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New Base-Free Alanes and Gallanes: Synthesis and Characterization of Monomeric Mes^*_2GaH ($Mes^* = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$), Dimeric $(Trip_2MH)_2$ ($Trip = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$; M = Al, Ga), and Related Sterically Crowded Arylaluminum Species

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The synthesis and characterization of several hydrido derivatives of aluminum and gallium which have bulky aryl substituents are described. The neutral derivatives Mes^*_2GaH (**1**), $(Trip_2GaH)_2$ (**2**), and $(Trip_2AlH)_2$ (**3**) ($Mes^* = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$; $Trip = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$) were synthesized by the reaction of *t*-BuLi with the corresponding halide derivatives. The X-ray crystal structures of **1**−**3** were also determined, and these showed that **1** was monomeric whereas **2** and **3** were dimeric with hydrogen bridging. VT NMR data for **2** indicated that it underwent significant dissociation in solution whereas **3** remains almost completely associated in toluene-d_8 at room temperature. The synthesis and structural characterization of the aluminate species $[TriphAlH_3Li(Et_2O)_{1.5}]_2$ (**4**) ($Triph = 2,4,6\text{-}Ph_3C_6H_2$) and $[Mes^*AlH_3Li(THF)_2]_2$ (**5**) and the neutral adduct $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3AlH_2(NMe_3)]$ (**6**) are also reported. These compounds are of importance in the synthesis of neutral uncomplexed hydrido derivatives. Crystal data at 130 K with Cu Kα (**1**−**3**, $\lambda = 1.541\,78$ Å) or Mo Kα (**4**−**6**, $\lambda = 0.710\,73$ Å) radiation: **1**, $C_{36}H_{59}Ga$, $a = 9.919(2)$ Å, $b = 29.443(3)$ Å, $c = 11.388(2)$ Å, $\beta = 94.72(2)°$, monoclinic, space group $P2_1/c$, $Z = 4$, $R = 0.044$ for 3694 ($I > 2\sigma(I)$) data; **2**, $C_{60}H_{94}Ga_2$, $a = 14.994(7)$ Å, $b = 10.263(4)$ Å, $c = 37.375(13)$ Å, $\beta = 95.56(3)°$, monoclinic, space group $P2_1/c$, $Z = 4$, $R = 0.068$ for 6112 ($I > 2\sigma(I)$) data; **3**·PhMe, $C_{67}H_{102}Al_2$, $a = 21.254(4)$ Å, $b = 23.318(3)$ Å, $c = 25.197(3)$ Å, orthorhombic, space group *Ibca*, $Z = 8$, $R = 0.069$ for 3244 ($I > 2\sigma(I)$) data; **4**, $C_{60}H_{70}Al_2Li_2O_3$, $a = 21.960(9)$ Å, $b = 15.835(7)$ Å, $c = 16.363(5)$ Å, $\beta = 102.30(3)°$, monoclinic, space group $C2/c$, $Z = 4$, $R = 0.073$ for 4011 ($I > 3\sigma(I)$) data; **5**, $C_{52}H_{96}Al_2Li_2O_4$, $a = 13.882(4)$ Å, $b = 19.038(5)$ Å, $c = 10.534(3)$ Å, $\beta = 101.02(2)°$, monoclinic, space group $P2_1/c$, $Z = 2$, $R = 0.084$ for 2703 ($I > 2\sigma(I)$) data; **6**, $C_{29}H_{40}AlN$, $a = 6.225(2)$ Å, $b = 17.016(2)$ Å, $c = 12.668(3)$ Å, $\beta = 102.57(2)°$, monoclinic, space group $P2_1$, $Z = 2$, $R = 0.035$ for 2883 ($I > 2\sigma(I)$) data.

Introduction

A recent review[1] has described the current state of knowledge of base-free, unsaturated hydride derivatives of Al−Tl as a "wasteland" compared to that of boron hydrides. A small number of results obtained over the past few years have, however, suggested that this situation is in the process of changing rapidly.[1,2] In particular, the use of sterically crowding groups and the availability of a new generation of unassociated metal halide precursors[3−6] suggest that a new advance in the chemistry of heavier main group 3 hydride derivatives is beginning. Normally, the neutral metal hydride derivatives are strongly associated as exemplified by the structures of the binary hydride derivatives $[AlH_3]_n$[7] or $[GaH_3]_n$.[8] Substituted derivatives, exemplified by the gas phase structures of $[Me_2GaH]_2$[9] or $[H_2Ga(\mu\text{-}NMe_2)]_2$[10] or the solid state structures of $[t\text{-}Bu_2AlH]_3$[11] or $[(TMP)_2AlH]_2$[12] (TMP = 2,2,6,6-tetramethylpiperidyl) show that the degree of aggregation may be reduced considerably by the use of crowding groups. The long Al−H distances in the latter compound were interpreted to indicate that dissociation into monomers was possible, and an IR spectrum of the monomeric $(TMP)_2AlH$ was indeed obtained upon dilution in an argon matrix.[12] More recent results have shown that the intramolecularly complexed hydride $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaH_2$[13] has terminal Ga−H bonds. In addition, use of the Mes* substituent on gallium which possesses an ortho *t*-Bu group which possibly interacts agostically with the metal has allowed the preparation[14] of Mes^*GaH_2 and $Mes^*(3,5\text{-}t\text{-}Bu_2C_6H_3CMe_2CH_2)GaH$ via the reaction of Mes^*GaCl_2[3,4] or Mes^*_2GaCl[5] ($Mes^* = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) with $LiGaH_4$. In this paper, the synthesis and characterization of the monomeric compound Mes^*_2GaH (**1**), the less crowded dimeric species $(Trip_2GaH)_2$ (**2**) and $(Trip_2AlH)_2$ (**3**) ($Trip = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$), the related aluminate species $[TriphAlH_3Li(OEt_2)_{1.5}]_2$ (**4**) ($Triph = 2,4,6\text{-}Ph_3C_6H_2$) and $[Mes^*AlH_3Li(THF)_2]_2$ (**5**), and the neutral $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3AlH_2(NMe_3)]$ (**6**) are reported. The neutral species **1**−**3** were synthesized by an alkene elimination

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Table 1. Crystallographic Data[a] for **1**−**6**

