

# Synthesis and Thermolysis of Aluminum Amidinates: A Ligand-Exchange Route for New Mixed-Ligand Systems

Allison L. Brazeau,<sup>†</sup> Zhaohui Wang,<sup>†</sup> Chris N. Rowley,<sup>‡</sup> and Seán T. Barry<sup>†,\*</sup>

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6, and Department of Chemistry, University of Ottawa, 10 Rue Marie-Curie, Ottawa, Ontario, Canada K1N 5N6

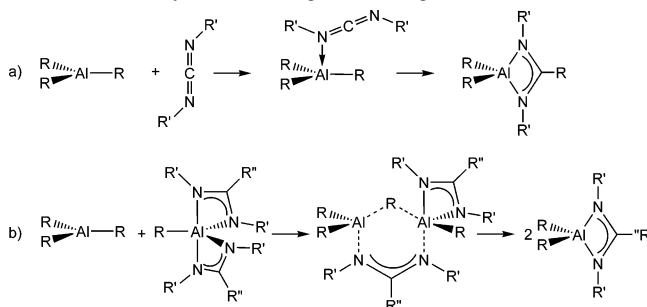
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A novel ligand-exchange route for the synthesis of amidinate-containing compounds of aluminum is explored. Syntheses of three new compounds,  $\text{MeC}(\text{N}^i\text{Pr})_2\text{AlEt}_2$  (**4**),  $\text{EtC}(\text{N}^i\text{Pr})_2\text{AlMe}_2$  (**5**), and  $(\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2)_2\text{AlH}$  (**6**), are presented. These mixed-ligand compounds are difficult to make in high yields by the more traditional routes of carbodiimide insertion or salt metathesis. The thermal reactivities of these compounds and their parent homoeleptic compounds  $[\text{MeC}(\text{N}^i\text{Pr})_2]_3\text{Al}$  (**1**),  $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3\text{Al}$  (**2**), and  $[\text{EtC}(\text{N}^i\text{Pr})_2]_3\text{Al}$  (**3**) are explored in detail and analyzed with respect to their utility as potential atomic-layer-deposition precursors for aluminum-containing films. The major mechanism of thermal decomposition is found to be carbodiimide deinsertion to form aluminum alkyls or amides. Because of their thermal characteristics, both compounds **3** and **5** hold promise for use as precursors.

## Introduction

Amidines of group 13 have appeared often in recent literature.<sup>1</sup> These compounds appear in diverse applications: they have been investigated as main group Zeigler-Natta catalysts,<sup>2</sup> potential vapor-deposition precursors,<sup>3,4</sup> and in C–H bond activation.<sup>5</sup> Very recently, an excellent example of a family of amidinate hydrides has been reported.<sup>6</sup> Generally, amidinates can be formed by several different mechanisms. The most common synthetic method is a salt metathesis reaction between a lithium amidinate and an aluminum halide. Jordan has previously employed this method, as well as carbodiimide insertion into an aluminum

**Scheme 1.** Formation of a Metal Amidinate (a) by Carbodiimide Insertion and (b) by Amidinate Ligand Exchange<sup>a†</sup>



alkyl bond, for amidinate synthesis.<sup>7</sup> Carbodiimide insertion has been thoroughly studied experimentally<sup>8</sup> and theoretically (Scheme 1 a).<sup>9</sup> As well, reaction of the parent amidine with an aluminum alkyl is a facile method of amidinate formation if the parent amidine is available.<sup>10</sup>

\* To whom correspondence should be addressed. E-mail: sbarry@ccs.carleton.ca.

<sup>†</sup> Carleton University.

<sup>‡</sup> University of Ottawa.

- (1) N. B. Amidinate will hereafter be used to denote any bidentate ligand that forms an N–C–N cycle with a metal center. Guanidinates are a subclass of this ligand in which the ligand's exocyclic group is an amide.
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Our interest in these systems lies in the synthesis and characterization of mixed-ligand systems for aluminum and gallium that incorporate both a chelate and a monodentate ligand. These compounds are intended as precursors for atomic layer deposition (ALD). In the ALD reaction cycle, a precursor must chemisorb onto the surface to form a self-limiting monolayer.<sup>11</sup> This monolayer subsequently reacts with a second vaporous precursor to deposit an atomic layer of target film. This process is rapidly becoming a staple of both microelectronics manufacturing and emerging nanotechnology applications.<sup>12</sup>

