

# Aluminum Complexes Incorporating Bulky Nitrogen and Sulfur Donor Ligands

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The synthesis and structures of aluminum complexes incorporating bulky thioamidate (RC(NR')S<sup>-</sup>), thioureido (R'HNC(NR')S<sup>-</sup>), and amidinate (RC(NR')<sub>2</sub><sup>-</sup>) ligands are described. The reaction of AlMe<sub>3</sub> with AdN=C=S (Ad = 1-adamantyl) affords the insertion product {MeC(NAd)S}AlMe<sub>2</sub> (**1**), which binds 1 equiv of AlMe<sub>3</sub> to generate {MeC(NAd)S}AlMe<sub>2</sub>·AlMe<sub>3</sub> (**2**). The alkane elimination reaction of AlMe<sub>3</sub> and N,N'-disubstituted thiourea derivatives, (R'HN)<sub>2</sub>C=S, affords thioureido complexes {R'HNC(NR')S}AlMe<sub>2</sub> (**3a**, R' = Ad; **3b**, R' = Ar = 2,6-*i*-Pr<sub>2</sub>-Ph). Carbodiimides, R'N=C=NR', react with AlMe<sub>3</sub> to afford acetamidinate compounds {MeC(NR')<sub>2</sub>}AlMe<sub>2</sub> (**4a**, R' = Ad; **4b**, R' = Ar). Sequential addition of <sup>t</sup>BuLi and AlX<sub>2</sub>Cl (X = Cl, Me) to R'N=C=NR' affords pivamidinate compounds {<sup>t</sup>BuC(NR')<sub>2</sub>}AlCl<sub>2</sub> (**5b**, R' = Ar) and {<sup>t</sup>BuC(NR')<sub>2</sub>}AlMe<sub>2</sub> (**6a**, R' = Ad; **6b**, R' = Ar). Complexes **1**, **3a**, **6a**, and **6b** have been characterized by X-ray crystallography.

## Introduction

Cationic aluminum alkyl species of general form {L-X}Al(R)<sup>+</sup>, which are stabilized by monoanionic, bidentate ancillary ligands ({L-X}<sup>-</sup>), are promising candidates for catalytic applications because the enhanced Lewis acidity of the cationic Al center and the presence of a reactive Al-R bond may promote insertion reactions.<sup>1</sup> Dimethyl aluminum compounds that contain bulky amidinate ligands, {RC(NR')<sub>2</sub>}AlMe<sub>2</sub> (R = Me, <sup>t</sup>Bu; R' = <sup>i</sup>Pr, cyclohexyl), are converted to {RC(NR')<sub>2</sub>}Al(Me)(L)<sup>+</sup> cations by abstraction of one methyl group. In these species, the {RC(NR')<sub>2</sub>}AlMe<sup>+</sup> cations are stabilized by an additional donor group (L' = {RC(NR')<sub>2</sub>}AlMe<sub>2</sub>, NMe<sub>2</sub>Ph, PMe<sub>3</sub>).<sup>1d</sup> We are investigating the synthesis and structures of other {L-X}AlR<sub>2</sub> compounds containing more diverse ancillary {L-X}<sup>-</sup> ligands, with the ultimate aim of developing new {L-X}AlR<sup>+</sup> cations with controlled structures and reactivity.<sup>2,3</sup> Amidinate ligands with extremely bulky substituents (R') at the donor nitrogen atoms, and related ligands incorporating other donor atoms, are of interest in this context because they may favor 3-coordinate {L-X}Al(R)<sup>+</sup> structures. Here we describe new {L-X}AlX<sub>2</sub> complexes (X = Cl, Me) containing bulky

thioamidate (RC(NR')S<sup>-</sup>), thioureido (R'HNC(NR')S<sup>-</sup>), and amidinate (RC(NR')<sub>2</sub><sup>-</sup>) ligands (R = Me, <sup>t</sup>Bu; R' = 1-adamantyl, 2,6-*i*-Pr<sub>2</sub>-Ph).

## Results and Discussion

**Ligand Syntheses.** The ligands used in this work were prepared by literature methods which are summarized in Scheme 1.<sup>4-6</sup> Addition of 1-adamantylamine to 1-adamantyl isothiocyanate yields *N,N*-diadamantylthiourea, and condensation of 2,6-diisopropylaniline with CS<sub>2</sub> yields *N,N*-bis(2,6-diisopropylphenyl)thiourea. These thioureas are oxidized to the corresponding carbodiimides AdN=C=NAd (Ad = 1-adamantyl) and ArN=C=NAr (Ar = 2,6-*i*-Pr<sub>2</sub>-Ph) by reaction with NaOCIO or NaOCl.

**Synthesis of Aluminum Thioamidate Complexes.** Insertion reactions of heteroallene compounds, including CO<sub>2</sub>,<sup>7,8</sup> CS<sub>2</sub>,<sup>9</sup> isocyanates (R'N=C=O),<sup>10</sup> and isothiocyanates (R'N=C=S),<sup>11</sup> into Al-X (X = R, OR, SR, NR<sub>2</sub>, AlR<sub>2</sub>) bonds are well-known.<sup>12</sup> The reaction of 1-adamantyl isothiocyanate and AlMe<sub>3</sub> yields {MeC(NAd)S}-

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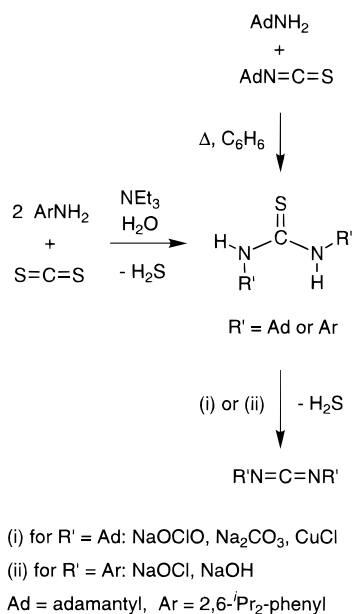
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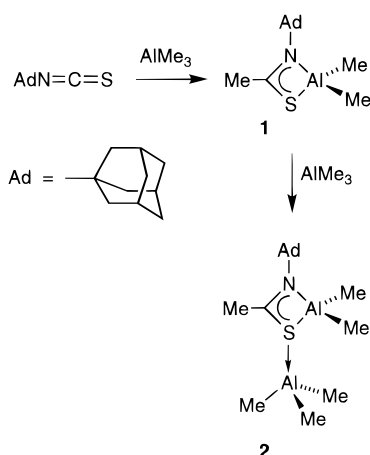
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Scheme 1

