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Halide Effects in the Formation of Four-Coordinate, Cationic Aluminum

David Atwood* and Jolin Jegier

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

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This work was conducted as part of a broad-based effort to determine the factors that affect cation formation for organometallic aluminum complexes. In this study the adduct species $R_2AlX\cdot NH_2{}^tBu$ (R, X: Me, F (**1**); Me, Cl (**2**); Et, Cl (**3**); Me, Br (**4**)) and cationic complexes $[R_2Al(NH_2{}^tBu)_2]X$ (R, X: Me, Br (**5**); Et, Br (**6**); Me, I (**7**)) were examined. These complexes demonstrate that the reaction of R_2AlX with excess $NH_2{}^tBu$ produces cationic complexes only when X = Br or I. All of the compounds were characterized by melting points, ^1H NMR, IR, elemental analyses, and, in some cases, X-ray crystallography. X-ray data: **2**, triclinic, $P\bar{1}$, $a = 6.277(3)$ Å, $b = 8.990(3)$ Å, $c = 10.393(3)$ Å, $\alpha = 71.97(1)°$, $\beta = 80.25(3)°$, $\gamma = 81.97(3)°$, $V = 547.0(4)$ Å^3, $Z = 2$, 1032 reflections with $F > 4.0\ \sigma(F)$, $R = 0.0520$; **5**, monoclinic, $P2_1/c$, $a = 9.099(1)$ Å, $b = 10.292(1)$ Å, $c = 17.255(2)$ Å, $\beta = 104.81(1)°$, $V = 1562.1(3)$ Å^3, $Z = 4$, 1464 reflections with $F > 4.0\ \sigma F$, $R = 0.0387$; **6**, monoclinic, $P2_1/c$, $a = 14.122(2)$ Å, $b = 13.539(2)$ Å, $c = 21.089(2)$ Å, $\beta = 107.73(1)°$, $V = 3841.2(9)$ Å^3, $Z = 4$, 781 reflections with $F > 5.0\ \sigma F$, $R = 0.0873$; **7**, monoclinic, $P2_1/n$, $a = 9.071(1)$ Å, $b = 10.529(1)$ Å, $c = 17.714(2)$ Å, $\beta = 103.67(1)°$, $V = 1644.0(3)$ Å^3, $Z = 4$, 1723 reflections with $F > 4.0\ \sigma F$, $R = 0.0451$.

Introduction

Although the first group 13 cation $[Me_2Ga(NH_3)_2]^+$ was synthesized in 1933 by Kraus and Toonder,[1] it was only in 1962 that the compound was correctly postulated to be cationic by Shriver and Parry.[2] Since that time four-coordinate cations have been reported sporadically in the literature. Representative examples include the cations $[Al(2\text{-}C(SiMe_3)_2C_5H_4N)_2]^+$,[3] $[{}^tBu_2Al(TMEDA)]^+$,[4] and $[Me_2Ga(NH_2{}^tBu)_2]^+$.[5]

Far more work has been reported on cationic complexes with a coordination number greater than 4. Perhaps the most historically well-developed cations are the six- and seven-coordinate complexes of general formula $[R_2Al(\text{crown ether})]^+$ (where R = alkyl or chloride).[6] Other examples of group 13 cations include those incorporating azamacrocycles[7] and multidentate ligands.[8] More recently, systematic studies of aluminum cations supported by the Salen class of ligands of general formula $[SalenAl(base)_2]^+$ have been reported.[9]

The lack of a systematic study into four-coordinate aluminum cations is surprising in view of the fact that aluminum cations may be expected to find as much relevance in organic transformations and catalysis as the traditional neutral derivatives.[10] For instance, they may possess enhanced Lewis acidity based upon the positive charge on the aluminum atom. Initial work toward this end appears promising. For example, four-

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Table 1. Selected Spectroscopic Data for Compounds **1**−**7**[a]

	^{1}H, ppm			
compound	Al−R (ppm)	N−^{t}Bu	N−H	ν(N−H) cm^{-1}
$Me_2AlF\cdot NH_2{}^tBu$ (**1**)	−0.40 (s)	0.61 (s)	1.74 (s)	3288, 3242
$Me_2AlCl\cdot NH_2{}^tBu$ (**2**)	−0.27 (s)	0.66 (s)	2.47 (s)	3240, 3207
$Et_2AlCl\cdot NH_2{}^tBu$ (**3**)	0.24 (q), 1.40 (t)	0.69 (s)	2.54 (s)	3231, 3200
$Me_2AlBr\cdot NH_2{}^tBu$ (**4**)	−0.19 (s)	0.65 (s)	2.62 (s)	3271, 3202
$[Me_2Al(NH_2{}^tBu)_2]Br$ (**5**)	−0.60 (s)	1.26 (s)	4.16 (s)	3053
$[Et_2Al(NH_2{}^tBu)_2]Br$ (**6**)	0.31 (q), 1.41 (t)	1.00 (s)	not obsd	3122
$[Me_2Al(NH_2{}^tBu)_2]I$ (**7**)	−0.55	1.37 (s)	5.81 (s)	3121, 3067

[a] All NMR data are given in C_6D_6 except those for **5** and **7**, which were taken in THF-d_8.

