Unusual Alkylaluminum Amides, Adducts, and Aluminates Containing Lithium

Drew Rutherford and David A. Atwood*

Contribution from the Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

Received April 15, 1996[⊗]

Abstract: Herein is presented the synthesis and characterization of the alkylaluminum lithium amides of the general formula $[R_2AlNLi(THF)_nR']_2$ (where R, R′ = Me, ^tBu (n = 1) (**1**); ^iBu, Ph (n = 1) (**2**); $SiMe_3$, Ph (n = 2) (**3**)). When the relatively bulky groups Mes or Dipp (Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl) are used, the unusual adducts $Me_2(^tBu)Al{-}NHLi(THF)_3Dipp$ (**4**) and $Mes_2(Me)Al{-}NLi(THF)_2(SiMe_3)_2$ (**6**) and aluminate $[^iBu_2(^tBu)AlNHDipp]^-[Li(THF)_4]^+$ (**5**) result. One other type of aluminate of relevance to this study is the related complexes $[Mes_2Al(NH^tBu)_2]Li(THF)_n$ (where n = 1 (**7**) and 2 (**8**)). Crystal data for **1**: triclinic, $P\bar{1}$, $a = 9.018(2)$ Å, $b = 9.056(1)$ Å, $c = 9.429(2)$ Å, $\alpha = 109.23(1)°$, $\beta = 90.29(1)°$, $\gamma = 102.82(1)°$, $V = 706.4(2)$ Å^3, $Z = 2$, with 1070 reflections with $F > 6.0\ \sigma(F)$, $R = 0.0697$. Crystal data for **2**: monoclinic, $P2_1/n$, $a = 10.584(1)$ Å, $b = 14.469(1)$ Å, $c = 13.599(1)$ Å, $\beta = 94.40(1)°$, $V = 2076.4(3)$ Å^3, $Z = 4$, with 1323 reflections with $F > 6.0\ \sigma(F)$, $R = 0.0741$. Crystal data for **4**: monoclinic, Cc, $a = 18.215(3)$ Å, $b = 10.498(1)$ Å, $c = 18.217(4)$ Å, $\beta = 106.12(1)°$, $V = 3347(1)$ Å^3, $Z = 4$, with 1423 reflections with $F > 4.0\ \sigma(F)$, $R = 0.065$. Crystal data for **5**: monoclinic, $P2_1/n$, $a = 10.262(1)$ Å, $b = 26.899(5)$ Å, $c = 16.687(2)$ Å, $\beta = 99.72(1)°$, $V = 4540(1)$ Å^3, $Z = 4$, with 1958 reflections with $F > 6.0\ \sigma(F)$, $R = 0.0755$. Crystal data for **7**: monoclinic, $P2_1/n$, $a = 17.005(2)$ Å, $b = 10.925(2)$ Å, $c = 17.138(2)$ Å, $\beta = 95.52(1)°$, $V = 3169.2(8)$ Å^3, $Z = 4$, with 1361 reflections with $F > 6.0\ \sigma(F)$, $R = 0.0657$. Crystal data for **8**: monoclinic, Cc, $a = 14.28(2)$ Å, $b = 19.829(5)$ Å, $c = 16.160(7)$ Å, $\beta = 111.33(1)°$, $V = 4264(5)$ Å^3, $Z = 8$, with 1172 reflections with $F > 4.0\ \sigma(F)$, $R = 0.0933$.

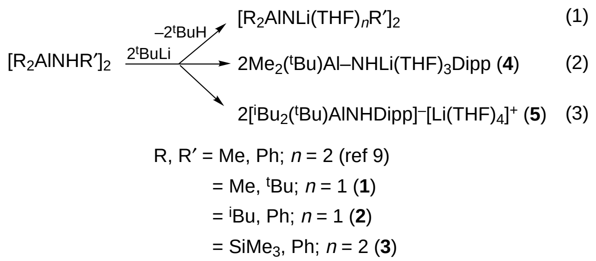
Introduction

Organometallic combinations between the group 13 and 15 elements have generated widespread interest over the last decade. This renaissance has been driven, in part, by applications in materials science[1] and catalysis.[2] Of fundamental interest is the possibility of multiple bonding between these two groups of elements.[3] Explorations into these areas have primarily involved the preparation of neutral complexes. Comparatively little has been accomplished with regard to charged group 13 complexes. This research group has actively been seeking to develop the chemistry of such species. This has primarily involved the utilization of the Salen and Salan classes of ligands in the quest to prepare new types of cationic[4] and anionic[5] complexes. Anionic complexes clearly hold the most promise in the search for 13−15 multiple bonding. This is particularly true in view of the fact that the first 13−15 multiple bond was, in fact, reported for a charged species (e.g. $[Mes_2B{=}AsPh]^-[Li(THF)_4]^+$).[6]

Toward understanding how such charged species form, the present paper represents a systematic exploration of alkylaluminum lithium amides of the general formula $[R_2AlNLi(THF)_nR']_2$ (where R, R′ = Me, ^tBu (n = 1) (**1**); ^iBu, Ph (n = 1) (**2**); $SiMe_3$, Ph (n = 2) (**3**)). These are formed by the deprotonation and lithiation of the corresponding primary amido alane, $[R_2AlNHR']_2$. In some cases the attempted lithiation produces surprising results. For instance, the unusual adducts $Me_2(^tBu)Al{-}NHLi(THF)_3Dipp$ (**4**) and $Mes_2(Me)Al{-}NLi(THF)_2(SiMe_3)_2$ (**6**) and aluminate $[^iBu_2(^tBu)AlNHDipp]^-[Li(THF)_4]^+$ (**5**) result when the relatively bulky Mes or Dipp groups are incorporated into the complex. One other type of aluminate of relevance to this study is the structurally similar complexes, $[Mes_2Al(NH^tBu)_2]Li(THF)_n$ (where n = 1 (**7**) and 2 (**8**)). A discussion of these new types of compounds and their relevance to 13−15 multiple bonding will be presented. Preliminary reports on compounds **1**[7] and **4**[8] have appeared.

Results and Discussion

$[Me_2AlNLi(THF)^tBu]_2$ (1), $[^iBu_2AlNLi(THF)Ph]_2$ (2), and $[(SiMe_3)_2AlNLi(THF)_2Ph]_2$ (3). Compounds **1**−**3** are prepared by the addition of ^tBuLi to the respective primary amido alane in THF (eq 1). This was also the route used to prepare the first



[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1996.

[1] (a) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. (b) Stringfellow, G. B. *Organometallic Vapor Phase Epitaxy*; Academic: San Diego, CA, 1989. (c) Kuech, T. F.; Jensen, K. F. In *Thin Film Processes II*; Vossen, J. L., Kern, W., Eds.; Academic: San Diego, CA, 1991; p 369. (d) Wells, R. L. *Coord. Chem. Rev.* **1992**, *112*, 273. (e) Cowley, A. H.; Jones, R. A. *Polyhedron* **1994**, *13*, 1149.