	1	**2**	**3**·PhMe	**4**	**5**	**6**
formula	$\mathrm{C_{36}H_{59}Ga}$	$\mathrm{C_{60}H_{94}Ga_2}$	$\mathrm{C_{67}H_{102}Al_2}$	$\mathrm{C_{60}H_{70}Al_2Li_2O_3}$	$\mathrm{C_{52}H_{96}Al_2Li_2O_4}$	$\mathrm{C_{29}H_{40}AlN}$
fw	561.6	954.8	961.5	907.0	853.0	429.6
color and habit	colorless plates	colorless needles	colorless blocks	colorless plates	colorless cubes	colorless prisms
cryst system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	*Ibca*	$C2/c$	$P2_1/c$	$P2_1$
a, Å	9.919(2)	14.994(7)	21.254(4)	21.960(9)	13.882(4)	6.225(2)
b, Å	29.443(3)	10.263(4)	23.318(3)	15.835(7)	19.038(5)	17.016(2)
c, Å	11.388(2)	37.375(13)	25.197(3)	16.363(5)	10.534(3)	12.668(3)
β, deg	94.72(2)	95.56(3)		102.30(3)	101.02(2)	102.57(2)
V, Å^3	3314.7(6)	5725(4)	12488(3)	5560(4)	2732.4(13)	1309.6(10)
Z	4	4	8	4	2	2
cryst dimens, mm	0.31 × 0.31 × 0.13	0.72 × 0.16 × 0.12	0.62 × 0.42 × 0.38	0.20 × 0.35 × 0.53	0.30 × 0.44 × 0.70	1.0 × 1.0 × 1.2
d_{calc}, g cm^{-3}	1.125	1.108	1.02	1.084	1.010	1.089
μ, mm^{-1}	1.263	1.386	0.674	0.093	0.091	0.093
no. of obsd rflcns	3694 ($I > 2\sigma(I)$)	6112 ($I > 2\sigma(I)$)	3244 ($I > 2\sigma(I)$)	4011 ($I > 3\sigma(I)$)	2703 ($I > 2\sigma(I)$)	2883 ($I > 2\sigma(I)$)
R, R_w	0.044, 0.052	0.068, 0.074	0.069, 0.174	0.073, 0.076	0.084, 0.115	0.035, 0.052

[a] Data were collected at 130 K with a Siemens R3m/V diffractometer using Mo Kα (λ = 0.710 73 Å) radiation (**4**−**6**) or with a Syntex P2$_1$ diffractometer using Cu Kα (λ = 1.547 18 Å) radiation (**1**−**3**).

route involving the treatment of the monohalide precursors with *t*-BuLi, whereas **4**−**6** were synthesized by the reaction of lithium aryls with various aluminum hydrides.

Experimental Section

General Procedures. All reactions were performed under $\mathrm{N_2}$ 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. $\mathrm{Mes^*{}_2GaCl}$,[5] $\mathrm{Trip_2GaBr}$,[3] $\mathrm{Trip_2AlBr}$,[3] $\mathrm{TriphLi(Et_2O)_2}$,[15] Mes*Br,[16] $\mathrm{AlH_3NMe_3}$,[17] and $\mathrm{IC_6H_3\text{-}2,6\text{-}(C_6H_4\text{-}4\text{-}}t\mathrm{\text{-}Bu)_2}$[18] were prepared by literature procedures. $\mathrm{LiAlH_4}$ was purified by crystallization from $\mathrm{Et_2O}$. 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. $\mathbf{Mes^*{}_2GaH}$ (**1**). A solution of 1.17 g (1.96 mmol) of $\mathrm{Mes^*{}_2GaCl}$ in ca. 40 mL of *n*-hexane was treated dropwise with 1.2 mL (2.0 mmol) of a pentane solution of 1.7 M *t*-BuLi with rapid stirring and cooling in an ice bath. The mixture was then allowed to come to room temperature and stirred overnight. Filtration, concentration to ca. 10 mL, and storage in a −20 °C freezer for 3 days afforded the product **1** as colorless crystals. Yield 0.50 g (46%). Mp: 147−152 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.44 (s, *m*-H, 4H), 1.38 (s, *o*-$\mathrm{CH_3}$, 36H), 1.33 (s, *p*-$\mathrm{CH_3}$, 18H). ^{13}C NMR (coupled) ($\mathrm{C_6D_6}$): δ 157.9 (s, br, *o*-C), 150.0 (m, *p*-C), 140.7 (d of t, *i*-C), $^2J_{\mathrm{C-H}}$ = 22.1 Hz (d), $^3J_{\mathrm{C-}m\mathrm{-H}}$ = 5.9 Hz (t), δ 122.1 (dd, *m*-C), $^1J_{\mathrm{C-H}}$ = 150.6 Hz, $^3J_{\mathrm{C-}m\mathrm{-H}}$ = 6.2 Hz, δ 38.6 (s, br, *o-C* ($\mathrm{CH_3)_3}$), 34.7 (s, br, *p-C* ($\mathrm{CH_3)_3}$), 33.3 (qm, *o*-$\mathrm{CH_3}$), $^1J_{\mathrm{C-H}}$ = 125.4 Hz, δ 31.5 (qm, *p*-$\mathrm{CH_3}$), $^1J_{\mathrm{C-H}}$ = 125.7 Hz. IR: $\nu_{\mathrm{Ga-H}}$ 1867 cm^{-1} (s).

($\mathbf{Trip_2GaH}$)$_2$ (**2**). A solution of 1.62 g (2.9 mmol) of $\mathrm{Trip_2GaBr}$ in *n*-hexane (40 mL) was treated dropwise with 1.8 mL (3.06 mmol) of a 1.7 M *t*-BuLi solution in pentane with cooling in an ice bath. The solution became yellow, and after warming to room temperature, it was stirred for a further 16 h. Filtration of the pale yellow solution, concentration to ca. 10 mL, and cooling in a −20 °C freezer for 2 days afforded 0.50 g of pale yellow needles. Concentration of the mother liquor and subsequent crystallization led to another 0.35 g of crude **2**. Recrystallization from *n*-hexane or toluene afforded **2** as colorless crystals. Yield: 0.85 g (61%). Mp: 192−4 °C (melts with gas evolution and turns gray). Crystals suitable for X-ray diffraction were grown in an NMR tube from a concentrated solution in $\mathrm{C_7D_8}$ at room temperature (90 mg in ca. 0.4 mL) over a period of 1 week. ^{1}H NMR ($\mathrm{C_6D_6}$), 20 °C: δ 7.03 (s, *m*-H, 8H), 6.09 (s, μ-H, 2H), 3.30 (s, br, $\Delta\nu_{1/2} \approx$ 60 Hz, *o*-CH, 8H), 2.73 (sept, *p*-CH, 4H), $^3J_{\mathrm{HH}}$ = 6.9 Hz, δ 1.47 (s, br, *o*-$\mathrm{CH_3}$, 12H), 1.36 (s, br, *o*-$\mathrm{CH_3}$, 12H), 1.16 (d, *p*-$\mathrm{CH_3}$, 24H), 1.02 (s, br, *o*-$\mathrm{CH_3}$, 12H), 0.58 (s, br, *o*-$\mathrm{CH_3}$, 12H). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 1.55.2 (*o*-C), 150.0 (*p*-C), 140.9 (*i*-C), 121.9 (s, br, *m*-C), 121.1 (s, br, *m*-C), 39.0 (s, br, *o*-CH), 37.8 (s, br, *o*-CH), 34.7 (*p*-CH), 24.7 (s, br, *o*-$\mathrm{CH_3}$), 24.1 (*p*-$\mathrm{CH_3}$). IR: $\nu_{\mathrm{Ga-H}}$ ~1180 cm^{-1} (st, br, ca. 1000−1300 cm^{-1}), 1755 cm^{-1} (w).

