(THF)₂]₂,¹⁰ or [(PhMe₂Si)₃CAIH₃Li(THF)₂]₂²⁷ or the amide [(Me₃Si)₂NAlH₃LiOEt₂]₂.²⁸ Treatment of **1** with either 1 or 3 equiv of Me₃-

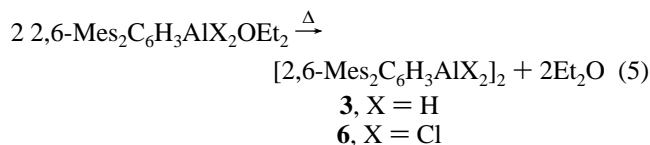
(27) Eaborn, C.; Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D.; Tavakkoli, K. *Organometallics* **1994**, *13*, 4243.

(28) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854.

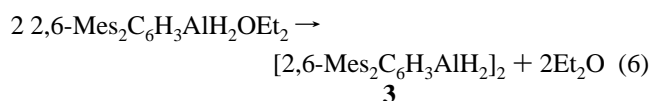
SiCl gives 2,6-Mes₂C₆H₃AlH₂OEt₂, **2**, or 2,6-Mes₂C₆H₃AlCl₂OEt₂, **4**, respectively, in good yields as in eqs 3 and 4.



The effectiveness of this synthetic route, i.e. the treatment of hydridoaluminates with a reactive halide like MeI⁷ or Me₃-SiCl,¹³ has been demonstrated recently in the syntheses of (Mes*AlH₂)₂,⁷ Mes*Al(H)Cl,¹³ and Mes*AlCl₂¹³ from [Mes*-AlH₃Li(THF)₂]₂.¹⁰ Compounds **2** and **4** are easily desolvated by heating to ca. 90–120 °C under reduced pressure.



Interestingly, **2** dissociates Et₂O in a benzene solution at room temperature.



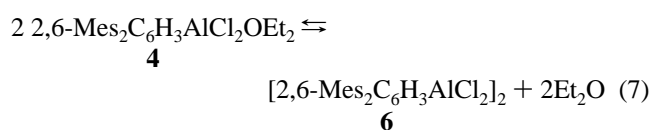
For example, a 0.3 M (0.05 g in 0.4 mL) solution of **2** in C₆D₆ at 20 °C consists of ca. 74% **2** and 26% **3** (viewed as a monomer). Heating to 80 °C causes the signals of **2** to disappear almost completely. The signals for **3** also became broad whereas the Et₂O resonances became sharp and very close to chemical shifts of free Et₂O.

Reducing the concentration of **2** to ca. 0.08 M shifts the equilibrium to 53% (**2**) and 47% (**3**) at 22 °C where the Et₂O resonances are considerably broadened (3.13, OCH₂, w_{1/2} ≈ 40 Hz, 0.86, CH₃, w_{1/2} ≈ 90 Hz). Thus, the desolvation of **2** is easily accomplished by either heating finely ground crystals of **2** to 110–120 °C under reduced pressure for ca. 10 min or by distilling off the solvent of a benzene solution of **2** under normal pressure. Slow cooling of the remaining, highly concentrated solution yields well-formed crystals of **3**.

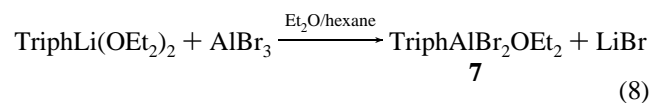
Spectroscopic investigations (IR and NMR) of **3** were consistent with the structure determined in the solid. In the infrared spectrum a sharp and strong peak at 1872 cm⁻¹ for ν_{Al-H(terminal)} was observed. The ν_{Al-H(bridging)} absorptions were in the range 1200–1400 cm⁻¹. Unfortunately, these peaks could not be distinguished clearly due to overlap with δ_{C-H} absorptions of **3** and the Nujol bands. In the ¹H NMR spectrum the Al-H resonance appears as a broad peak at 3.5 ppm (w_{1/2} ≈ 30 Hz) at 20 °C but the integration amounts only to one hydrogen per aluminum. Apparently, the terminal and bridging Al-H resonance appear at different chemical shifts and exchange between them is relatively slow on the NMR time scale at room temperature. The second Al-H resonance could not be located, however. It is probably obscured by the aryl ligand resonances. For VT-NMR (C₇D₈) in the range of -95 → +100 °C, cooling causes the Al-H resonance at 3.5 ppm to sharpen: w_{1/2} = ca. 22 Hz at -60 °C compared to ca. 50 Hz at 20 °C. Heating to ca. 100 °C leads to the virtual disappearance of the Al-H signal. The ligand hydrogen signals remain largely unaffected by the temperature changes. Although the NMR and IR data showed **3** to be pure, the crystal chosen for crystallography contained

