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New Routes to Synthetically Useful, Sterically Encumbered Arylaluminum Halides and Hydride Halides

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The synthesis and structural characterization of the compounds Mes*AlCl$_2$(THF) (**1**), Mes*AlCl$_2$ (**2**), Mes*Al(H)Cl(THF) (**3a**), Mes*Al(H)Cl (**4a**), and (Mes*AlH$_2$)$_2$ (**5**) (Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2^-$) are described as well as those for two compounds **3b** and **4b** that are analogs of **3a** and **4a** but have H:Cl ratios that are less than 1:1. All compounds were characterized by ^{1}H, ^{13}C NMR, and IR spectroscopy, and **1**, **2**, **3a**, and **4b** were additionally characterized by X-ray crystallography. Compound **1** is best synthesized by the reaction of [(THF)$_2$LiH$_3$AlMes*]$_2$ (**6**) with 6 equiv of Me$_3$SiCl. A more conventional route involving the addition of (THF)$_2$LiMes* to 2 equiv of AlCl$_3$ in toluene usually affords a mixture of **1** and AlCl$_3$·THF. Recrystallization of **1** from *n*-hexane results in a species that has less than 1 equiv of THF per Mes*AlCl$_2$. The THF free complex **2** may be obtained in quantitative yield by heating **1** for 20 min at 90 °C under reduced pressure. Compound **3a** may be obtained by treating a 1:1 mixture of Mes*Li(THF)$_2$ and LiAlH$_4$ with 2 equiv of Me$_3$SiCl or by the addition of slightly less than 4 equiv of Me$_3$SiCl to **6**. The THF can be removed from **3a** by sublimation to give **4a**. The related compounds **3b** and **4b**, which display an aluminum-bound H:Cl ratio that is deficient in H, can be obtained by reactions with slightly more than 2 equiv of Me$_3$SiCl. Crystal data at 130 K with Cu Kα ($\lambda = 1.541\ 78$ Å) radiation: **1**, C$_{22}$H$_{37}$AlCl$_2$O, $a = 11.889(3)$ Å, $b = 9.992(3)$ Å , $c = 19.704(5)$ Å, orthorhombic, space group $Pca2_1$, $Z = 4$, $R = 0.068$ for 1556 ($I > 2\sigma(I)$) data; **2**, C$_{18}$H$_{29}$AlCl$_2$, $a = 12.147(5)$ Å, $b = 18.042(6)$ Å, $c = 17.771(7)$ Å, $\beta = 95.77(3)°$, monoclinic, space group $P2_1/n$, $Z = 8$, $R = 0.032$ for 4610 ($I > 2\sigma(I)$) data; **3a**, C$_{22}$H$_{38}$AlClO, $a = 16.887(7)$ Å, $b = 16.333(6)$ Å, $c = 8.739(3)$ Å, $\beta = 101.41(3)°$, monoclinic, space group $P2_1/c$, $Z = 4$, $R = 0.073$ for 2752 ($I > 2\sigma(I)$) data; **4b**, C$_{18}$H$_{29.64}$AlCl$_{1.36}$, $a = 12.077(3)$ Å, $b = 17.920(3)$ Å, $c = 17.634(5)$ Å ; $\beta = 95.21(2)$ Å, monoclinic, space group $P2_1/n$, $Z = 8$, $R = 0.070$ for 4261 ($I > 2\sigma(I)$) data.

Introduction

Sterically hindered, neutral organohalide derivatives of the heavier main group III elements Al, Ga, and In are key starting materials for a variety of compounds with unusual bonding and structures.[1,2] Among the most crowded, well-characterized organohalides are the recently reported Mes* (Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) derivatives of formula Mes*MX$_2$ (M/X = Al/Br,[3] Ga/Cl,[3,4] Ga/Br,[4] In/Cl,[3,4] In/Br[4]) or Mes*$_2$MX (M/X = Ga/Cl,[5] In/Cl,[6] In/Br[7]). A notable feature of the dihalides is that they are monomeric in the solid state whereas all previously known uncomplexed organodihalide derivatives were associated through halide bridging. In addition, it was noted[3] that neither Mes*AlBr$_2$, Mes*GaCl$_2$, nor Mes*InCl$_2$ formed stable complexes with Et$_2$O even though they were synthesized in an Et$_2$O solvent mixture. The synthesis of all the Mes*-substituted metal halide derivatives has involved the familiar lithium halide salt elimination reaction. For the Ga and In derivatives, moderate to good yields of the product were obtained by stoichiometric reaction of LiMes* (generated from Mes*Br and Li(*n*-Bu)) with the metal halide.[3,4] For the only currently known, well-characterized aluminum derivative Mes*AlBr$_2$, it was reported that more than 2 equiv of LiMes* (generated from Li(*n*-Bu) and relatively expensive Mes*Br) reagent was required to obtain a good (65%) yield of the product.[3] Subsequent experience has shown that the use of less than this amount of LiMes* afforded mixtures of products from which it proved very difficult to obtain a pure Mes*AlX$_2$ sample due to contamination with aluminum halide and/or aluminate complexes. Given the key role of the Mes*AlX$_2$ halides as starting materials, it was a priority to develop reliable and efficient routes to such species. In addition, it was desired to examine the tendency of Mes*AlX$_2$ compounds to form complexes with Et$_2$O or THF, the two most commonly used ether donor solvents.

In this paper, the synthesis of Mes*AlCl$_2$(THF) (**1**) in good yield by two separate routes and its X-ray crystal structure are described. It is also shown that **1** readily desolvates under mild conditions to give the hitherto uncharacterized species Mes*AlCl$_2$ (**2**). The previously unreported hydride halide compounds Mes*Al(H)Cl(THF), **3a**, and its desolvated analogue, **4a**, as well as the related species **3b** and **4b**, involving ratios of aluminum-bound H:Cl that are less than 1:1, are now reported.

Experimental Section

General Procedures. All reactions were performed under N$_2$ by using either modified Schlenk techniques or a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled from sodium−potassium alloy and degassed twice before use. Mes*Br[8] and [(THF)$_2$-LiH$_3$AlMes*]$_2$[9] were prepared by literature procedures. AlCl$_3$ and Me$_3$SiCl were purchased from Aldrich and used as received. 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, and NMR spectra were recorded on a General Electric GE-300 spectrometer.