[2] Yamamoto, H. In *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley & Sons Ltd.: West Sussex, England, 1994; Chapter 7.

[3] (a) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1135. (b) Petrie, M. A.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1993**, 1737.

[4] (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (b) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem.* **1996**, *35*, 63.

[5] Atwood, D. A.; Rutherford, D. *Inorg. Chem.* **1995**, *34*, 4008.

[6] Petrie, M. A.; Shoner, S. C.; Rasika Dias, H. V.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1033.

[7] Atwood, D. A.; Rutherford, D. *Main Group Chem.* **1996**, *4*, 431.

[8] Atwood, D. A.; Rutherford, D. *J. Chem. Soc., Chem. Commun.* **1996**, 1251.

S0002-7863(96)01244-9 CCC: $12.00

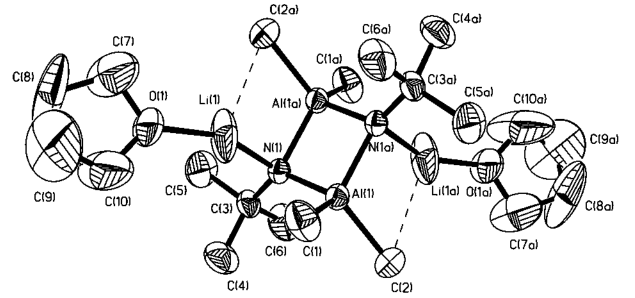


Figure 1. Molecular structure and atom numbering scheme for $[Me_2AlNLi(THF)^tBu]_2$ (**1**).

reported example of such complexes, $[Me_2AlNLi(THF)_2Ph]_2$.[9] Unlike the neutral precursors, the lithiated derivatives are insoluble in hydrocarbon solvents. They are, however, soluble in benzene, toluene, THF, and Et_2O. Another indication of deprotonation for **1**−**3** is the fact that they do not show N−H resonances in either the ^1H NMR or the IR spectra. Otherwise, there is very little change in the spectroscopic characterization on going from an N−H to an N−Li. For instance, the Me−Al chemical shift in $[Me_2AlNH^tBu]_2$ appears[10] at δ −0.39 ppm, while for **1** it appears at −0.32 ppm. Moreover, the Me group in the adduct, $Me_3Al{-}NH_2{}^tBu$, is found in the same region of the spectrum (δ −0.41 ppm).[10]

The NMR data indicates the presence of THF in each molecule. The number of THF molecules correlates with the overall steric bulk of each complex. Thus, those possessing ^{t}Bu and ^{i}Bu groups coordinate one THF, while the less sterically encumbered coordinate two (relatively longer Si−C bonds in the TMS group make it less sterically encumbered than ^{t}Bu).

Perhaps the most diagnostic spectroscopic evidence for the lithiation of the primary amides is the large downfield shift observed for the *ipso*-carbon of the *N*-aryl substituents in the ^{13}C NMR. In $[Me_2AlNLi(THF)_2Ph]_2$, a shift of δ 20.2 ppm was reported on going from the neutral to the lithiated compound (δ 143.3 to 163.6 ppm).[9] A similar downfield shift was observed for **2** and **3**. The *ipso*-carbon of **2** shifted δ 13.9 ppm, whereas a downfield shift of δ 9.7 ppm was recorded for **3**. This effect is a consequence of the increased electron density centered on the anionic nitrogen and can be explained by partial delocalization of the negative charge into the π-system of the phenyl ring. This results in a deshielding of the carbon resonance and a shift to lower field. This model is partly born out in the examination of the solid state structure of **2** (see Figure 2). Furthermore, this type of shift in the ^{13}C NMR was not observed for **1**. The parent amide has a shift of δ 51.4 ppm, while that of the lithiated derivative is δ 51.3 ppm.

The presence and number of THF molecules in **1** and **2** is confirmed by X-ray crystallography. In each structure (Figures 1 and 2) the lithium atoms are closely associated with the nitrogen atoms (N−Li = 1.91(2) and 1.980(17) Å, respectively). Each Li atom is further coordinated to one THF molecule (av Li−O = 1.84(2) Å). In the structure of $[Me_2AlNLi(THF)_2Ph]_2$, which contains two coordinated THF molecules, the N−Li distance is somewhat larger 2.023(12) Å.[9] The shorter distance observed for **1** can be attributed to the more negative charge on nitrogen compared to that on the derivatives possessing an aryl ring which may be partially delocalized.

A general structural feature present in dimeric primary amido alanes with an aryl group on the nitrogen is that the alignment of the phenyl group is nearly orthogonal to the Al_2N_2 four-membered ring. The precursor to **2** has such an alignment (dihedral angle = 90.4°).[10] Upon lithiation, a significant perturbation is observed; the phenyl ring in **2** twists to a nearly planar alignment with the Al_2N_2 four-membered ring (dihedral angle = 13.3°). This observation is in agreement with the delocalization of charge into the phenyl ring, as the planarization of the aryl group relative to the Al−N bonds enhances overlap of the orbitals. In addition, a decrease in bond length between N1 and C1 would be expected, and this is observed [1.445(5) to 1.390(9) Å]. A similar phenyl group twist was observed in $[Me_2AlNLi(THF)_2Ph]_2$.[9]

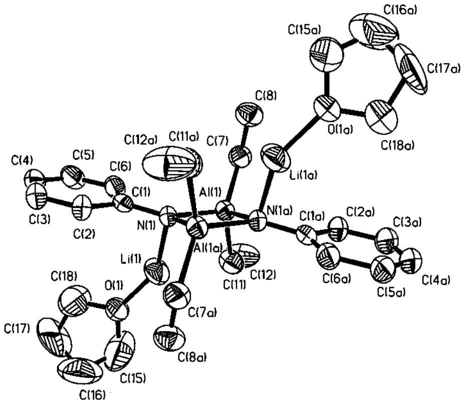


Figure 2. Molecular structure and atom numbering scheme for $[^iBu_2AlNLi(THF)Ph]_2$ (**2**).

Beyond these observations the effect of the lithiation on the original structure of the amino alanes is surprisingly slight. Thus, the lithiated products remain dimeric with relatively unchanged bond lengths and angles. See, for example, the Al−C distance and the N−Al−N′, Al−N−Al′, and C−N−Al angles (Table 1). However, there is a dramatic change in the Al−N bond distances. For **1** and **2** these distances are 1.873(5) and 1.888(5) Å, respectively (Table 2). This compares to distances of 1.955(3) and 1.978(3) Å for the starting materials. Similarly, for $[Me_2AlNLi(THF)_2Ph]_2$, the distance is 1.885(5) Å.

The ultimate goal of this research was to isolate monomeric compounds possessing short bonds that could be attributed to π-bonding. In the present case, the dimeric four-coordinate nature of the complexes obviates such bonding. The short distances in **1** and **2**, then, may be attributed to an increased electrostatic attraction between the Al and N atoms. In the case of **2**, the negative charge is delocalized into the phenyl ring on the nitrogen.