ca. 13% OH in place of hydride. The reason for this may be that the X-ray crystals were grown fortuitously in an NMR tube which was capped with a plastic cap for 1 week. This may have permitted contamination by moisture and subsequent hydrolysis of **3**. The 2,6-Mes₂C₆H₃- and even more so the 2,6-Trip₂C₆H₃- derivatives show a tendency to form single crystals of mixed compounds with halides or OH groups, as in the case of **3a** which may be formulated as [2,6-Mes₂C₆H₃-AlH_{0.88}(OH)_{0.12}(μ-H)_{0.86}(μ-OH)_{0.14}]₂ when partially hydrolyzed.

The compound 2,6-Mes₂C₆H₃AlCl₂OEt₂, **4**, was conveniently prepared in ca. 75% yield by the reaction of **1** with 3 equiv of Me₃SiCl in Et₂O/hexane. Attempts to generate **4** by the reaction of [2,6-Mes₂C₆H₃Li]₂²¹ with AlCl₃ in different solvent systems did not lead to **4**. Instead, low yields of a compound were observed, which, on the basis of NMR evidence and its lattice parameters, is probably [2,6-Mes₂C₆H₃AlCl₃LiOEt₂]₂ (**5**). Such a compound has precedent in the case of [TripGaCl₃LiOEt₂]₂.²⁹ These difficulties were similar to those observed in the preparation of Mes*AlCl₂.¹³ While the OEt₂ in **2** is relatively easily removed, the synthesis of [2,6-Mes₂C₆H₃AlCl₂]₂ requires somewhat more rigorous conditions: 2.5 h at 120–130 °C under reduced pressure. The difference is probably due to the larger δ⁺ charge on aluminum in **4** owing to the more electronegative chloride substituents. An equilibrium (eq 7), similar to that in eq 6 can also be seen in solution, albeit here it lies more to the



left, i.e. toward **4**. At room temperature no signal due to **6** was observed (0.035 g in 0.4 mL C₆D₆) while, at 80 °C, the *o*- and *p*-Me groups have the same chemical shift (2.20 ppm) in the ¹H NMR spectrum. Considering the fact that the *o*- and *p*-Me resonances exchange their positions in **4** and **6**, this may be indicative of some exchange according to eq 7 at 80 °C. Heating a solution of **6** in C₆D₆ to 80 °C only slightly affects the shift of the signals in the ¹H NMR spectrum. In contrast to the synthesis of **4** and Mes*AlCl₂THF,¹³ TriphAlBr₂OEt₂ (**7**) can be obtained directly by reaction of TriphLi(OEt₂)₂ with AlBr₃, but only in moderate (36.7%) yields (eq 8). This complex was

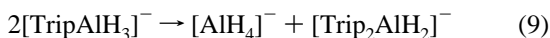


originally synthesized with a view to its subsequent reaction with Li₂PCy (Cy = cyclohexyl) to give the compound (TriphAlPCy)₃ which (it was hoped) should have had an unsaturated ring structure similar to (TriphGaPCy)₃.³⁰ Unfortunately, the product obtained could not be purified sufficiently for structural characterization. The relatively low solubility of **7** in Et₂O/hexane probably facilitates the separation of **7** from AlBr₃·OEt₂ and other side products, which is a major problem in the other cases (vide supra). In addition, some side reactions in the Mes*, 2,6-Mes₂C₆H₃- and 2,6-Trip₂C₆H₃- systems may be due to an attack of the strongly Lewis acidic AlCl₃ or AlBr₃ on the ligand. In effect this retro-Friedel-Crafts reaction does not occur so easily at the Triph ligand because of its smaller size and possibly less electron density in its aromatic system.

(29) Petrie, M. A.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.

(30) Hope, H.; Pestana, D. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 691.