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Mes*Li(THF)$_2$. Mes*Li(THF)$_2$ was synthesized by a slightly modified literature procedure.[10] A solution of 12.93 g (39.7 mmol) of Mes*Br in 20 mL of THF/80 mL *n*-pentane was treated at *ca.* −78 °C with 30 mL (48.0 mmol) of a 1.6 M *n*-BuLi solution in hexanes and stirred for 4 h at this temperature. The colorless precipitate was washed twice with *n*-pentane (2 × 50 mL) at −78 °C, collected on a sintered-glass frit, and dried under reduced pressure. The ^{1}H NMR spectrum shows the presence of two THF molecules per Mes* unit. Yield: 68%. ^{1}H NMR (C_6D_6): 7.59 (s, *m*-H, 2H), 3.38 (m, OC*H*$_2$, 8H), 1.64 (s, *o*-CH$_3$, 18H), 1.57 (s, *p*-CH$_3$, 9H), 1.24 ppm (m, CH$_2$, 8H).

Mes*AlCl$_2$·THF (1). Method A. A slurry of 0.48 g (0.55 mmol) of [(THF)$_2$LiH$_3$AlMes*]$_2$ in THF/hexane (30 mL of a 1:2 mixture) was treated with 0.42 mL (3.3 mmol, 0.36 g) of Me$_3$SiCl at −78 °C. The resulting clear colorless solution was warmed to room temperature and stirred overnight. After removal of volatile materials, the colorless solid was extracted with *n*-hexane (40 mL). Concentration to *ca.* 20 mL followed by crystallization at −20 °C overnight gave 0.28 g of small colorless crystals of **1**. Yield: 61%. Mp: 99−100 °C. ^{1}H NMR (C_6D_6): 7.45 (s, *m*-H, 2H), 3.58 (m, OC*H*$_2$, 4H), 1.59 (s, *o*-CH$_3$, 18H), 1.33 (s, *p*-CH$_3$, 9H), 1.02 ppm (m, CH$_2$, 4H). ^{13}C{^{1}H} NMR (C_6D_6): 161.1 (*o* -C), 150.4 (*p*-C), 121.3 (*m*-C), 72.6 (O*C*H$_2$), 39.3 (*o*-*C*(CH$_3$)$_3$), 34.7 (*p*-*C*(CH$_3$)$_3$), 33.5 (*o*-CH$_3$), 31.5 (*p*-CH$_3$), 24.7 ppm (CH$_2$). ^{27}Al NMR: 108 ppm (s, broad, $\Delta\nu_{1/2}$ = *ca.* 6300 Hz).

Method B. Mes*Li(THF)$_2$ (3.00 g, 7.5 mmol) was added to a slurry of AlCl$_3$ (2.00 g, 15.0 mmol) in PhMe (40 mL) at −78 °C via a solids-addition funnel in several portions (*ca.* 30 min). The colorless slurry was kept at *ca.* −78 °C for an additional 1 h, slowly warmed to room temperature, and stirred for a further 16 h. The volatile materials were removed from the slightly cloudy solution under reduced pressure, after which the remaining colorless sticky solid was warmed to *ca.* 40 °C for 1 h under reduced pressure. The colorless solid was then extracted twice with 80 and 40 mL of *n*-hexane, respectively. The combined hexane extracts were concentrated to *ca.* 50 mL and slowly cooled to −20 °C for 24 h to yield **1** as large (>1 mm) colorless plates of sufficient quality for X-ray diffraction studies. The sample also contains *ca.* 0.3 equiv of AlCl$_3$·THF (by ^{1}H, ^{27}Al NMR). This contaminant can be removed by sublimation to afford **2** (vide infra), and pure **1** may be reconstituted by adding THF. Yield of the mixture of **1** and AlCl$_3$·THF: 2.29 g, 73.4% (or 56% crude Mes*AlCl$_2$·THF). Mp: softens at 60 °C, melts at 85−90 °C. ^{1}H NMR (C_6D_6): 7.45 (s, *m*-H, 2H), 3.63 (m, OC*H*$_2$, 5.3H), 1.58 (s, *o*-CH$_3$, 18H), 1.32 (s, *p*-CH$_3$), 1.00 ppm (m, CH$_2$, 5.3H). ^{13}C{^{1}H} NMR (C_6D_6): 160.9 (*o*-C), 150.6 (*p*-C), 121.3 (*m*-C), 72.7 (O*C*H$_2$), 39.1 (*o*-*C*(CH$_3$)$_3$), 34.7 (*p*-*C*(CH$_3$)$_3$), 33.5 (*o*-CH$_3$), 31.5 (*p*-CH$_3$), 24.6 ppm (*C*H$_2$). ^{27}Al NMR (C_6D_6, ν_o = 78.340 477 MHz): 87.4 ppm (s, $\nu_{1/2}$ = *ca.* 430 Hz, AlCl$_3$·THF). Concentration of the supernatant liquid to *ca.* 4−5 mL, followed by cooling in a −20 °C freezer overnight, gave 0.18 g of a mixture of **1** and **2** in the form of large (>1.5 mm) colorless plates with the average composition (by ^{1}H NMR) of Mes*AlCl$_2$·0.35THF. The crystal used for the structure determination of **2** was taken from this batch.

Removal of Excess AlCl$_3$·THF. Method A. A mixture of 1 equiv of Mes*AlCl$_2$·THF and *ca.* 0.4 equiv of AlCl$_3$·THF (1.83 g containing *ca.* 1.5 mmol of AlCl$_3$·THF) in *n*-pentane (50 mL) was reacted with 0.59 g (1.5 mmol) of Mes*Li(THF)$_2$ at −78 °C. The resultant mixture was warmed to room temperature and stirred overnight. The colorless precipitate (LiCl) was removed, and the colorless solution was concentrated to *ca.* 30 mL to yield 0.59 g of colorless pyramid-shaped (*ca.* 1 mm) crystals after 20 h at room temperature. Cooling of the mother liquor to −20 °C for 4 days gave another 0.68 g of **1**. Yield: 59%. AlCl$_3$·THF content: <5% according to ^{1}H and ^{27}Al NMR.