$Me_2(^tBu)Al{-}NHLi(THF)_3Dipp$ (4) and $[^iBu_2(^tBu)AlNHDipp]^-[Li(THF)_4]^+$ (5). When ^{t}BuLi is added to either $[Me_2AlNHDipp]_2$[11] or $[^iBu_2AlNHDipp]_2$,[10] the unusual adduct complex **4** and aluminate **5** result (eqs 2 and 3). In compound **4** the ^{t}BuLi does not deprotonate the amine as seen for **1**−**3**, but rather metalates it. The ^{t}Bu group alkylates the aluminum atom. Formation of the monomeric adduct allows more room around the N−Li moiety (compared to the dimers), and the lithium can then bind three THF molecules. The NMR data for **4** shows Al−Me resonances that are somewhat more shielded (δ −0.60 ppm) than in the starting material (δ −0.31 ppm). This is in keeping with the fact that the compound has been changed from an amide with a covalent bond to an amine adduct with a dative bond (**4**).[12] A similar transformation occurs when the dimeric complex $[^iBu_2AlNHDipp]_2$ is combined with 2 equiv of ^{t}BuLi. However, due to the presence of bulky groups on both the Al and N atoms (^{i}Bu and Dipp, respectively), the lithium atom is prevented from bonding to the N atom and the anion−cation pair $[^iBu_2{}^tBuAlNHDipp]^-[Li(THF)_4]^+$ (**5**) is formed.

---

[9] Atwood, D. A.; Rutherford, D. *Organometallics* **1996**, *15*, 436.

[10] Rutherford, D.; Atwood, D. *Main Group Chem.*, in press.

[11] Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

[12] For a discussion of covalent and dative bonding, see: Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

Table 1. Comparison of Structural Data for **1**, **2**, **4**, **5**, **7**, and Related Compounds

	bond lengths (Å)			angles (deg)			
compound	Al−C (av)	Al−N	N−Li	N−Al−N′	Al−N−Al′	C−N−Al	ref
$[Me_2AlNLi(THF)_2Ph]_2$	1.99(1)	1.885(5)	2.023(12)	88.3(2)	92.7(2)	134.0(3)	9
$[Me_2AlN(H)^tBu]_2$	1.969(3)	1.955(3)		86.1(1)	93.9(1)	126.1(3)	10
$[Me_2AlNLi(THF)^tBu]_2$ (**1**)	2.007(8)	1.873(5)	1.91(2)	89.2(3)	90.8(2)	128.6(5)	7
$[^iBu_2AlNHPh]_2$	1.96(2)	1.978(3)		86.5(1)	93.5(1)	123.0(2)	10
$[^iBu_2AlNLi(THF)Ph]_2$ (**2**)	2.00(4)	1.888(5)	1.980(17)	86.7(2)	93.3(2)	134.4(4)	
$[Me_2AlNHDipp]_2$	1.96(1)	1.99(1)		82.6(4)	94.7(5)	132(1)	11
$Me_2{}^tBuAl-NHLi(THF)_3Dipp$ (**4**)	1.99(1)	1.976(9)	2.171(21)			125.9(6)	8
$Mes_2AlN(SiMe_3)_2$	1.982(3)	1.813(7)				119.1(4)	10
$[^iBu_2AlNHDipp]_2$	1.965(9)	1.995(1)		84.4(3)	94.5(3)	129(11)	10
$[^iBu_2{}^tBuAlNHDipp]Li(THF)_4$ (**5**)	2.01(1)	1.883(8)					
$[Me_3AlNLi(SiMe_3)_2]_\infty$	2.03(3)	1.944(3)	2.027(7)				12
$[Mes_2Al(NH^tBu)_2]Li(THF)$ (**7**)	1.904(7)	2.045(10)	2.02(3)	96.2(3)		132(5)	

Table 2. Bond Lengths (Å) and Angles (deg) for $[Me_2AlNLi(THF)^tBu]_2$ (**1**), $[^iBu_2AlNLi(THF)Ph]_2$ (**2**), $Me_2{}^tBuAlNHLi(THF)_3Dipp$ (**4**), $[^iBu_2{}^tBuAlNHDipp][Li(THF_4)]$ (**5**), and $Mes_2Al(NH^tBu)_2Li(THF)$ (**7**)

1	**2**	**4**	**5**	**7**
		bond length		
Al(1)−N(1) 1.873(5)	Al(1)−N(1) 1.888(5)	Al(1)−N(1) 1.976(9)	Al(1)−N(1) 1.883(8)	Al(1)−N(1) 1.908(7)
Al(1)−Li(1) 2.862(21)	Al(1)−Li(1) 2.725(16)	Al(1)−C(1) 1.997(13)	Al(1)−C(13) 2.009(10)	Al(1)−N(2) 1.912(8)
Al(1)−C(1) 2.000(6)	Al(1)−C(7) 1.977(8)	Al(1)−C(2) 1.988(11)	Al(1)−C(17) 1.992(10)	Al(1)−Li(1) 2.655(18)
Al(1)−C(2) 2.014(9)	Al(1)−C(11) 2.040(8)	Al(1)−C(15) 2.037(13)	Al(1)−C(21) 2.012(11)	Al(1)−C(1) 2.038(11)
O(1)−Li(1) 1.862(21)	N(1)−Li(1) 1.980(17)	N(1)−C(3) 1.396(14)	N(1)−C(1) 1.383(13)	Al(1)−C(10) 2.042(9)
N(1)−Li(1) 1.915(18)	N(1)−C(1) 1.390(9)	N(1)−Li(1A) 2.171(21)	O(1)−Li(1) 1.901(20)	N(1)−Li(1) 2.036(19)
N(1)−C(3) 1.441(7)	O(1)−Li(1) 1.828(16)	O(1)−Li(1) 2.059(20)	O(2)−Li(1) 1.939(19)	N(2)−Li(1) 2.007(19)
		O(2)−Li(1) 1.937 (22)	O(3)−Li(1) 1.941(18)	N(2)−C(23) 1.480(14)
		O(3)−Li(1) 1.979(27)	O(4)−Li(1) 1.944(20)	O(1)−Li(1) 1.881(20)
		angles		
N(1)−Al(1)−C(1) 112.2(3)	N(1)−Al(1)−C(7) 121.1(3)	N(1)−Al(1)−C(1) 103.5(5)	N(1)−Al(1)−C(13) 108.5(4)	N(1)−Al(1)−N(2) 96.3(3)
N(1)−Al(1)−C(2) 117.7(2)	N(1)−Al(1)−C(11) 109.0(3)	N(1)−Al(1)−C(2) 117.2(5)	N(1)−Al(1)−C(17) 114.3(4)	N(1)−Al(1)−C(1) 108.8(3)
C(1)−Al(1)−C(2) 108.1(4)	C(7)−Al(1)−C(11) 110.9(3)	C(1)−Al(1)−C(2) 106.2(6)	N(1)−Al(1)−C(21) 102.3(4)	N(2)−Al(1)−C(1) 112.9(4)
N(1)−Al(1)−N(1A) 89.2(2)	N(1)−Al(1)−N(1A) 86.7(2)	N(1)−Al(1)−C(15) 109.6(5)	C(13)−Al(1)−C(17) 109.5(4)	N(1)−Al(1)−C(10) 119.8(4)
C(1)−Al(1)−N(1A) 119.1(3)	C(7)−Al(1)−N(1A) 115.2(3)	C(1)−Al(1)−C(15) 109.5(5)	C(17)−Al(1)−C(21) 110.6(5)	N(2)−Al(1)−C(10) 108.2(4)
C(2)−Al(1)−N(1A) 110.0(3)	C(11)−Al(1)−N(1A) 111.8(3)	C(2)−Al(1)−C(15) 110.4(5)	C(13)−Al(1)−C(21) 111.5(4)	C(1)−Al(1)−C(10) 110.2(4)
Al(1)−N(1)−Al(1A) 90.8(2)	Al(1)−N(1)−Al(1A) 93.3(2)	Al(1)−N(1)−C(3) 125.9(6)	Al(1)−N(1)−C(1) 143.6(7)	Al(1)−N(1)−Li(1) 84.6(6)
		Al(1)−N(1)−Li(1A) 111.9(7)	Al(1)−N(1)−H(1A) 108.7(2)	Al(1)−N(1)−C(19) 135.3(7)
		C(3)−N(1)−Li(1A) 113.4(9)	C(1)−N(1)−H(1A) 107.7(6)	Al(1)−N(2)−Li(1) 85.3(6)
				Al(1)−N(2)−C(23) 128.1(6)
				Li(1)−N(2)−C(23) 105.3(8)
				N(1)−Li(1)−N(2) 89.4(8)
				N(1)−Li(1)−O(1) 137.7(10)
				N(2)−Li(1)−O(1) 132.8(10)