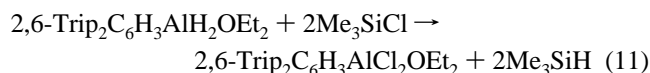
Attempts to use the Trip (Trip = 2,4,6-*i*-Pr₃C₆H₂) ligand according to eqs 1–3 were unsuccessful. The reaction of [TripLiOEt₂]₂²³ with LiAlH₄ gave the expected product [TripAlH₃Li·OEt₂]_n (*n* = probably 2), but only in moderate yield (35%) owing to its high solubility even in pentane and hexane. It was characterized by NMR (¹H, ¹³C, ⁷Li, ²⁷Al) and by IR spectroscopy. Further reaction with Me₃SiCl resulted in the formation of [Trip₂AlH]₂ and not TripAlH₂OEt₂. This result is in agreement with the findings of Eaborn, Smith et al.²⁷ who reported [*t*-Bu₂AlH₂(THF)₂] to be the only isolable product from the reaction of *t*-BuLi with LiAlH₄. Apparently, even the Trip substituent is not sufficiently bulky to suppress the disproportionation shown in eqs 9 or 10



It was thought that the employment of the very bulky ligand 2,6-Trip₂C₆H₃– would allow the isolation of the monomeric alane 2,6-Trip₂C₆H₃AlH₂ since this substituent is capable of stabilizing mononuclear compounds such as 2,6-Trip₂C₆H₃Li·C₆H₆.³¹ The reaction of 2,6-Trip₂C₆H₃LiOEt₂²⁰ with AlH₃NMe₃²² proceeded smoothly and gave [2,6-Trip₂C₆H₃AlH₃LiOEt₂]_n (**8**) (*n* is probably 2) in nearly quantitative yields. Removal of the LiH in **8** by reaction with one equiv of Me₃SiCl gave 2,6-Trip₂C₆H₃AlH₂OEt₂ (**9**) in good yield, which then can be easily desolvated to form the dimeric [2,6-Trip₂C₆H₃AlH₂]₂, **10**, in high yield. As in the case of **2**, a benzene solution of **9** consists of **9**, **10**, and free Et₂O in equilibrium with each other. Increasing the temperature from 25 to 85 °C shifts this equilibrium to the right. For example, a solution of ca. 35 mg of **9** in 0.4 mL C₆D₆ at 24 °C consists of ca. 60% of **9** and 40% of **10** with broad Et₂O signals, while at 85 °C 40% **9**, 60% **10** (based on monomeric **10**), and sharp Et₂O signals are observed. This is in good agreement with the ease of desolvation of **9** in the solid state: 30 min at 95 °C under reduced pressure.

The compound [2,6-Trip₂C₆H₃AlH₂]₂, **10**, is dimeric, with bridging hydrogens, in the solid state. According to ¹H NMR data this structure is retained in solution, even up to 85 °C. The ¹H NMR spectrum of **10** shows bridging and terminal hydrogen resonances as separate signals: a broad (*w*_{1/2} ca. 66 Hz) signal at 3.30 ppm and a somewhat sharper (*w*_{1/2} ca. 10 Hz) signal at 2.72 ppm. However, for [Mes*AlH₂]₂,⁷ only one Al–H resonance for both terminal and bridging hydrogens is observed, and for **3** one of the two hydrogens is obscured by methyl peaks. Warming to 80 °C causes the signals to broaden the 2.72 ppm resonance, indicating some fluxionality of the hydride substituents in exchanging their position, which at room temperature appears to be frozen out.

Preliminary investigation of the reactions of **10** with Me₃SiCl in Et₂O did not give the expected 2,6-Trip₂C₆H₃AlCl₂OEt₂ product. Changing the solvent to THF gave a mixture of compounds from which a small amount of crystals with the composition [2,6-Trip₂C₆H₃Al(Cl)_{0.68}(H)_{0.32}(μ-OH)]₂·2C₆H₆, **12**, were eventually obtained. This result illustrates that it is, in principle, possible to obtain 2,6-Trip₂C₆H₃AlCl₂OEt₂, **11**, according to eq 11 but this reaction appears to be so sluggish that



when using only small amounts of starting material **9** (<1 mmol) adventitious moisture competes successfully in forming OH-

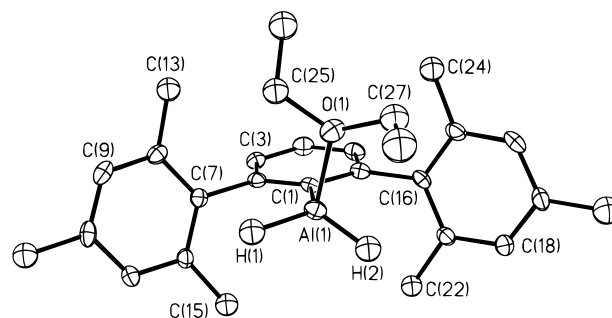


Figure 1. Thermal ellipsoid plot (30%) of one of the two independent molecules of **2**. H atoms except those bound to aluminum are omitted for clarity.