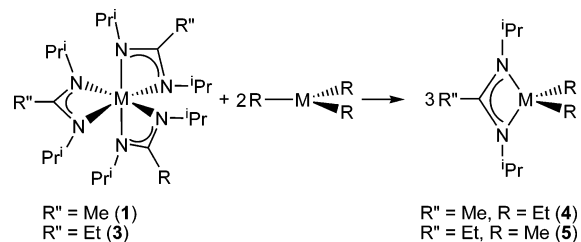
As synthetic chemists, our interest is in designing precursors that incorporate several characteristics important to vapor-phase deposition techniques. The compounds must be volatile so that they can be entrained into deposition reactors. Ideally, these compounds would be distillable liquids to avoid kinetic problems associated with volatilizing solid precursors. They must exhibit thermal robustness at moderate temperatures (~100 °C) so that they may be heated over long periods of time to promote volatility. Finally, and very importantly, these compounds must be able to chemisorb to a substrate or growing target film to form a single monolayer of excellent coverage, without undergoing further chemical reaction. This places strict requirements on the volatility and thermal stability of potential precursors that must be balanced with the high reactivity needed in the ALD reaction cycle.

By designing precursors with mixed-ligand systems, we hope to incorporate self-limiting behavior. The monodentate ligand can act as an “anchor” that readily reacts with surface sites, whereas the chelate ligand will sterically protect the newly formed monolayer from further reaction, promoting self-limiting behavior.<sup>13</sup> Herein, we will report a novel synthetic method for the formation of mixed-ligand systems: amidinate ligand exchange. This important synthetic method allows for the flexible alteration of the anchor ligand without altering the nature of the exocyclic group on the chelate ligand (Scheme 1).

In carbodiimide insertion reactions, the exocyclic group must be the same as the metal-bound monodentate ligand if a homoleptic starting metal species is used. If a mixed-monodentate-ligand system is used, the bond that the carbodiimide species inserts into relies on more complicated steric considerations that were described by Chang (Scheme 1a).<sup>8</sup> The preference of carbodiimide insertion depends on both the metal-bonded species and the alkyl groups of the carbodiimide.

In contrast, ligand-exchange reactions transfer the entire amidinate from one metal center to another, allowing easy control over the nature of the exocyclic group on the chelate ligand, regardless of the identity of the monodentate ligand. This allows for a very easy route for modification of the compound to tune thermal reactivity, among other characteristics. To the best of our knowledge, our group is the first

**Scheme 2.** General Ligand-Exchange Reaction for Alkyl Aluminum Compounds **4** and **5**



to exploit ligand exchange of amidinates.<sup>4</sup> We are presently exploring the mechanism of this reaction, as well as its generality for different metal centers.

We have applied the ligand-exchange approach to the synthesis of three potential precursors for vapor deposition. To do so, we have employed two homoleptic amidinate compounds previously reported in the literature:  $[\text{MeC}(\text{N}^i\text{Pr})_2]_3\text{Al}$  (**1**) and  $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3\text{Al}$  (**2**).<sup>4</sup> Additionally, we report a third homoleptic amidinate,  $[\text{EtC}(\text{N}^i\text{Pr})_2]_3\text{Al}$  (**3**). Through ligand exchange, we have synthesized three potential precursors:  $\text{MeC}(\text{N}^i\text{Pr})_2\text{AlEt}_2$  (**4**),  $\text{EtC}(\text{N}^i\text{Pr})_2\text{AlMe}_2$  (**5**), and  $(\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2)_2\text{AlH}$  (**6**). Additionally, we have explored the thermal reactivity of these compounds to ascertain thermal stability and to consider what common thermochemical reaction pathways exist. Specifically, we consider how the reverse of insertion (“deinsertion”) affects the thermochemistry of each compound.

## Results and Discussion

**Homoleptic Six-Coordinate Amidinates.** To attempt these ligand-exchange reactions with aluminum alkyls, we first made the homoleptic amidinates **1** and **3** by carbodiimide insertion into trimethylaluminum and triethylaluminum, respectively (Scheme 2).

Both **1** and **3** form over a few days at elevated temperatures and have excellent yields. The <sup>1</sup>H NMR spectra for each of these compounds give two doublets (1.32 and 1.17 ppm for **1** and 1.40 and 1.24 ppm for **3**), which is an indication of the steric bulk around the metal center. All four isopropyl methyl groups are inequivalent in the amidinate ligand in the static structure but can equilibrate through both a racemization step and a rotation around the ligand’s C<sub>2</sub> axis.<sup>14</sup> The increased steric hindrance prevents the C<sub>2</sub> rotation, as we have previously discussed.<sup>4</sup>

Because of a lack of anchoring ligands, these compounds are not considered to be very good candidates as precursors for ALD. Both homoleptic amidinates have good volatility under a roughing pump vacuum (128 °C for **1** and 140 °C for **3**) but are solids at these temperatures; both compounds decompose without melting above 310 °C.