($\mathbf{Trip_2AlH}$)$_2$ (**3**). A solution of 0.53 g (1.0 mmol) of $\mathrm{Trip_2AlBr}$ in 20 mL of *n*-hexane was treated dropwise with 0.6 mL (1.0 mmol) of a 1.7 M *t*-BuLi solution in pentane with cooling in an ice bath. A finely divided colorless solid began to precipitate immediately. The mixture was then warmed to room temperature and stirred overnight. After some colorless needle-shaped crystals, which had formed at the flask wall, were redissolved, the mixture was filtered, concentrated to ca. 10 mL, and cooled to −20 °C for 2 days to afford 0.30 g (yield 69%) of colorless needles of **3**. Mp: turns opaque at 230 °C, melts with gas evolution at 245−7 °C, and decomposes into a gray material. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.01 (s, *m*, 4H), 6.98 (s, *m*-H, 4H), 5.61 (s, μ-H, 2H), 3.24, 3.22 (2 sept, *o*-CH, 8H), $^3J_{\mathrm{HH}}$ = 6.6 Hz, δ 2.73 (sept, *p*-CH, 4H), $^3J_{\mathrm{HH}}$ = 6.9 Hz, δ 1.51 (d, *o*-$\mathrm{CH_3}$, 12H), 1.37 (d, *o*-$\mathrm{CH_3}$, 12H), 1.18, 1.15 (2d, *p*-$\mathrm{CH_3}$, 24H), 1.05 (d, *o*-$\mathrm{CH_3}$, 12H), 0.55 (d, *o*-$\mathrm{CH_3}$, 12H). ^{13}C {^{1}H} NMR ($\mathrm{C_6D_6}$): δ 157.3, 157.0 (*o*-C), 150.6 (*p*-C), 138.0 (br, *i*-C), 121.9, 120.4 (*m*-C), 41.0, 39.0 (*o*-CH), 34.8 (*p*-C), 25.8, 25.4, 24.5, 24.1 (*o*-$\mathrm{CH_3}$), 24.2. (*p*-$\mathrm{CH_3}$). IR: $\nu_{\mathrm{Al-H}}$ 1350 cm^{-1} (st, br, 1150−1450 cm^{-1}, partially obscured by $\delta_{\mathrm{CH_3}}$ of **3** and mineral oil, 1760 cm^{-1} (w). Crystals suitable for X-ray crystallography were grown from a concentrated toluene solution in a −20 °C freezer over a period of 2 weeks.

[$\mathbf{TriphAlH_3Li(OEt_2)_{1.5}}$]$_2$ (**4**). A solution of 0.92 g (2.0 mmol) of $\mathrm{TriphLi(OEt_2)_2}$ in 50 mL of $\mathrm{Et_2O}$ was added to a solution of 0.076 g (2.0 mmol) of $\mathrm{LiAlH_4}$ in $\mathrm{Et_2O}$ (30 mL) at room temperature. A fine colorless precipitate (LiH) was formed immediately. After being stirred for a further 5 h, the mixture was kept at 5 °C for 2 days to allow the precipitate to settle. Filtration, concentration, and cooling to −20 °C for a week afforded 0.51 g (56% yield) of **4** as colorless crystals. Mp: 114 °C (melts with gas evolution). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.77 (s, *m*-H, 4H), 7.73 (d), J = 7.1 Hz, δ 7.62 (d), J = 7.2 Hz, δ 7.24 (q), J = 7.3 Hz, δ 7.13 (m, obscured by $\mathrm{C_6D_5H}$)- (aryl H, ~34H), 3.11 (q, $\mathrm{OCH_2}$, 12H), $^3J_{\mathrm{HH}}$ = 6.9 Hz, δ 2.51 (s, br, $\Delta\nu_{1/2} \approx$ 60 Hz, Al−H, 6H), 0.94 (t, $\mathrm{CH_3}$, 18H). IR: $\nu_{\mathrm{Al-H}}$ 1710 cm^{-1} st, vbr, 1550−1850 cm^{-1}).

[$\mathbf{Mes^*AlH_3Li(THF)_2}$]$_2$ (**5**). Mes*Li was generated in situ by the addition of *n*-BuLi (1.6 M in hexanes, 9.4 mL, 15 mmol) to a well-stirred solution of Mes*Br (4.88 g, 15 mmol) in a 10:1 pentane−tetrahydrofuran mixture (50 mL) with cooling in a dry ice bath. After 2 h, a precipitate formed which was allowed to settle. The supernatant liquid was removed via cannula. The remaining precipitate was dissolved in diethyl ether, and the solution was cooled in a dry ice bath. After 2 h of stirring, $\mathrm{AlH_3(NMe_3)}$ (1.34 g, 15 mmol) was added via solid-addition funnel. The solution was allowed to warm slowly to room temperature and stirred overnight. The volume was reduced to incipient crystallization. Cooling overnight in a −30 °C freezer produced large colorless crystals of **5** in ca. 80% yield. Mp: 140 °C followed by desolvation, leaving a colorless solid which decomposes at 250 °C to a gray solid. IR (Nujol, ν in cm^{-1}): 1755 s, 1650 s, 1585

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m, 1515 m, 1295 w, 1240 s, 1210 w, 1190 m, 1165 m, 1125 m, 1045 s, 935 w, 915 w, 870 s, 780 s, 750 w, 660 w, 645 m, 600 s, 475 m, 320 s. ^{1}H NMR (300 MHz, PhMe-d_8): δ 1.37 (s, 8H, THF), 1.40 (s, 9H, 4-*t*-Bu), 1.77 (s, 18H, *o*-*t*-Bu), 3.44 (s, 8H, THF), 3.81 (s, 3H, Al−H), 7.44 (s, 2H, *m*-H). ^{13}C NMR (75.5MHz, PhMe-d_8): δ 25.5 (s, THF), 32.1 (s, *p*-CH_3), 34.1 (s, *o*-CH_3), 34.7 (s, *p*-*C*$(CH_3)_3$, 39.4 (s, *o*-*C*$(CH_3)_3$, 68.5 (s, THF), 120.1 (s, *m*-C), 147.2 (s, *p*-C), 160.4 (s, *o*-C).

