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Articles

Monomeric Alanes: Synthesis, Structure, and Thermolysis of Mes*Al(H)N($SiMe_3$)$_2$ and a One-Pot Synthetic Route to Mes*$_2$AlH (Mes* = $-C_6H_2$-2,4,6-*t*-Bu_3)

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The reaction of (Mes*AlH_2)$_2$ (Mes* = $-C_6H_2$-2,4,6-*t*-Bu_3) with HN($SiMe_3$)$_2$ affords the monomeric amidoarylalane Mes*Al(H)N($SiMe_3$)$_2$, **1**. This product can also be synthesized by the reaction of [Mes*AlH_2]$_2$ with LiN($SiMe_3$)$_2$, which, in addition, yields the byproducts $LiAlH_2\{N(SiMe_3)_2\}_2$, **3**, and Mes*H. Thermolysis of **1** at 175−180 °C affords three different products: Mes*AlC_6H_2-2,4-*t*-Bu_2-6-CMe_2CH_2, **2**, the related species $(Me_3Si)_2NAlC_6H_2$-2,4-*t*-Bu_2-6-CMe_2CH_2, **4**, and the imide [Mes*AlN($SiMe_3$)]$_n$, **5**. In addition, the previously reported monomeric alane Mes*$_2$AlH was synthesized in ca. 70% yield by a one-pot reaction between LiMes* (generated in situ) and $AlH_3 \cdot NMe_3$. All products were spectroscopically characterized, and the structure of **1** was determined by X-ray crystallography. The Al−N distance (1.819(2) Å) in **1** is relatively long. However, it has a substantial, 18.5 kcal mol^{-1}, Al−N rotation barrier which is attributed to steric congestion rather than Al−N π bonding.

Introduction

Trimethylhalosilane elimination is a convenient route for the formation of group 13−15 or 13−16 compounds.[1] These reactions generally take place under mild conditions, and the volatile byproduct Me_3SiX (X = Cl, Br) can be removed easily by distillation. This procedure also avoids the need to filter the reaction mixture to separate the metal halide salt, as is required in the more conventional salt elimination route. A further advantage of the halosilane elimination reaction is that it proceeds in hydrocarbon solvent, whereas the salt elimination reaction often requires the presence of ethers, which may form undesirable, strong adducts with the product or may even react with the group 13 starting material to form ether cleavage products with the appropriate halide. The trimethylhalosilane elimination has been shown to work well for B−S,[2] Ga−P,[3] Ga−As,[1b] Ga−S,[4] In−P,[5] and In−As[6] bond formation. However, it is only rarely observed for aluminum halides,[7] although cleavage of silyl ethers by aluminum halide species to form Al−O species has been reported.[8] We recently showed that Al−O[9] and Al−S[10] bonds can be formed under mild conditions by the reaction of aluminum hydrides with $[Me_2SiO]_3$ or $(Me_3Si)_2S$ with elimination of Me_2SiH_2 or Me_3SiH. Similar investigations involving amine/aluminum-hydride systems such as $Me_3N \cdot AlH_2N(SiMe_3)_2$ and $H_3Al \cdot N(H)(SiMe_3)_2$ found that both compounds decomposed around 100 °C into aluminum, hydrogen and amine instead of eliminating Me_3SiH with concomitant imide or amide formation.[11] In order to compare the reactivity of these Si−N bonded species with the corresponding Si−O or Si−S compounds we have investigated the reaction of [Mes*AlH_2]$_2$[12] with HN($SiMe_3$)$_2$ as well as the subsequent thermolysis of the initial amide product Mes*Al(H)N($SiMe_3$)$_2$.

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,[13] $AlH_3 \cdot NMe_3$,[14] [Mes*AlH_2]$_2$,[12] and LiN($SiMe_3$)$_2$,[15] were prepared by literature procedures. $(Me_3Si)_2NH$ was 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.