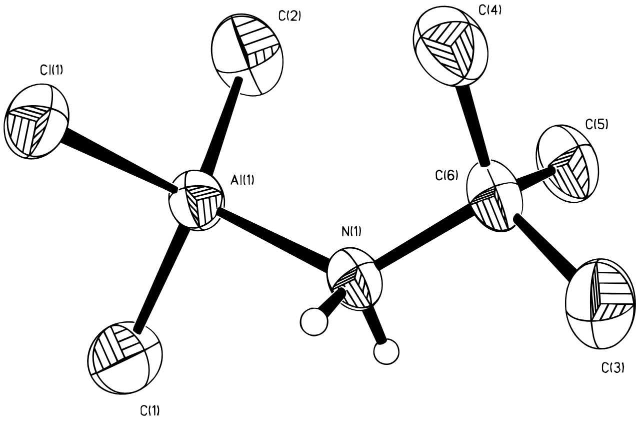


Figure 1. Molecular structure and atom-numbering scheme for $Me_2AlCl\cdot NH_2{}^tBu$ (**2**).

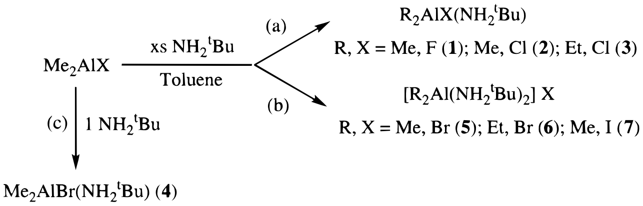
coordinate aluminum cations have been postulated to promote certain Diels−Alder reactions.[11] Additionally, we recently reported the use of six-coordinate cations of the form $[SalenAl(MeOH)_2]^+$ as propylene oxide oligomerization catalysts.[12]

As a corollary to our work on six-coordinate, cationic complexes, we have been exploring the guidelines for which analogous four-coordinate species may form. This marks the first instance where a systematic study into the factors that affect cation formation has been presented. It will expand upon an earlier communication[13] and focus on what types of halide may be displaced from R_2AlX (X = halide) by *tert*-butylamine to form the cations, $[R_2Al(NH_2{}^tBu)_2]X$. The specific compounds to be discussed are the adducts $R_2AlX\cdot NH_2{}^tBu$ (R, X: Me, F (**1**); Me, Cl (**2**); Et, Cl (**3**); Me, Br (**4**)) and cationic complexes $[R_2Al(NH_2{}^tBu)_2]X$ (R, X: Me, Br (**5**); Et, Br (**6**); Me, I (**7**)).

Results and Discussion

The four-coordinate cationic aluminum complexes that have been reported in the literature have three things in common: (1) they employ alkyl groups on aluminum, (2) they displace halide in forming the cation, and (3) a strong base (usually nitrogen) is used to effect this displacement. Although there are not enough examples of four-coordinate cations to determine a trend for the type of halide that is displaced, taken together with the six-coordinate cations, it can be seen that the type of halide that is displaced is generally chloride (forming the anion, usually $[R_nAlCl_{4-n}]^-$). For the present study, we wanted to determine what halides could be displaced by a monodentate base, while keeping the type of ligand (and base) constant. Cases where the halide = F, Cl, Br, and I will be examined. A future installment in this program will be an examination of what effect changing one of the alkyls to alkoxide has on cation formation.[14]

Scheme 1. General Syntheses of the Adducts (**1**−**4**) and the Cationic (**5**−**7**) Complexes



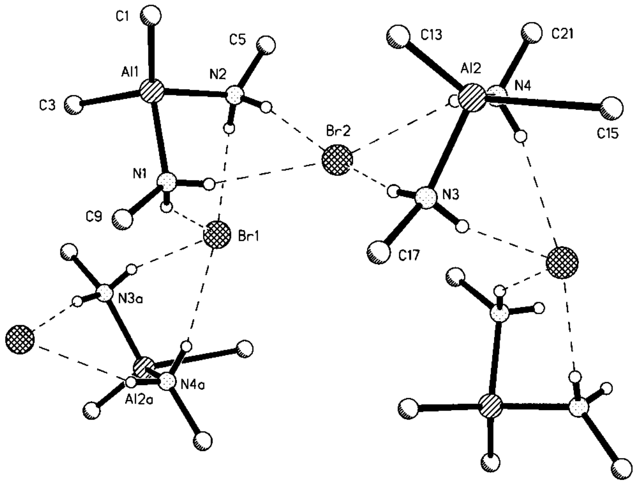


Figure 2. Network of hydrogen bonding in $[Et_2Al(NH_2{}^tBu)_2]Br$ (**6**).