[2,6-(Ph-4-*t*-Bu)$_2$C$_6$H$_3$AlH$_2$(NMe$_3$)] (6). IC_6H_3-2,6-(Ph-4-*t*-Bu)$_2$ (2.34 g, 5 mmol) was dissolved in 30 mL of diethyl ether, and the solution was treated with *n*-BuLi (1.6 M in hexanes, 3.1 mL, 5 mmol) with cooling in an ice bath. After 2 h of stirring the solution was added dropwise to $AlH_3(NMe_3)$ (0.45 g, 5 mmol) in 20 mL of diethyl ether. The mixture became cloudy and was left to stir overnight. The mixture was filtered through a fine porosity frit, and the volume was reduced to incipient crystallization. Cooling overnight in a −30 °C freezer produced colorless crystals of **6** in ca. 75% yield. Mp: 160 °C (with immediate loss of NMe_3); a white solid forms which decomposes above 325 °C. IR (Nujol, ν in cm^{-1}): 1935 w, 1920 w, 1910 w, 1890 w, 1860 w, 1780 br, s, 1570 w, 1560 w, 1545 w, 1505 m, 1305 w, 1265 m, 1235 m, 1200 m, 1170 w, 1110 s, 1020 s, 995 s, 965 w, 945 w, 920 m, 900 w, 845 s, 830 s, 800 s, 700 br, s, 605 m, 570 s, 550 m, 515 s, 475 m, 425 w, 400 m, 380 m, 350 m, 295 s. ^{1}H NMR (300 MHz, Tol-d_8): δ 1.27 (s, 18H, *p*-*t*-Bu), 1.37 (s, 9H, NMe_3), 3.85 (br, s, 2H, Al−H), 7.34−7.44 (m, 7H, aryl H) 7.67 (d, 4H, *m*-(*t*-BuPh)). ^{13}C NMR (75.5 MHz, C_7D_8): δ 31.6 (s, *p*-CH_3), 34.5 (s, *p*-*C*$(CH_3)_3$), 47.9 (s, NMe_3), 125.3−130.2 (various −CH carbons), 144.8−153.4 (various quaternary carbons).

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 stream as described in ref 19.

All data were collected near 130 K with either a Syntex $P2_1$ (using Cu Kα, λ = 1.541 78 Å radiation) in the cases of **1**−**3** or with a Siemens R3m/v diffractometer (using Mo Kα, λ = 0.710 73 Å radiation) in the cases of **4**−**6**. Both diffractometers were equipped with a graphite monochromator and a locally modified Enraf-Nonius universal low-temperature device for low-temperature work.

Crystallographic programs used for the structure solutions of **1**, **2**, and **4**−**6** and refinements were those of SHELXTL-Plus installed on a MicroVax 3200 workstation. The structure of **3** was solved using SHELXTL-93 installed on an IBM 486 computer. Scattering factors were obtained from ref 20a. An absorption correction was applied by using the method described in ref 20b. 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 supplementary material. 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 $U_H \cong 1.3U_C$. Hydrogen atoms bound to aluminum or gallium were located on Fourier difference maps and, with the exception of those in **3**, were allowed to refine freely with fixed isotropic parameters. The structures of **2**−**5** were also subject to minor disorder problems. In the case of **2**, several of the carbon atoms of the C(16) Trip group as well as the methyl groups of a *p*-*i*-Pr substituent of the C(46) Trip group were found to occupy two positions and were refined with 50% occupancy in each.

For **3**, the C(26) of the *p*-*i*-Pr group was found to be disordered and refined with partial occupancies of 50.16 and 49.84%. The toluene molecule in the structure of **3**·PhMe was also disordered around a C_2 axis through C(41) and refined with partial occupancies for C(40)−

Table 2. Atom Coordinates (*x*, *y*, *z*; ×10^4) for Important Atoms in **1**−**6**