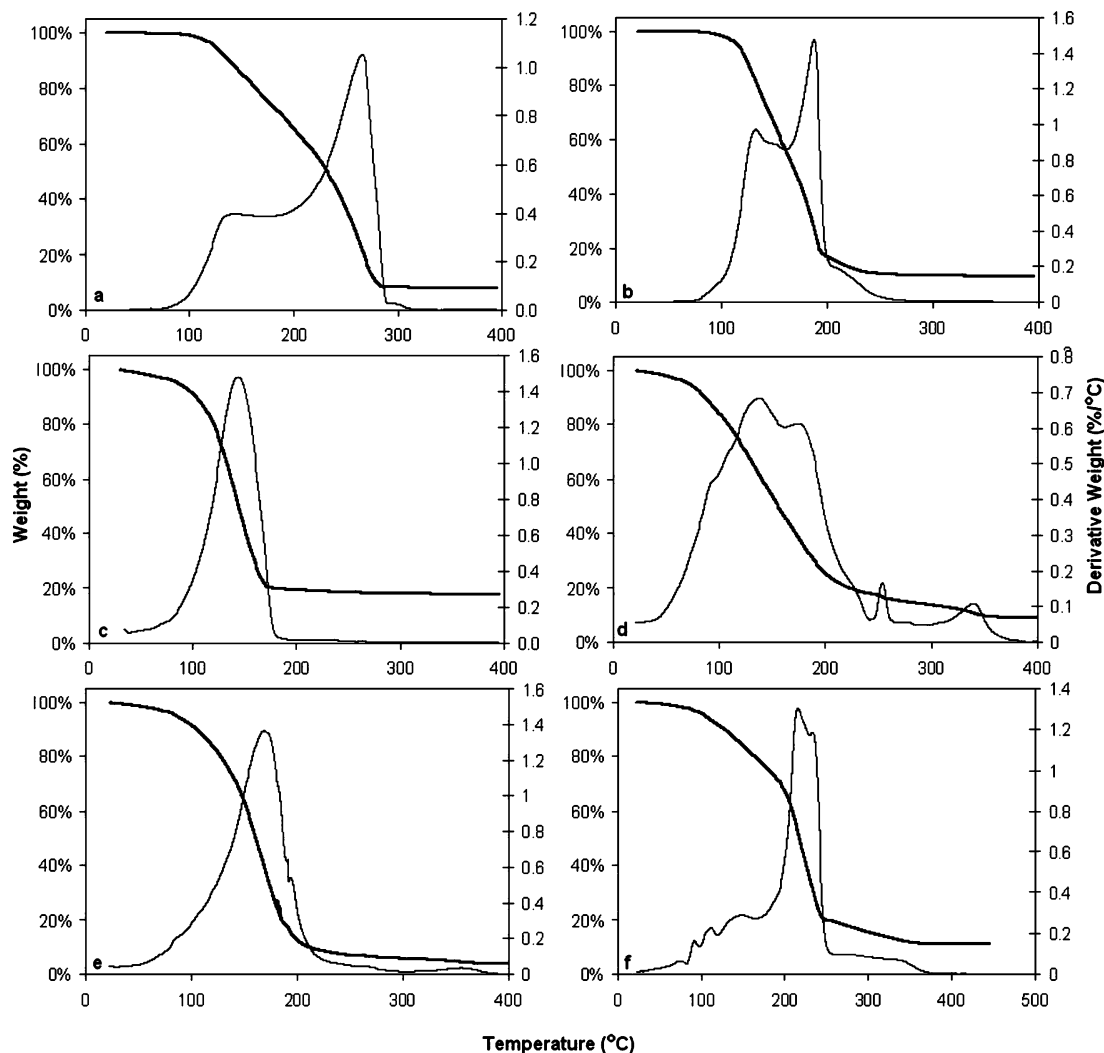
The thermogravimetric (TG) curve for **1** shows two distinct features (Figure 1a). We were able to monitor evolved species during the TG run by condensing the off-gas in an NMR tube. These NMR tubes were changed at temperature intervals determined by the observed thermal events

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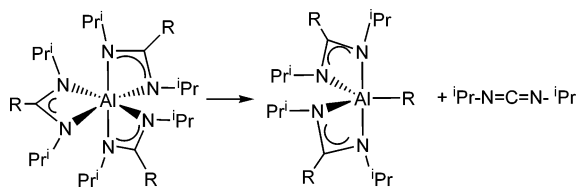
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**Figure 1.** thermal gravimetric analysis (with derivative curve) for compounds (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

**Scheme 3.** Deinsertion of Carbodiimide from an Amidinate to Produce an Aluminum Alkyl and Diisopropyl Carbodiimide



in the TG. Below 200 °C, the TG showed a relatively slow weight loss; it was apparent in the  $^1\text{H}$  NMR that diisopropylcarbodiimide was deinserting from the acetamidinate ligand (Scheme 3). This is not very surprising, as trisamidinates of group 13 are easily synthesized by multiple carbodiimide insertion reactions.<sup>9</sup> The thermal feature above 200 °C appears to be volatilization of either **1** or its deinsertion products. Because of experimental constraints, we can monitor only species that are moderately air-stable.