Method B. A crystalline mixture of Mes*AlCl$_2$·THF and AlCl$_3$·THF (approximate ratio 1:0.4; 1.09 g) was heated for 3 h to 80 °C under reduced pressure (0.02 mmHg). A colorless microcrystalline solid (AlCl$_3$·THF) sublimed. The remaining off-white powder was pure Mes*AlCl$_2$ (**2**). Yield: 0.64 g, 85%.

Mes*AlCl$_2$ (2). Compound **1** (0.31 g, 0.75 mmol) was heated under reduced pressure (*ca.* 0.02 mmHg) to 90 °C for 20 min. The colorless solid, which is essentially pure Mes*AlCl$_2$, was dissolved in *n*-hexane (30 mL), the solution was filtered, and the filtrate was concentrated to *ca.* 10 mL and cooled in a −20 °C freezer. After 3 days, 0.15 g of large (>1 mm) colorless crystals (parallelepipeds) formed. Yield: 58.2%. Mp: turns opaque at 100 °C, melts at 146−150 °C. ^{1}H NMR (C_6D_6): 7.37 (s, *m*-H, 2H), 1.45 (s, *o*-CH$_3$, 18H), 1.27 ppm (s, *p*-CH$_3$, 9H). ^{13}C{^{1}H} NMR: 158.6 (*o*-C), 152.7 (*p*-C), 121.2 (*m*-C), 37.5 (*o*-*C*(CH$_3$)$_3$), 35.0 (*p*-*C*(CH$_3$)$_3$), 32.9 (*o*-CH$_3$), 31.3 ppm (*p*-CH$_3$). ^{27}Al NMR (C_6D_6, 80 °C): 130 ppm (s, broad, $\nu_{1/2}$ = *ca.* 4700 Hz).

Mes*Al(H)Cl·THF (3a). Method A. A *ca.* −78 °C slurry of Mes*Li(THF)$_2$ in 1:1 *n*-pentane/Et$_2$O (80 mL) (generated in situ from 6.08 g (18.7 mmol) of Mes*Br and 12.2 mL of 1.6 M *n*-BuLi in hexane) was transferred via a cannula to a slurry of LiAlH$_4$ (0.64 g, 17.0 mmol) in Et$_2$O (30 mL) at −78 °C, the mixture was warmed to room temperature and stirred for a further 16 h. After cooling to −78 °C, the colorless, cloudy (LiH) solution was treated dropwise with Me$_3$SiCl (4.5 mL, 35 mmol, 3.80 g). The mixture was then warmed to room temperature and stirred for an additional 1 h. The clear, colorless supernatant was decanted, and the volatile materials were removed under reduced pressure. The colorless solid was then extracted with *n*-hexane (80 mL), the extract was filtered, and the filtrate was concentrated to *ca.* 50 mL and cooled in a −20 °C freezer for 24 h to yield 1.4 g of **3a** as large colorless crystals. Yield: 21.6%. The crystal used for the structure determination was taken from this batch. ^{1}H NMR (C_6D_6): 7.47 (s, *m*-H, 2H), 4.8 (s, broad, $\nu_{1/2}$ = *ca.* 60 Hz, Al−H, 1H), 3.43 (m, OCH$_2$, 4H), 1.60 (s, *o*-CH$_3$, 18H), 1.36 (s, *p*-CH$_3$, 9H), 1.04 ppm (m, CH$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 160.2 (*o*-C), 149.8 (*p*-C), 121.0 (*m*-C), 70.6 (O*C*H$_2$), 39.0 (*o*-*C*(CH$_3$)$_3$), 34.8 (*p*-*C*(CH$_3$)$_3$), 33.5 (*o*-CH$_3$), 31.6 (*p*-CH$_3$), 24.8 ppm (CH$_2$). IR: $\nu_{\mathrm{Al-H}}$ 1880 (sh), 1832 (st), 1785 (m), 1757 cm^{-1} (m). Concentration of the mother liquor to *ca.* 30 mL and crystallization at −20 °C afforded 2.04 g of a *ca.* 1:1 mixture (by NMR) of **3a** and Mes*AlH$_2$.[11]

Method B. A slurry of [(THF)$_2$LiH$_3$AlMes*]$_2$ (3.8 mmol) in PhMe (50 mL) was treated dropwise with Me$_3$SiCl (1.93 mL, 1.65 g, 15.2 mmol) at −78 °C. The mixture was warmed to room temperature and stirred overnight (16 h). After removal of the volatile materials under reduced pressure the colorless, slightly sticky solid was extracted with *n*-hexane (60 mL). The supernatant was decanted, concentrated to 20 mL, and cooled to −20 °C for 4 days. As no crystals had formed, THF (1 mL) was added and the solution was concentrated to *ca.* 5 mL and cooled in −20 °C freezer. After 2 days, large, colorless crystals of **3b** (Mes*Al(H)$_{0.64}$Cl$_{1.36}$·THF) had formed. Yield: 1.78 g. Mp: 77−95 °C. ^{1}H NMR (C_6D_6): 7.48, 7.46 (2s *m*-H, 2H), 4.8 (s, broad, $\nu_{1/2}$ = *ca.* 60 Hz, Al−H, 0.66H), 3.43 (m, OC*H*$_2$, 4H), 1.60 (s, *o*-CH$_3$, 18H), 1.36 (s, *p*-CH$_3$, 9H), 1.04 ppm (m, CH$_2$, 4H). IR: $\nu_{\mathrm{Al-H}}$ 1885 (sh), 1836 (st), 1810 (sh), 1770 cm $^{-1}$ (w). The reaction of 2.07 g (2.4 mmol) of [(THF)$_2$LiH$_3$AlMes*]$_2$ with 3.4 equiv (1.05 mL, 8.2 mmol, 0.90 g) of Me$_3$SiCl affords Mes*Al(H)$_{0.9}$Cl$_{1.1}$·THF in 49% yield. ^{27}Al NMR: 121 ppm (s, br, $\Delta\nu_{1/2}$ = *ca.* 8300 Hz). IR: $\nu_{\mathrm{Al-H}}$ = 1832 cm^{-1} (st).