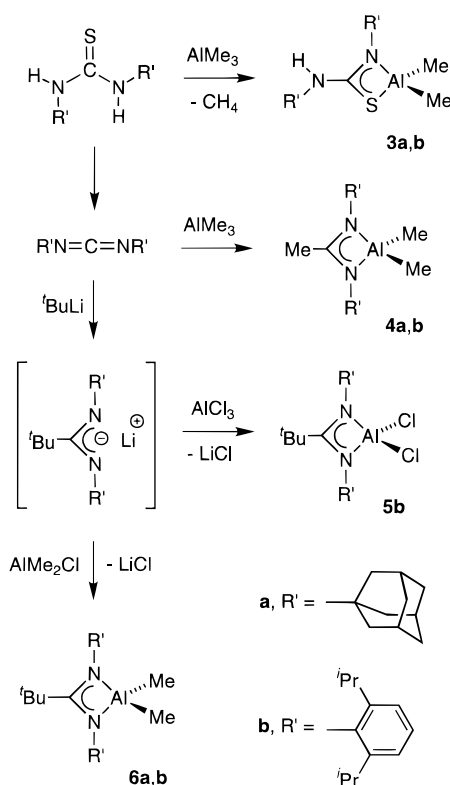


Scheme 2



AlMe<sub>2</sub> (**1**, Scheme 2), which is isolated as an orange solid by recrystallization from Et<sub>2</sub>O at -30 °C. An X-ray crystallographic analysis (*vide infra*) establishes that **1** is monomeric in the solid state; that is, this compound does not dimerize by bridging through the sulfur atom. However, NMR studies show that **1** forms an adduct with AlMe<sub>3</sub>. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of {MeC(NAd)S}AlMe<sub>2</sub>·AlMe<sub>3</sub> (**2**, Scheme 2) contain adamantyl resonances that are shifted from the corresponding resonances of **1**. The <sup>1</sup>H NMR spectrum contains two Al–Me resonances (δ -0.48, -0.64) in a 2/3 intensity ratio that are shifted from the resonances of **1** and AlMe<sub>3</sub>,<sup>13</sup> and the <sup>13</sup>C NMR spectrum also contains two Al–Me resonances (δ -6.9, -8.5). Presumably coordination of **1** to AlMe<sub>3</sub> occurs through the sulfur atom of the thioamidate ligand, similar to the O–Al bonding in {O=CPhNPhC(H)MeO}AlMe<sub>2</sub>·AlMe<sub>3</sub>, {pyCRR'O}AlMe<sub>2</sub>·AlMe<sub>3</sub> and related compounds.<sup>14,15</sup> No attempt was

Scheme 3



made to isolate **2**. Several *N*-phenylthioacetamidate aluminum complexes, {MeC(NPh)S}AlR<sub>2</sub> (R = Me, Et, *i*-Pr) have been reported previously.<sup>16</sup> Analogous amidate complexes, {RC(NR')O}AlR<sub>2</sub>, have been prepared previously by alkane elimination reactions of acid amides and AlR<sub>3</sub> compounds.<sup>14,17</sup>

#### Synthesis of Aluminum Thioureido Complexes.

The methane elimination reaction of AlMe<sub>3</sub> and the thioureas (R'HN)<sub>2</sub>C=S (R' = Ad, Ar) affords thioureido complexes {R'HNC(NR')S}AlMe<sub>2</sub> (**3a**, R' = Ad; **3b**, R' = Ar, Scheme 3). Complex **3a** is isolated as colorless platelike crystals by recrystallization from Et<sub>2</sub>O at 0 °C, and **3b** is isolated as colorless, hexagonal crystals by recrystallization from hot toluene. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3a** and **3b** are consistent with C<sub>s</sub>-symmetric structures. The NMR spectra of **3b** contain four isopropyl methyl resonances and one Al–Me resonance, which is consistent with a structure in which the H–N–C(ipso) plane of the amino group is parallel to the Al–N–C–S plane, and rotation around the N–Ar bonds is slow on the NMR time scale. It is likely that the Ar groups are oriented perpendicular to the Al–N–C–S plane. Analogous aluminum thioureido complexes containing smaller nitrogen substituents have been prepared previously by SiMe<sub>3</sub>Cl elimination reactions of *N*-silylated thioureas (R'<sub>2</sub>NC(S)NR'SiMe<sub>3</sub>; R' = Me, Et, Ph) with AlR<sub>2</sub>Cl (R = Me, Et, *i*-Bu) compounds.<sup>16</sup>

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**Table 1. Summary of Crystal Data for Compounds 1, 3a, 6a, and 6b**

	<b>1</b>	<b>3a</b>	<b>6a</b>	<b>6b</b>
formula	C <sub>14</sub> H <sub>24</sub> AlNS	C <sub>23</sub> H <sub>37</sub> AlN <sub>2</sub> S	C <sub>27</sub> H <sub>45</sub> AlN <sub>2</sub>	C <sub>31</sub> H <sub>49</sub> AlN <sub>2</sub>
fw	265.38	400.59	424.63	476.70
cryst size (mm)	0.20 × 0.20 × 0.13	0.44 × 0.39 × 0.10	0.35 × 0.39 × 0.50	0.30 × 0.28 × 0.23
color/shape	yellow/block	colorless/plate	colorless/prismatic	colorless/irreg block
<i>d</i> (calc) (Mg/m <sup>3</sup> )	1.197	1.164	1.142	1.071
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	6.8455(6)	16.865(6)	14.405(2)	10.1845(1)
<i>b</i> (Å)	9.2486(8)	13.198(6)	14.835(2)	11.0117(2)
<i>c</i> (Å)	13.072(1)	10.285(3)	12.893(2)	14.4123(3)
$\alpha$ (deg)	107.370(1)		112.54(1)	74.284(1)
$\beta$ (deg)	96.595(1)	93.42(3)	99.69(1)	77.687(1)
$\gamma$ (deg)	107.070(2)		95.35(1)	73.882(1)
<i>V</i> (Å <sup>3</sup> )	736.2(1)	2285(2)	2470.5(6)	1477.99(4)
<i>Z</i>	2	4	4	2
<i>T</i> (K)	173(2)	213(2)	213(2)	173(2)
diffractometer	Siemens SMART Platform CCD	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Siemens SMART Platform CCD
radiation, $\lambda$ (Å)	Mo K $\alpha$ , 0.710 73	Mo K $\alpha$ , 0.710 73	Mo K $\alpha$ , 0.710 73	Mo K $\alpha$ , 0.710 73
2 $\theta$ range (deg)	3.3 < 2 $\theta$ < 50.1	4.0 < 2 $\theta$ < 50.0	4.0 < 2 $\theta$ < 50.0	3.0 < 2 $\theta$ < 50.0
data collected: <i>h</i> ; <i>k</i> ; <i>l</i>	±8; ±10; 0,15	±19; -1,15; -12,2	±17; -17,16; -2,15	-11,12; -12,13; 0,17
no. of reflns	4136	5051	10292	8096
no. of unique reflns	2485	3912	8534	4944
<i>R</i> <sub>int</sub>	0.0208	0.0337	0.0143	0.0244
no. of obsd reflns	<i>I</i> > 2 $\sigma$ ( <i>I</i> ), 2045	<i>I</i> > 2 $\sigma$ ( <i>I</i> ), 2178	<i>I</i> > 2 $\sigma$ ( <i>I</i> ), 7351	<i>I</i> > 2 $\sigma$ ( <i>I</i> ), 3712
$\mu$ (mm <sup>-1</sup> )	0.260	0.190	0.098	0.089
transmission range (%)	76–100	83–100	96–100	72–100
structure solution	direct methods <sup>a</sup>	direct methods <sup>b</sup>	direct methods <sup>b</sup>	direct methods <sup>a</sup>
no. of data/parameters	2485/157	3912/273	8534/757	4943/321
GOF on <i>F</i> <sup>2</sup>	1.032	1.027	1.062	1.036
<i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>c,d</sup>	<i>R</i> 1 = 0.0465, w <i>R</i> 2 = 0.1124	<i>R</i> 1 = 0.0489, w <i>R</i> 2 = 0.1058	<i>R</i> 1 = 0.0397, w <i>R</i> 2 = 0.1045	<i>R</i> 1 = 0.0551, w <i>R</i> 2 = 0.1299
<i>R</i> indices (all data) <sup>c,d</sup>	<i>R</i> 1 = 0.0599, w <i>R</i> 2 = 0.1201	<i>R</i> 1 = 0.1256, w <i>R</i> 2 = 0.1376	<i>R</i> 1 = 0.0493, w <i>R</i> 2 = 0.1145	<i>R</i> 1 = 0.0792, w <i>R</i> 2 = 0.1440
max resid density (e/Å <sup>3</sup> )	0.30	0.34	0.30	0.31

<sup>a</sup> SHELXTL-Plus Version 5, Siemens Industrial Automation, Inc., Madison, WI. <sup>b</sup> MULTAN, Multan80, University of York, York, England. <sup>c</sup> *R*1 =  $\sum||F_o| - |F_c||/\sum|F_o|$ . <sup>d</sup> w*R*2 =  $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ , where  $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ .

### Synthesis of Aluminum Amidinate Complexes.

Aluminum acetamidinate compounds, {MeC(NR')<sub>2</sub>}-AlMe<sub>2</sub>, have been prepared previously by the reaction of AlMe<sub>3</sub> and the appropriate carbodiimide.<sup>2,18</sup> Analogous compounds containing bulkier substituents at the central carbon of the amidinate ligand can be prepared by treating the carbodiimide with lithium alkyl reagents to generate Li[RC(NR')<sub>2</sub>] salts, followed by reaction with aluminum halides.<sup>2,19</sup> Both approaches were utilized to prepare aluminum amidinate compounds with Ad or 2,6-*i*-Pr<sub>2</sub>-Ph substituents at nitrogen (Scheme 3). The reaction of AlMe<sub>3</sub> with R'N=C=NR' in hexane affords the acetamidinate complexes {MeC(NR')<sub>2</sub>}AlMe<sub>2</sub> (**4a**, R' = Ad; **4b**, R' = 2,6-*i*-Pr<sub>2</sub>-Ph). Both compounds are isolated as white solids in good yield by simple removal of the volatiles from the reaction mixture. Sequential treatment of the carbodiimides with <sup>t</sup>BuLi (0 °C, Et<sub>2</sub>O) and AlCl<sub>3</sub> or AlMe<sub>2</sub>Cl (-78 °C, Et<sub>2</sub>O) affords the pivamidinate compounds {<sup>t</sup>BuC(NAr)<sub>2</sub>}AlCl<sub>2</sub> (**5b**) and {<sup>t</sup>BuC(NR')<sub>2</sub>}AlMe<sub>2</sub> (**6a**, R' = Ad; **6b**, R' = 2,6-*i*-Pr<sub>2</sub>-Ph), respectively. The presumed intermediate Li[<sup>t</sup>BuC(NR')<sub>2</sub>] salts were not isolated. Compounds **5b**, **6a**, and **6b** are isolated as white or colorless crystals by recrystallization from cold pentane. The relatively low isolated yields (13–20%) are attributed to the high solubility of these compounds in the recrystallization solvent. The NMR data for **4–6** are consistent with *C*<sub>2v</sub>-sym-

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

Al(1)–N(1)	1.953(2)	Al(1)–S(1)	2.340(1)
Al(1)–C(1)	1.960(3)	Al(1)–C(2)	1.953(3)
N(1)–C(3)	1.300(3)	S(1)–C(3)	1.744(3)
N(1)–C(5)	1.494(3)	C(3)–C(4)	1.502(4)
N(1)–Al(1)–C(1)	111.1(1)	N(1)–Al(1)–C(2)	117.7(1)
C(1)–Al(1)–C(2)	118.8(1)	N(1)–Al(1)–S(1)	72.44(7)
C(1)–Al(1)–S(1)	113.8(1)	C(2)–Al(1)–S(1)	114.4(1)
C(3)–S(1)–Al(1)	74.51(9)	C(3)–N(1)–Al(1)	99.5(2)
N(1)–C(3)–S(1)	113.4(2)	C(5)–N(1)–Al(1)	131.8(2)
C(3)–N(1)–C(5)	128.1(2)	N(1)–C(3)–C(4)	129.2(2)
S(1)–C(3)–C(4)	117.3(2)		

metric structures and, for **4b–6b**, slow rotation around the Ar–N bonds.

**Molecular Structures of {MeC(NAd)S}AlMe<sub>2</sub> (1) and {AdNHC(NAd)S}AlMe<sub>2</sub> (3a).** Crystal data for **1** and **3a** are summarized in Table 1, refinement details are discussed in the Experimental Section, and selected bond distances and angles are listed in Tables 2 and 3. Molecular geometries and atom labeling schemes are shown in Figures 1 and 2.

Complexes **1** and **3a** are monomeric and exhibit distorted tetrahedral geometry at aluminum. The ligand bite angles (N–Al–S: **1**, 72.44(7)°; **3a**, 73.16(9)°) are in the range observed for {RC(NR')<sub>2</sub>}AlX<sub>2</sub> (X = Cl, R) amidinate and {R<sub>2</sub>NC(NR')<sub>2</sub>}AlCl<sub>2</sub> guanidinate complexes (N–Al–N = 68–72°).<sup>2,3</sup> The C–Al–C angles (**1**, 118.8(1)°; **3a**, 117.9(3)°) are similar to those in {RC(NR')<sub>2</sub>}AlR<sub>2</sub> compounds.<sup>2</sup> The N–Al–S–C metacycles are approximately planar in both **1** and **3a**

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**Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3a**

Al(1)–N(1)	1.910(3)	Al(1)–S(1)	2.342(2)
Al(1)–C(2)	1.951(6)	Al(1)–C(3)	1.943(5)
N(1)–C(1)	1.320(4)	S(1)–C(1)	1.758(3)
N(1)–C(11)	1.495(4)	C(1)–N(2)	1.337(4)
N(2)–C(21)	1.479(4)		
N(1)–Al(1)–C(2)	113.8(3)	N(1)–Al(1)–C(3)	116.1(2)
C(2)–Al(1)–C(3)	117.9(3)	N(1)–Al(1)–S(1)	73.16(9)
C(2)–Al(1)–S(1)	111.0(2)	C(3)–Al(1)–S(1)	116.8(2)
C(1)–S(1)–Al(1)	74.0(1)	C(1)–N(1)–Al(1)	100.5(2)
N(1)–C(1)–S(1)	111.6(2)	C(11)–N(1)–Al(1)	132.1(2)
C(1)–N(1)–C(11)	127.0(3)	N(1)–C(1)–N(2)	125.4(3)
S(1)–C(1)–N(2)	123.0(3)	C(1)–N(2)–C(21)	132.4(3)

(dihedral angle N–Al–S–C = 2.5° for **1**; 4.9° for **3a**), with distorted trigonal planar coordination at the carbon and nitrogen atoms (sum of angles ca. 360°).

The C–N distance within the metallacycle of **1** (1.300(3) Å) is slightly shorter than the corresponding C–N distances in aluminum amidinate complexes (ca. 1.34 Å), and the C–S bond length (**1**, 1.744(3) Å) is in the normal range for C(sp<sup>2</sup>)–S single bonds (1.75 Å; compare to C(sp<sup>2</sup>)=S double-bond length of 1.68 Å in thioureas).<sup>20,21</sup> These results indicate that resonance structure **B** in Scheme 4 dominates the bonding within the thioamidate ligand of **1** and reflect the fact that C–N π bonding is stronger than C–S π bonding.

The C–N and C–S distances (1.320(4) and 1.758(3) Å) within the metallacycle of **3a** are similar to those in **1**. Additionally, the AdHN–C bond length (1.337(4) Å) is intermediate between normal C(sp<sup>2</sup>)–N single- and double-bond distances,<sup>22</sup> and the Ad–N–H and metallacycle planes are essentially coplanar (angle between planes: Ad–N2–H/Al1–N1–C1–S1 = 4.8°; dihedral angle S1–C1–N2–C21 = 5.0°). These results indicate that the AdHN–C bond has significant double-bond character and that resonance structures **D** and **E** in Scheme 4 dominate the bonding in the thioureido ligand of **3a**. A similar bonding situation has been observed in the guanidinate complex {Me<sub>2</sub>NC(N<sup>i</sup>Pr)<sub>2</sub>}AlCl<sub>2</sub>.<sup>3,23</sup>

**Molecular Structures of {‘BuC(NAd)<sub>2</sub>}AlMe<sub>2</sub> (6a) and {‘BuC(NAR)<sub>2</sub>}AlMe<sub>2</sub> (6b).** Crystal data for **6a** and **6b** are summarized in Table 1, refinement details are discussed in the Experimental Section, and selected bond distances and angles are listed in Tables 4 and 5. Molecular geometries and atom-labeling schemes are shown in Figures 3 and 4, and selected bond angles are given in Figure 5.