Compound  $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3\text{Al}$  (**2**) exhibits thermolysis very similar to that of compound **1**, although the onset of thermolysis (88 °C) is lower (Figure 1b). Decomposition by carbodiimide deinsertion starts to become apparent at 120 °C and continues until about 250 °C. This very small window between onset of volatilization and thermal decomposition

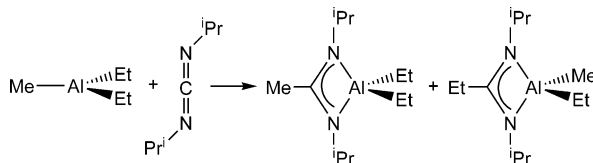
renders this compound useless as a vapor-phase precursor. Handily, it is an excellent starting material for ligand exchange.

Compound **3** is stable in air for a number of minutes and has considerably better thermal chemistry than **1** and **2** (Figure 1c). The TG weight loss was dominated by volatilization, with a very early onset (34.3 °C). Off-gas analysis by  $^1\text{H}$  NMR confirmed the absence of carbodiimide below 150 °C and showed characteristic peaks for **3**. The derivative curve showed a slow onset/rapid decline that is a characteristic peak shape for volatilization. Between 200 and 250 °C, there is evidence of carbodiimide deinsertion in the  $^1\text{H}$  NMR, although the feature in the TG is a minor weight loss. Although **3** would be a solid at any vapor-deposition process temperature, its excellent volatility and low residual mass (17% when loaded under air) suggest it is a promising aluminum precursor. Subsequent reactivity studies are under way to determine what, if any, reactivity it might have with silicon surfaces.

**Dialkyl Monoamidinates.** It is worth noting here that the process of ligand exchange allows for the inclusion of both methyl and ethyl groups in these products, which subsequently allows control over melting point and volatility.

## Amidinate Exchange Mechanism for Aluminum

**Scheme 4.** Lack of Carbodiimide Insertion Selectivity between Methyl and Ethyl Groups at an Aluminum Center

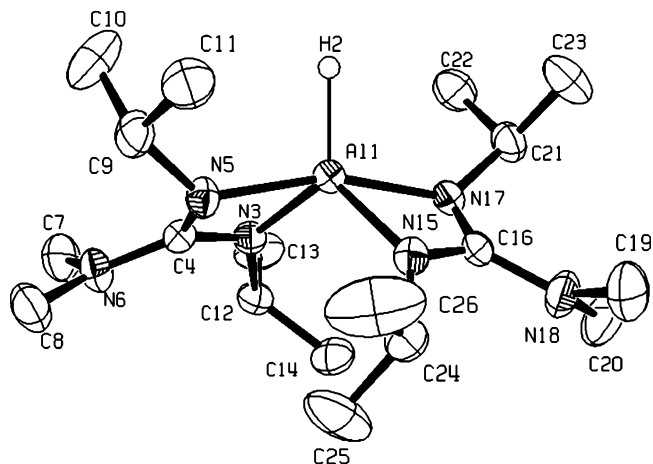


When synthesis of either compound was attempted by carbodiimide insertion, the result was a mixture of compounds that had both exocyclic methyl and ethyl groups (Scheme 4). The selectivity of insertion between these two alkyl groups appears to be sufficiently small that this synthetic pathway cannot produce a reasonable yield of either compound.

The ligand-exchange reactions to form compounds **4** and **5** were facile, occurring at room temperature with stirring. Both of these compounds are distillable liquids at room temperature, with **4** having a melting point below  $-30\text{ }^{\circ}\text{C}$ , likely because of its less symmetrical nature and the inclusion of ethyl groups to frustrate crystallization.<sup>15</sup> Although the final yields of these compounds are moderate (77% for **4** and 71% for **5**), this was after purification by distillation of less than a gram of material in each case: the crude  $^1\text{H}$  NMRs for these compounds showed very little proton-containing impurities. Also, the  $^1\text{H}$  NMR spectrum showed only a single doublet for the isopropyl methyl groups, indicating that the ligand rotation for these compounds is fast on the NMR time scale. This demonstrates the expected alleviation of steric hindrance at the metal center. To compare synthetic methods, we also synthesized compound **4** by a salt metathesis reaction between  $\text{Et}_2\text{AlCl}$  and  $\text{MeC}(\text{N}^i\text{Pr})_2\text{Li}$ . The crude yield was 96.8%, showing little difference from that of the ligand-exchange synthesis (95.7%).