Mes*Al(H)Cl (4a). A 0.23 g (0.6 mmol) sample of Mes*Al(H)Cl·THF (**3a**) was sublimed at *ca.* 110−120 °C under reduced pressure, and 0.13 g of colorless microcrystalline Mes*Al(H)Cl (**4a**) was recovered. ^{1}H NMR (C_6D_6): 7.38 (s, *m*-H, 2H), 5.25 (s, broad, $\nu_{1/2} \approx$ 40 Hz, Al−H, 1H), 1.44 (s, *o*-CH$_3$, 18H), and 1.30 (s, *p*-CH$_3$, 9H). ^{13}C{^{1}H} NMR (C_6D_6): 158.5 (*o*,C), 121.0 (*m*-C), 38.3 (*o*-*C*(CH$_3$)$_3$), 34.9 (*p*-*C*(CH$_3$)$_3$), 32.9 (*o*-CH$_3$), 31.4 ppm (*p*-CH$_3$). IR: $\nu_{\mathrm{Al-H}}$ 1882 (st), 1813 cm^{-1} (w). Mp: softens at 85 °C, melts from 100−110 °C.

Mes*AlH$_{0.64}$Cl$_{1.36}$ (4b). A 0.92 g (2.4 mmol) sample of Mes*Al(H)$_{0.64}$Cl$_{1.36}$·THF (**3b**) was sublimed at *ca.* 110−120 °C under reduced pressure. The colorless microcrystalline sublimate (0.63 g) was crystallized from *n*-hexane by cooling at *ca.* −20 °C for 3 days. Yield: 0.28 g. ^{1}H NMR (C_6D_6): 7.38 (s, *m*-H, 2H), 5.25 (s, broad, $\nu_{1/2}$ = *ca.* 60 Hz, Al−H, 0.6H), 1.44 (s, *o*-CH$_3$), 1.30 ppm (s, *p*-CH$_3$). ^{13}C{^{1}H } NMR (C_6D_6): 158.4 (*o*-C), 151.8 (*p*-C), 121.0 (*m*-C), 38.2 (*o*-C(CH$_3$)$_3$), 34.9 (*p*-*C*(CH$_3$)$_3$), 32.9 (*o*-CH$_3$), 31.4 ppm (*p*-CH$_3$). IR: $\nu_{\mathrm{Al-H}}$ 1877 (st), 1849 (sh), 1805 cm^{-1} (w). Mp: 110−121 °C.

X-ray Crystallographic Studies. The crystals were removed from the Schlenk tube under a stream of N$_2$ 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

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Table 1. Crystallographic Data[a] for **1**, **2**, **3a**, and **4b**

	1	**2**	**3a**	**4b**
formula	$C_{22}H_{37}AlCl_2O$	$C_{18}H_{29}AlCl_2$	$C_{22}H_{38}AlClO$	$C_{18}H_{29.64}AlCl_{1.36}$
fw	415.40	343.29	380.95	321.34
color and habit	colorless plate	colorless plate	colorless plate	colorless prism shaped fragment
cryst system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pca2_1$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	11.889(3)	12.147(5)	16.887(7)	12.077(3)
b, Å	9.992(3)	18.042(6)	16.333(6)	17.920(3)
c, Å	19.704(5)	17.771(7)	8.739(3)	17.634(5)
β, deg		95.77(3)	101.41(3)	95.21(2)
V, Å^3	2341(1)	3875(2)	2363(2)	3801(2)
Z	4	8	4	8
cryst dimens, mm	0.61 × 0.60 × 0.10	0.58 × 0.46 × 0.40	0.56 × 0.55 × 0.22	0.90 × 0.52 × 0.28
d_{calc}, g cm^{-3}	1.179	1.177	1.071	1.123
μ, mm^{-1}	2.906	3.373	1.823	2.602
no. of obsd rflcns	1556 ($I > 2\sigma(I)$)	4610 ($I > 2\sigma(I)$)	2752 ($I > 2\sigma(I)$)	4261 ($I > 2\sigma(I)$)
R, wR_2	0.068, 0.174	0.032, 0.079	0.073, 0.189	0.070, 0.187

[a] Data were collected at 130 K with a Syntex $P2_1$ diffractometer (**1**, **3a**, **4b**) or a Siemens P4/RA diffractometer (**2**) using Cu Kα (λ = 1.541 78 Å) radiation.

stream as described in ref 12. All data were collected near 130 K with either a Syntex $P2_1$ (graphite monochromator) in the cases of **1**, **3a**, and **4b** or a Siemens P4/RA diffractometer (nickel foil monochromator) in the case of **2** using Cu Kα (λ = 1.541 78 Å) radiation. Both diffractometers were equipped with a locally modified Enraf-Nonius universal low-temperature device for low-temperature work.

Crystallographic programs used for the structure solutions were those of the SHELXTL Version 5.03 (1994) program package installed on an IBM-compatible 486 computer. Scattering factors were obtained from ref 13. An absorption correction was applied by using the method described in ref 14. Some details of the data collection and refinement are given in Table 1. Coordinates for selected atoms are given in Table 2, and selected bond distances and angles are given in Table 3. 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. Hydrogen atoms attached to the carbons were included in the refinement at calculated positions using a riding model with C−H = 0.96 Å and $U_H = 1.2U_C$ and $1.5U_C$ for methyl hydrogens. Hydrogen atoms bound to aluminum were located on Fourier difference maps and, with the exception of those in **4b**, were allowed to refine freely with fixed isotropic parameters.

Discussion

The main objectives of this work were the development of a more practical route to a Mes*AlX_2 (X = halide) starting material and the study of some of its properties. The work may be summarized by Scheme 1, which presents an overall view of the relationships among the compounds under discussion.