Compound **1**			
Ga	1552(1)	3721(1)	3448(1)
H(1)	421(49)	3563(16)	4246(40)
C(1)	3247(4)	3384(1)	3958(3)
C(2)	4220(3)	3564(1)	4801(3)
C(6)	3504(3)	2949(1)	3473(3)
C(7)	4026(4)	4002(1)	5553(3)
C(8)	4006(4)	3858(1)	6854(3)
C(9)	5182(4)	4340(1)	5439(3)
C(10)	2094(4)	4249(1)	5223(3)
C(15)	2485(4)	2668(1)	2668(3)
C(16)	1294(4)	2943(1)	2080(3)
C(17)	3167(4)	2439(1)	1652(3)
C(18)	1897(4)	2304(1)	3426(3)
C(19)	1040(3)	4107(1)	2020(3)
C(20)	1840(4)	4118(1)	1042(3)
C(24)	−367(3)	4202(1)	635(3)
C(25)	3406(3)	4153(1)	1119(3)
C(26)	3971(4)	4349(1)	2314(3)
C(27)	4007(4)	3094(1)	914(3)
C(28)	3837(4)	4488(1)	177(3)
C(33)	−1338(3)	4337(1)	2741(3)
C(34)	−2264(4)	4730(1)	2262(3)
C(35)	−617(4)	4523(1)	3883(3)
C(36)	−2248(4)	3934(1)	3014(3)
Compound **2**			
Ga(1)	2872(1)	8071(1)	1477(1)
Ga(2)	1406(1)	0562(1)	1049(1)
H(1)	1929(50)	7193(78)	1282(20)
H(2)	2237(50)	7270(77)	1303(19)
C(1)	2808(4)	8149(7)	2004(2)
C(16)	3908(5)	7559(7)	1219(2)
C(31)	290(4)	8701(6)	1290(2)
C(46)	1594(4)	8791(6)	540(2)
Compound **3**			
Al(1)	2561(1)	0	2500
Al(2)	1292(1)	0	2500
C(1)	2957(2)	574(1)	2029(1)
C(2)	2906(2)	592(2)	1469(1)
C(3)	3125(2)	1074(2)	1194(1)
C(4)	3385(2)	1543(2)	1447(1)
C(5)	3456(2)	1514(2)	1995(1)
C(6)	3251(2)	1040(1)	2285(1)
C(16)	892(2)	−434(2)	3086(1)
C(17)	924(2)	−1028(2)	3184(1)
C(18)	684(2)	−1249(2)	3659(1)
C(19)	406(2)	−909(2)	4043(2)
C(20)	351(2)	−327(2)	3936(1)
C(21)	585(2)	−88(2)	3468(1)
Compound **4**			
Al(1)	4043(1)	2971(2)	1379(1)
C(1)	3949(1)	2880(2)	128(2)
H(1)	3435(17)	2875(23)	1770(23)
H(2)	4366(18)	2167(23)	1754(24)
H(3)	4518(17)	3808(24)	1774(22)
Li(1)	5000	1633(6)	2500
O(1)	5121(3)	463(4)	2704(4)
Li(2)	5000	4395(6)	2500
O(2)	5563(1)	5028(2)	1949(2)
Compound **5**			
Al(1)	6196(1)	9707(1)	1971(1)
Li(1)	5054(6)	9144(5)	−605(9)
H(1a)	6069(39)	9707(29)	472(54)
H(1b)	5942(36)	8967(29)	2390(50)
H(1c)	5371(38)	10251(28)	2223(52)
C(1)	7541(3)	10041(3)	2878(5)
O(1)	5730(3)	8374(2)	−1313(4)
O(2)	3981(3)	8611(2)	−157(4)
Compound **6**			
Al(1)	2238(1)	7152(1)	3457(1)
C(1)	−346(3)	6428(1)	2940(2)
N(1)	781(3)	8078(1)	4047(2)
H(1)	3272	7568	2595
H(2)	4099	6962	4472

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(19) 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.

(20) (a) *International Tables for Crystallography*; D. Reidel Publishing Co.: Dordrechtt, The Netherlands, 1993; Vol. C. (b) Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds **1**−**6**

	Compound **1**		
Ga−C(1)	1.995(3)	C(1)−Ga−C(19)	131.9(1)
Ga−C(19)	2.009(3)	C(1)−Ga−H(1)	108.0(1.7)
Ga−H(1)	1.572(48)	C(19)−Ga−H(1)	119.2(1.6)
	Compound **2**		
Ga(1)- -Ga(2)	2.638(2)	C(1)−Ga(1)−C(16)	127.7(3)
Ga(1)−C(1)	1.983(7)	C(31)−Ga(2)−C(46)	129.6(3)
Ga(1)−C(16)	1.979(7)	Ga(1)−H(1)−Ga(2)	95.5(3.7)
Ga(2)−C(31)	1.978(7)	Ga(1)−H(2)−Ga(2)	105.7(4.4)
Ga(2)−C(46)	1.966(7)	H(1)−Ga(1)−H(2)	79.9(3.6)
Ga(1)−H(1)	1.773(76)	H(1)−Ga(2)−H(2)	78.3(3.6)
Ga(1)−H(2)	1.650(70)		
Ga(2)−H(1)	1.792(70		
Ga(2)−H(2)	1.659(70)		
	Compound **3**		
Al(1)- -Al(2)	2.698(2)	Al(1)−C(1)	1.977(3)
C(1)−C(2)	1.414(5)	Al(2)−C(16)	1.982(3)
C(4)−C(5)	1.393(5)	C(1)−C(6)	1.409(5)
C(5)−C(6)	1.394(5)	C(2)−C(3)	1.401(5)
C(16)−C(17)	1.408(5)	C(3)−C(4)	1.380(5)
C(17)−C(18)	1.398(5)	C(16)−C(21)	1.415(5)
C(18)−C(19)	1.383(5)	C(19)−C(20)	1.388(5)
C(1)−Al−C(1)′	129.7(2)	C(20)−C(21)	1.395(5)
C(16)−Al−C(16)′	129.3(2)		
	Compound **4**		
Al(1)−C(1)	2.018(4)	H(1)−Al(1)−C(1)	119.8(1.3)
Al(1)−H(1)	1.545(41)	H(2)−Al(1)−C(1)	106.7(1.5)
Al(1)−H(2)	1.521(35)	H(1)−Al(1)−H(2)	96.0(2.1)
Al(1)−H(3)	1.725(35)	H(1)−Al(1)−H(3)	113.9(1.9)
Li(1)−H(2)	1.849(35)	H(2)−Al(1)−H(3)	107.4(1.8)
Li(2)−H(3)	1.692(35)	H(2)−Li(1)−H(2a)	125.6(2.3)
Li(1)−O(1)	1.892(11)	Li(1)−H(2)−Al(1)	150.4(2.4)
Li(2)−O(2)	1.954(6)	Li(2)−H(3)−Al(2)	157.5(2.4)
		O(2)−Li(2)−O(2a)	118.4(5)
	Compound **5**		
Al(1)−C(1)	2.030(5)	C(1)−Al(1)−H(1a)	113.2(20
Al(1)−H(1a)	1.555(57)	C(1)−Al(1)−H(1b)	113.1(17)
Al(1)−H(1b)	1.537(55)	C(1)−Al(1)−H(1c)	110.0(18)
Al(1)−H(1c)	1.603(55)	H(1a)−Al(1)−H(1b)	107.7(28)
Li(1)−H(1a)	1.953(51)	H(1a)−Al(1)−H(1c)	102.8(28)
Li(1)−H(1c)	2.048(53)	H(1b)−Al(1)−H(1c)	109.5(28)
Li(1)−O(1)	1.962(11)	Al(1)−H(1a)−Li(1)	121.1(31)
Li(1)−O(2)	1.934(11)	Al(1)−H(1c)−Li(1a)	109.3(28)
Li(1)- -Al(1)	3.063(9)	H(1)−Li(1)−H(1a)	103.5(21)
Al(1)- -Li(1a)	2.986(9)	O(1)−Li(1)−O(2)	98.5(5)
	Compound **6**		
Al(1)−C(1)	2.018(2)	C(1)−Al(1)−H(1)	118.5(10)
Al(1)−N(1)	2.039(3)	C(1)−Al(1)−H(2)	122.3(11)
Al(1)−H(1)	1.626(34)	H(1)−Al(1)−H(2)	108.0(14)
Al(1)−H(2)	1.583(23)	N(1)−Al(1)−C(1)	101.8(1)
		N(1)−Al(1)−H(1)	102.8(12)
		N(1)−Al(1)−H(2)	99.3(11)

C(42), C(44), and C(45). The bridging hydride atoms in **3** appear to be asymmetric with respect to the Al atoms. Due to the crystallographic 2-fold axis passing through the two Al's, any asymmetry in the hydride positions gives rise to disorder. Several refinement strategies were used in order to define the hydride positions, but all resulted in poor convergence and the presence of extra difference map intensity. This is not unexpected, since the separation between the two hydride positions is small (<0.4 Å) and the overall contribution to the scattering is minimal. If the hydride is modeled as a single anisotropic atom, it becomes non-positive definite. Consequently, the two most consistently appearing hydride sites were assigned 0.5 occupancy and their positions fixed using a fixed isotropic thermal parameter of 0.04 Å^2 for each.