Mes*Al(H)N($SiMe_3$)$_2$, 1. Method A. A solution of [Mes*AlH_2]$_2$ (0.60 g, 1.1 mmol) in PhMe (30 mL) was treated with HN($SiMe_3$)$_2$

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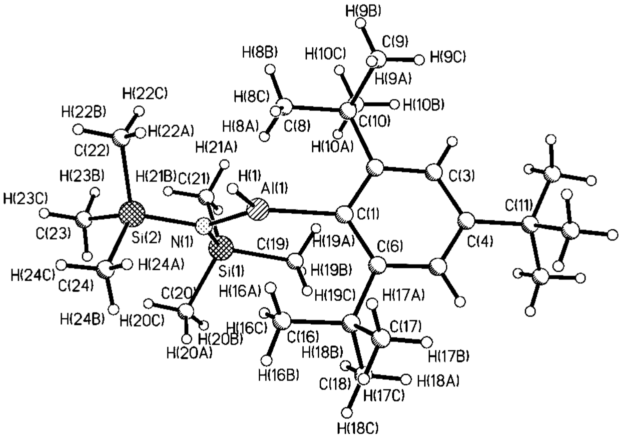

Figure 1. Computer-generated drawing for **1**. Selected bond distances and angles are listed in Table 2.

(0.46 mL, 2.2 mmol) at room temperature. It was then heated to 100−105 °C for 40 h, after which time the mixture was stripped of volatile materials under reduced pressure. The remaining colorless solid was dissolved in *n*-hexane (30 mL), and after decantation, the clear colorless solution was concentrated to about 2 mL. The precipitated microcrystalline solid was redissolved by gentle warming (30−40 °C). Cooling to about −20 °C overnight afforded 0.51 g of colorless X-ray quality crystals of **1** (Figure 1). Yield: 54%. Removal of the supernatant liquid followed by crystallization of the residue from *n*-pentane (1 mL) at −20 °C for 1 week gave 0.11 g of an about 50:50 mixture of **1** and **2** (for data for **2** vide infra). Mp: 121−122 °C. IR: $\nu_{Al-H} = 1836$ cm^{-1} (st). ^{1}H NMR (C_7D_8): 7.37 (s, *m*-H, 2H), 5.12 (s, broad, Al−H, 1H), 1.54 (s, *o*-CH$_3$, 18H), 1.31 (s, *p*-CH$_3$, 9H), 0.43 (s, Si−CH$_3$, 9H), 0.01 (s, Si−CH$_3$, 9H). ^{13}C{^{1}H} NMR (C_7D_8): 157.1 (*o*-C), 150.7 (*p*-C), 121.4 (*m*-C), 38.4 (*o*-*C*(CH$_3$)$_3$), 34.8 (*p*-*C*(CH$_3$)$_3$), 33.1 (*o*-CH$_3$), 31.5 (*p*-CH$_3$), 5.5, 5.1 (SiCH$_3$). ^{27}Al{^{1}H} NMR (C_7D_8, 100 °C, $\nu_o = 78.340\,477$ MHz): 143 (s, broad). $w_{1/2} \approx 5500$ Hz.

Mes*Al(H)N(SiMe$_3$)$_2$, 1. Method B. A solution of LiN(SiMe$_3$)$_2$ (0.33 g, 2.0 mmol) in *n*-pentane (10 mL) was added dropwise to a solution of [Mes*AlH$_2$]$_2$ (0.55 g, 1.0 mmol) in *n*-pentane (10 mL) at room temperature, immediately after which a fine colorless precipitate formed. The slurry was stirred for another 2 h and then left standing to allow the precipitate to settle overnight. The precipitate was collected on a glass frit and dried under reduced pressure. Yield: 0.30 g. The IR spectrum displayed both broad bands centered near 1750 and 800 cm^{-1} and bands due to the presence of the Mes* moiety. A sample dissolved easily and almost completely in C_6D_6, and the soluble part was identified as Mes*H by ^{1}H NMR. Concentration of the filtrate to about 3−5 mL followed by cooling to −20 °C for 3 weeks afforded 0.075 g of large (1 cm in length) colorless needles of LiAlH$_2$[N(SiMe$_3$)$_2$]$_2$, **3**. ^{1}H NMR (C_6D_6): 3.6 (s, broad, Al−H, 2H), 0.39 (s, Si−CH$_3$, 36H). ^{7}Li NMR (C_6D_6): 0.14 (s). Concentration of the supernatant liquid to about 1−2 mL and subsequent cooling to −20 °C for 3 weeks gave 0.34 g of impure **1**, which was purified by recrystallization from *n*-hexane (1 mL) at about −20 °C for 1 week.