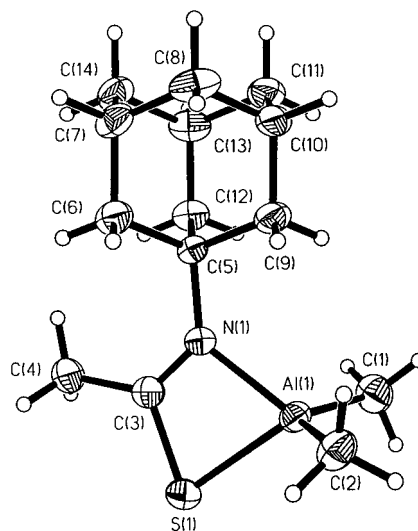
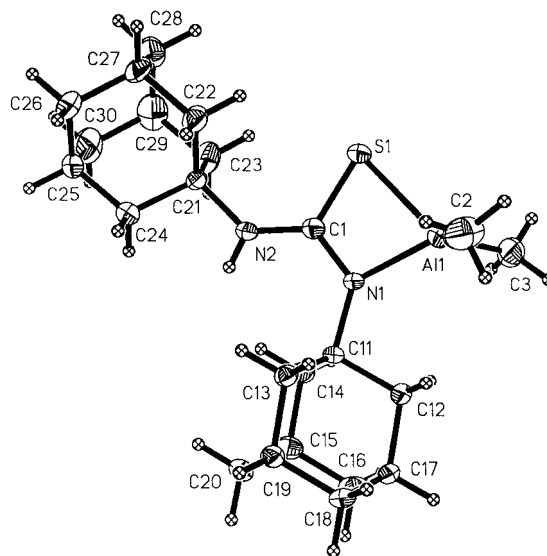
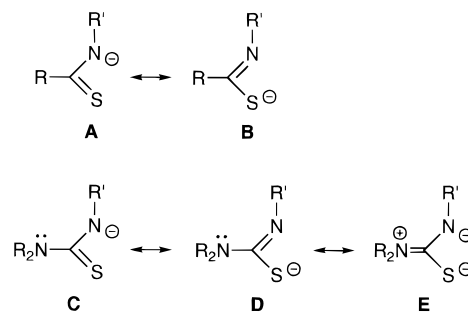
Complexes **6a** and **6b** are monomeric with distorted tetrahedral geometries at aluminum. The N–Al–N–C metallacycles are planar (dihedral angles N–Al–N–C = 0.8, 1.9° for **6a**; –1.0° for **6b**) and are structurally very similar to those in {RC(NR')<sub>2</sub>}AlMe<sub>2</sub> (R = Me, 'Bu; R' = Cy) amidinate complexes.<sup>2</sup> It was noted previously that enhancement of steric interactions

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(23) However, the donor nitrogen atoms of {Me<sub>2</sub>NC(N<sup>i</sup>Pr)<sub>2</sub>}AlCl<sub>2</sub> exhibit some pyramidal character (sum of angles = 348.4° average, N–R' substituents 26.3° (average) out of the plane of the metallacycle). In contrast, in compound **3a** there is no evidence for sp<sup>3</sup>-character at the donor nitrogen atom (sum of angles = 359.6°, R' substituent in the plane of the metallacycle).

**Figure 1.** Molecular structure of {MeC(NAd)S}AlMe<sub>2</sub> (**1**).**Figure 2.** Molecular structure of {AdHNC(NAd)S}AlMe<sub>2</sub> (**3a**).**Scheme 4**

between the C–R and N–R' substituents in {RC(NR')<sub>2</sub>}AlX<sub>2</sub> complexes forces the N–R' substituents closer to the metal center and increases the cone angle of the amidinate ligand. This structural effect strongly influences the amidinate bonding mode (i.e., bridging vs chelating)<sup>24</sup> and the chemistry that occurs at the metal center.<sup>1,25</sup> Key bond angles in the relatively crowded {‘BuC(NCy)<sub>2</sub>}AlMe<sub>2</sub> and in **6a** and **6b** are shown in Figure 5.<sup>2</sup> The C–N–R' and R'–N–Al angles in **6b** are similar to those in {‘BuC(NCy)<sub>2</sub>}AlMe<sub>2</sub>;

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6a**

Molecule 1			
Al(1)–N(1)	1.920(1)	Al(1)–N(2)	1.916(1)
Al(1)–C(6)	1.965(2)	Al(1)–C(7)	1.963(2)
N(1)–C(1)	1.360(2)	N(1)–C(21)	1.478(2)
N(2)–C(1)	1.353(2)	N(2)–C(11)	1.483(2)
C(1)–C(2)	1.553(2)		
N(1)–Al(1)–N(2)	69.02(6)	C(6)–Al(1)–C(7)	114.2(1)
N(1)–Al(1)–C(6)	116.49(9)	N(1)–Al(1)–C(7)	117.08(9)
N(2)–Al(1)–C(6)	116.79(9)	N(2)–Al(1)–C(7)	116.06(9)
C(1)–N(1)–Al(1)	92.1(1)	C(1)–N(2)–Al(1)	92.4(1)
N(1)–C(1)–N(2)	106.5(1)	C(21)–N(1)–Al(1)	129.5(1)
C(11)–N(2)–Al(1)	128.7(1)	C(1)–N(1)–C(21)	138.2(1)
C(1)–N(2)–C(11)	138.8(1)	N(1)–C(1)–C(2)	126.7(1)
N(2)–C(1)–C(2)	126.7(1)		
Molecule 2			
Al(2)–N(31)	1.912(1)	Al(2)–N(32)	1.915(1)
Al(2)–C(36)	1.963(2)	Al(2)–C(37)	1.969(3)
N(31)–C(31)	1.355(2)	N(31)–C(51)	1.479(2)
N(32)–C(31)	1.358(2)	N(32)–C(41)	1.481(2)
C(31)–C(32)	1.554(2)		
N(31)–Al(2)–N(32)	69.12(6)	C(36)–Al(2)–C(37)	115.8(2)
N(31)–Al(2)–C(36)	117.0(1)	N(31)–Al(2)–C(37)	114.5(1)
N(32)–Al(2)–C(36)	117.5(1)	N(32)–Al(2)–C(37)	114.6(1)
C(31)–N(31)–Al(2)	92.4(9)	C(31)–N(32)–Al(2)	92.1(1)
N(31)–C(31)–N(32)	106.3(1)	C(51)–N(31)–Al(2)	128.5(1)
C(41)–N(32)–Al(2)	129.0(1)	C(31)–N(31)–C(51)	139.2(1)
C(31)–N(32)–C(41)	138.6(1)	N(31)–C(31)–C(32)	127.0(1)
N(32)–C(31)–C(32)	126.6(1)		