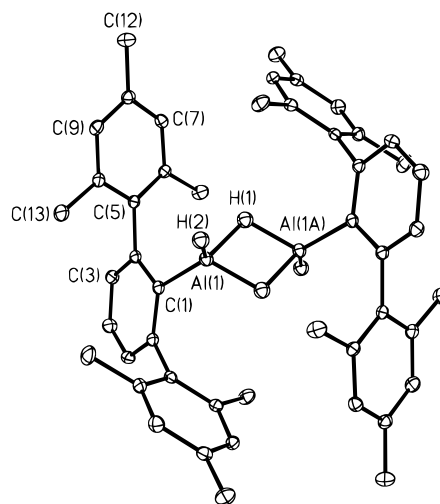


Figure 2. Thermal ellipsoid plot (30%) of **3a**. H atoms except those bound to aluminum and the partially present OH groups are omitted for clarity.

containing species such as **12**. In addition, related experiments with [Mes*AlH₂]₂¹³ indicate that the reaction of the corresponding lithium aluminate with Me₃SiCl is superior to the use of the alane. Interestingly, the direct reaction of 2,6-Trip₂C₆H₃LiOEt₂ with a 2-fold excess of AlCl₃ in toluene followed by crystallization from hexane/Et₂O gave 2,6-Trip₂C₆H₃AlCl₂OEt₂, **11**, in low yield. In addition, samples of **11** always contained some crystallized AlCl₃OEt₂ which could not be removed by recrystallization. In this respect the synthesis of **11** by the reaction of the aryllithium compound 2,6-Trip₂C₆H₃LiOEt₂ with AlCl₃ is similar to the reaction of Mes*Li(THF)₂ with AlX₃ (X = Cl, Br) which gave Mes*AlX₂, but the yields were consistently low and the products were contaminated by AlX₃.

Structures

The structures of **2** and **3** (as the mixture **3a** of formula 2,6-Mes₂C₆H₃Al(H)_{0.88}(OH)_{0.12}(μ-H)_{0.86}(μ-OH)_{0.14}]₂ are illustrated in Figures 1 and 2. The formation of the ether complex **2** does not, at present, have a counterpart in [Mes*AlH₂]₂ chemistry, which does not form a complex with either Et₂O or THF. It is not known, at present, whether this difference in behavior is a result of a difference in strength in the bonding in the bridging Al(μ-H)₂Al units or the blocking of strong Al–O bonding by Al···H–C interactions involving the *o*-*t*-butyl groups in a putative Mes*AlH₂OEt₂ complex. The lack of formation of an Et₂O complex with Mes*AlCl₂¹³ or Mes*AlBr₂,²⁹ which are both monomers (whereas the complex 2,6-Mes₂C₆H₃AlCl₂OEt₂, **4**, is readily formed) seems to support the latter view. Nonetheless, it should be borne in mind that the complex **2** is not a strong one and the ether can be removed under mild conditions

(31) Schiemenz, B.; Power, P. P. *Angew. Chem., Int. Ed. Engl.*, in press.

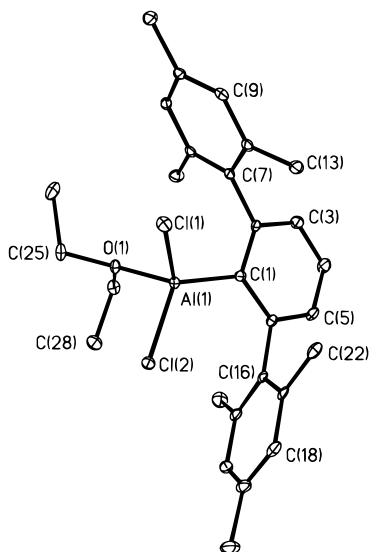


Figure 3. Thermal ellipsoid plot (30%) of **4**. H atoms are omitted for clarity.

to afford **3**. The Al–O distance, 1.922(3) Å, is at the long end of the scale for R_3AlOEt_2 ³² complexes and the Al–C bond length, 2.002(4) Å is slightly longer than the Al–C distance 1.983(5) Å in $Mes^*Al(H)CITHF$ ¹³ or the 1.956(3) Å found in **3**. Thus, the structural data for **2** suggest significant crowding, and are consistent with ease of removal of Et_2O . The Al---H distances involve the usual large standard deviations and no subtle structural inferences can be drawn from them.