The original preparation of Mes*$AlBr_2$ required the use of 2.5 equiv of the expensive Mes*Br precursor.[3] Attempts to react Mes*Li (generated by treatment of Mes*Br with *n*-BuLi in a THF/*n*-pentane 1:4 mixture at *ca.* −78 °C, followed by two washings with *n*-pentane) with 1 equiv of $AlBr_3$ in either *n*-hexane or toluene led to impure oils from which Mes*$AlBr_2$ could eventually be isolated (after several crystallizations and sublimation) in yields that were often less than 20%.[15] Interestingly, the reaction of Mes*Li with 1 equiv of $GaCl_3$ under the same conditions led to a mixture of Mes*$_2$GaCl and Mes*$GaCl_2$.[15] A different approach using the Grignard reagent Mes*MgBr and the addition of 1 equiv of $AlBr_3$ does not lead to Mes*$AlBr_2$ but to the isolation of Mes*$_2$Mg[16] in *ca.* 50% yield. Mes*$GaCl_2$ can be conveniently synthesized by the reaction of Mes*Li(THF)$_2$ with 2 equiv of $GaCl_3$ in *n*-pentane.[15]

It seems that in the 1:1 reactions with the MX_3 (M = Al, Ga) salt the LiCl, LiBr, and $MgBr_2$ byproducts form insoluble or relatively inert complexes such as $LiMCl_4$, $LiMBr_4$, and $MgBrMBr_4$ with unreacted MX_3. In contrast to its gallium and indium congeners, Mes*$_2$AlX (X = Cl, Br) has not yet been reported. Bearing the probable formation of aluminate salts in mind, it was decided to react Mes*Li, which was isolated as Mes*Li(THF)$_2$, with 2 equiv of $AlCl_3$ in toluene. This resulted in a milky solution. Removal of the volatile materials and extraction with *n*-hexane, followed by crystallization at −20 °C, gives large (*ca.* 1−2 mm) colorless crystals, which are Mes*$AlCl_2$·THF (**1**) according to the X-ray structure determination. NMR spectroscopic examinations nevertheless reveal a THF:Mes* ratio that is greater than 1:1, and the ^{27}Al NMR spectrum displays a narrow line in the 80−90 ppm range, consistent with the presence of some $AlCl_3$·THF contamination of the product in the crystals.[17] The excess (cocrystallized) $AlCl_3$·THF can be removed either (a) by reaction of this mixture with the appropriate amount of Mes*Li(THF)$_2$ in *n*-pentane or (b) by sublimation at 80 °C under reduced pressure, which leaves pure **2** as a powder. Pure **1** can then be obtained by the addition of THF.

The solvent-free Mes*$AlCl_2$ (**2**) can be isolated in the form of large (*ca.* 2 mm) colorless plates either by repeated crystallization of **1** from *n*-hexane or by heating of **1** to 90 °C under reduced pressure.

The alternative (and higher yielding) method for the synthesis of **1** arose from parallel work involving the synthesis of (Mes*AlH_2)$_2$ (**5**).[11] This molecule was originally synthesized by the reaction of MeI with [(THF)$_2$LiH$_3$AlMes*]$_2$ as described by eq 1. It was later found that Me_3SiCl could be used instead

$$\underset{\mathbf{6}}{[(\mathrm{THF})_2\mathrm{LiH_3AlMes^*}]_2} + 2\mathrm{MeI} \rightarrow 2\mathrm{LiI} + 2\mathrm{MeH} + \underset{\mathbf{5}}{(\mathrm{H_2AlMes^*})_2} \quad (1)$$

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Table 2. Atom Coordinates ($\times 10^4$) for Important Atoms in **1**, **2**, **3a**, and **4b**

Compound **1**			
Al(1)	8360(2)	−1614(2)	523(1)
Cl(1)	8857(2)	479(2)	557(1)
Cl(2)	7024(2)	−1769(2)	−194(1)
O(1)	9630(4)	−2099(5)	−10(2)
C(1)	8485(6)	−2585(7)	1392(4)
C(2)	9102(6)	−3809(7)	1454(4)
C(3)	9719(6)	−4069(7)	2043(4)
C(4)	9713(6)	−3216(7)	2595(4)
C(5)	8981(6)	−2142(7)	2580(4)
C(6)	8325(6)	−1854(7)	2005(4)
Compound **2**			
Al(1)	7577(1)	1718(1)	1374(1)
Cl(1)	7334(1)	872(1)	547(1)
Cl(2)	9268(1)	2051(1)	1488(1)
C(1)	6597(2)	2203(1)	2019(1)
C(2)	6492(2)	1945(1)	2760(1)
C(3)	5932(2)	2371(1)	3256(1)
C(4)	5468(2)	3055(1)	3058(1)
C(5)	5547(2)	3295(1)	2321(1)
C(6)	6090(2)	2892(1)	1803(1)
Al(2)	2657(1)	5657(1)	1653(1)
Cl(3)	1878(1)	6532(1)	1001(1)
Cl(4)	4362(1)	5576(1)	1492(1)
C(19)	1779(2)	5017(1)	2231(1)
C(20)	1238(2)	4373(1)	1921(1)
C(21)	566(2)	3964(1)	2350(1)
C(22)	377(2)	4162(1)	3085(1)
C(23)	892(2)	4796(1)	3380(1)
C(24)	1591(2)	5222(1)	2978(1)
Compound **3a**			
Al(1)	8749(1)	9666(1)	2485(2)
Cl(1)	9581(1)	8897(1)	1523(2)
H(1)	8856(31)	9606(32)	4491(62)
O(1)	9183(2)	10740(2)	2407(4)
C(1)	7576(3)	9830(3)	1684(5)
C(2)	7082(3)	9532(3)	2698(5)
C(3)	6395(3)	9983(3)	2894(5)
C(4)	6158(3)	10690(3)	2083(5)
C(5)	6583(3)	10909(3)	926(5)
C(6)	7261(3)	10491(3)	691(5)
Compound **4b**			
Al(1)	2674(1)	673(1)	1553(1)
Cl(1)	4449(1)	429(1)	1562(1)
Cl(2)	1845(8)	1574(5)	1031(5)
H(1)	2482(58)	1300(37)	903(36)
C(1)	1742(3)	62(2)	2147(3)
C(2)	1567(3)	272(2)	2900(2)
C(3)	926(4)	−172(2)	3338(2)
C(4)	437(4)	−837(2)	3063(2)
C(5)	605(4)	−1031(2)	2321(2)
C(6)	1228(3)	−608(2)	1859(2)
Al(2)	7316(1)	1662(1)	3654(1)
Cl(3)	5565(1)	1951(1)	3522(1)
Cl(4)	7557(2)	808(1)	4492(1)
H(2)	7915(94)	1053(67)	4047(73)
C(19)	8300(3)	2173(2)	3009(2)
C(20)	8814(3)	2867(2)	3231(2)
C(21)	9411(4)	3258(2)	2723(2)
C(22)	9547(4)	3004(2)	1995(2)
C(23)	9064(3)	2322(2)	1787(2)
C(24)	8453(3)	1906(2)	2275(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds **1**, **2**, **3a**, and **4b**