**Table 5. Selected Bond Lengths (Å) and Angles (deg) for 6b**

Al(1)–N(1)	1.940(2)	Al(1)–N(2)	1.936(2)
Al(1)–C(1)	1.952(3)	Al(1)–C(2)	1.955(3)
N(1)–C(3)	1.356(3)	N(1)–C(8)	1.440(3)
N(2)–C(3)	1.339(3)	N(2)–C(20)	1.439(3)
C(3)–C(4)	1.539(3)		
N(1)–Al(1)–N(2)	68.15(7)	C(1)–Al(1)–C(2)	115.8(1)
N(1)–Al(1)–C(1)	118.0(1)	N(1)–Al(1)–C(2)	116.4(1)
N(2)–Al(1)–C(1)	115.9(1)	N(2)–Al(1)–C(2)	114.1(1)
C(3)–N(1)–Al(1)	91.9(1)	C(3)–N(2)–Al(1)	92.6(1)
N(1)–C(3)–N(2)	107.4(2)	C(8)–N(1)–Al(1)	137.1(1)
C(20)–N(2)–Al(1)	135.4(1)	C(3)–N(1)–C(8)	131.0(2)
C(3)–N(2)–C(20)	132.0(2)	N(1)–C(3)–C(4)	125.3(2)
N(2)–C(3)–C(4)	127.3(2)		

however, the former compound is more crowded due to the presence of the four isopropyl groups. The aryl rings in **6b** are oriented perpendicular to the metallacycle (angles between aryl and metallacycle planes = 86.7°, 85.5°), and the isopropyl groups are positioned above and below the metallacycle plane, which minimizes <sup>t</sup>Bu/Ar steric contacts.<sup>26</sup> In contrast, the R'–N–Al angle in **6a** is ca. 6° smaller than those in {<sup>t</sup>BuC(NCy)<sub>2</sub>}AlMe<sub>2</sub> and **6b** due to close H–H contacts between the <sup>t</sup>Bu and adamantyl groups.<sup>27</sup>

## Conclusions

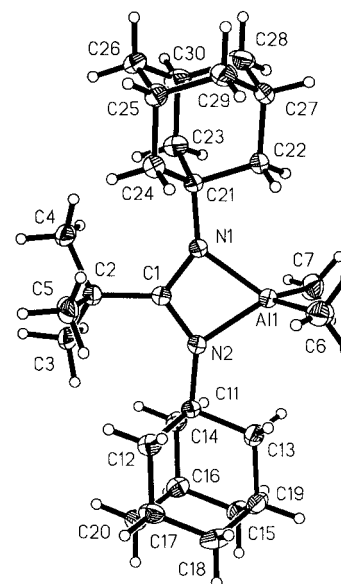
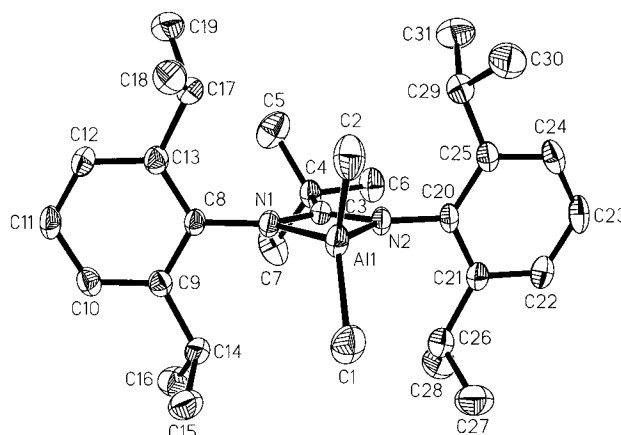
New {L–X}AlR<sub>2</sub> compounds containing bulky adamantyl- or aryl-substituted N,S<sup>–</sup> and N,N<sup>–</sup> donor ligands

(24) (a) Hausen, H.-D.; Gerstner, F.; Schwarz, W. *J. Organomet. Chem.* **1978**, *145*, 277. (b) Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1996**, *35*, 2448. (c) Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1996**, *35*, 1423.

(25) Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1997**, *36*, 501.

(26) Close H–H contacts: H(6B)–H(28A) = 2.3 Å; H(6C)–H(31A) = 2.3 Å; H(5C)–H(19A) = 2.3 Å; H(7B)–H(16A) = 2.4 Å. Sum of van der Waals radii = 2.4 Å.

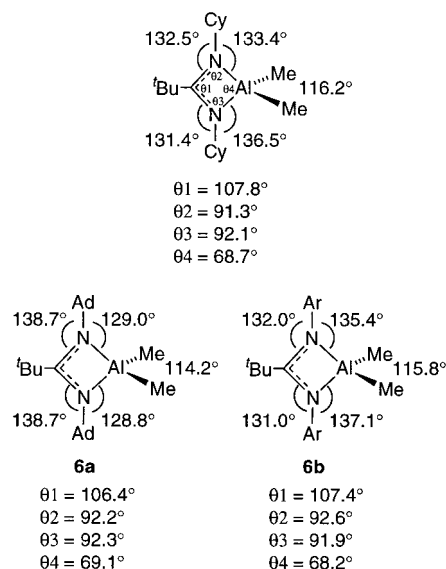
(27) Close H–H contacts: H(5C)–H(12B) = 2.2 Å; H(3C)–H(12B) = 1.8 Å; H(3C)–H(14A) = 2.0 Å; H(3A)–H(14A) = 2.2 Å; H(5B)–H(24A) = 2.2 Å; H(4B)–H(24A) = 1.9 Å; H(4A)–H(23B) = 2.1 Å.

**Figure 3.** Molecular structure of {<sup>t</sup>BuC(NAd)<sub>2</sub>}AlMe<sub>2</sub> (**6a**).**Figure 4.** Molecular structure of {<sup>t</sup>BuC(NAr)<sub>2</sub>}AlMe<sub>2</sub> (**6b**; Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>-Ph).

have been prepared and characterized. The thioamidate and thioureido compounds {MeC(NAd)S}AlMe<sub>2</sub> (**1**) and {R'HNC(NR')S}AlMe<sub>2</sub> (**3a**, R' = Ad; **3b**, R' = 2,6-<sup>i</sup>Pr-Ph) exhibit planar metallacycle structures with C–S single bonds and sterically open Al and S centers. The “superbulky” amidinate complexes {<sup>t</sup>BuC(NAd)<sub>2</sub>}AlMe<sub>2</sub> (**6a**) and {<sup>t</sup>BuC(NAr)<sub>2</sub>}AlMe<sub>2</sub> (**6b**; Ar = 2,6-<sup>i</sup>Pr-Ph) exhibit a greater degree of steric crowding around the Al centers than the most crowded case described previously, i.e., {<sup>t</sup>BuC(NCy)<sub>2</sub>}AlMe<sub>2</sub>. Studies of cationic {L–X}AlR<sup>+</sup> complexes derived from these neutral precursors will be discussed in subsequent contributions.

## Experimental Section

**General Procedures.** All manipulations were performed on a high-vacuum line or in a glovebox under a purified N<sub>2</sub> atmosphere. Solvents were distilled from Na/benzophenone ketyl, except for chlorinated solvents, which were distilled from activated molecular sieves (3 Å) or CaH<sub>2</sub>. The compounds (AdNH)<sub>2</sub>C=S,<sup>4</sup> (ArNH)<sub>2</sub>C=S,<sup>5</sup> AdN=C=NAd,<sup>4</sup> and ArN=C=NAr<sup>6</sup> (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>-Ph) were prepared by literature methods. All other chemicals were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker AMX 360 spectrometer in sealed or Teflon-valved tubes at ambient probe temperature unless otherwise indicated. <sup>1</sup>H and <sup>13</sup>C chemical



**Figure 5.** Key bond angles in {BuC(NCy)<sub>2</sub>}AlMe<sub>2</sub>, **6a** and **6b**. The data for **6a** are averaged values from the two independent molecules.

shifts are reported versus SiMe<sub>4</sub> and were determined by reference to the residual <sup>1</sup>H and <sup>13</sup>C solvent peaks. Coupling constants are reported in hertz. Elemental analyses were performed by Desert Analytics Laboratory (Tucson, AZ). E-mass spectra were obtained using the direct insertion probe method with a VG Analytical Trio I instrument operating at 70 eV. Data for key peaks (*m/z*, relative % intensity vs base peak, assignment) are listed.