Removal of the ether affords the dimer **3**, the structure of which (i.e. **3a**) is contaminated by the presence of –OH impurities (14%) at the bridging and terminal hydride sites. The structure may be compared with that of $[Mes^*AlH_2]_2$.⁷ There can be no doubt that they are very similar with very close bridging and terminal Al–H distances. The Al–C bond length observed in **3**, 1.956(3) Å, is almost identical to the 1.966(3) Å seen in $[Mes^*AlH_2]_2$. The Al---Al separations 2.630(2) Å in **3** and 2.652(2) Å in $[Mes^*AlH_2]_2$ ⁷ are also very similar.

The structure of 2,6- $Mes_2C_6H_3AlCl_2OEt_2$, **4** (Figure 3), also has no counterpart in the case of Mes^*AlCl_2 , which does not form a stable complex with ether.^{13,29} The Al–Cl distances 2.140(1) and 2.132(2) Å are slightly longer than those observed in Mes^*AlCl_2THF ,¹³ which have the values 2.120(1) and 2.129(1) Å. A notable feature of the structure of **4** is the Al–O bond length of 1.877(2) Å, which is shorter than the 1.922(3) Å observed in **2**. The shorter distance in **4** is consistent with the greater difficulty in removing the ether from this molecule.

When ether is removed from **4**, a dimeric, halide-bridged structure is observed for the product **6** (Figure 4). This configuration may be contrasted with the monomeric structure observed for the corresponding Mes^* derivative Mes^*AlCl_2 .¹³ The difference may be attributed to the presence of significant interactions between the aluminum and C–H bonds from the *o-t*-Bu group of the Mes^* ligand and their absence in a putative 2,6- $Mes_2C_6H_3AlCl_2$ monomer which can then associate through chloride bridging to the more available aluminums. The bridging Al–Cl distances are *ca.* 0.07 Å longer than those in the terminal Al–Cl bonds. The terminal Al–Cl bond lengths are very similar to those seen in Mes^*AlCl_2 , 2.125(5) Å. The Al–C distances, average 1.937(15) Å, are surprisingly short in view of the fact that the aluminum is four-coordinate. This lack of large variations in the Al–C (and to a lesser extent the

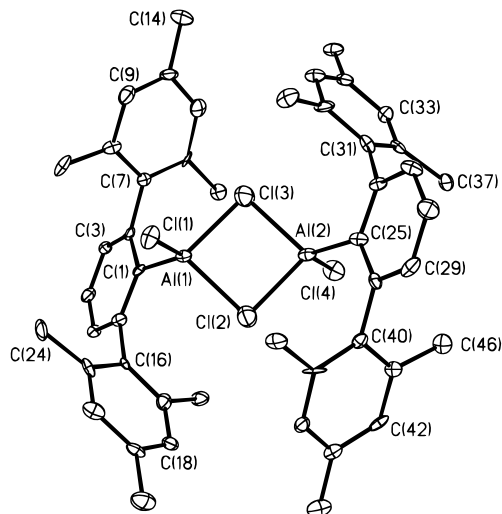


Figure 4. Thermal ellipsoid plot (30%) of **6**. H atoms are omitted for clarity.

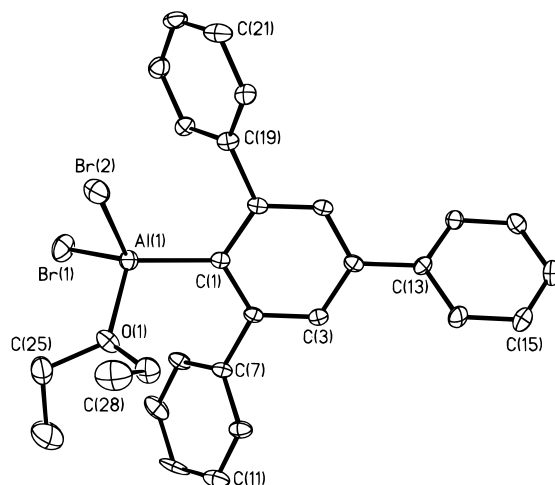


Figure 5. Thermal ellipsoid plot (30%) of **7**. H atoms are omitted for clarity.