Compounds **1**−**3** were prepared by mixing the dialkylaluminum halide reagent with an excess of *tert*-butylamine in toluene and allowing the mixture to stir for a minimum of 2 h at ambient temperature. In the cases where the halide = F or Cl the corresponding adduct species (**1**−**3**) resulted (Scheme 1a). This type of adduct can also be prepared by the reaction of Me_3Al with $[H_3N^tBu]X$ (X = Cl, Br, I).[15] The adduct species for X = Br (**4**) can be prepared by adding 1 equiv of *tert*-butylamine to Me_2AlBr (Scheme 1c). The successful adduct formation in this reaction is in contrast to the same reaction conducted using a bidentate base (tetramethylethylenediamine (TMEDA)). When 1 equiv of TMEDA is added to $[^tBu_2AlX]_2$, the product $[^tBu_2Al(TMEDA)]^+[^tBu_2AlX_2]^-$ appears to result from the unsymmetrical cleavage of the dialkylaluminum halide dimer.[4] In the preparation of **4**, there was no evidence for this type of reaction. All of the adducts were soluble in toluene and were isolated by recrystallization from hexane at low temperature.

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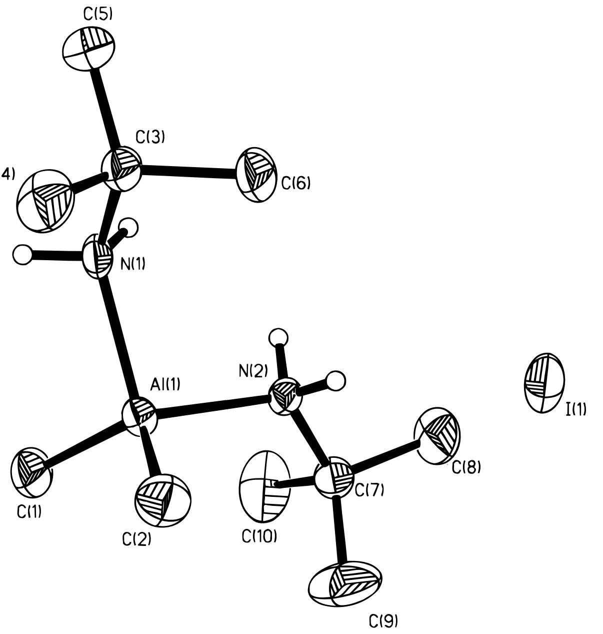

Figure 3. Molecular structure and atom-numbering scheme for [$Me_2Al(NH_2{}^tBu)_2$]I (**7**).

The presence of one coordinated *tert*-butylamine in **1**−**4** was determined by the integration of the ^1H NMR data. This indicated a ratio of 2:3 for the methyl and *tert*-butyl hydrogens. The effect of decreasing halide electronegativity can be seen in the change in Al−Me ^1H chemical shifts for **1**, **2**, and **4** (Table 1). This group shifts to lower field, becoming progressively more deshielded as the electron-withdrawing potential of the halide becomes weaker. This can be interpreted in terms of a synergy within in the X−Al−C−H linkage. There is an increase in p character in the Al−X bond maximized at X = F. The Al−Me bonds then possess more s character and, in turn, the C−H bonds more p character. Since p orbitals are less electronegative than s orbitals, the net effect is a relatively more deshielded proton moving from F to Br.

The molecular structure of **2** exemplifies the adduct motif (Figure 1). The Al atom possesses a distorted T_d geometry. The most significant deviations occur in the C−Al−C bond angle which is wider (121.2(3)°), and the N−Al−Cl angle, which is correspondingly more narrow (99.5(1)°). This is in keeping with an increase in p character (narrower angles) in the bonds to the more electronegative atoms. A similar, although more pronounced, distortion is observed in the molecular structure of $Mes_2GaF{\cdot}NH_2{}^tBu$.[16] In this complex the F−Ga−N bond angle is 94.0(2)°.

When the halide is changed to Br or I (Scheme 1b), the second *tert*-butylamine molecule acts to break the Al−X bond and displace the halide to form the cation. A significant change occurs in the ν_{N-H} IR stretches when this takes place (Table 1). In **1**−**4**, both the symmetric and asymmetric stretching modes were apparent. In **5** and **6**, this group is manifested as a broad peak shifted to lower frequency. In **7**, the N−H stretches appear as broad peaks 150−200 cm^{-1} lower than the adducts. These changes can be explained by the presence of hydrogen bonding between the $-NH_2$ groups and the halide. This is apparent in the crystal packing diagrams of **5**−**7** (provided in the Supporting Information). As a representative example, the network of hydrogen bonding for **6** is shown in Figure 2 (the terminal CH_3 groups on the ethyls and *tert*-butyls have been omitted for clarity). In the structure, each bromide ion bridges two cations and hydrogen bonds with one hydrogen on each of the amine groups. This leads to a total of four bonds which range from 2.53 to 2.74 Å and give the bromide a distorted square planar geometry.

The molecular structures of **5** and **7** are very similar (Figure 3 depicts **7**; compound **5** is isomorphous and has the same atom-labeling scheme). Each possesses a central four-coordinate aluminum cation in a distorted T_d geometry. The distortions are evident in widened C−Al−C bond angles and narrowed N−Al−N bond angles (see Table 2). Additionally, the Al−C and Al−N bond distances are quite similar.

A primary motivation for our study of cationic aluminum complexes is to determine their utility in organic synthesis and catalysis. Along these lines, we have previously reported that $SalenAl^+$ complexes oligomerize propylene oxide.[12] We were interested to see whether complex **2** would also be catalytically active. In the experiment, both **1** and **2** were dissolved in liquid propylene oxide and the resulting solutions were stirred for 72 h. After a standard workup, the ^1H NMR spectra indicated that there was no polyether present. Although no concrete conclusions may be drawn from this negative result, it is interesting to note that the successful polymerization catalysts were six-coordinate[12] while the cation reported here is four-coordinate.