Mes*$_2$AlH. A slurry of LiMes* in THF/*n*-pentane (20 mL, 60 mL) (generated in situ at ca., −78 °C from Mes*Br (6.10 g, 18.7 mmol) and *n*-BuLi (19.0 mmol, 11.9 mL of a 1.6 M hexane solution)) was added to a slurry of AlH$_3$·NMe$_3$ (0.80 g, 9.0 mmol) in Et$_2$O (20 mL) at −78 °C, which was slowly warmed to room temperature and stirred overnight. After removal of the volatile materials under reduced pressure, the remaining slightly sticky, colorless solid was extracted with *n*-hexane (60 mL). The colorless precipitate (LiBr) was separated, and the remaining pale yellow solution was concentrated to about 30 mL and cooled to −20 °C for 2 days to give 3.24 g of large colorless plates of Mes*$_2$AlH. Yield: 69%. Occasionally, Mes*$_2$AlH may be contaminated with small amounts of [Mes*AlH$_3$Li(THF)$_2$]$_2$,[16] which may be removed by recrystallization from *n*-hexane. The compound was authenticated by melting point and ^{1}H and ^{13}C NMR spectroscopic data.

Mes*AlC$_6$H$_2$-2,4-*t*-Bu$_2$-6-CMe$_2$CH$_2$, 2. Mes*$_2$AlH (0.30 g, 0.58 mmol) was placed in a Schlenk tube in a preheated oil bath at 155 °C. After about 10 min, the sample began to melt with a slight gas evolution and solidified after about 30 min. NMR spectroscopic studies of the crude product showed an almost complete conversion to **2** with about 7% of unreacted starting material. Attempts to grow crystals suitable for X-ray crystallographic studies were unsuccessful. ^{1}H NMR (C_6D_6): 7.70 (d, *m*-H, 1H), $^4J_{HH} = 1.3$ Hz, 7.60 (d, *m*-H, 1H), 7.49 (s, *m*-H (Mes*), 2H), 1.70 (s, C(CH$_3$)$_2$, 6H), 1.53 (s, *o*-C(CH$_3$)$_3$ (Mes*), 18H), 1.38, 1.37, 1.33 (s, C(CH$_3$)$_3$, 9H each), 0.91 (s, Al−CH$_2$, 2H). ^{13}C{^{1}H} NMR (C_6D_6): 166.4, 157.5, 157.3, 151.6, 150.4, 137.4, 133.8 (quaternary carbons), 121.9 (*m*-C(Mes*)), 121.0, 119.7 (*m*-C), 41.9 (*C*(CH$_3$)$_2$), 38.6 (*o*-*C*(CH$_3$)$_3$ (Mes*)), 38.0, 35.0, 34.8 (*C*(CH$_3$)$_3$), 37.6 (C(*C*H$_3$)$_2$), 33.9, 31.7, 31.5 (C(*C*H$_3$)$_3$), 33.0 (*o*-C(*C*H$_3$)$_3$(Mes*)), 29.3 (Al−CH$_2$).