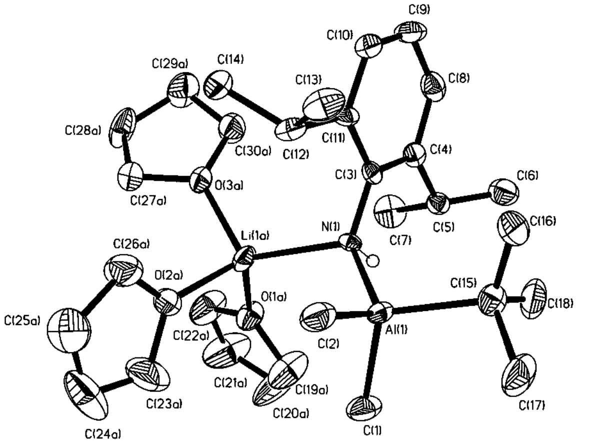


Figure 3. Molecular structure and atom numbering scheme for $Me_2{}^tBuAlNLi(THF)_3Dipp$ (**4**).

The crystal structure of **4** confirms the presence of three THF molecules around the four-coordinate Li atom (Figure 3). Several significant changes occur upon lithiation. Most obviously, a monomeric complex, which possesses close to idealized tetrahedral angles around Al, is formed. The groups around Al and N adopt a sterically less encumbered staggered arrangement. This leads to a somewhat eclipsed conformation for the N and Li groups. The Al−N bond distance in **4** (1.976(9) Å) is roughly equivalent to that observed before alkylation/lithiation (av 1.99(1) Å). The generally short distances found in **1**, **2**, **4**, and **5** may be attributed to an increase in the electrostatic attraction between the Al and N atoms resulting from the lithiation. The greater negative charge on **4** compared to the starting material is evident from a comparison of the Al−Me ^1H chemical shifts (δ −0.60 for **4** vs δ −0.31 ppm). The N−Li distance in **4** (2.171(21) Å) is similar to that observed for other lithiated amides with the lithium in a T_d coordination geometry.[13] The effect of removing the lithium atom from such a complex is observed in the structure of **5** (Figure 4). This leads to a substantially shorter Al−N bond distance of 1.883(8) Å. The angles around Al approximate T_d. Compounds **4** and **5** are the first structurally characterized trialkylaluminum adducts of primary lithium amides. However, they bear a close resemblance to the recently reported secondary lithium amide adducts, $[LiN(SiMe_3)_2MMe_3]_\infty$ (where M = Al, Ga).[14] In this latter complex the Al−N and N−Li bond distances are 1.944(3) and 2.027(7) Å, respectively. The primary difference between this complex and **4**−**6** lies in the fact that the synthesis was performed in the absence of a donor solvent. Thus, in order to increase the Li atom coordination number, the complex adopts a polymeric structure in the solid state.

---

(13) W. N. Stetzer, P. v. R. Schleyer. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press, Inc.: New York, 1985; Vol. 24, p 353.

(14) Niemeyer, M.; Power, P. P. *Organometallics* **1995**, *14*, 5488.

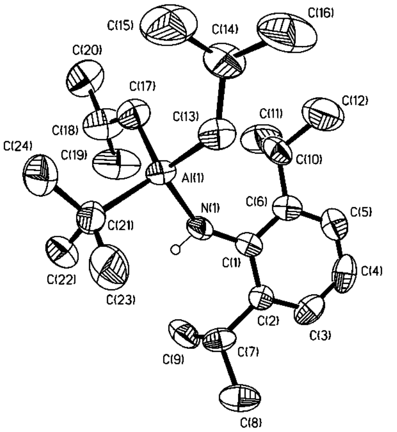


Figure 4. Molecular structure and atom numbering scheme for the anion of [^{i}Bu$_2$^{t}BuAlNHDipp][Li(THF$_4$)] (**5**).

Mes$_2$(Me)Al−NLi(THF)$_2$(SiMe$_3$)$_2$ (6). It was originally hoped that the addition of MeLi to Mes$_2$Al−N(SiMe$_3$)$_2$ would result in elimination of SiMe$_4$ to form the lithium aluminum amide, [Mes$_2$Al═N(SiMe$_3$)]$^-$Li$^+$. This would follow the precedent set by destannylation reactions[15] and would represent a new synthetic strategy in the context of group 13 chemistry. Additionally, we hoped to detect the presence of π-bonding in this complex. However, the reaction proceeded in a manner analogous to the formation of **4** (eq 4). The MeLi adds to both

$$\mathrm{Mes_2AlN(SiMe_3)_2} \xrightarrow{\mathrm{MeLi}} \mathrm{Mes_2(Me)Al{-}NLi(THF)_2(SiMe_3)_2}\ (\mathbf{6}) \quad (4)$$

the Al and N atoms, forming the trialkylaluminum lithium amide adduct. The presence of the Li atom in this molecule results in a ^{1}H SiMe$_3$ chemical shift of δ 0.57 ppm compared to that for the starting material of δ 0.23 ppm.