Conclusion

This work was conducted as part of a broad-based program to understand the limits for which cationic aluminum complexes are formed. In so doing, factors such as ligand, base, and halide may be varied. The current study was concerned with what effect the type of halide has on cation formation and has demonstrated that the demarcation for cation formation in complexes of general formula R_2AlX with excess $NH_2{}^tBu$ lies between Cl and Br. Thus, only adducts are isolated when X = *F* or Cl, and cations are formed when X = Br and I. Current work is focused on the effect of changing the R group on Al from alkyl to alkoxide.[14]

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert-atmosphere glovebox. All solvents were rigorously dried prior to use. *tert*-Butylamine was dried over CaH_2 and distilled prior to use. The Me_2AlF used in the synthesis of **1** was prepared according to the literature method but employing a 20 h, rather than 3 h, reflux.[17] Propylene oxide was dried over CaH_2, distilled, and used immediately. NMR data were obtained on JEOL GSX-400 and -270 instruments at 270.17 Hz (^1H). 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}.

$Me_2AlF{\cdot}H_2N^tBu$ (1). To a stirred suspension of sodium fluoride (58.35 mmol, 2.450 g) in toluene (10 mL) was added a solution of dimethlyaluminum chloride (54.05 mmol, 5.00 g) in toluene (5 mL). To this suspension was added xylene (20 mL) and the mixture refluxed for 20 h. The volatiles were distilled from the solid under vacuum, and to the resulting colorless solution was added 4 equiv of *tert*-butylamine (0.216 mol, 22.7 mL). The solution was stirred at 25 °C for 12 h, and the volatiles were removed under reduced pressure, yielding an oily white solid. The solid was dissolved in hexane (30 mL), the solution filtered, and the filtrate stirred at −78 °C for 12 h, yielding **1** as colorless needles (5.483 g, 68%). Mp: 52−6 °C. ^1H-NMR (C_6D_6): δ −0.40 (s, 6H, $AlCH_3$), 0.61 (s, 9H, $C(CH_3)_3$), 1.74 (s (br), 2H, NH_2). IR: ν 3288 s, 3242 s, 2972 m, 2930 s, 2818 w, 1577 s, 1475 m, 1402 m, 1377 s, 1284 m, 1178 s (br), 1026 w, 900 m, 711

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Table 2. Bond Lengths (Å) and Angles (deg) for **2**, **5**, and **7**[a]

$Me_2AlCl\cdot NH_2{}^tBu$ (**2**)		$[Me_2Al(NH_2{}^tBu)_2]Br$ (**5**)		$Me_2Al(NH_2{}^tBu)_2]I$ (**7**)	
Al(1)−Cl(1)	2.204(2)	Al−N(1)	2.000 (4)	Al(1)−N(1)	1.988(7)
Al(1)−N(1)	1.993(4)	Al−N(2)	1.989(4)	Al(1)−N(2)	1.996(6)
Al(1)−C(1)	1.937(6)	Al−C(1)	1.955(7)	Al(1)−C(1)	1.960(8)
Al(1)−C(2)	1.946(5)	Al−C(2)	1.951(6)	Al(1)−C(2)	1.929(9)
N(1)−C(6)	1.519(6)	N(1)−C(3)	1.510(7)	N(1)−C(3)	1.509(10)
C(3)−C(6)	1.520(8)	N(2)−C(7)	1.501(6)	N(2)−C(7)	1.509(11)
C(4)−C(6)	1.508(6)	C(3)−C(4)	1.520(8)	C(3)−C(4)	1.514(13)
C(5)-C(6)	1.510(6)	C(3)−C(5)	1.516(8)	C(3)−C(5)	1.520(14)
		C(3)−C(6)	1.525(8)	C(3)−C(6)	1.539(10)
		C(7)−C(8)	1.468(10)	C(7)−C(8)	1.519(12)
		C(7)−C(9)	1.494(10)	C(7)−C(9)	1.505(15)
		C(7)-C(10)	1.488(10)	C(7)-C(10)	1.526(13)
Cl(1)−Al(1)−N(1)	99.5(1)	N(1)−Al−N(2)	97.5(2)	N(1)−Al(1)−N(2)	98.2(3)
Cl(1)−Al(1)−C(1)	108.0(2)	N(1)−Al−C(1)	103.3(2)	N(1)−Al(1)−C(1)	102.8(3)
N(1)−Al(1)−C(1)	102.5(2)	N(2)−Al−C(1)	114.7(2)	N(2)−Al(1)−C(1)	114.1(4)
Cl(1)−Al(1)−C(2	108.5(2)	N(1)−Al−C(2)	116.7(2)	N(1)−Al(1)−C(2)	115.1(4)
N(1)−Al(1)−C(2)	114.8(2)	N(2)−Al−C(2)	106.8(2)	N(2)−Al(1)−C(2)	107.2(3)
C(1)−Al(1)−C(2)	121.2(3)	C(1)−Al−C(2)	116.6(3)	C(1)−Al(1)−C(2)	117.9(4)
Al(1)-N(1)-C(6)	126.8(3)	Al−N(1)−C(3)	124.2(3)	Al(1)−N(1)−C(3)	126.7(5)
N(1)-C(6)-C(3)	107.9(3)	Al−N(2)−C(7)	123.5(4)	Al(1)−N(2)−C(7)	123.7(5)
N(1)-C(6)-C(4)	108.6(4)	N(1)−C(3)−C(4)	108.1(4)	N(1)−C(3)−C(4)	107.6(7)
C(3)-C(6)-C(4)	111.4(4)	N(1)−C(3)−C(5)	108.2(5)	N(1)−C(3)−C(5)	109.9(7)
N(1)-C(6)-C(5)	107.7(4)	C(4)−C(3)−C(5)	111.8(5)	C(4)−C(3)−C(5)	110.2(8)
C(3)-C(6)-C(5)	110.1(4)	N(1)-C(3)-C(6)	108.0(5)	N(1)−C(3)−C(6)	107.0(6)
C(4)-C(6)-C(5)	111.1(4)	C(4)-C(3)-C(6)	110.0(5)	C(4)-C(3)-C(6)	112.0(8)
		C(5)-C(3)-C(6)	110.6(4)	C(5)-C(3)-C(6)	110.0(7)
		N(2)-C(7)-C(8)	108.5(5)	N(2)-C(7)-C(8)	107.6(7)
		N(2)-C(7)-C(9)	109.3(5)	N(2)-C(7)-C(9)	108.2(8)
		C(8)-C(7)-C(9)	111.1(6)	C(8)-C(7)-C(9)	112.2(8)
		N(2)-C(7)-C(10	108.6(5)	N(2)-C(7)-C(10)	107.9(7)
		C(8)-C(7)-C(10)	110.7(6)	C(8)-C(7)-C(10)	109.0(8)
		C(9)-C(7)-C(10)	108.6(6)	C(9)-C(7)-C(10)	111.7(9)