Al–halide) bond lengths with coordination number has also been remarked upon in a previous publication.²⁹

The structure of the Triph derivative $TriphAlBr_2OEt_2$, **7** (Figure 5), has many features in common with that of **4**. The Al–O distances, 1.877(2) Å in **4** and 1.868(8) Å in **7**, are very similar. The Al–C bond length in **4**, 1.992(3) Å, is slightly longer than the 1.983(9) Å in **7** although this difference may be of marginal significance owing to the higher standard deviation in Al–C distance. Even though the Triph ligand is the least sterically demanding aryl substituent in the compounds under discussion, **7** displays the largest distortion from the expected geometry. The Al–C(1) vector is bent by 14.4° from the C(1)–C(4) vector. Since the ionic character of the Al–C bond may permit flexibility in angular distortion, the observed distortion may be due to packing forces in the crystal.

The structures of the compounds featuring the bulky 2,6- $Triph_2C_6H_3$ ligand **9–12** (Figures 6–9) are very similar to those of their 2,6- $Mes_2C_6H_3$ – counterparts **2–4**. As already mentioned, compounds containing the 2,6- $Triph_2C_6H_3$ – group tend to crystallize as mixtures but nevertheless form large well-formed crystals that afford good diffraction data. With the sole exception of 2,6- $Triph_2C_6H_3AlCl_2OEt_2$ (**11**), compounds **9a**, **10a**, **10b**, and **12** crystallized as the mixed species with co-crystallized benzene as illustrated by the following formulas: 2,6- $Triph_2C_6H_3Al(H)_{1.76}(Cl)_{0.24}(OEt_2)_{0.58}(THF)_{0.42}$ (**9a**), [2,6- $Triph_2C_6H_3Al(H)_{0.74}(u-OH)_{0.26}$] $\cdot 2C_6H_6$ (**10a**), [2,6- $Triph_2C_6H_3$ –

(32) Haaland, A. In *Coordination Chemistry of Aluminum*, Robinson, G. H., Ed.; VCH: New York, 1993; Chapter 1.

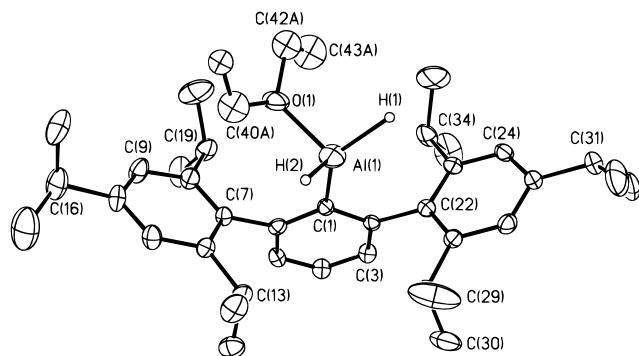


Figure 6. Thermal ellipsoid plot (30%) of **9a**. H atoms except those bound to aluminum and the partially occupied Cl atom and THF are omitted for clarity.

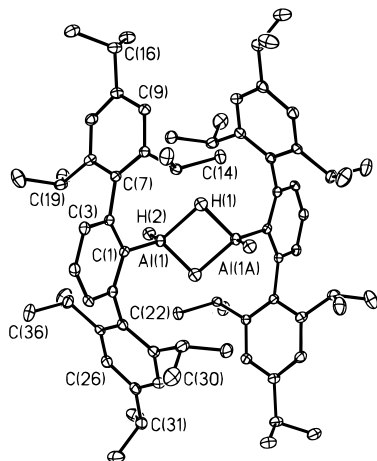


Figure 7. Thermal ellipsoid plot (30%) of **10a**. H atoms except those bound to aluminum and the partially occupied OH groups are omitted for clarity.

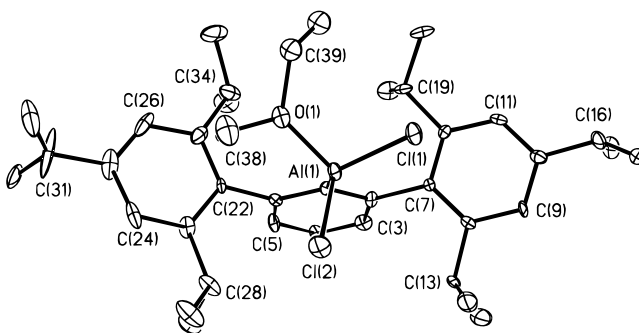


Figure 8. Thermal ellipsoid plot (30%) of **11**. H atoms are omitted for clarity.