Compound **1**			
Al(1)−Cl(1)	2.173(3)	Al(1)−C(1)	1.975(7)
Al(1)−Cl(2)	2.131(3)	Al(1)−O(1)	1.902(5)
Cl(1)−Al(1)−Cl(2)	107.1(1)	C(1)−Al(1)−O(1)	107.1(3)
C(1)−Al(1)−Cl(1)	115.2(2)	Cl(1)−Al(1)−O(1)	92.7(2)
C(1)−Al(1)−Cl(2)	126.5(2)	Cl(2)−Al(1)−O(1)	102.0(2)
Compound **2**			
Al(1)−Cl(1)	2.120(1)	Al(2)−Cl(3)	2.123(1)
Al(1)−Cl(2)	2.129(1)	Al(2)−Cl(4)	2.123(1)
Al(1)−C(1)	1.942(2)	Al(2)−C(19)	1.936(2)
Cl(1)−Al(1)−Cl(2)	109.6(1)	Cl(3)−Al(2)−Cl(4)	111.4(1)
Cl(1)−Al(1)−C(1)	133.1(1)	Cl(3)−Al(2)−C(19)	119.6(1)
Cl(2)−Al(1)−C(1)	117.4(1)	Cl(4)−Al(2)−C(19)	128.8(1)
Compound **3a**			
Al(1)−Cl(1)	2.174(2)	Al(1)−H(1)	1.73(5)
Al(1)−C(1)	1.983(5)	Al(1)−O(1)	1.908(3)
Cl(1)−Al(1)−C(1)	128.2(2)	C(1)−Al(1)−O(1)	103.2(2)
Cl(1)−Al(1)−O(1)	103.6(1)	C(1)−Al(1)−H(1)	105(2)
Cl(1)−Al(1)−H(1)	114(2)	O(1)−Al(1)−H(1)	97(2)
Compound **4b**			
Al(1)−Cl(1)	2.186(2)	Al(2)−Cl(3)	2.169(2)
Al(1)−Cl(2)	2.070(10)	Al(2)−Cl(4)	2.130(2)
Al(1)−H(1)	1.61(6)	Al(2)−H(2)	1.45(12)
Al(1)−C(1)	1.944(4)	Al(2)−C(19)	1.947(4)
Cl(1)−Al(1)−C(1)	119.88(14)	Cl(3)−Al(2)−C(19)	117.78(14)
Cl(1)−Al(1)−H(1)	103(3)	Cl(3)−Al(2)−Cl(4)	108.41(9)
Cl(1)−Al(1)−Cl(2)	126.4(3)	Cl(3)−Al(2)−H(2)	132.(5)
Cl(2)−Al(1)−C(1)	113.5(3)	Cl(4)−Al(2)−C(19)	133.8(2)
C(1)−Al(1)−H(1)	137(3)	C(19)−Al(2)−H(2)	109(5)

of MeI to afford elimination of Me_3SiH instead of methane. The addition of further Me_3SiCl leads to the substitution of further hydrogens on the aluminum by chlorine. Thus, the addition to **6** of 4 instead of 2 equiv of Me_3SiCl gives **3a** in the presence of THF whereas 6 equiv of Me_3SiCl affords compound **1** in which all the hydrogens are replaced by chlorine (eqs 2 and 3). Care has to be exercized in adding exactly the correct number of equiv of Me_3SiCl in the case of eq 2 since the addition of more than 4 equiv will result in a species which has less than one aluminum hydrogen per chlorine, i.e. a species such as **3b**. The synthesis of **3a** may also be accomplished in

$$[(THF)_2LiH_3AlMes^*]_2 + 4Me_3SiCl \rightarrow 2LiCl + 4Me_3SiH + \underset{\mathbf{3a}}{2Mes^*Al(H)Cl(THF)} \quad (2)$$

$$[(THF)_2LiH_3AlMes^*]_2 + 6Me_3SiCl \rightarrow 2LiCl + 6Me_3SiH + \underset{\mathbf{1}}{2Mes^*AlCl_2(THF)} \quad (3)$$

reduced yield by the one-pot reaction of $Mes^*Li(THF)_2$ with $LiAlH_4$, followed by treatment with Me_3SiCl. The route to $(H_2AlMes^*)_2$ described by eq 4 was investigated in order to avoid

$$2Mes^*Li(THF)_2 + 2LiAlH_4 \rightarrow \underset{\mathbf{6}}{[(THF)_2LiH_3AlMes^*]_2} + 2LiH \xrightarrow{4Me_3SiCl} \underset{\mathbf{5}}{(Mes^*AlH_2)_2} + 4LiCl + 4Me_3SiH + 4THF \quad (4)$$

the necessity of isolating $[(THF)_2LiH_3AlMes^*]_2$, **6**. Apparently, $(Mes^*AlH_2)_2$, **5**, reacts with Me_3SiCl at a rate competitive with that of LiH, thereby giving some **3** as product. Attempts to synthesize **3a** by exchange reactions involving **1** and **5** led to mixtures of products which according to ^1H NMR consisted mainly of $Mes^*AlH_nCl_{2-n}\cdot THF$ species.