[a] The best structure obtained for **6** suffered serious disorder problems. The bond length and angle data were not of sufficient quality to be used in the discussion.

Table 3. Summary of Crystal Data for $Me_2AlCl\cdot NH_2{}^tBu$ (**2**), $[Me_2Al(NH_2{}^tBu)_2]Br$ (**5**), $[Et_2Al(NH_2{}^tBu)_2]Br$ (**6**), and $[Me_2Al(NH_2{}^tBu)_2]I$ (**7**)

	2	**5**	**6**	**7**
formula	$C_6H_{17}AlClN$	$C_{10}H_{28}AlBrN_2$	$C_{24}H_{64}Al_2Br_2N_4$	$C_{10}H_{28}AlIN_2$
fw	547.0	283.2	622.6	330.2
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	6.277(3)	9.099(1)	14.122(2)	9.071(1)
b, Å	8.990(3)	10.292(1)	13.539(2)	10.529(1)
c, Å	10.393(3)	17.255(2)	21.089(2)	17.714(2)
α, deg	71.97(1)			
β, deg	80.25(3)	104.81(1)	107.73(1)	103.67(1)
γ, deg	81.97(3)			
V, Å^3	547.0(4)	1562.1(3)	3841.2(9)	1644.0(3)
Z	2	4	4	4
D_{calc}, g/cm^3	1.006	1.204	1.077	1.334
crystal size, mm	$(0.8)^2 \times 0.3$	$(0.4)^3$	$0.6 \times (0.1)^2$	$0.7 \times 0.4 \times 0.2$
T, K	298	298	298	298
2θ range, deg	3.5−45	3.5−45	3.5−45	3.5−45
scan type	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$
scan speed, deg/min	8−60	6−60	6−60	12−60
scan range, deg	0.72	0.40	0.40	0.50
no. of reflns collcd	1886	4704	6001	2970
no. of indp reflns	1421	2003	4741	2150
no. of obsd reflns	1032	1464	781	1723
x ($F > x\sigma(F)$)	4	4	5	4
no. of params	82	127	235	127
R	0.0520	0.0387	0.0873	0.0451
R_w	0.0511	0.0395	0.0974	0.0465
GOF	0.56	1.37	7.54	2.16
max diff peak, e/Å^3	0.33	0.47	0.36	0.81

s (br). Anal. Calcd: C, 48.30; H, 11.49. Found: C, 47.14; H, 11.13. The relatively low values for the analysis of **1** may be attributed to the fact that in the solid it decomposes rapidly at room temperature.