Compounds **4** and **5** are promising vapor precursors because of their very low melting points. However, TG analysis shows very different thermal behaviors for these two compounds (Figures 1d,e). Both compounds show an onset of volatilization almost immediately in the TG experiment: compound **4** starts evaporating at  $32.8\text{ }^{\circ}\text{C}$  and compound **5** starts at  $20\text{ }^{\circ}\text{C}$ . Both compounds have excellent residual masses (8.8% for **4** and 3.6% **5**).

The TG thermolysis of compound **4** showed no carbodiimide deinsertion up to  $130\text{ }^{\circ}\text{C}$  by  $^1\text{H}$  NMR analysis of the off-gas, during which the TG shows a weight loss typical of volatilization (Figure 1d). The derivative curve of the TG showed a second process partially overlapping with volatilization in the temperature region between  $130$  and  $240\text{ }^{\circ}\text{C}$ , where the characteristic peaks of diisopropyl carbodiimide were dominant in the  $^1\text{H}$  NMR of the off-gas. Further thermolysis continued between  $250$  and  $350\text{ }^{\circ}\text{C}$  but did not show the carbodiimide. This suggests there is a thermolysis window between  $150$  and  $250\text{ }^{\circ}\text{C}$  where carbodiimide deinsertion occurs. Considering the low melting point, the low residual mass, and early onset of thermal decomposition



**Figure 2.** Crystal structure diagram of  $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{AlH}$  (**6**). The thermal ellipsoids are shown at the 50% level of probability, and all hydrogen atoms except the aluminum-bonded hydride are excluded for simplicity.

of **4** in the TG, this compound would only be suitable for low-temperature deposition processes.

Compound **5** shows much more encouraging thermal characteristics (Figure 1e). A dominant single feature in the TG showed evaporation below  $210\text{ }^{\circ}\text{C}$  with no production of carbodiimide, as monitored from  $^1\text{H}$  NMR of the off-gas. A subsequent minor feature between  $300$  and  $400\text{ }^{\circ}\text{C}$  produced a number of unidentifiable products, with only a small amount of carbodiimide. This suggests that carbodiimide is likely produced through a high-temperature decomposition of the ligand itself. With its very low onset of volatilization, its below room-temperature melting point, and excellent thermal stability, compound **5** is a very encouraging potential precursor.

The utility of ligand exchange is most noteworthy in the synthesis of  $(\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2)_2\text{AlH}$  (**6**) from **2** and  $\text{AlH}_3\cdot\text{NMe}_2\text{Et}$ . This synthesis uses alane rather than lithium aluminum hydride to avoid lithium impurities in the product that could become problematic when using the compound as a thin film precursor. As with the previous ligand-exchange products, this compound forms at room temperature with stirring and can be precipitated in high yield as a crystalline solid. The  $^1\text{H}$  NMR shows one doublet for the isopropyl methyl groups, indicating only a small steric effect around the metal center, unlike compounds **1** and **3**.

Thermolysis of compound **6** shows an early onset of decomposition (Figure 1f). Below  $150\text{ }^{\circ}\text{C}$ , TG off-gas monitoring by  $^1\text{H}$  NMR showed production of the parent guanidine. The large weight loss between  $150$  and  $250\text{ }^{\circ}\text{C}$  shows both rapid volatilization and carbodiimide deinsertion by NMR. Although the melting point for compound **6** is quite low ( $61\text{ }^{\circ}\text{C}$ ), the thermal behavior suggests that this compound would be a poor precursor for vapor deposition. Interestingly, it is not carbodiimide deinsertion that is the lowest-temperature decomposition route but rather the release of the guanidine.