Thermolysis of 1. Crystals of **1** (0.50 g, 1.2 mmol) in a Schlenk tube were placed in a preheated oilbath at 175−180 °C. After about 1 min a clear colorless liquid had formed and a smooth gas evolution commenced and continued for about 20 min, during which time the temperature was slowly raised to 190 °C. The liquid became opaque during that time, and after cooling to room temperature, the product mixture had become a sticky solid. A ^{1}H NMR spectroscopic investigation of this solid showed the presence of three different compounds with the approximate distribution of 66% (Me$_3$Si)$_2$NAlC$_6$H$_2$-2,4-*t*-Bu$_2$-6-Me$_2$CH$_2$, **4**, 27% **2**, and 7% [Mes*AlNSiMe$_3$]$_n$, **5**. Compound **5** could be separated in the form of a colorless, microcrystalline solid by crystallization from *n*-hexane (ca. 3−5 mL) at about −20 °C for 1 week. Yield: 0.015 g, 3%. Separation of **4** and **2** was unsuccessful. ^{1}H NMR data (C_6D_6) **4**: 7.66 (d, *m*-H, 1H), $^4J_{HH} = 1.5$ Hz, 7.57 (d, *m*-H, 1H), 1.56 (s, C(CH$_3$)$_2$, 6H), 1.54, 1.35 (s, C(CH$_3$)$_3$, 9H each), 0.58 (s, Al−CH$_2$, 2H), 0.22 (s, SiCH$_3$, 18H). **5**: 7.56 (s, *m*-H, 2H), 1.82 (s, *o*-CH$_3$,18H), 1.31 (s, *p*-CH$_3$, 9H), 0.05 (s, Si−CH$_3$, 9H).

X-ray Structure Determination. Crystals of **1** 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 glass fiber, and immediately placed in the low-temperature nitrogen stream as described in ref 17. The data were collected at 130 K with a Siemens P4-RA diffractometer (nickel foil monochromator equipped with a locally modified Enraf-Nonius universal low-temperature device using Cu Kα ($\lambda = 1.541\,78$ Å) radiation).

Crystallographic programs used for the structure solution were those of the SHELXTL Version 5.03 (Siemens, 1994) program package. Scattering factors were obtained from ref 18. An absorption correction was applied by using the method described in ref 19. Some details of the data collection and refinement are given in Table 1, and selected bond distances and angles are given in Table 2. Further details are provided in the Supporting Information. The crystal structure was solved by direct methods and 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. H(1) was located in the Fourier difference map and refined freely with a fixed isotropic thermal parameter of $U_{H(1)} = 1.5U_{Al(1)}$. The *p-tert*-butyl group displayed rotational disorder which was modeled with split occupancies for C(12)−C(14) and C(12a)−C(14a) of 0.572(8) and 0.428(8).

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Table 1. Crystallographic Data for **1**

formula	$C_{24}H_{48}AlNSi_2$
fw	433.79
space group	$P\bar{1}$
a, Å	9.615(2)
b, Å	11.684(2)
c, Å	13.781(2)
α, deg	70.890(12)
β, deg	76.688(13)
γ, deg	89.479(13)
V, Å^3	1419.8(4)
Z	2
T, K	130
γ, Å	1.541 78
δ_{calcd}, g cm^{-3}	1.015
μ, mm^{-1}	1.482
R1,^{a} %	4.90
wR2^b, %	13.08

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

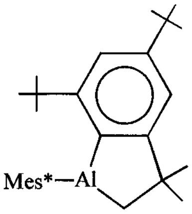
Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Al(1)−N(1)	1.819(2)	H(1)−Al(1)−N(1)	114.5(10)
Al(1)−C(1)	1.974(2)	H(1)−Al(1)−C(1)	118.0(10)
Al(1)−H(1)	1.51(3)	C(1)−Al(1)−N(1)	127.54(10)
N(1)−Si(1)	1.740(2)	Al(1)−N(1)−Si(1)	123.87(11)
N(1)−Si(2)	1.744(2)	Al(1)−N(1)−Si(2)	114.27(12)
		Si(1)−N(1)−Si(2)	121.82(12)

Results and Discussion

The following compounds are relevant to this discussion.