$Me_2AlCl\cdot H_2N^tBu$ (2). To a stirred solution of dimethylaluminum chloride (21.62 mmol, 2.000 g) in toluene (60 mL) at 25 °C was added *tert*-butylamine (86.48 mmol, 9.1 mL). The resulting colorless solution was stirred at 25 °C for 2 h, and the volatiles were removed under reduced pressure, resulting in a nearly quantitative yield of **2** as a white powder. Recrystallization by dissolution in hexane (90 mL) followed by storage at −30 °C for several days afforded 2.976 g (83%) of **2** as colorless needles. X-ray-quality crystals were obtained from a concentrated solution in toluene stored at −20 °C for 1 day. Mp: 61−3 °C. ^{1}H-NMR (C_6D_6): δ −0.27 (s, 6H, AlCH_3), 0.66 (s, 9H, C(CH_3)$_3$), 2.47 (s (br), 2H, NH_2). IR: ν 3240 s, 3207 s, 3130 m, 2976 s, 2945

Table 4. Atomic Coordinates ($\times 10^5$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^4$) for $Me_2AlCl\cdot NH_2{}^tBu$ (**2**)

atom	*x*	*y*	*z*	*U*(eq)
Al(1)	13054(23)	8125(16)	21329(14)	598(6)
Cl(1)	−18734(20)	4522(16)	34065(14)	845(6)
N(1)	26781(54)	17910(36)	32271(34)	529(14)
C(1)	29726(99)	−12146(62)	23800(67)	1042(33)
C(2)	8337(108)	21713(68)	3222(52)	1031(31)
C(3)	36001(89)	37012(60)	42517(53)	826(25)
C(4)	2396(79)	42012(56)	31299(56)	794(24)
C(5)	38809(85)	43000(54)	17333(50)	799(24)
C(6)	25825(73)	35316(47)	30831(46)	584(19)

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Me_2Al(NH_2{}^tBu)_2]Br$ (**5**)

atom	*x*	*y*	*z*	*U*(eq)
Al	1276(2)	7082(2)	1191(1)	41(1)
Br	491(1)	1195(1)	1474(1)	60(1)
N(1)	−435(5)	8186(4)	575(2)	40(2)
N(2)	1712(5)	8077(4)	2212(2)	41(2)
C(1)	2813(7)	7257(7)	586(4)	71(3)
C(2)	764(7)	5316(5)	1440(4)	68(3)
C(3)	−2085(6)	7963(5)	551(3)	46(2)
C(4)	−2223(7)	7886(7)	1410(3)	63(3)
C(5)	−2593(7)	6715(6)	95(4)	67(3)
C(6)	−2996(7)	9116(6)	124(4)	68(3)
C(7)	3252(6)	8133(6)	2793(3)	49(2)
C(8)	3773(9)	6798(8)	3004(5)	128(4)
C(9)	3148(8)	8879(9)	3520(4)	101(4)
C(10)	4312(8)	8824(9)	2405(4)	127(5)

m, 2879 m, 1579 s, 1475 m, 1402 s, 1377 s, 1302 s, 1197 s, 898 w, 696 s (br). Anal. Calcd: C, 43.51; H, 10.35. Found: C, 43.19; H, 10.27.

$Et_2AlCl\cdot H_2N^tBu$ (3). The procedure was as for **2** using diethylaluminum chloride (10.81 mmol, 1.303 g), toluene (30 mL), *tert*-butylamine (48.24 mmol, 4.6 mL), and hexane (45 mL), yielding **3** as colorless needles (1.456 g, 70%). Mp: 69−70 °C. ^{1}H-NMR (C_6D_6): δ 0.24 (q, 4H, Al(CH_2CH$_{3)2}$), 0.69 (s, 9H, C(CH_3)$_3$), 1.40 (t, 6H, Al(CH$_2$CH_3), 2.54 (s (br), 2H, NH_2). IR: ν 3231 m, 3200 m, 2980 s, 2897 m, 2598 m, 1577 m, 1512 w, 1402 s, 1377 s, 1302 m, 1246 w, 798 m (br), 692 m. Anal. Calcd: C, 49.61; H, 10.93. Found: C, 49.49; H, 10.56.

$Me_2AlBr\cdot H_2N^tBu$ (4). Dimethylaluminum bromide was prepared *in situ* by addition of a solution of aluminum bromide (3.75 mmol, 1.000 g) in toluene (20 mL) to a stirred solution of trimethylaluminum (7.50 mmol, 0.541 g) in toluene (30 mL). The solution was allowed to stir for 20 min and then cooled to −78 °C. *tert*-Butylamine (11.50 mmol, 1.21 mL) was added slowly and the solution stirred for 30 min. The solution was slowly warmed to room temperature and stirred an additional 2 h. The volatiles were removed under reduced pressure, and the white solid was dissolved in hexane (70 mL). The solution was filtered to remove a small amount of insoluble material, and the filtrate was cooled to −30 °C for 48 h, yielding **4** as colorless plates (1.782 g, 75%). Mp: 73−7 °C. ^{1}H-NMR (C_6D_6): δ −0.19 (s, 6H, AlCH_3), 0.65 (s, 9H, C(CH_3)$_3$), 2.62 (s (br), 2H, NH_2). IR: ν 3271 w, 3202 w, 2976 s, 2889 m, 1602 s, 1570 m, 1502 s, 1477 m, 1477 s, 1404 s, 1296 s, 1261 m, 1199 s, 1093 m, 1030 m, 798 s, 707 s. Anal. Calcd: C, 34.30; H, 8.16. Found C, 34.48; H, 8.03.