Although compounds **4** and **6** would appear to be isolated intermediates in the formation of the corresponding aluminum amides (eq 1), they are surprisingly stable. Heating of either one in THF for 24 h to effect this transformation results, after workup, in the isolation of each unchanged. This would imply that the formation of such an adduct species is not an intermediate in the synthesis of compounds **1** and **2**. Moreover, attempts to isolate adduct species in the synthesis of **1** and **2** (and others) have been unsuccessful. In all cases, this reaction leads directly to the formation of complexes having the general formulas shown in eq 1. Although **4** is unique, it does bear some similarity to the LiH adduct formed from the reaction of ^{t}BuLi with R$_3$Al[16] and the lithium oxide species, R$_3$AlOLiAlR$_2$.[17]

Mes$_2$Al(NH^{t}Bu)$_2$Li(THF) (7) and Mes$_2$Al(NH^{t}Bu)$_2$Li(THF)$_2$ (8). Compounds **7** and **8** are prepared by the addition of lithium amide to Mes$_2$AlCl·THF. When the reaction is run in toluene, the aluminate possessing a singly solvated three-coordinate lithium atom is obtained as the final product (**7**). When the reaction is run in THF, however, the expected tetracoordinate tetrahedral lithium atom is obtained in the product (**8**). Compound **7** can be cleanly converted to **8** by dissolution in THF (eq 5). These compounds were originally

$$\mathrm{Mes_2Al(NH^tBu)_2Li(THF)}\ (\mathbf{7}) \xrightarrow{\mathrm{THF}} \mathrm{Mes_2Al(NH^tBu)_2Li(THF)_2}\ (\mathbf{8}) \quad (5)$$

prepared in order to explore whether intramolecular protonolysis

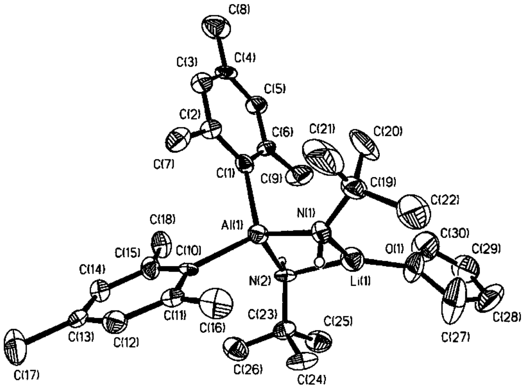


Figure 5. Molecular structure and atom numbering scheme for Mes$_2$Al(NH^{t}Bu)$_2$Li(THF) (**7**).

could be used to create lithium aluminum amides (Me$_2$AlN(Li(THF)$_n$)^{t}Bu in this case). However, extended reflux of **7** or **8** in toluene does not effect this transformation.

The molecular structure of **7** is shown in Figure 5. Unfortunately, the X-ray data for **8** was not of sufficient quality to warrant comparison of anything but overall morphological features with **7**. With the exception of having one additional THF molecule, compound **8** is isostructural to **7**. In **8** the lithium atom is in a distorted T_d geometry while in **7** it adopts a trigonal planar geometry. The aluminum atom is in a surprisingly undistorted T_d geometry in view of the steric bulk of the Mes groups and the constraints imposed by the AlN$_2$Li four-membered ring. Thus, the largest deviation is seen for N(1)−Al(1)−C(10), 119.9(4)°. The *N*-^{t}Bu groups adopt orientations trans to one another but are not equivalent. This is evident from the disposition of the AlN$_2$Li four-membered ring in which the N2 atom is displaced 0.54 Å from the plane defined by the other atoms. Additionally, the Al(1)−N(2) bond distance (1.913(7) Å) is longer than that of Al(1)−N(1) (1.896(7) Å). Both of these distances are shorter than what is observed in the structurally similar complex [^{t}Bu$_2$Al(NHC(Ph)$_3$)$_2$]Li, in which the distances are 1.933(3) and 1.938(3) Å.[3a] Other relevant comparisons to **7** and **8** are examples such as [Me$_2$Si(N^{t}Bu)$_2$(AlMe$_2$)(MgI)]$_2$[18] and the series [Me$_2$Al(^{i}Pr$_2$N)$_2$MgR]$_2$ (where R is a wide range of organic functionalities).[19] A common structural feature among these examples and **7** and **8** is the presence of an AlN$_2$M four-membered ring (where M = Li and MgR).

^{7}Li NMR Data for Compounds 1−8. It was of interest to see if a correlation could be obtained between the number and type of coordinating atom around lithium and its ^{7}Li chemical shift. In this manner, the actual coordination of the solvent and nitrogen around the lithium atom in an unknown sample could be determined. Additionally, the formation of monomeric compounds of the formula [R$_2$Al═NR′]$^-$[Li(solvent)$_4$]$^+$ might be observed in solution. The results are listed in Table 4. In general, the chemical shift range observed for ^{7}Li is not very large.[20] For the present compounds, the greatest disparity occurs between compounds **7** (with two N and one O coordinating) and **8** (with two N and two O coordinating). However, these values do not have further precedent in **1**−**6**. One of the seminal studies correlating ^{7}Li chemical shift and coordination environment followed the change on going from [Li(THF)$_4$]$^+$ (δ −1.53 ppm) to [Li(HMPA)]$^+$ (δ −0.5 ppm).[21] Compound **5**, which

---

(15) Stille, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201.

(16) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37.

(17) (a) Aoyagi, T.; Araki, T.; Oguni, N.; Tani, H. *Inorg. Chem.* **1973**, *12*, 817. (b) Aoyagi, T.; Araki, T.; Oguni, N.; Mikumo, M.; Tani, H. *Inorg. Chem.* **1973**, *12*, 2702.

(18) Veith, M.; Frank, W.; Töllner, F.; Lange, H. *J. Organomet. Chem.* **1987**, *326*, 315.

(19) Chang, C.-C.; Srinivas, B.; Wu, M.-L.; Chiang, W.-H.; Chiang, M. Y.; Hsiung, C.-S. *Organometallics* **1995**, *14*, 5150.

(20) *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 105−147.

(21) Reich, H. J.; Borst, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1835.

Table 3. Crystal Data for [Me$_2$AlNLi(THF)^{t}Bu]$_2$ (**1**), [^{i}Bu$_2$AlNLi(THF)Ph]$_2$ (**2**), Me$_2{}^t$BuAlNLi(THF)$_3$Dipp (**4**), [^{i}Bu$_2{}^t$BuAlNHDipp][Li(THF$_4$)] (**5**), and Mes$_2$Al(NH^{t}Bu)$_2$Li(THF) (**7**)