$Mes^*Al(H)N(SiMe_3)_2$ **1**



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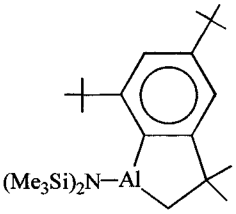
$LiAlH_2[N(SiMe_3)_2]_2$ **3**



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$[Mes^*AlNSiMe_3]_n$ **5**

Synthesis and Spectroscopy. The amide Mes*Al(H)N(SiMe$_3$)$_2$, **1**, was obtained in 54% yield by the reaction of [Mes*AlH$_2$]$_2$ with 2 equiv of HN(SiMe$_3$)$_2$ in toluene at 100−105 °C for 40 h followed by crystallization from *n*-hexane (method A, eq 1). A small amount of an about 50:50 mixture

$$[Mes^*AlH_2]_2 + 2HN(SiMe_3)_2 \xrightarrow[\text{PhMe, 40 h}]{100-105\ °C} 2\ Mes^*Al(H)N(SiMe_3)_2 + 2H_2 \quad (1)$$

of **1** and Mes*$\overline{AlC_6H_2\text{-}2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}CMe_2C}H_2$, **2** (vide infra) could be isolated from the supernatant liquid. The reaction of [Mes*AlH$_2$]$_2$ with 2 equiv of LiN(SiMe$_3$)$_2$ according to eq 2 (method B) was also investigated for two reasons: (a) to avoid possible competing Al−C(Mes*) cleavage in reaction 1; (b) to check its possible applicability to the synthesis of, for example, Mes*Al(H)E(R)SiMe$_3$ (E = P, As) from [Mes*AlH$_2$]$_2$ and LiE(R)SiMe$_3$. Upon mixing, the starting materials in *n*-pentane, a colorless precipitate formed immediately, which, upon isolation, was shown to be a mixture of LiH and/or LiAlH$_4$ and LiMes* by IR and ^{1}H NMR spectroscopy. The latter compound decomposes into Mes*H(D) upon addition of C$_6$D$_6$. Fractional crystallization of the filtrate afforded a small amount of LiAlH$_2$[N(SiMe$_3$)$_2$]$_2$, **3**, and finally **1** in less than 40% yield. Apparently, LiMes* elimination competes successfully with LiH elimination in this reaction system. The ^{1}H and ^{13}C NMR spectra of **1** display two separate sets of signals for the N(SiMe$_3$)$_2$ groups at room temperature, and the IR spectrum features a strong $\nu_{\text{Al-H}}$ absorption at 1836 cm^{-1}, which indicated the presence of a terminal Al−H moiety. A VT ^{1}H NMR study showed the SiMe$_3$ signals coalesced at 117(2) °C and displayed a maximum peak separation of 136.5 Hz at −70 °C, from which an activation energy of 18.5(2) kcal mol^{-1} for the dynamic process may be estimated.[20]

$$[Mes^*AlH_2]_2 + 2LiN(SiMe_3)_2 \rightarrow 2\ Mes^*Al(H)N(SiMe_3)_2 + 2LiH \quad (2)$$

Structure. The X-ray diffraction data for **1** confirmed its monomeric nature. It is only the second crystal structure determination of a monomeric, three-coordinate alane derivative.[21] The aluminum coordination is distorted trigonal planar, and the Al−C, Al−H, and Al−N distances of 1.974(2), 1.51(3), and 1.819(2) Å lie within the range previously observed for three-coordinate aluminum compounds,[22] although the Al−N distance is at the upper end of its range. There is a small torsion angle of 1.8° between the normals to the planes at Al and N ($\Sigma°(N) = 359.96$), which implies almost perfect alignment of the Al and N p orbitals for Al−N π bonding. The Al−N bond length, however, suggests that π bonding is quite weak and that the high Al−N rotation barrier is instead a consequence of steric congestion. The crowded nature of **1** is indicated by a number of short intramolecular H···H distances, for example, 2.43 Å between H(18B) (*o*-*t*-Bu) and H(19C) (Me$_3$Si). It may also be noted that the Al−N rotation barrier of 18.5 kcal mol^{-1} is the highest such barrier reported to date.[22] Previous studies on three-coordinate aluminum amides reported an upper limit of 8−10 kcal mol^{-1} for the Al−N barrier. The Al−C distance in **1** is normal and is comparable to those seen in other Mes*Al derivatives.[22,24] Another feature that **1** has in common with many other Mes*/Al compounds are the close contacts (ca. 2.27 Å) between the aluminum center and the *o*-*t*-Bu hydrogens.