$[Me_2Al(H_2N^tBu)_2]Br$ (5). Dimethylaluminum bromide was prepared *in situ* by addition of a solution of aluminum bromide (7.50 mmol, 2.000 g) in toluene (30 mL) to a stirred solution of trimethylaluminum (15.00 mmol, 1.081 g) in toluene (30 mL) at 25 °C. The solution was allowed to stir for 20 min, and then excess (4 equiv) *tert*-butylamine (89.99 mmol, 9.5 mL) was added. The colorless solution was allowed to stir for 3 h during which a white precipitate formed. The volatiles were removed under reduced pressure, yielding the product as a white powder. Dissolution in THF (150 mL) followed by slow cooling and storage at −5 °C for 1 day afforded 1.024 g of **5** as colorless X-ray-quality crystals. Storage of the filtrate at −30 °C for several days afforded 2.968 g of **5** as colorless crystals (combined yield 63%). Mp: 148−51 °C. ^{1}H-NMR (THF-d_8): δ −0.60 (s, 6H, AlCH_3), 1.26 (s, 18H, C(CH_3)$_3$), 4.16 (s (br), 4H, NH_2). IR: ν 3053 s (br), 2995 m, 1581 s, 1481 m, 1400 s, 1375 s, 1311 s, 1192 s, 1097 w, 893 m, 752 s, 705 s, 673 m. Anal. Calcd: C, 42.41; H, 9.96. Found: C, 41.98; H, 9.82.

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Et_2Al(NH_2{}^tBu)_2]Br$ (**6**)

atom	*x*	*y*	*z*	*U*(eq)
Al(1)	7085(14)	2104(14)	7093(9)	114(11)
Al(2)	8603(21)	−2366(20)	9318(10)	180(16)
Br(1)	6649(6)	−633(5)	7886(3)	148(4)
Br(2)	4111(5)	1271(4)	6214(3)	113(3)
N(1)	6158(29)	1887(28)	7612(18)	124(27)
N(2)	6600(27)	887(27)	6585(16)	111(24)
N(3)	7384(40)	−1743(30)	9410(19)	161(35)
N(4)	7891(27)	−2850(30)	8382(18)	127(27)
C(1)	8501(46)	2010(47)	7570(29)	141(22)
C(2)	8913(81)	1212(87)	8001(53)	185(47)
C(2b)	9017(88)	2934(97)	7998(57)	102(46)
C(3)	6376(89)	3422(74)	6406(50)	228(51)
C(4)	5755(167)	3693(179)	6185(112)	318(150)
C(4b)	7361(97)	3430(83)	6548(54)	133(48)
C(5)	6891(47)	392(45)	5984(26)	101(19)
C(6)	8019(76)	37(79)	6342(47)	112(45)
C(6b)	7937(103)	501(107)	6110(60)	72(50)
C(7)	6808(70)	1311(69)	5545(41)	90(34)
C(7b)	6182(91)	1084(85)	5361(52)	58(43)
C(8)	6471(72)	−674(74)	5863(40)	39(35)
C(8b)	6016(87)	−343(89)	5707(51)	84(47)
C(9)	6203(61)	2480(56)	8278(38)	138(27)
C(10)	5286(37)	2130(41)	8485(22)	156(38)
C(11)	7168(37)	2237(47)	8801(26)	220(52)
C(12)	6117(47)	3509(46)	8129(31)	249(39)
C(13b)	10189(112)	−1609(105)	9105(72)	167(62)
C(13)	9553(94)	−1378(102)	9532(61)	143(46)
C(14)	9435(76)	−568(85)	8931(50)	126(42)
C(14b)	10437(99)	−1902(93)	9586(66)	148(55)
C(15)	8819(83)	−4067(80)	9818(47)	88(40)
C(15b)	8649(83)	−3367(89)	10065(54)	108(46)
C(16)	9557(110)	−3666(116)	9804(71)	186(62)
C(16b)	9737(97)	−3518(96)	10484(63)	166(51)
C(17)	7267(58)	−1058(55)	10071(35)	143(24)
C(18)	6094(94)	−1182(113)	9968(60)	86(44)
C(18b)	6258(70)	−539(69)	9720(40)	103(34)
C(19)	6814(86)	−1920(70)	10384(45)	117(34)
C(19b)	7869(131)	−2045(115)	10603(67)	124(57)
C(20)	8433(171)	−1195(201)	10575(106)	193(92)
C(20b)	8043(73)	−286(74)	10030(44)	175(40)
C(21)	8351(62)	−3437(57)	7863(39)	163(28)
C(22)	9189(87)	−4023(89)	8252(51)	115(47)
C(22b)	8555(97)	−4468(91)	8254(53)	127(49)
C(23)	8985(67)	−2514(66)	7766(44)	141(36)
C(23b)	8332(160)	−2801(162)	7337(98)	126(84)
C(24)	7347(43)	−3740(43)	7330(27)	135(21)

$[Et_2Al(H_2N^tBu)_2]Br$ (6). The procedure was as for **5** using aluminum bromide (7.50 mmol, 2.00 g), triethylaluminum (14.99 mmol, 1.712 g), *tert*-butylamine (90.00 mmol, 9.46 mL), and (toluene (60 mL). The resulting colorless solution was concentrated to 15 mL, and hexane (20 mL) was added. The solution was stored at −30 °C for 1 week, yielding **6** as colorless needles (6.050 g, 86%). Crystals suitable for X-ray diffraction were grown from a concentrated solution in THF which was stored at −10 °C for several days. Mp: 92−5 °C. ^{1}H-NMR (C_6D_6): δ 0.31 (q, 4H, AlCH_2CH$_3$), 1.00 (s, 18H, C(CH_3)$_3$), 1.41 (t, 6H, AlCH$_2$CH_3). IR: ν 3122 s (br), 3055 s (br), 2972 s, 1591 s, 1475 m, 1402 s, 1375 s, 1311 m, 1205 m, 1184 s, 1080 m, 982 m, 895 m, 740 s, 634 m (br). Anal. Calcd: C, 46.30; H, 10.36. Found: C, 45.97; H, 9.82.