In **4**, the ether molecule attached to Li(1) was disordered and modeled on the basis of equal occupancy of two sites. In addition, a *p*-*t*-Bu group of the Mes* substituent showed rotational disorder and was refined successfully with carbon site occupancies as described in the supplementary material.

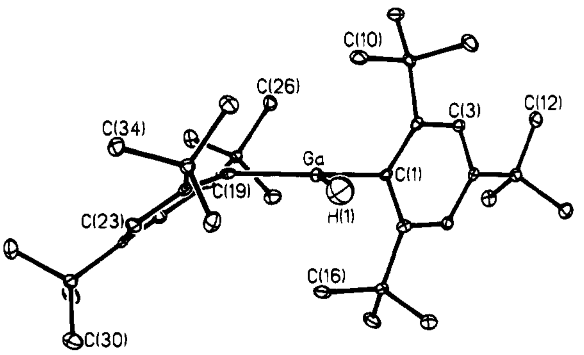

Figure 1. Computer-generated thermal ellipsoid plot (30%) of **1**. Hydrogen atoms, except the one bound to gallium, are omitted for clarity.

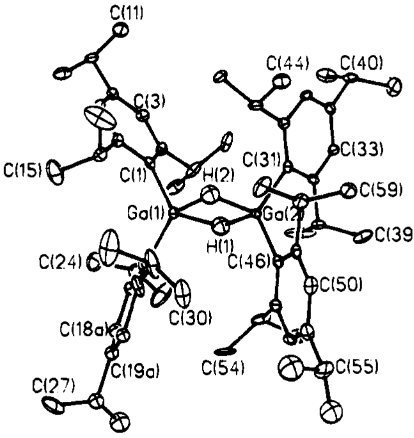

Figure 2. Thermal ellipsoid plot (30%) of **2**. Hydrogen atoms except those bound to gallium, are omitted for clarity.

Results

Syntheses. The neutral compounds **1**−**3** were synthesized by treatment of the corresponding halide with *t*-BuLi to afford the product with concomitant elimination of isobutene and lithium halide. In each case, the reaction proceeded smoothly in good (50−70%) yield. The aluminate compounds **4** and **5** were synthesized by using the aryllithium reagent in conjunction with $LiAlH_4$ or AlH_3NMe_3. It was found that **4** and **5** crystallized best with ether (**4**) and THF (**5**) donors. The neutral adduct **6** probably results from the reaction of $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2\text{-}C_6H_3AlH_3(LiOEt_2)_n]_m$ with *n*-BuI to give LiI, *n*-BuH, and **6**.

Structural Descriptions. Mes*$_2$GaH (1). The crystallographic data for **1** show that the structure (Figure 1) consists of noninteractive monomers of formula Mes*$_2$GaH. There is no crystallographically required symmetry. The gallium is coordinated in an essentially trigonal planar fashion (Σ°Ga = 359.1°) by two Mes* groups and a hydrogen. The C−Ga−C angle 131.9(1)° is significantly wider than either of the C−Ga−H angles, which have the values 108.0(1.7)° for C(1)-Ga−H(1) and 119.2(1.6)° for C(19)-Ga−H(1). A feature of the structure is the distortion from normal geometry in the Ga−C(19)Mes* ring moiety. For example, there is an angle of 33.6° between the Ga−C(19) and C(19)- -C(24) vectors. The Ga−C distances, 1.995(3) and 2.009(3) Å, are almost equal and the Ga−H distance is 1.572(48) Å. In addition, three hydrogens (from *o*-*t*-Bu groups) are found at distances of 2.00 Å (H(16b)), 2.35 Å (H(10b)), and 2.37 Å (H(10c)). There is an angle of 88.1° between the perpendiculars to the averaged plane of the C(1) ring and the coordination plane at gallium.

(Trip$_2$GaH)$_2$ (2). Molecules of **2** (Figure 2) are dimerized through hydrogen bridging in the solid state. Each gallium is

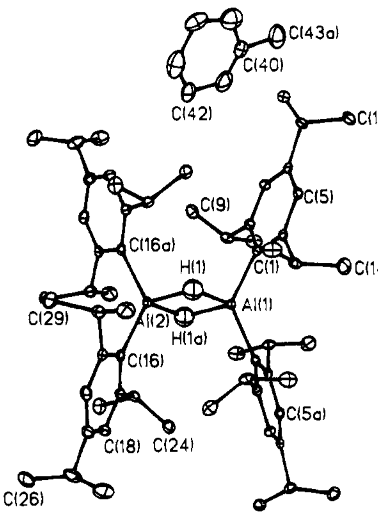

Figure 3. Thermal ellipsoid plot (30%) of **3**·PhMe. Hydrogen atoms, except those bound to aluminum, are omitted for clarity. The bridging hydrogen is depicted in one of the disordered positions.

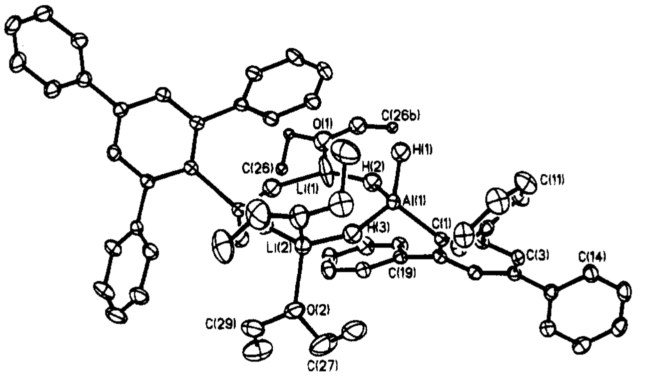

Figure 4. Thermal ellipsoid plot (30%) of **4**. Hydrogen atoms, except those bound to aluminum, are omitted for clarity.

four-coordinate and bound to two bridging hydrogens and two terminal Trip groups. The average Ga–C distance is 1.977(5) Å. The Ga–H bond lengths range from 1.650(70) to 1.792(70) Å. The Ga_2H_2 core of the molecule is approximately planar with the more acute internal angles averaging 79(4)° at the galliums. The Ga- -Ga separation is 2.638(2) Å.