$\text{Al}(\text{H})_{0.72}(\text{OH})_{0.28}(\mu\text{-H})_{0.48}(\mu\text{-OH})_{0.52}]_2 \cdot 2(\text{C}_6\text{H}_6)$ (**10b**), $[2,6\text{-Trip}_2\text{C}_6\text{H}_3\text{Al}(\text{Cl})_{0.68}(\text{H})_{0.32}(\mu\text{-OH})_2]_2 \cdot 2\text{C}_6\text{H}_6$ (**12**). The structure of 2,6-Trip₂C₆H₃AlH₂OEt₂ (**9**) compares closely with that of **2**. Despite the larger substituent in **9**, both Al–O (1.903(5) Å) and Al–C (1.983(5) Å) bond distances are slightly shorter than in **2**. Compounds **10a**, **10b**, and **12** are all dimeric and differ only in the amount of included OH or Cl (in the case of **12**) substituents instead of hydride. Their structures closely resemble that of **3**. They all feature a distorted tetrahedral environment at the aluminums. The Al–C distances are 1.963–(4) (**10a**), 1.966(2) (**10b**), and 1.949(3) Å (**12**), which are close to 1.956(3) Å in **3** and 1.966(3) Å in [Mes*AlH₂]₂.⁷ With increasing OH substitution in the bridging position the Al–Al separation increases from 2.635(3) (**10a**) and 2.704(1) (**10b**) to

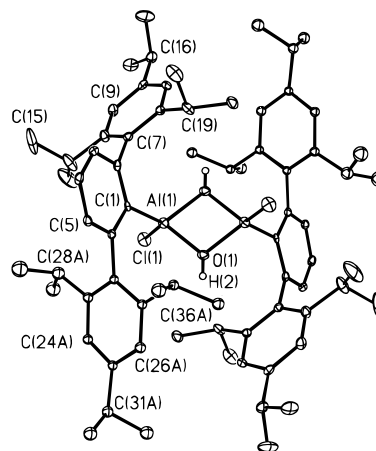


Figure 9. Thermal ellipsoid plot (30%) **12**. H atoms except those bound to oxygen are omitted for clarity.

2.788(2) (**12**). The Trip substituents groups of the ligand are trans to each other in the dimers and lie approximately parallel to each other. In this way, the bulky ortho Trip groups do not interfere with each other and the dimeric form rather than the desired monomer is the most stable. The compound **11** closely resembles **4** except that the Al–C distance is significantly shorter in **11** (1.954(11) Å) than in 1.992(3) Å in **4**.

An additional feature of interest in these compounds is the Al–C distance. The monomeric etherates **2**, **4**, **7**, and **9a** display Al–C bonds in the range 1.983(9)–2.02(2) Å whereas in the dimers the Al–C bond length varies between 1.922(12) Å and 1.966(2) Å with **11** being an exception (Al–C 1.954(11) Å). Two factors may be responsible: electron density from the Et₂O lowers the ionic character of the Al–C bond, thereby weakening (and lengthening) it. In addition, the Et₂O molecule is more sterically demanding than the bridging H, Cl, or OH ligands.

Conclusions

The synthesis and structure of several sterically encumbered terphenyl derivatives of aluminum hydrides and halides have been presented. These results show that the presence of one such group at the metal is not as effective as Mes* in preventing further coordination at aluminum. One of the major reasons for this is the lack of any significant interaction between the ortho aryl group of the terphenyl ligand substituent and the aluminum. A further reason lies in the nature of the ortho aryl groups themselves which, being effectively two-dimensional in their steric properties, can arrange themselves so that steric and electronic masking of the vacant metal coordination site is not observed. In contrast, where two sterically encumbering terphenyl ligands are present, steric congestion becomes unavoidable. In this case, lower coordination numbers or more distorted interligand angles at the metal (to an extent greater than those observed for two Mes* groups) are the result.^{16,17}

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Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **2**, **3a**, **4**, **6**, **7**, **9a**, **10a**, **10b**, **11**, and **12** and figures showing alternate structures taking into account disorder for **2**, **3a**, and **9a–12** (112 pages). Ordering information is given on any current masthead page.