compound	**1**	**2**	**4**	**5**	**7**
formula	$C_{10}H_{23}AlLiNO$	$C_{18}H_{31}AlLiON$	$C_{30}H_{57}AlLiNO_3$	$C_{40}H_{77}AlLiNO_4$	$C_{30}H_{50}AlLiN_2O$
formula weight	207.2	311.4	513.7	669.9	488.6
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	Cc	$P2_1/n$	$P2_1/n$
a (Å)	9.018(2)	10.584(1)	18.215(3)	10.262(1)	17.005(2)
b (Å)	9.056(1)	14.469(1)	10.498(1)	26.899(5)	10.925(2)
c (Å)	9.429(2)	13.599(1)	18.217(4)	16.687(2)	17.138(2)
α (deg)	109.23(1)				
β (deg)	90.29(1)	94.40(1)	106.12(1)	99.72(1)	95.52(1)
γ (deg)	102.82(1)				
V (Å^3)	706.4(2)	2076.4(3)	3347(1)	4540(1)	3169.2(8)
Z	2	4	4	4	4
D_{calc} (g/cm^3)	0.974	0.996	1.020	0.980	1.024
crystal size (mm)	0.8 × 0.3 × 0.2	0.9 × 0.8 × 0.3	1.3 × 0.6 × 0.4	0.6 × 0.6 × 0.4	0.4 × 0.3 × 0.15
temperature (K)	298	298	278	298	298
2θ range (deg)	3.5−45	3.5−45	3.5−45	3.5−45	3.5−45
scan type	$2\theta - \theta$	$2\theta - \theta$	$2\theta - \theta$	$2\theta - \theta$	$2\theta - \theta$
scan speed (deg/min)	10−60	10−60	18−60	8−60	8−60
scan range (deg)	0.55	0.41	0.60	0.39	0.36
reflections collected	2228	3549	1983	7392	4003
indp reflections	1810	2718	1983	5889	3096
obsd reflections	1070	1323	1423	1958	1384
$F > x\sigma(F)$	6	6	4	6	4
number of parameters	127	199	323	428	316
R	0.0697	0.0741	0.0650	0.0755	0.0657
R_w	0.0679	0.0692	0.0611	0.0678	0.0649
GOF	0.75	1.41	2.44	2.10	2.30
LarDiff. Peak (e/Å^3)	0.26	0.20	0.24	0.17	0.18

Table 4. ^{7}Li NMR Data for Compounds **1**−**8**

compound	chemical shift (ppm)
[Me$_2$AlNLi(THF)^{t}Bu]$_2$ (**1**)	0.708
[^{i}Bu$_2$AlNLi(THF)Ph]$_2$ (**2**)	−0.415
[Me$_2$AlNLi(THF)$_2$Ph]$_2$ (ref 7)	−0.586
[(SiMe$_3$)$_2$AlNLi(THF)$_2$Ph]$_2$ (**3**)	−0.342
Me$_2{}^t$BuAlNHLi(THF)$_3$Dipp (**4**)	−0.865
[^{i}Bu$_2{}^t$BuAlNHDipp] Li(THF)$_4$ (**5**)	−1.684, −0.952
Mes$_2$MeAlNLi(THF)$_2$(SiMe$_3$)$_2$ (**6**)	−0.146
Mes$_2$Al(NH^{t}Bu)$_2$Li(THF) (**7**)	1.464
Mes$_2$Al(NH^{t}Bu)$_2$Li(THF)$_2$ (**8**)	−0.073

exists as a separated ion pair in the solid state, exhibited one peak corresponding to the tetrasolvate (δ −1.684 ppm) and another corresponding to displacement of one THF by coordination to the nitrogen of the aluminate (δ −0.952 ppm). This latter value is mirrored in that demonstrated by **4**, which possesses three coordinating THF molecules and one nitrogen atom in the solid state (δ −0.865 ppm). Unfortunately, there was not a clear trend continuing through the series corresponding to coordination of three through one molecule of solvent. However, there appears to be a ligand effect as evidenced by the similarity of the shifts for those bound to an N−Ph moiety.

Summary

Three methods were explored for the synthesis of lithium amido alanes: deprotonation of the neutral amido complex, elimination of Me$_4$Si (from **6**), and elimination of amine (from **7** and **8**). Only the first method was successful. In going from a neutral amido alane to the lithiated derivatives (**1**−**3**), the overall dimeric morphology of the molecule is maintained. The primary change occurs in the Al−N bond distance which, in general, shortens by 0.08−0.09 Å. The shortening may be attributed to a slight increase in the electrostatic attraction between the aluminum and nitrogen atom. Attempts to prepare the analogous monomeric derivatives by incorporating bulky groups into the molecular framework led to isolation of products resulting from alkylation of the aluminum and metalation of the nitrogen (**4** and **5**). However, these are among the first structurally characterized adducts between an aluminum trialkyl and lithium amide. In the most sterically encumbered case, alkylation also occurs but the lithium atom is dissociated. On the basis of the ^{7}Li NMR, there appears to be some reassociation of the lithium, however. Current work has been directed toward using sequestering agents such as TMEDA and 12-crown-4 to dissociate the lithium and produce discrete anionic aluminates. Unfortunately, preliminary results show that this is not a straightforward process.

Experimental Procedure

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glovebox. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and −270 instruments at 270.17 (^{1}H) and 62.5 (^{13}C) MHz. Chemical shifts are reported relative to SiMe$_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The primary amido alanes [R$_2$AlNHR′]$_2$ (where R, R′ = Me, ^{t}Bu; ^{i}Bu, Ph; SiMe$_3$, Ph; ^{i}Bu, Dipp;[10] and Me, Dipp[11]) and monomeric Mes$_2$AlN(SiMe$_3$)$_2$[10] were prepared as previously described.

[Me$_2$AlNLi(THF)^{t}Bu]$_2$ (1). [Me$_2$AlNH^{t}Bu]$_2$ (0.700 g, 2.7 mmol) was dissolved in 25 mL of THF, and ^{t}BuLi (3.0 mL, 5.5 mmol, 1.82 M in pentane) was added at 25 °C. Upon addition the solution turned orange and then colorless. The exothermic reaction mixture was stirred for 1 h at 25 °C, and then solvents were removed to give a white solid which was subsequently washed with 25 mL of dry hexanes and filtered to give 0.863 g of a colorless solid (79%): mp 183−191 °C. Dissolution of the solid in 5 mL of toluene and storage at −20 °C for several weeks yielded crystals suitable for X-ray analysis: ^{1}H NMR (270 MHz, C$_6$D$_6$) δ −0.32 (s, 6H, AlCH_3), 1.13 (m, 4H, THF), 1.54 (s, 9H, CCH_3), 3.41 (m, 4H, THF); ^{13}C NMR (100 MHz, C$_6$D$_6$) δ −3.91 (AlCH$_3$), 25.1 (THF), 38.0 (CCH$_3$), 51.3 (NCMe$_3$), 68.7 (THF); ^{27}Al NMR (104 MHz, THF-d_8) δ 138 ($W_{1/2}$ = 800); IR (KBr) 2951, 1624, 1460, 1411, 1175, 1044, 885, 845, 762, 671 cm^{-1}. Anal. Calcd for C$_{10}$H$_{23}$NOAlLi: C, 57.97; H, 11.11. Found: C, 57.76; H, 11.08.