$[Me_2Al(H_2N^tBu)_2]I$ (7). Dimethylaluminum iodide was prepared *in situ* by addition of a solution of trimethylaluminum (7.50 mmol, 0.541 g) in toluene (30 mL) to a suspension of aluminum iodide (3.75 mmol, 1.529 g) in toluene (40 mL). The flask was protected from light, and the contents were refluxed for 3 h. After the mixture was cooled to 25 °C, *tert*-butylamine (45.00 mmol, 4.73 mL) was added. A white precipitate formed almost immediately. The suspension was stirred at 25 °C for 3 h, and the volatiles were removed under reduced pressure. The residue was dissolved in THF (125 mL), the mixture filtered to remove a small amount of insoluble material, and the filtrate cooled to −5 °C for 2 days, yielding 1.503 g of **7** as colorless plates suitable for X-ray diffraction. Concentration of the filtrate and storage at −30 °C for 1 day yielded 0.518 g of **7** as colorless needles (combined yield 54%). Mp: 178−80 °C. ^{1}H-NMR (THF-d_8): δ −0.55 (s, 6H, AlCH_3), 1.37 (s, 18H, C(CH_3)$_3$), 5.81 (s (br), 4H, NH_2). IR: ν 3121 s (br), 3067 s (br), 2970 s, 2928 m, 1568 m, 1479 m, 1400 s, 1375 s, 1307 s, 1201 s (br), 891 m, 744 s, 669 m. Anal. Calcd: C, 36.37; H, 8.54. Found: C, 36.14; H, 8.31.

Attempted Polymerization of Propylene Oxide with 2. To **2** (3.02 mmol, 0.500 g) was added propylene oxide (0.357 mol, 25.0 mL) at 0 °C. The mixture was then allowed to warm to 25 °C. After 45 min, all of the original solid was in solution. The solution was allowed to stir for 72 h, and the volatiles were removed under reduced pressure, resulting in a small amount of an oily solid. Nearly all of the original volume of monomer was recovered. The solid was dissolved in CH_2Cl_2 (50 mL), and the solution was washed with 0.01 M HCl (50 mL). The CH_2Cl_2 layer was then washed with H_2O (50 mL) and dried with Na_2SO_4. CH_2Cl_2 was removed under reduced pressure, resulting in a very small amount of an oily solid of which the major component was determined by ^{1}H-NMR to be silicone grease.

Attempted Polymerization of Propylene Oxide with 5. The procedure was as described for the attempted polymerization above using **5** (1.77 mmol, 0.500 g) and propylene oxide (0.357 mol, 25.0 mL), resulting in a very small amount of an oily solid of which the major component was determined by ^{1}H-NMR to be silicone grease.

X-ray Experimental Work. Data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα (0.710 73 Å) radiation. The check reflections, measured every 100 reflections, indicated a less than 5% decrease in intensity over the course of data collection for each compound, 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 for **2**, **5**, and **7**. There were two problems in the solution of **6**. First, the ethyl groups were disordered. Second, the best crystal obtained still led to a weak data set. Combined, these two problems precluded the anisotropic refinement of all of the heavy atoms in **6**. They also led to high standard deviations for the metrical and positional parameters, so much so that the bond lengths and angles were not listed for comparison in Table 2. Regardless, the structure is unambiguous and the *R* values are reasonable. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

Table 7. Atomic Coordinates ($\times 10^5$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times 10^4$) for $[Me_2Al(NH_2{}^tBu)_2]I$ (**7**)

atom	*x*	*y*	*z*	*U*(eq)
Al(1)	50642(25)	79742(24)	88141(13)	404(8)
I(1)	8377(7)	87571(6)	64941(3)	578(2)
N(1)	38878(61)	69152(62)	93937(31)	412(22)
N(2)	45305(62)	70462(61)	78037(30)	380(21)
C(1)	71622(92)	77182(104)	94008(50)	703(39)
C(2)	43518(107)	96963(82)	86152(53)	644(37)
C(3)	22526(85)	71007(87)	94229(44)	495(30)
C(4)	21599(110)	83212(96)	98618(55)	723(42)
C(5)	17253(105)	59858(97)	98365(53)	726(42)
C(6)	13170(91)	71695(113)	85773(47)	749(41)
C(7)	55068(87)	70474(87)	72217(45)	503(31)
C(8)	46618(115)	63145(121)	65121(49)	906(49)
C(9)	57932(151)	84051(104)	70323(71)	1049(62)
C(10)	69793(108)	63524(133)	75859(61)	1042(57)

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Supporting Information Available: Unit cell diagrams and listings of X-ray experimental details, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters (33 pages). Ordering information is given on any current masthead page.

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