**{MeC(NAd)S}AlMe<sub>2</sub> (1).** A suspension of 1-adamantyl isothiocyanate (1.35 g, 7.00 mmol) in hexanes (50 mL) was added to a rapidly stirred solution of AlMe<sub>3</sub> (0.70 mL, 7.3 mmol) in hexanes (20 mL). The mixture was stirred at room temperature for 15 h to afford a slurry of a flocculent white precipitate in a yellow solution. The volatiles were removed under vacuum, and {MeC(NAd)S}AlMe<sub>2</sub> was extracted with Et<sub>2</sub>O and isolated from the extract by crystallization at -30 °C. Yield: 1.52 g, 78%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.58 (s, 3H, CMe), 2.10 (br s, 3H, Ad-H<sub>γ</sub>), 1.95 (br d, *J*<sub>HH</sub> = 3.2, 6H, Ad-H<sub>β</sub>), 1.71 (br d, *J*<sub>HH</sub> = 14, 3H, Ad-H<sub>δ</sub>), 1.67 (br d, *J*<sub>HH</sub> = 14, 3H, Ad-H<sub>δ</sub>), -0.58 (s, 6H, AlMe<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 196.0 (s, CMe), 58.9 (s, Ad-C<sub>α</sub>), 42.3 (t, <sup>1</sup>*J*<sub>CH</sub> = 127, Ad-C<sub>β</sub>), 36.3 (t, <sup>1</sup>*J*<sub>CH</sub> = 126, Ad-C<sub>δ</sub>), 29.9 (d, <sup>1</sup>*J*<sub>CH</sub> = 133, Ad-C<sub>γ</sub>), 29.4 (q, <sup>1</sup>*J*<sub>CH</sub> = 130, CMe), -8.8 (br q, <sup>1</sup>*J*<sub>CH</sub> = 115, AlMe<sub>2</sub>). Anal. Calcd for C<sub>14</sub>H<sub>24</sub>AlNS: C, 63.36; H, 9.11; N, 5.28. Found: C, 63.32; H, 9.10; N, 5.11. MS (*m/z*): 250 (99, M<sup>+</sup> - Me).

**Generation of {MeC(NAd)S}AlMe<sub>2</sub>·AlMe<sub>3</sub> (2).** A solution of {MeC(NAd)S}AlMe<sub>2</sub> (0.063 g, 0.24 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (400 μL) was added to a solution of AlMe<sub>3</sub> (0.017 g, 0.24 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (200 μL), and NMR spectra were recorded. The spectra showed that 100% conversion to {MeC(NAd)S}AlMe<sub>2</sub>·AlMe<sub>3</sub> had occurred. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.64 (s, 3H, CMe), 2.15 (br s, 3H, Ad-H<sub>γ</sub>), 2.01 (br s, 6H, Ad-H<sub>β</sub>), 1.71 (br m, 6H, Ad-H<sub>δ</sub>), -0.48 (s, 6H, AlMe<sub>2</sub>), -0.64 (s, 9H, AlMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 191.9 (s, CMe), 60.8 (s, Ad-C<sub>α</sub>), 42.1 (t, <sup>1</sup>*J*<sub>CH</sub> = 128, Ad-C<sub>β</sub>), 36.1 (t, <sup>1</sup>*J*<sub>CH</sub> = 127, Ad-C<sub>δ</sub>), 29.9 (d, <sup>1</sup>*J*<sub>CH</sub> = 134, Ad-C<sub>γ</sub>), 29.5 (q, <sup>1</sup>*J*<sub>CH</sub> = 131, CMe), -6.9 (br q, <sup>1</sup>*J*<sub>CH</sub> = 113, AlMe<sub>2</sub>), -8.5 (br q, <sup>1</sup>*J*<sub>CH</sub> = 116, AlMe<sub>3</sub>).

**{AdHNC(NAd)S}AlMe<sub>2</sub> (3a).** A solution of AlMe<sub>3</sub> (0.210 g, 2.91 mmol) in hexanes (10 mL) was added to a suspension of *N,N*-bis(adamantyl)thiourea (1.00 g, 2.90 mmol) in hexanes (80 mL). The solution became clear and a gas was evolved. After 15 h the volatiles were removed under vacuum to afford {AdHNC(NAd)S}AlMe<sub>2</sub> as a white solid (1.08 g, 93%). Analytically pure samples were obtained by recrystallization in Et<sub>2</sub>O at 0 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 5.38 (s, 1H, NH), 2.14 (s,

6H, Ad), 2.10 (br d, *J*<sub>HH</sub> = 11, 6H, Ad), 1.90 (br d, *J*<sub>HH</sub> = 2.8, 6H, Ad), 1.69 (s, 6H, Ad), 1.70 (br d, 3H, *J*<sub>HH</sub> = 13, Ad), 1.64 (br d, *J*<sub>HH</sub> = 13, 3H, Ad), -0.64 (s, 6H, AlMe<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 171.1 (s, CNHAD), 54.8 (s, Ad-C<sub>α</sub>, two signals coincident), 42.7 (t, <sup>1</sup>*J*<sub>CH</sub> = 129, Ad-C<sub>β</sub>), 42.4 (t, <sup>1</sup>*J*<sub>CH</sub> = 127, Ad-C<sub>β</sub>), 36.6 (t, <sup>1</sup>*J*<sub>CH</sub> = 127, Ad-C<sub>δ</sub>), 36.5 (t, <sup>1</sup>*J*<sub>CH</sub> = 128, Ad-C<sub>δ</sub>), 30.2 (d, <sup>1</sup>*J*<sub>CH</sub> = 133, Ad-C<sub>γ</sub>), 29.9 (d, <sup>1</sup>*J*<sub>CH</sub> = 128, Ad-C<sub>γ</sub>), -7.7 (br q, <sup>1</sup>*J*<sub>CH</sub> = 114, AlMe<sub>2</sub>). Anal. Calcd for C<sub>23</sub>H<sub>37</sub>AlN<sub>2</sub>S: C, 68.96; H, 9.31; N, 6.99. Found: C, 68.78; H, 9.30; N, 6.91. MS (*m/z*): 385 (100, M<sup>+</sup> - Me).

**{ArHNC(NAr)S}AlMe<sub>2</sub> (3b).** This compound was prepared by the procedure described for **3a**, using 1.00 g of *N,N*-bis(2,6-diisopropylphenyl)thiourea (2.52 mmol) in 80 mL of pentane. After 15 h the volatiles were removed under vacuum, yielding {ArHNC(NAr)S}AlMe<sub>2</sub> as a white solid. Yield: 0.946 g, 83% based on AlMe<sub>3</sub>. Analytically pure samples were obtained as colorless hexagonal crystals by cooling a hot (70 °C) saturated toluene solution to room temperature. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.36 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.9, 1H, Ar-H<sub>para</sub>), 7.27 (m, 3H, Ar), 7.19 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8, 2H, Ar-H<sub>meta</sub>), 6.41 (br s, 1H, NH), 3.26 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.7, 2H, CHMe<sub>2</sub>), 3.06 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.8, 2H, CHMe<sub>2</sub>), 1.34 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8, 6H, CHMe<sub>2</sub>), 1.33 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8, 6H, CHMe<sub>2</sub>), 1.21 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.1, 6H, CHMe<sub>2</sub>), 1.08 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8, 6H, CHMe<sub>2</sub>), -0.51 (s, 6H, AlMe<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 177.9 (s, CNHAr), 147.6 (s, Ar-C<sub>ortho</sub>), 145.8 (s, Ar-C<sub>ortho</sub>), 135.6 (s, Ar-C<sub>ipso</sub>), 131.8 (s, Ar-C<sub>ipso</sub>), 129.7 (d, <sup>1</sup>*J*<sub>CH</sub> = 162, Ar-C<sub>para</sub>), 128.0 (d, <sup>1</sup>*J*<sub>CH</sub> = 160, Ar-C<sub>para</sub>), 124.9 (d, <sup>1</sup>*J*<sub>CH</sub> = 158, Ar-C<sub>meta</sub>), 124.3 (d, <sup>1</sup>*J*<sub>CH</sub> = 163, Ar-C<sub>meta</sub>), 28.7 (d, <sup>1</sup>*J*<sub>CH</sub> = 128, CHMe<sub>2</sub>), 28.6 (d, <sup>1</sup>*J*<sub>CH</sub> = 134, CHMe<sub>2</sub>), 26.4 (q, <sup>1</sup>*J*<sub>CH</sub> = 126, CHMe<sub>2</sub>), 24.6 (q, <sup>1</sup>*J*<sub>CH</sub> = 126, CHMe<sub>2</sub>), 24.1 (q, <sup>1</sup>*J*<sub>CH</sub> = 126, CHMe<sub>2</sub>), 24.0 (q, <sup>1</sup>*J*<sub>CH</sub> = 126, CHMe<sub>2</sub>), -7.9 (q, <sup>1</sup>*J*<sub>CH</sub> = 114, AlMe<sub>2</sub>). Anal. Calcd for C<sub>27</sub>H<sub>41</sub>AlN<sub>2</sub>S: C, 71.63; H, 9.13; N, 6.19. Found: C, 71.60; H, 9.37; N, 5.92. MS (*m/z*): 437 (100, M<sup>+</sup> - Me).