Thermolyses. The cis alignment of H(1) and Si(2)Me$_3$ (H(1)···Si(2) = 3.17 Å) suggested the possibility of intramolecular aluminum imide formation (i.e., [Mes*AlNSiMe$_3$]$_n$). Thermolysis of **1** at 180−190° for 20 min led to a smooth gas evolution and the formation of a sticky solid. No Me$_3$SiH was detected in the gas phase above the reaction, although an as yet unidentified silylmethyl peak, which was not attributable to (Me$_3$Si)$_2$NH, (Me$_3$Si)$_2$O, or silicon grease, was observed by

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^{1}H NMR spectroscopy. ^{1}H NMR spectroscopic investigation of the solid residue showed the presence of three species: 27%, **2**, 66% $(Me_3Si)_2N\overline{AlC_6H_2\text{-}2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}CMe_2C}H_2$, **4**, and 7% $[Mes^*AlNSiMe_3]_n$, **5**. The compound **5** could be separated by crystallization from *n*-hexane and tentatively characterized as $[Mes^*AlNSiMe_3]_n$ by ^{1}H NMR spectroscopy. It crystallizes from C_6D_6 in the form of very thin plates which have, so far, proved unsuitable for X-ray crystallography. Most probably, the structure of **5** is dimeric (i.e., $n = 2$), with parameters similar to those seen for $(Mes^*AlNPh)_2$.[24] The cyclized species **2** was identified in the mixture by comparison to an independently synthesized sample (vide infra). The related cyclized derivative **4** was identified by analysis of the remaining signals in the ^{1}H NMR spectrum. Unfortunately, **2** and **4** could not be separated by fractional crystallization. The presence of **4** as the major product of the thermolysis of **1** suggests that C−H activation of the *o*-*t*-Bu C−H bonds occurs at a rate faster than Me_3SiH elimination, which would have afforded **5** in a higher yield. The fact that **2** is formed in both the synthesis of **1** via method A and in the thermolysis of **1** points to a significant degree of ligand migration/exchange at high temperatures, although **1** is monomeric in the solid state.

Independent Syntheses of 2 and Mes*$_2$AlH. Mes^*_2AlH was first described by Cowley and co-workers[21] as the product of transmetalation of Mes^*_2GaCl or Mes^*_2InCl with $LiAlH_4$ as in eq 3. During our work on the chemistry of $[Mes^*AlH_2]_2$,

$$Mes^*_2MCl \xrightarrow[Et_2O]{LiAlH_4} Mes^*_2AlH \qquad (M = Ga, In) \tag{3}$$

Mes^*_2AlH was occasionally observed as a side product during the synthesis of its precursor, $[Mes^*AlH_3Li(THF)_2]_2$.[16] While attempting to rationalize this result, we found a convenient one-pot synthesis (eqs 4 and 5), which affords Mes^*_2AlH in

$$Mes^*Br + n\text{-}BuLi \xrightarrow[-78\ °C]{THF/pentane} LiMes^* + n\text{-}BuBr \tag{4}$$

$$2\ LiMes^* + 2n\text{-}BuBr + AlH_3{\cdot}NMe_3 \rightarrow Mes^*_2AlH + 2\ n\text{-}BuH + 2\ LiBr + NMe_3 \tag{5}$$

moderate to good yield. Lithiation of Mes*Br with *n*-BuLi in THF at about −78 °C affords Mes*Li and *n*-BuBr. Addition of this mixture to $AlH_3{\cdot}NMe_3$ in Et_2O gives Mes^*_2AlH and LiH. The LiH reacts quickly with the butylbromide to afford butane and LiBr. Heating of Mes^*_2AlH slightly above its melting point (144−146 °C)[21] to 155 °C for about 30 min results (after gas evolution) in the new compound **2**, which is solid at 160 °C. Spectroscopic studies (^{1}H, ^{13}C NMR, IR) established the formulation of **2** as the orthometalated species $Mes^*\overline{AlC_6H_2\text{-}2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}CMe_2C}H_2$.[23]

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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 **1** (9 pages). Ordering information is given on any current masthead page.

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