The THF from **3** can be easily removed by sublimation at 110−120 °C under reduced pressure without affecting the H:Cl ratio. It is notable, however, that the synthesis of $Mes^*Al(H)Cl\cdot THF$ (H:Cl ratio 1:1) according to eq 2 can be further complicated by an equilibrium involving $(Mes^*AlH_2)_2$, $Mes^*Al(H)Cl\cdot THF$, and $Mes^*AlCl_2\cdot THF$. It should be noted that $Mes^*Al(H)_nCl_{2-n}\cdot THF$ ($n > 1$) is less soluble than $(Mes^*AlH_2)_2$

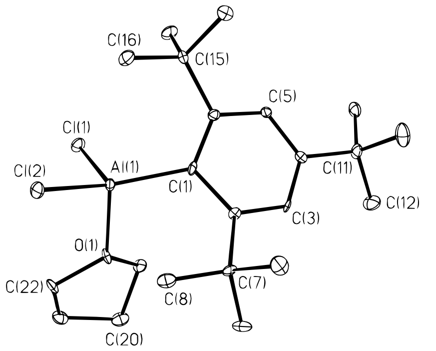


Figure 1. Thermal ellipsoidal plot (30%) of **1**. H atoms are omitted for clarity.

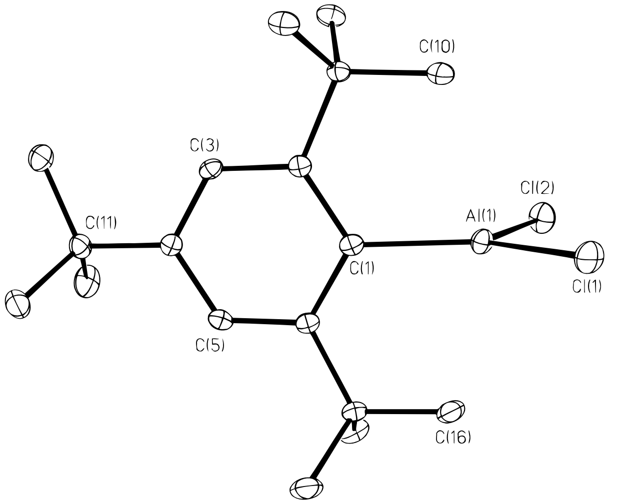


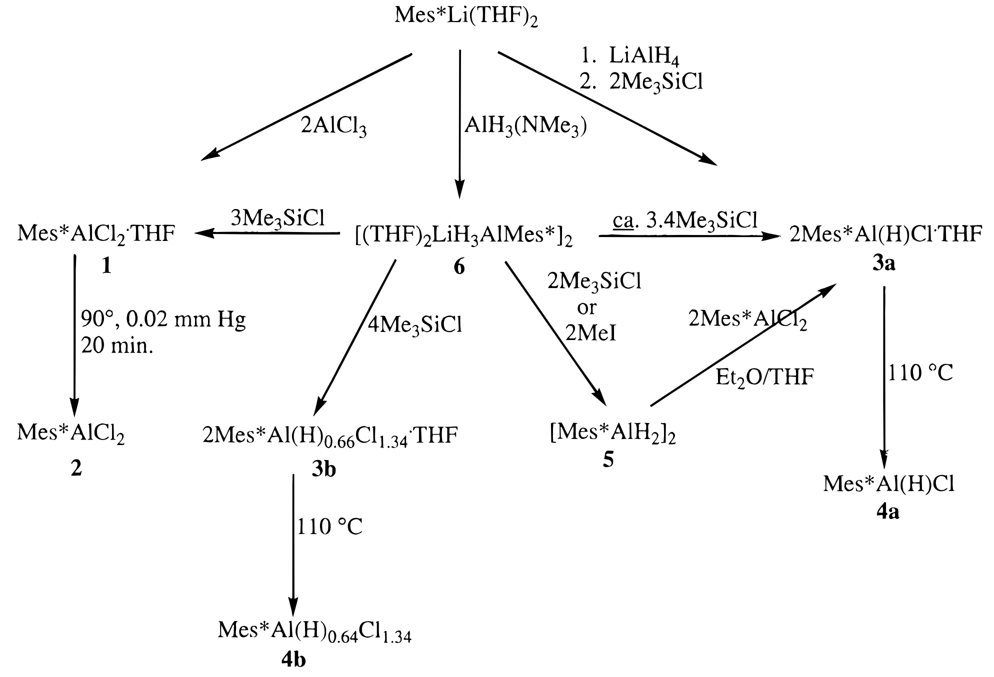
Figure 2. Thermal ellipsoidal plot (30%) of one of the independent molecules of **2**. H atoms are omitted for clarity.

in hexane or pentane solutions which contain small amounts (*ca.* 5−10 equiv) of THF. Thus, a synthesis following the exact stoichiometry given by eq 2 can lead to $Mes^*Al(H)_n Cl_{2-n}\cdot THF$ with $n < 1$ in the isolated crystals. The employment of less than 4 equiv of Me_3SiCl per $[(THF)_2LiH_3AlMes^*]_2$ increases the H:Cl ratio to 0.9:1.1.

Structures. The structures of compounds **5**[11] and **6**[9] have been described elsewhere. The structure of **1**, which is illustrated in Figure 1, bears a resemblance to the structure of the less sterically encumbered $MesAlCl_2(THF)$.[3] There are important differences in structural detail, however, that may be attributed to the greater size of the Mes* group in comparison to Mes. The Al−C and Al−O distances in **1** are *ca.* 0.05 Å longer than the corresponding lengths in $MesAlCl_2(THF)$. The Cl−Al−Cl angle is *ca.* 3° narrower in **1** and the C−Al−Cl angles in **1** can be up to 11° wider than the same feature in $MesAlCl_2(THF)$. The higher steric crowding in **1** is also manifested in the distortion of the C(1)−C(6) phenyl ring. The C(1)−C(4) vector deviates by 30.5° from the Al−C(1) vector. Furthermore, the ring itself is also distorted toward a boat conformation so that the planes defined by C(1)−C(2)−C(6) and C(3)−C(4)−C(5) are folded toward the plane C(2)−C(3)−C(5)−C(6) by angles of 13.2 and 4.8°, respectively. Removal of THF from **1** under mild conditions results in the three-coordinate species **2**. The lowering of the aluminum coordination number from 4 to 3 results in slightly shorter metal−carbon and metal−halide bonds as well as wider interligand angles. The crystals of **2** are not isomorphous with their Ga or In analogues, nor are they isomorphous with the Al species Mes^*AlBr_2 although all the compounds bear a close structural resemblance. They are, however, isomorphous with **4b** (vide infra). The two crystallographically independent molecules in **2** have almost identical structures; the only significant differences relate to slight changes in the orientation of the *t*-Bu groups. There are also close approaches (2.1 Å) of two H atoms from ortho *t*-Bu groups to the Al center which are similar to those observed in Mes^*AlBr_2. The positioning of the aromatic ring plane approximately perpendicular to the metal coordination plane thus appears to take place for two reasons: to minimize steric congestion and to permit agostic interactions between the *t*-Bu hydrogens and the metal.