**{MeC(NAd)<sub>2</sub>}AlMe<sub>2</sub> (4a).** A solution of AlMe<sub>3</sub> (0.132 g, 1.84 mmol) in hexane (10 mL) was added dropwise to a rapidly stirred solution of 1,3-diadamantylcarbodiimide (0.500 g, 1.61 mmol) in hexane (30 mL). The reaction mixture was stirred at room temperature for 18 h, and the volatiles were removed under vacuum, affording pure {MeC(NAd)<sub>2</sub>}AlMe<sub>2</sub> as a white solid (0.62 g, 88%). Analytically pure samples were obtained by recrystallization from Et<sub>2</sub>O at -30 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.22 (s, 3H, CMe), 2.03 (br s, 6H, Ad-H<sub>γ</sub>), 1.79 (br d, *J*<sub>HH</sub> = 2.9, 12H, Ad-H<sub>β</sub>), 1.65 (br s, 12H, Ad-H<sub>δ</sub>), -0.82 (s, 6H, AlMe<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 172.6 (s, CMe), 51.5 (s, Ad-C<sub>α</sub>), 44.6 (t, <sup>1</sup>*J*<sub>CH</sub> = 129, Ad-C<sub>β</sub>), 36.8 (t, <sup>1</sup>*J*<sub>CH</sub> = 126, Ad-C<sub>δ</sub>), 30.3 (d, <sup>1</sup>*J*<sub>CH</sub> = 132, Ad-C<sub>γ</sub>), 19.7 (q, <sup>1</sup>*J*<sub>CH</sub> = 128, CMe), -9.6 (br q, <sup>1</sup>*J*<sub>CH</sub> = 112, AlMe<sub>2</sub>). Anal. Calcd for C<sub>24</sub>H<sub>39</sub>AlN<sub>2</sub>: C, 75.35; H, 10.27; N, 7.32. Found: C, 74.96; H, 10.35; N, 7.30.

**{MeC(NAr)<sub>2</sub>}AlMe<sub>2</sub> (4b).** This compound was prepared by the procedure described for **4a**, using 0.525 g of 1,3-bis(2,6-diisopropylphenyl)carbodiimide (1.45 mmol) in 40 mL of hexane and 0.111 g of AlMe<sub>3</sub> (1.53 mmol) in 10 mL of hexane. After 18 h the volatiles were removed under vacuum, yielding pure {MeC(NAr)<sub>2</sub>}AlMe<sub>2</sub> as an off-white solid (0.491 g, 74%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.19 (m, 6H, NAr), 3.35 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.8, 4H, CHMe<sub>2</sub>), 1.49 (s, 3H, CMe), 1.23 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.6, 12H, CHMe<sub>2</sub>), 1.21 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.2, 12H, CHMe<sub>2</sub>), -0.53 (s, 6H, AlMe<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 176.1 (s, CMe), 145.1 (s, Ar-C<sub>ortho</sub>), 138.4 (s, Ar-C<sub>ipso</sub>), 126.3 (d, <sup>1</sup>*J*<sub>CH</sub> = 160, Ar-C<sub>para</sub>), 123.8 (d, <sup>1</sup>*J*<sub>CH</sub> = 156, Ar-C<sub>meta</sub>), 28.5 (d, <sup>1</sup>*J*<sub>CH</sub> = 126, CHMe<sub>2</sub>), 24.7 (q, <sup>1</sup>*J*<sub>CH</sub> = 126, CHMe<sub>2</sub>), 23.9 (q, <sup>1</sup>*J*<sub>CH</sub> = 126, CHMe<sub>2</sub>), 14.4 (q, <sup>1</sup>*J*<sub>CH</sub> = 129, CMe), -9.9 (q, <sup>1</sup>*J*<sub>CH</sub> = 113, AlMe<sub>2</sub>).

**{'BuC(NAr)<sub>2</sub>}AlCl<sub>2</sub> (5b).** A solution of 1,3-bis(2,6-diisopropylphenyl)carbodiimide (2.85 g, 7.86 mmol) in Et<sub>2</sub>O (80 mL) was cooled to 0 °C. <sup>t</sup>BuLi (4.6 mL of a 1.7 M solution in hexanes, 7.9 mmol) was added slowly by syringe. The resulting mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was cooled to -78 °C, and a solution of AlCl<sub>3</sub> (1.05 g, 7.86 mmol) in Et<sub>2</sub>O (30 mL) was added. The resulting solution was allowed to warm to room

temperature and was stirred for 18 h. The volatiles were removed under vacuum, yielding an oily yellow solid.  $\{\text{BuC}(\text{NAr})_2\}\text{AlCl}_2$  was extracted from LiCl with pentane and isolated from the extract by crystallization at  $-30^\circ\text{C}$ . Yield: 0.687 g, 17% based on  $\text{AlCl}_3$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.27 (d,  $^3J_{\text{HH}} = 6.5$ , 1H, Ar), 7.24 (d,  $^3J_{\text{HH}} = 6.8$ , 1H, Ar), 7.19 (s, 3H, Ar), 7.17 (d,  $J_{\text{HH}} = 6.7$ , 1H, Ar), 3.41 (sept,  $^3J_{\text{HH}} = 6.7$ , 4H,  $\text{CHMe}_2$ ), 1.36 (d,  $^3J_{\text{HH}} = 6.5$ , 12H,  $\text{CHMe}_2$ ), 1.27 (d,  $^3J_{\text{HH}} = 6.8$ , 12H,  $\text{CHMe}_2$ ), 0.98 (s, 9H,  $\text{CMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  187.3 (s,  $\text{CCMe}_3$ ), 145.3 (s, Ar- $C_{\text{ortho}}$ ), 136.6 (s, Ar- $C_{\text{ipso}}$ ), 127.4 (d,  $^1J_{\text{CH}} = 159$ , Ar- $C_{\text{para}}$ ), 124.2 (d,  $^1J_{\text{CH}} = 157$ , Ar- $C_{\text{meta}}$ ), 42.5 (s,  $\text{CMe}_3$ ), 29.4 (q,  $^1J_{\text{CH}} = 128$ ,  $\text{CMe}_3$ ), 29.1 (d,  $^1J_{\text{CH}} = 128$ ,  $\text{CHMe}_2$ ), 27.3 (q,  $^1J_{\text{CH}} = 131$ ,  $\text{CHMe}_2$ ), 23.0 (q,  $^1J_{\text{CH}} = 126$ ,  $\text{CHMe}_2$ ). Anal. Calcd for  $\text{C}_{29}\text{H}_{43}\text{AlN}_2\text{Cl}_2$ : C, 67.30; H, 8.76; N, 5.41. Found: C, 67.03; H, 8.39; N, 5.43. MS ( $m/z$ ,  $^{35}\text{Cl}$ ): 516 (2,  $\text{M}^+ - \text{Me}$ ), 473 (2,  $\text{M}^+ - \text{Pr}$ ).