[^{i}Bu$_2$AlNLi(THF)Ph]$_2$ (2). A solution of [^{i}Bu$_2$AlNHPh]$_2$ (2.122 g, 4.55 mmol) in 30 mL of THF was cooled to −78 °C, and then ^{t}BuLi (5.00 mL, 1.83 M, 9.10 mmol) was added over a 4 min period. The solution was stirred a −78 °C for 4 h, the solvents were removed in vacuo, and the oil was dissolved in 20 mL of toluene and stored at −30 °C. After 2 days a light yellow layer separated from the toluene. The top layer was removed, and the yellow oil was pumped on until it solidified (36 h at 25 °C). Dissolution of the yellow solid in 5 mL of toluene and storage at −15 °C for 1 day resulted in colorless crystals suitable for X-ray analysis (2.43 g, 86%): mp 188−195 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 0.40 (m, 4H, $\mathrm{AlC}H_2$), 1.04 (m, 4H, THF), 1.26−1.29 (m, 12H, $\mathrm{CHC}H_3$), 2.20 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 3.04 (m, 4H, THF), 6.60 (m, 1H, Ph−*H*), 7.01−7.21 (m, 4H, Ph−*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 25.1 (THF), 25.5 ($\mathrm{Al}C\mathrm{H}_2$), 27.9 ($C\mathrm{HCH}_3$), 29.2 ($\mathrm{CH}C\mathrm{H}_3$), 68.4 (THF), 114.5 (Ph), 121.9, 130.0, 158.1; IR (KBr) 3059, 2945, 2857, 1584, 1473, 1276, 1175, 1034, 876, 764, 675 cm^{-1}. Anal. Calcd for $C_{36}H_{62}N_2O_2Al_2Li_2$: C, 69.45; H, 10.00. Found: C, 69.09; H, 10.16.

$[(SiMe_3)_2AlNLi(THF)_2Ph]_2$ (3). $[(SiMe_3)_2AlNHPh]_2$ (1.103 g, 2.08 mmol) was dissolved in 20 mL of THF, and then ^{t}BuLi (2.3 mL, 1.80 M in pentane, 4.1 mmol) was added at 25 °C. The solution changed from a light yellow to dark yellow-orange and then back to a light yellow during the course of addition and was accompanied by a vigorous evolution of gas. The solution was stirred for 3 h at 25 °C, and then the volatiles were removed under reduced pressure to yield 1.44 g of a sticky yellow semisolid (83%): mp 83−87 °C dec; ^{1}H NMR (270 MHz, C_6D_6) δ 0.49 (s, 18H, $\mathrm{SiC}H_3$), 1.18 (m, 8H, THF), 3.17 (m, 8H, THF), 6.65−7.15 (m, 5H, Ph−*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 4.0 ($\mathrm{Si}C\mathrm{H}_3$), 25.2 (THF), 68.4 (THF), 117.7 (Ph), 118.9, 129.4, 154.5; ^{29}Si NMR (C_6D_6) δ −21.8; IR (KBr) 2958, 1618, 1490, 1401, 1261, 1044, 820, 753 cm^{-1}. Anal. Calcd for $C_{40}H_{78}N_2O_4Al_2Si_4Li_2$: C, 57.83; H, 9.40. Found: C, 57.42; H, 9.22.

$Me_2{}^tBuAlNHLi(THF)_3(2,6\text{-}{}^iPr_2Ph)$ (4). $[Me_2AlNH(2,6\text{-}{}^iPr_2Ph)]_2$ (1.184 g, 2.54 mmol) was dissolved in 25 mL of freshly distilled dry THF, and the solution was stirred at 25 °C. ^{t}BuLi (2.73 mL, 1.86 M in pentane, 5.08 mmol) was added, and the solution momentarily turned orange, but changed to a light yellow upon complete addition. The slightly exothermic reaction mixture was stirred for 1 h at 25 °C, and then the volatiles were removed under reduced pressure to give a thick yellow oil. The oil was washed with 50 mL of hexane, and a yellow solid precipitated. The solvent was filtered to give 1.883 g of a light yellow semisolid. Recrystallization from toluene at −10 °C yielded 1.767 g of colorless crystals suitable for X-ray analysis (68%): mp 28−34 °C; ^{1}H NMR (270 MHz, C_6D_6) δ −0.60 (s, 6H, $\mathrm{AlC}H_3$), 1.14 (m, 12H, THF), 1.17 (d, J = 7 Hz, 12H, $\mathrm{CHC}H_3$), 1.24 (s, 9H, $\mathrm{CC}H_3$), 2.90 (br s, 1H, N*H*), 3.08 (m, 12H, THF), 3.47 (m, 2H, $\mathrm{C}H\mathrm{CH}_3$), 6.72 (t, J = 6 Hz, 1H, Ph−*H*), 6.95 (d, J = 7 Hz, 2H, Ph−*H*); ^{13}C NMR (100 MHz, C_6D_6) δ −9.02 ($\mathrm{Al}C\mathrm{H}_3$), 24.2 ($C\mathrm{CH}_3$), 24.5 (THF), 25.3 ($\mathrm{C}C\mathrm{H}_3$), 27.7 ($C\mathrm{HCH}_3$), 32.0 ($\mathrm{CH}C\mathrm{H}_3$), 118.3 (Ph), 123.6, 136.6, 148.5; IR (KBr) 3049, 2928, 1462, 1429, 1238, 1167, 1044, 761, 686, 630, 565 cm^{-1}. Anal. Calcd for $C_{30}H_{57}NO_3AlLi$: C, 70.18; H, 11.11. Found: C, 69.77; H, 11.38.

$[{}^iBu_2{}^tBuAlNH(2,6\text{-}{}^iPr_2Ph)][Li(THF)_4]$ (5). A solution of $[{}^iBu_2AlNH(2,6\text{-}{}^iPr_2Ph)]_2$ (2.00 g, 3.15 mmol) in 30 mL of THF was cooled to −78 °C, and then ^{t}BuLi (3.42 mL, 1.86 M, 6.36 mmol) was added over 2 min. The solution was stirred at −78 °C for 2 h, the solvents were removed in vacuo, and the residual semisolid was dissolved in 15 mL of toluene and stored at −30 °C. After 2 days, a colorless preciptitate was isolated by removal of excess solvents at −78 °C. Redissolution of the precipitate in minimium toluene at 25 °C and storage at −10 °C yielded colorless crystals suitable for X-ray analysis (3.96 g, 94%): mp 62−64 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 0.18−0.51 (m, 4H, $\mathrm{AlC}H_2$), 1.25−1.41 (m, 40H, $\mathrm{CHC}H_3$ and THF), 1.44 (s, 9H, $\mathrm{CC}H_3$), 2.30 (m, 2H, $\mathrm{CH_2C}H$), 3.07 (s, 1H, N*H*), 3.34 (m, 16H, THF), 3.67 (sept, 2H, $\mathrm{PhC}H$), 6.81−7.15 (m, 3H, Ph−*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 22.6 ($C\mathrm{CH}_3$), 24.5 (THF), 24.5 ($\mathrm{Al}C\mathrm{H}_2$), 25.5 ($\mathrm{C}C\mathrm{H}_3$), 27.7 ($C\mathrm{HCH}_3$), 27.7 ($\mathrm{Ph}C\mathrm{H}$), 29.7 ($\mathrm{CH_2CH}C\mathrm{H}_3$), 32.9 ($\mathrm{PhCH}C\mathrm{H}_3$), 68.2 (THF), 117.5 (Ph), 123.5, 136.3, 149.5; IR (KBr) 3169, 2960, 1620, 1462, 1400, 1263, 1091, 812, 669 cm^{-1}. Anal. Calcd for $C_{40}H_{77}NO_4AlLi$: C, 71.75; H, 11.51. Found: C, 72.03; H, 11.23.