$(Trip_2AlH)_2$·PhMe (3·PhMe). The structure of 3·PhMe (Figure 3) is very similar to that of **2** although the crystals are not isomorphous. In addition, there is a crystallographically required 2-fold symmetry axis along the Al···Al vector and a noninteracting molecule of toluene per dimeric unit. The average Al–C distance and C–Al–C angle are 1.979(4) Å and 129.7(2)°. The Al–H distances and the internal angles in the Al_2H_2 unit are of limited significance owing to the disorder problem described above. The Al- -Al separation is 2.698(2) Å.

$[TriphAlH_3Li(OEt)_{1.5}]_2$ (4). Molecules of **4** (Figure 4) have a crystallographically imposed 2-fold axis of rotation along the Li(1)–Li(2) vector. The core of the molecule is composed of a puckered $Al_2Li_2H_4$ eight-membered ring with bridging hydrogens (Li–H = 1.77(4) Å (average), Al–H = 1.62(4) Å (average)). The terminal Al–H distance is 1.545(41) Å. Remarkably, Li(1) is bound to only one Et_2O molecule (Li(1)–O(1) = 1.892(11) Å), whereas Li(2) is coordinated by the expected two Et_2O molecules (Li(2)–O(2) = 1.954(6) Å).

$[Mes^*AlH_3Li(THF)_2]_2$ (5). This molecule (Figure 5) possesses a crystallographically required center of symmetry. The two H_3AlMes^* units are bridged by two lithiums, such that two hydrogens at each aluminum act as bridges to two separate lithium atoms whereas the remaining hydrogen is terminally bound. The core of the molecule is thus composed of a puckered $Al_2Li_2H_4$ ring. The aluminums, which are bound to two bridging hydrogens, a terminal hydrogen, and a Mes* group, are four-coordinate. The lithiums are bound to two bridging hydrogens and two THF molecules. The Al–C distance is 2.030(5) Å, and the bridging and terminal Al–H distances average 1.57(6) Å. The bridging Li–H distances are 1.95(5) and 2.05(5) Å. The Li–O distances are 1.934(11) and 1.962(11) Å.

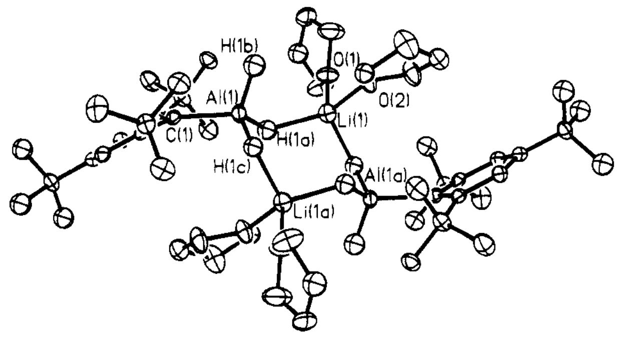

Figure 5. Thermal ellipsoid plot (30%) of **5**. Hydrogen atoms, except those bound to aluminum, are omitted for clarity.

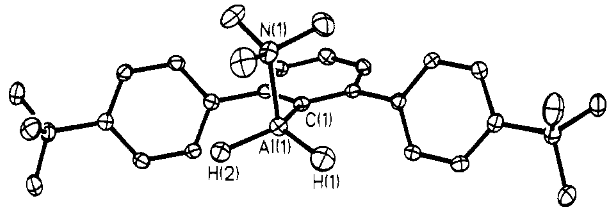

Figure 6. Thermal ellipsoid plot (30%) of **6**. Hydrogen atoms, except those bound to aluminum, are omitted for clarity.

$[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3AlH_2(NMe_3)]$ (6). This molecule (Figure 6) crystallizes as monomers. The aluminum is coordinated, in a distorted tetrahedral fashion, to the aryl group (Al–C(1) = 2.018(2) Å), two terminal hydrogens (Al–H (average 1.60(3) Å), and an NMe_3 donor (Al–N = 2.039(3) Å. Important angular data are given in Table 3.

Discussion

The major objective of the work described here was to develop simple routes to unassociated hydride derivatives of the heavier main group 3 elements. Recent work has shown that it is possible to use bulky aryl groups to synthesize unassociated aryl halide derivatives of aluminum, gallium, and indium.[3-6] Such compounds are normally strongly associated through halide bridging. However, employment of groups such as Trip($2,4,6\text{-}i\text{-}Pr_3C_6H_2$) or Mes*($2,4,6\text{-}t\text{-}Bu_3C_6H_2$) can prevent such bridging and in many instances block the formation of Lewis acid–base complexes with donors such as Et_2O or THF.[3] These observations suggested that it should be possible to achieve similar results for corresponding hydride and related derivatives. While the work described here was being written up, the syntheses and structures of the unassociated compounds Mes^*GaH_2 (**7**) and $(Mes^*)(3,5\text{-}t\text{-}Bu_2C_6H_3CMe_2CH_2)GaH$ (**8**) (which is an isomer of **1**) were reported.[14] These compounds were synthesized by the reaction of $LiGaH_4$ with Mes^*GaCl_2 or Mes^*_2GaCl. In this paper, a different synthetic route to the related compounds Mes_2GaH (**1**) and $(Trip_2MH)_2$ (M = Ga (**2**), Al (**3**)) is described. In addition, the syntheses and structures of two hindered aluminate species, which are possible precursors for neutral alanes of formula $ArAlH_2$ (Ar = Mes*[21] or Triph), and the neutral compound $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3AlH_2(NMe_3)]$ are described.