$\{\text{BuC}(\text{NAd})_2\}\text{AlMe}_2$  (**6a**). This compound was prepared by the procedure described for **5b**, using 2.64 g of 1,3-diadamantylcarbodiimide (8.50 mmol) in 80 mL of  $\text{Et}_2\text{O}$ , 5.0 mL of  $\text{tBuLi}$  (1.7 M solution in pentane, 8.5 mmol), and 0.79 mL of  $\text{AlMe}_2\text{Cl}$  (8.6 mmol) in 30 mL of  $\text{Et}_2\text{O}$ . After 18 h the volatiles were removed under vacuum, and the product was extracted from the LiCl with pentane. The pentane extract was concentrated and cooled to  $-30^\circ\text{C}$  to afford  $\{\text{BuC}(\text{NAd})_2\}\text{AlMe}_2$  as white crystals, which were isolated by filtration (0.47 g, 13% based on  $\text{AlMe}_2\text{Cl}$ ). The low isolated yield is due to the high solubility of the product.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.05 (br s, 6H, Ad- $H_\alpha$ ), 2.02 (s br, 12H, Ad- $H_\beta$ ), 1.62 (br s, 12H, Ad- $H_\gamma$ ), 1.47 (s, 9H,  $\text{CMe}_3$ ),  $-0.76$  (s, 6H,  $\text{AlMe}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  182.5 (s,  $\text{CCMe}_3$ ), 55.0 (s, Ad- $C_\alpha$ ), 46.0 (t,  $^1J_{\text{CH}} = 128$ , Ad- $C_\beta$ ), 38.5 (s,  $\text{CMe}_3$ ), 36.6 (t,  $^1J_{\text{CH}} = 126$ , Ad- $C_\gamma$ ), 32.6 (q,  $^1J_{\text{CH}} = 127$ ,  $\text{CMe}_3$ ), 30.7 (d,  $^1J_{\text{CH}} = 133$ , Ad- $C_\delta$ ),  $-6.8$  (br q,  $^1J_{\text{CH}} = 113$ ,  $\text{AlMe}_2$ ). Anal. Calcd for  $\text{C}_{27}\text{H}_{45}\text{AlN}_2$ : C, 76.37; H, 10.68; N, 6.60. Found: C, 76.43; H, 10.86; N, 6.65.

$\{\text{BuC}(\text{NAr})_2\}\text{AlMe}_2$  (**6b**). This compound was prepared by the procedure described for **5b**, using 2.71 g of 1,3-bis(2,6-diisopropylphenyl)carbodiimide (7.48 mmol) in 80 mL of  $\text{Et}_2\text{O}$ , 4.4 mL of  $\text{tBuLi}$  (1.7 M solution in pentane, 7.5 mmol), and 0.7 mL of  $\text{AlMe}_2\text{Cl}$  (7.48 mmol) in 30 mL of  $\text{Et}_2\text{O}$ . After 15 h the volatiles were removed under vacuum yielding an oily red-brown solid.  $\{\text{BuC}(\text{NAr})_2\}\text{AlMe}_2$  was extracted from LiCl with pentane and isolated from the extract by crystallization at  $-30^\circ\text{C}$ . Yield: 0.726 g, 20% based on  $\text{AlMe}_2\text{Cl}$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.18–7.12 (m, 6H, Ar), 3.45 (sept,  $^3J_{\text{HH}} = 6.8$ , 4H,  $\text{CHMe}_2$ ), 1.34 (d,  $^3J_{\text{HH}} = 7.2$ , 12H,  $\text{CHMe}_2$ ), 1.16 (d,  $^3J_{\text{HH}} = 6.8$ , 12H,  $\text{CHMe}_2$ ), 0.91 (s, 9H,  $\text{CMe}_3$ ),  $-0.6$  (s, 6H,  $\text{AlMe}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  180.5 (s,  $\text{CCMe}_3$ ), 145.0 (s, Ar- $C_{\text{ortho}}$ ), 139.6 (s, Ar- $C_{\text{ipso}}$ ), 125.9 (d,  $^1J_{\text{CH}} = 161$ , Ar- $C_{\text{para}}$ ), 123.7 (d,  $^1J_{\text{CH}} = 156$ , Ar- $C_{\text{meta}}$ ), 42.3 (s,  $\text{CMe}_3$ ), 29.7 (q,  $^1J_{\text{CH}} = 127$ ,  $\text{CMe}_3$ ), 28.7

(d,  $^1J_{\text{CH}} = 129$ ,  $\text{CHMe}_2$ ), 27.1 (q,  $^1J_{\text{CH}} = 128$ ,  $\text{CHMe}_2$ ), 22.8 (q,  $^1J_{\text{CH}} = 127$ ,  $\text{CHMe}_2$ ),  $-8.6$  (br q,  $^1J_{\text{CH}} = 113.4$ ,  $\text{AlMe}_2$ ). Anal. Calcd for  $\text{C}_{31}\text{H}_{49}\text{AlN}_2$ : C, 78.10; H, 10.36; N, 5.88. Found: C, 77.61; H, 10.28; N, 5.78. MS ( $m/z$ ): 461 (100,  $\text{M}^+ - \text{Me}$ ).

**X-ray Structure Determinations.** The structures of **1** and **6b** were determined at the University of Minnesota by V. G. Young, Jr. The structures of **3a** and **6a** were determined at the University of Iowa by D. C. Swenson. Crystal data, data collection details, and solution and refinement procedures are collected in Table 1. Additional comments specific to each structure follow.

$\{\text{MeC}(\text{NAd})\text{S}\}\text{AlMe}_2$  (**1**). Crystals were obtained by crystallization from  $\text{Et}_2\text{O}$  at  $-30^\circ\text{C}$ . All non-H atoms were refined anisotropically, and all H atoms were placed in ideal positions and refined as riding atoms with group isotropic displacement parameters.

$\{\text{AdN}(\text{H})\text{C}(\text{NAd})\text{S}\}\text{AlMe}_2$  (**3a**). Crystals were obtained by crystallization from  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$ . All non-H atoms were refined anisotropically. The H2, H2A–C and H3A–C H atoms were refined with isotropic displacement parameters. All other H atoms were included with the riding model (C–H = 0.98–0.99 Å), tetrahedral angles,  $U_{\text{iso}} = 1.2 \times U_{\text{iso}}$  (equiv C).

$\{\text{BuC}(\text{NAd})_2\}\text{AlMe}_2$  (**6a**). Crystals were obtained by recrystallization from pentane at  $-30^\circ\text{C}$ . Two independent molecules with nearly the same conformation were found in the asymmetric unit. All non H atoms were refined with anisotropic displacement parameters. All adamantyl H atoms were included with a modified riding model: tetrahedral angles, C–H refined (C–H equal for  $\text{CH}_2$  groups),  $U_{\text{iso}}$  refined. Methyl H atoms were refined with no restraints or constraints, and with independent isotropic displacement parameters.

$\{\text{BuC}(\text{NAr})_2\}\text{AlMe}_2$  (**6b**). Crystals were obtained by crystallization from pentane at  $-30^\circ\text{C}$ . All non-H atoms were refined anisotropically, and all H atoms were placed in ideal positions and refined as riding atoms with group isotropic displacement parameters.

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**Supporting Information Available:** Tables of atomic coordinates, isotropic displacement parameters, anisotropic displacement parameters, bond distances and bond angles, and hydrogen atom coordinates (31 pages). Ordering information is given on any current masthead page.

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