$Mes_2(Me)Al{-}NLi(THF)_2(SiMe_3)_2$ (6). $Mes_2AlN(SiMe_3)_2$ (0.911 g, 2.14 mmol) was dissolved in 30 mL of THF, and freshly prepared MeLi (1.40 mL, 1.60 M in Et_2O, 2.24 mmol) was added at 25 °C. The solution was stirred for 24 h at 25 °C, and then the volatiles were removed in vacuo to give a yellow semisolid (1.13 g): mp 132−137 °C dec; ^{1}H NMR (270 MHz, C_6D_6) δ −0.14 (s, 3H, $\mathrm{AlC}H_3$), 0.57 (s, 18H, $\mathrm{SiC}H_3$), 1.38 (m, XH, THF), 2.31 (s, 6H, p-$\mathrm{C}H_3$), 2.90 (s, 12H, m-$\mathrm{C}H_3$), 3.55 (m, XH, THF), 6.91 (s, 4H, Ph−*H*); ^{13}C NMR (100 MHz, C_6D_6) δ −12.3 ($\mathrm{Al}C\mathrm{H}_3$), 5.05 ($\mathrm{Si}C\mathrm{H}_3$), 18.5 (p-$C\mathrm{H}_3$), 25.2 (THF), 26.7 (m-$C\mathrm{H}_3$), 68.9 (THF), 125.7 (Ph), 126.9, 127.1, 127.2, 132.8, 146.7. Anal. Calcd for $C_{24}H_{40}NAlSi_2$: C, 66.92; H, 9.92. Found: C, 67.00; H, 9.98.

$Mes_2Al(NH{}^tBu)_2Li(THF)$ (7). *tert*-Butylamine (1.0 mL, 9.5 mmol) was dissolved in 30 mL of hexane, the solution was cooled to −78 °C, and then ^{t}BuLi (5.3 mL, 1.80 M in pentane, 9.5 mmol) was added slowly over 2 min. The milky white suspension was warmed to 25 °C and stirred for 1 h, and then cannulated into a solution of $Mes_2AlCl{-}THF$ (1.78 g, 4.77 mmol) in 30 mL of toluene. The reaction mixture was stirred at 25 °C for 12 h, the volatiles were removed under reduced pressure, and the residue was extracted with 75 mL of hexane. Filtration and concentration to $^1/_3$ volume yielded crystals suitable for X-ray analysis after storage at −30 °C for 5 days (1.88 g, 81%): mp softens at 132 °C, melts at 188−189 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 1.09 (m, 4H, THF), 1.15 (s, 18H, $\mathrm{CC}H_3$), 2.26 (s, 2H, $\mathrm{PhC}H_3$), 2.32 (s, 4H, $\mathrm{PhC}H_3$), 2.47 (s, 9H, $\mathrm{PhC}H_3$), 2.55 (s, 3H, $\mathrm{PhC}H_3$), 2.70 (br s, 2H, N*H*), 3.40 (m, 4H, THF), 6.86 (s, 4H, Ph−*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 21.3 ($\mathrm{Ph}C\mathrm{H}_3$), 21.4 ($\mathrm{Ph}C\mathrm{H}_3$), 24.9 ($\mathrm{Ph}C\mathrm{H}_3$), 25.4 ($\mathrm{Ph}C\mathrm{H}_3$), 27.4 (THF), 34.7 ($\mathrm{C}C\mathrm{H}_3$), 50.1 ($C\mathrm{CH}_3$), 69.6 (THF), 125.6 (Ph), 127.9, 128.1, 145.6; IR (KBr) 2953, 1601, 1446, 1369, 1211, 1035, 947, 846, 594, 488 cm^{-1}. Anal. Calcd for $C_{30}H_{50}N_2OAlLi$: C, 73.77; H, 10.25. Found: C, 74.07; H, 10.38.

$Mes_2Al(NH{}^tBu)_2Li(THF)_2$ (8). $Mes_2Al(NH{}^tBu)_2Li(THF)$ (**7**) (1.88 g, 3.85 mmol) was dissolved in 40 mL of dry THF and heated at reflux for 24 h, and then the volatiles were removed under reduced pressure to give a white solid. The solid was extracted in hexanes (50 mL) and the solution filtered. Concentration of the filtrate to ∼$^1/_2$ volume and storage at −30 °C for 2 days yielded colorless crystals suitable for X-ray analysis (1.62 g, 75%). The title compound may also be synthesized directly following the procedure described for **7** except lithiating *tert*-butylamine in THF instead of hexanes: mp 189−192 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 1.12 (s, 18H, $\mathrm{CC}H_3$), 1.30 (m, 8H, THF), 2.31 (s, 6H, $\mathrm{PhC}H_3$), 2.69 (br s, 12H, $\mathrm{PhC}H_3$), 3.44 (m, 8H, THF), 6.95 (s, 4H, Ph−*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 21.4 ($\mathrm{Ph}C\mathrm{H}_3$), 25.5 ($\mathrm{Ph}C\mathrm{H}_3$), 27.5 (THF), 34.7 ($\mathrm{C}C\mathrm{H}_3$), 50.1 ($C\mathrm{CH}_3$), 68.1 (THF), 125.6 (Ph), 127.8, 128.1, 145.2; IR (KBr) 2952, 1601, 1448, 1371, 1212, 1042, 932, 844, 594, 489 cm^{-1}. Anal. Calcd for $C_{34}H_{58}N_2O_2AlLi$: C, 72.86; H, 10.36. Found: C, 73.11; H, 10.37.

X-ray Experimental. Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 3. Data were collected on a Siemens P4 diffractometer using graphite monochromated Mo Kα (0.71073 Å) radiation. In each case the check reflections indicated a less than 5% decrease in intensity over the course of data collection, and hence, no correction was applied. All calculations were performed on a personal computer using the Siemens software package, SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms (all but the nitrogen hydrogens) were included in the refinement in calculated positions using fixed isotropic parameters. The nitrogen hydrogens were found from difference maps and allowed to refine isotropically without further restraints.

Acknowledgment. Gratitude is expressed to the National Science Foundation (NSF-OSR Grant 9452892) and the donors of the Petroleum Research Fund (Grant 30057-G3), administered by the American Chemical Society, for support. The receipt of an NSF-CAREER (1996−2000) award is also gratefully acknowledged.

Supporting Information Available: Tables of bond lengths and angles, positional parameters, anisotropic thermal parameters, and unit cell views (73 pages). See any current masthead page for ordering and Internet access instructions.

JA961244F