Compound **1** was synthesized, with elimination of isobutene, from the reaction of $Mes^*{}_2GaCl$ with *t*-BuLi, eq 1.

$$\text{Mes*}_2\text{GaCl} + t\text{-BuLi} \xrightarrow[0\ °\text{C}]{\text{hexane}} \text{LiCl} + \text{C}_4\text{H}_8 + \underset{\mathbf{1}}{\text{Mes*}_2\text{GaH}} \tag{1}$$

The mild reaction conditions are similar to those recently described[11] for the synthesis of the aluminum hydride $(t\text{-}Bu_2AlH)_3$ and are, presumably, a consequence of the great steric bulk of the organic substituents, which encourages elimination in order to ease steric congestion. Compound **1** is characterized by a strong IR band at 1867 cm^{-1} attributable to a terminal Ga−H bond stretch. Although the resonance for the hydrogen bound to gallium has not been observed in the ^1H NMR spectrum, there is indirect evidence for its presence in the ^{13}C NMR spectrum since it couples to the ipso carbons of the Mes* groups. The presence of a terminal Ga−H bond involving three-coordinate gallium was confirmed by the X-ray study in which the gallium hydrogen was located on a Fourier difference map and refined. The observed distance 1.572(48) Å is longer than the 1.43(10) Å recently reported[14] for **8**, but the difference is probably not significant owing to the relatively high standard deviations. This distance may also be compared to bond lengths in the range 1.49−1.59 Å for terminal Ga−H bonds in four- or five-coordinate Ga−H species.[9,10,13,22,23] The overall structure of **1** resembles those of $Mes^*{}_2GaCl$ (**9**)[5] and $Mes^*{}_2InCl$[6] most closely, particularly in the distortion at one of the Mes* groups in which the aromatic ring plane is bent by more than 30° from the Ga−C vector line. A similar distortion has been reported in the structure of the compound $Mes^*{}_2GaN(H)Ph$.[24] The remaining Mes* group in all these structures adopts a position such that there are close interactions between the metal and some of the hydrogens from ortho *t*-Bu groups. It is interesting to note that there was no evidence in the ^1H or ^{13}C NMR spectra of **1** for the existence of significant quantities of its isomer **8** when crystals of **1** were dissolved in toluene and heated to ca. 60−80 °C for a few hours.

The use of the less sterically crowding group Trip at gallium or aluminum allows the synthesis of **2** and **3** by a route that is essentially identical to that for **1**. The IR data for **2** showed a strong broad band at 1180 cm^{-1}, which is in a region appropriate for Ga−H bridging,[1] and a weak band at 1755 cm^{-1}. For **3**, a band, assigned to the bridging Al−H stretch, was observed at 1350 cm^{-1}. The ^1H NMR spectra of **2** and **3** in toluene-d_8, in addition to slightly broadened metal hydrogen peaks, show two sets of signals of equal intensity for the *o*- and *p*-CH groups as well as the meta C−H peaks (for **2** at −20 °C, for **3** at room temperature). The *o*-CH_3 resonances are observed as a set of four signals of equal intensity in the ^1H and $^{13}C\{^1H\}$ NMR spectra under these conditions. VT ^1H and ^{13}C NMR studies of **2** and **3** showed that in the case of **2** signals coalesce at ca. 40−50 °C to afford a barrier of 10.2 ± 2 kcal for the dynamic process.[25] For **3**, however, the corresponding peaks were only broadening (approaching coalescence) at temperatures as high as 115 °C, which leads to a barrier of at least 18.4 kcal mol^{-1} calculated for the *p*-$C(CH_3)_3$ peaks (at least 18.7 kcal mol^{-1} for the *m*-C). Coalescence for the *o*-C peaks occurs at 100 °C, giving a barrier of 19.0 kcal mol^{-1}, but this value is not very accurate due to the relatively low maximum peak separation of 24 Hz at room temperature. The metal hydrogen resonances in **2** and **3** were observed to shift slightly during the VT experiment, but no splitting was seen. These data were interpreted on the basis that **2** can dissociate to monomers in solution but that the aluminum compound **3** is more strongly associated due to the often greater Lewis acidity displayed by aluminum in comparison to gallium[26] (*cf.* the dimeric structure of Al_2Me_6[27] and the monomeric structure of $GaMe_3$[28]). Since the barriers for **2** and **3** are so different, it is unlikely that the dynamic process being observed is flipping of the Trip rings. The bridging Ga−H bonds in **2** are, as expected,[9] considerably longer than the terminal Ga−H distance seen in **1**. The large standard deviations, however, imply that caution needs to be used in interpreting such differences. The dissociation of **2** into monomers is apparently similar to the dissociation of the dimer $[(TMP)_2AlH]_2$ in an argon matrix. In addition, their unassociated structures should resemble that described for their monomeric, lighter, congener $Trip_2BH$.[29]

The structure of **3** bears a close resemblance to that of **2**. The disordered bridging Al−H distances were in the range 1.65(5)−1.94(5) Å. These values are comparable to those observed for $(t\text{-}Bu_2AlH)_3$ and $[(TMP)_2AlH]_2$. The Al- -Al separation is slightly longer than the Ga- -Ga distance, but both intermetallic distances are similar to those reported for the M−M single bonds in tetraalkyl- and tetraaryldimetalane compounds of formula R_2MMR_2 (M = Al, Ga; R = $-CH(SiMe_3)_2$[30] or Trip[31]).

The structures of the aluminate compounds **4** and **5**, although they were synthesized by different methods, have many similarities. Essentially, two $[ArAlH_3]^-$ (Ar = Triph, Mes*) are linked by two bridging Li^+ ions to form an eight-membered $Al_2Li_2H_4$ ring). The only significant difference in the structures relates to the solvation of the Li^+ ions which are both bound to two THF donors in **5**, whereas in **4** one of the Li^+ ions is solvated by one ether donor. The observation of the eight-membered $Al_2Li_2H_4$ rings has a precedent in the compound $[Li(Et_2O)H_3AlN(SiMe_3)_2]_2$.[32] The average Li−H distance of 2.00(5) Å in **5** is very similar to the values in $LiAlH_4$[33] or LiH[34] itself. The Al−H distances which are in the range 1.54−1.61 Å are similar to those observed in other aluminate species.[2]

The neutral adduct, compound **6**, resulted from the reaction between AlH_3NMe_3 and the lithium aryl. This synthetic method was very similar to that employed in the synthesis of **5**. In **5**, however, the NMe_3 donor was replaced by $[Mes^*]^-$ to give the $[H_3AlMes^*]^-$ anion. In **6**, LiI was probably eliminated along

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with *n*-BuH, and NMe_3 remains bound to a neutral AlH_2Ar moiety. The bond distances and angles observed in **6** are unremarkable and well within those observed for other amine complexes.[2,35]

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Supplementary Material Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1**, **2**, and **4**–**6** (54 pages). Ordering information is given on any current masthead page.

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