Compound **6** has been characterized by single-crystal XRD (Figure 2, Tables 1 and 2). It has a  $P2(1)/c$  space group and roughly  $C_2$  symmetry. The central aluminum has a 5-coordinate, distorted trigonal bipyramidal geometry, with N5 and N17 occupying the axial positions. These bonds (Al1–N5

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**Table 1.** Selected Crystal Data and Structure Refinement Parameters for **6**

empirical formula	C <sub>18</sub> H <sub>41</sub> AlN <sub>6</sub> ( <b>6</b> )
fw	368.55
<i>T</i> (K)	206(2)
$\lambda$ (Å)	0.71073
cryst syst	monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	13.709(4)
<i>b</i> (Å)	9.031(3)
<i>c</i> (Å)	19.025(6)
$\alpha$ (deg)	90
$\beta$ (deg)	98.108(5)
$\gamma$ (deg)	90
<i>V</i> (Å <sup>3</sup> )	2331.8(13)
<i>Z</i>	4
$\rho$ (calcd) (Mg/m <sup>3</sup> )	1.050
abs coeff (mm <sup>-1</sup> )	0.099
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
R indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	R1 = 0.0632, wR2 = 0.1408

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o| ; wR2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$$

**Table 2.** Selected Bond Lengths and Angles for **6**

Bond Length (Å)	
Al1–N3	1.947(2)
Al1–N15	1.950(2)
Al1–N5	1.995(2)
Al1–N17	2.009(2)
Al1–H2	1.58(2)
Bond Angle (deg)	
N3–Al1–N5	67.77(8)
N15–Al1–N17	67.78(8)
N5–Al1–N17	162.26(8)
N3–Al1–N15	116.66(8)
N3–Al1–H2	120.4(8)
N15–Al1–H2	122.9(8)
Torsion Angle (deg)	
Al1–N3–C4–N5	1.8(2)
Al1–N15–C16–N17	0.8(2)
Sum of Angles (deg)	
$\Sigma$ N6	358.9
$\Sigma$ N18	357.3

= 1.99 Å, Al1–N17 = 2.01 Å) are longer than the equatorial nitrogen metal bonds (Al1–N3 = 1.946 Å, Al1–N15 = 1.95 Å), giving the chelate rings a lopsided coordination enforced by the central geometry. The aluminum hydride bond is 1.58 Å, which is typical for this moiety.<sup>16</sup>

The N5–Al1–N17 angle is quite distorted (162.3°) because of the bite angle enforced by the chelate rings (67.8° in both rings). These bite angles are typical for two ligands of this type coordinated to aluminum.<sup>4</sup> The equatorial bonds are closer to the ideal (N3–Al1–N15 = 116.7°, N3–Al1–H2 = 120.4°, N15–Al1–H2 = 122.9°).

As is typical for this ligand, the exocyclic amide groups are nearly planar ( $\Sigma$ N6 = 158.9°,  $\Sigma$ N18 = 157.3°). This approach to planarity indicates that a p-orbital on the exocyclic nitrogen is participating in the  $\pi$  system of the ligand. However, this participation is not full, as indicated by the torsion angle of the plane of the exocyclic amide with respect to the ligand plane (N3–C4–N6–C7 = 40.8°, N5–C4–N6–C8 = –26.7(4)°, N15–C16–N18–C19 = 50.0°, N17–C16–N18–C20 = –27.8(3)°). The range of plane tilt

is caused by the minimal deviation from planarity of the exocyclic amide groups.

## Conclusions

Carbodiimide deinsertion appears to be the major thermal decomposition route for amidinates of aluminum. All of the reported compounds exhibited this reactivity to a greater or lesser extent as determined by analysis of the TG off-gas at varying temperatures. The homoleptic compounds [MeC(N<sup>i</sup>Pr)<sub>2</sub>]<sub>3</sub>Al<sup>9</sup> (**1**), [Me<sub>2</sub>NC(N<sup>i</sup>Pr)<sub>2</sub>]<sub>3</sub>Al (**2**),<sup>4</sup> and [EtC(N<sup>i</sup>Pr)<sub>2</sub>]<sub>3</sub>Al (**3**) showed the lowest temperature decompositions because of the available 5-coordinate geometries after deinsertion.

The process of ligand exchange allows for the synthesis of MeC(N<sup>i</sup>Pr)<sub>2</sub>AlEt<sub>2</sub> (**4**), EtC(N<sup>i</sup>Pr)<sub>2</sub>AlMe<sub>2</sub> (**5**), and (Me<sub>2</sub>NC(N<sup>i</sup>Pr)<sub>2</sub>)<sub>2</sub>AlH (**6**) in high yields and at room temperature. This synthetic route is more facile than salt metathesis reactions with comparable yields under room-temperature conditions. Also, mixed-ligand compounds such as **4** and **5** are very difficult to make by carbodiimide insertion because of insertion competition. Most importantly, this synthetic route provides a very simple, one-pot synthesis of hydrides such as **6**. Our novel route permits synthesis of new mixed-ligand systems with ease. The mechanism and kinetics of ligand exchange, as well as its greater general utility for various metal centers, is the subject of additional research by our group.