The structure of **3a** resembles that of **1** except the two formulas differ by the substitution of a hydrogen instead of a chlorine at the aluminum; however, the crystals of **1** and **3a** are not isomorphous. Nonetheless, the Al−Cl and Al−C bond lengths are very similar in the two compounds. The Al−H

Scheme 1. Summary of Relationships among Compounds **1**−**6**



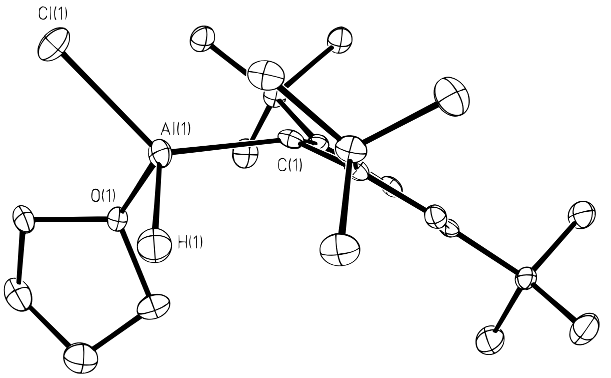


Figure 3. Thermal ellipsoidal plot (30%) of **3a**. H atoms are omitted for clarity.

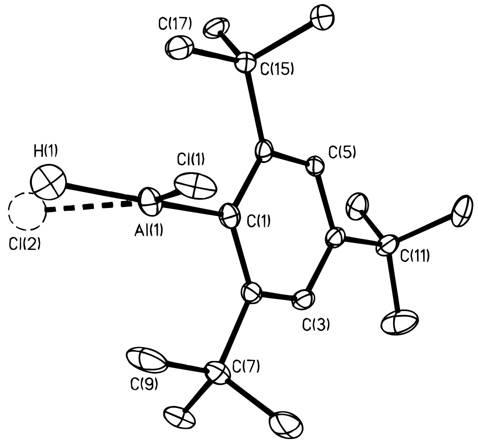


Figure 4. Thermal ellipsoidal plot (30%) of one of the independent molecules of **4b**. H atoms are omitted for clarity.

distance is 1.73(5) Å which is *ca.* 0.2 Å longer than the terminal Al−H bond in $(Mes^*AlH_2)_2$[11] or Mes^*_2AlH.[6] The high standard deviations, however, makes such comparisons of limited value. The Al−O distance 1.908(3) Å is essentially identical to the value observed in **1**.

Desolvation of **3b** by heating under reduced pressure invariably afforded species of formula $Mes^*Al(H)_{0.64}(Cl)_{1.36}$ (**4b**) upon recrystallization. The amount of Cl always exceeded that of the aluminum hydrogen in several preparations. The ratio of Al−H to Mes* can be determined approximately by integration of the ^1H NMR signals. Different ratios of H:Cl are also observed in the X-ray crystal structure where the two crystallographically independent molecules have H−Cl compositions of $H_{0.85}Cl_{1.15}$ and $H_{0.43}Cl_{1.57}$. The positions of the partially occupied H(1)/Cl(2) and H(2)/Cl(4) are exchanged with respect to each other. The hydrogen atoms H(1) and H(2) deviate slightly from the averaged Cl_2AlC plane, and the Al−H distances are 1.45(12) and 1.61(6) Å in good agreement with the values in $(Mes^*AlH_2)_2$[11] and Mes_2AlH.[6] There is a 90° torsion angle between the aluminum coordination plane and the plane of the aromatic ring. In addition, there are short contacts (*ca.* 2.1 Å) between hydrogens from the ortho *t*-Bu groups and the Al centers. It is interesting to note that the structure of **4b** closely resembles those of **2** and Mes^*AlBr_2 and is in sharp contrast to the dimeric arrangement of $(Mes^*AlH_2)_2$. A dimeric structure of the type $Mes^*(Cl)Al(\mu\text{-}H)_2Al(Cl)Mes^*$ might have been expected for **4** especially in view of the relative strength of the Al−H−Al bridge in $(Mes^*AlH_2)_2$ (**6**) which is apparently not cleaved by nucleophiles like THF. It is also notable that **2** and **4b** are essentially isomorphous with very similar cell constants. In effect, the structure of **4b** may be most simply described as consisting of Mes*Al(H)Cl contaminated with some Mes^*AlCl_2.

Conclusion

Reaction of $[(THF)_2LiH_3AlMes^*]_2$ with an appropriate number of equivalents of Me_3SiCl affords various arylaluminum halides in good yield. Although ether complexes of Mes^*AlX_2 (X = Cl, Br) have not been isolated, it is possible to crystallize the THF-complexed species $Mes^*AlCl_2(THF)$ and Mes*Al(H)Cl(THF). These compounds are the first Lewis-base complexes of Mes*-substituted Al derivatives. However, even the THF can be removed by mild heating under reduced pressure. The relatively weak coordinating ability of the Al center with regard to Et_2O or THF is due to the large size of the Mes* substituent and the presence of agostic interactions involving the metal and C−H bonds from the ortho *t*-Bu groups.

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Supporting Information Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (35 pages). Ordering information is given on any current masthead page.

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