The most encouraging potential precursor for ALD was EtC(N<sup>i</sup>Pr)<sub>2</sub>AlMe<sub>2</sub> (**5**). It is a liquid at room temperature and boils under vacuum at 28 °C. Additionally, it is very thermally stable and shows only modest carbodiimide production at very high temperatures.

## Experimental Section

**General Procedures.** All manipulations were performed in a nitrogen-filled drybox. The chemicals: alane *N*-dimethylethylamine, deuterated benzene, trimethylaluminum, triethylaluminum, diethylaluminum chloride, and 1,3-diisopropyl carbodiimide were purchased from Aldrich Chemical Co. and used as received. All solvents used were anhydrous grade, also purchased from Aldrich and used as received. The synthesis of [MeC(N<sup>i</sup>Pr)<sub>2</sub>]<sub>3</sub>Al (**1**),<sup>9</sup> (Me<sub>2</sub>NC(N<sup>i</sup>Pr)<sub>2</sub>)<sub>3</sub>Al (**2**),<sup>4</sup> and MeC(N<sup>i</sup>Pr)<sub>2</sub>Li<sup>7</sup> followed literature procedures. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on a Varian Gemini-200 and a Bruker 400 MHz spectrometer, using the residual protons in the deuterated solvent for reference. Mass spectra were obtained using the electron impact method on a VG ZAB-2HF triple-focusing spectrometer. Guelph Chemical Laboratories performed combustion analysis. Thermogravimetric analysis was performed on a TA Instruments Q50 apparatus.

**Thermolysis Monitoring by NMR.** Under a normal atmosphere, the TG off-gas was piped into NMR tubes that were partially submerged in liquid nitrogen. The NMR tube was switched during the data collection to separate specific temperature ranges defined by thermolysis events in the TG. After condensation of the off-gas, deuterated benzene was added to the tube by syringe, and a <sup>1</sup>H NMR was collected.

[EtC(N<sup>i</sup>Pr)<sub>2</sub>]<sub>3</sub>Al (**3**). In a 150 mL pressure vessel, triethylaluminum (1.0 M in hexane, 4 mL, 4 mmol) was added dropwise to 1,3-diisopropyl carbodiimide (3.137 g, 24.8 mmol) while the solution was stirred rapidly over 20 min; the solution remained colorless. The reaction mixture was heated in an oil bath at 130 °C

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for 96 h with the pressure vessel submerged to the level of the solution; the solution turned yellow. The volatiles were removed under vacuum, and a yellow powder remained (3.77 mmol, 94.3%). Compound **3** was purified by sublimation at 140 °C to yield a white powder (93%). Mp: >310 °C (decomp.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 3.62 (sept, 6H, CH(Me)<sub>2</sub>), 2.09 (quart, 6H, NC(CH<sub>2</sub>-CH<sub>3</sub>)N), 1.40 (d, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.00 (t, 9H, NC(CH<sub>2</sub>CH<sub>3</sub>)N). <sup>13</sup>C NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 171.6 (NC(CH<sub>2</sub>CH<sub>3</sub>)N), 46.0 (NCH(CH<sub>3</sub>)<sub>2</sub>), 26.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.6 (NC(CH<sub>2</sub>CH<sub>3</sub>)N), 11.0 (NC(CH<sub>2</sub>CH<sub>3</sub>)N). Mass spectrum (EI, *m/z*) (rel intensity, %): 492 (1.6, M<sup>+</sup>). Anal. Calcd for AlC<sub>27</sub>H<sub>57</sub>N<sub>6</sub>: C, 65.81; H, 11.66; N, 17.05. Found: C, 65.94; H, 12.00; N, 16.99.

**MeC(N<sup>i</sup>Pr)<sub>2</sub>AlEt<sub>2</sub> (4)**. Method 1. In a 50 mL round-bottom flask, 1,3-diisopropylcarbodiimide (1.67 g, 13.2 mmol) was dissolved in hexane (20 mL). Methylolithium (1.6 M in ether, 8.4 mL, 13.4 mmol) was added to the solution dropwise with stirring. The solution had a white precipitate and was stirred at room temperature for 24 h. Diethylaluminum chloride (1.0 M in hexane, 13.4 mL, 13.4 mmol) was added to the solution dropwise with stirring, and the solution was left to stir for 48 h. The white precipitate was filtered, and the volatiles from the colorless filtrate were removed under vacuum. A slightly yellow viscous liquid remained (12.8 mmol, 96.8%).

Method 2. In a 50 mL round-bottom flask, compound **1** (1.129 g, 2.5 mmol) was dissolved in hexane (20 mL). Triethylaluminum (1.0 M in hexane, 5.0 mL, 5.0 mmol) was added to the solution dropwise with stirring. The cloudy yellow solution was left to stir at room temperature for 19 h, and the volatiles were then removed under vacuum, leaving a yellow viscous liquid (7.2 mmol, 95.7%). The liquid was stored at -30 °C for a week, and remained as a liquid.

Compound **4** was distilled at 36 °C, 85 mTorr to yield a colorless liquid (77.2%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 3.12 (sept, 2H, CH(Me)<sub>2</sub>), 1.38 (t, 6H, CH<sub>2</sub>CH<sub>3</sub>), 1.297 (s, 3H, (iPrN)<sub>2</sub>CCH<sub>3</sub>), 0.96 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.30 (quart, 4H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 172.2 (NC(CH<sub>3</sub>)N), 44.8 (NCH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 10.1 (NC(CH<sub>3</sub>)N), 9.68 (CH<sub>2</sub>CH<sub>3</sub>). Mass spectrum (EI, *m/z*) (rel intensity, %): 225 (4.8, M<sup>+</sup>). Anal. Calcd for AlC<sub>12</sub>H<sub>27</sub>N<sub>2</sub>: C, 63.68; H, 12.02; N, 12.38. Found: C, 63.96; H, 11.84; N, 11.94.

**EtC(N<sup>i</sup>Pr)<sub>2</sub>AlMe<sub>2</sub> (5)**. In a 50 mL round-bottom flask, compound **3** (0.385 g, 0.8 mmol) was dissolved in hexane (4 mL). Trimethylaluminum (2.0 M in hexane, 0.8 mL, 1.6 mmol) was added to the solution with stirring. The solution was stirred at room temperature for 18 h, and the volatiles were then removed under vacuum, leaving

a slightly yellow liquid. The liquid was stored at -30 °C overnight, and a yellow solid resulted (1.9 mmol, 82.6%). Compound **5** was distilled at 28 °C, 110 mTorr to yield a colorless liquid (1.62 mmol, 71.0%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 3.19 (sept, 2H, CH(Me)<sub>2</sub>), 1.80 (quart, 2H, (iPrN)<sub>2</sub>CCH<sub>2</sub>CH<sub>3</sub>), 0.98 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.76 (t, 3H, (iPrN)<sub>2</sub>C CH<sub>2</sub>CH<sub>3</sub>), -0.28 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 175.8 (NC(CH<sub>2</sub>CH<sub>3</sub>)N), 44.8 (NCH(CH<sub>3</sub>)<sub>2</sub>), 25.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.0 (NC(CH<sub>2</sub>CH<sub>3</sub>)N), 11.6 (NC(CH<sub>2</sub>CH<sub>3</sub>)N), -9.25 (CH<sub>3</sub>). Anal. Calcd for AlC<sub>11</sub>H<sub>25</sub>N<sub>2</sub>: C, 62.23; H, 11.87; N, 13.19. Found: C, 61.79; H, 11.45; N, 12.87.

**[Me<sub>2</sub>NC(N<sup>i</sup>Pr)<sub>2</sub>]<sub>2</sub>AlH (6)**. In a 50 mL flask, 1.5 g of compound **2** (2.8 mmol) was dissolved in approximately 15 mL of toluene. To this solution was added 2.8 mL of AlH<sub>3</sub>·N(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>CH<sub>3</sub>) (0.5 M in toluene, 1.4 mmol) dropwise to the flask over 10 min while the solution was stirred rapidly. The reaction mixture was left at room temperature to stir for 24 h and then cooled to -30 °C for 18 h. Compound **6** precipitated at -30 °C as clear crystals (1.33 g, 86%). Mp: 61 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 3.54 (sept, 4H, CH(Me)<sub>2</sub>), 2.47 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 1.40 (d, 24H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 169.47 NC(NMe<sub>2</sub>)N, 46.14 (CHMe<sub>2</sub>), 39.27 (N(CH<sub>3</sub>)<sub>2</sub>), 25.06 (CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for AlC<sub>18</sub>H<sub>41</sub>N<sub>6</sub>: C, 58.66; H, 11.21; N, 22.80. Found: C, 58.30; H, 11.43; N, 22.44.

**Single-Crystal X-ray Analysis.** A single crystal was mounted on a thin glass fiber using viscous oil and then cooled to the data collection temperature. Crystal data and details of the measurements are included in the Supporting Information. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in *f*. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*<sup>2</sup>. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library.

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**Supporting Information Available:** Crystallographic information files (CIF) for compound **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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