

Two Types of Intramolecular Addition of an Al–N Multiple-Bonded Monomer LAlNAr' Arising from the Reaction of LAlI with N₃Ar' (L = HC[(CMe)(NAr)]₂, Ar' = 2,6-Ar₂C₆H₃, Ar = 2,6-*i*Pr₂C₆H₃)

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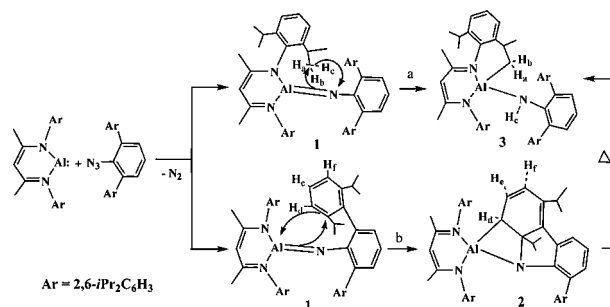
Considerable attention has been attracted to the heavier group 13 imides, since they can be used as single-source precursors for metal nitrides, which have interesting electronic properties and therefore important applications for technological materials.¹ In recent years, studies of the syntheses and characterization of such compounds have shown that they have a strong tendency to associate, even to oligomerize.² However, the modification of the substituents on both metal and nitrogen of the (MN)_n core have a great effect on their aggregation. The preparation of di- and tricoordinate imido monomers Ar'MNL'' (M = Ga, In; Ar' = 2,6-Ar₂C₆H₃, Ar = 2,6-*i*Pr₂C₆H₃, L'' = 2,6-(4-*t*Bu-Xyl)₂C₆H₃) and LMNL' (M = Al, Ga; L = HC[(CMe)(NAr)]₂, L' = 2,6-Trip₂C₆H₃, Trip = 2,4,6-*i*Pr₃C₆H₂), which have the lowest degree of association and the unique M–N multiple bond, demonstrates the stabilization of Al (Ga or In) imido monomers by the large bulky ligands.³ Nonetheless, the syntheses of compounds containing a Ga₂N₂ or an AlN₄ ring,^{2e,4a} which are proposed to proceed through the monomeric Al(Ga) imide, in the absence of steric protection, suggests the high reactivity of such monomers. Herein we show that the latent reactivity of a monomeric Al–N multiple-bonded species initiates further intramolecular addition. The reaction of the β-diketiminato LAlI^{4b} with the bulky N₃Ar' can afford two different isomers **2** and **3** derived from their parent imide LAlNAr' (**1**, Scheme 1). Also of great interest is the thermal conversion of **2** into **3**. This indicates the difference of the thermal stability between **2** and **3**.

The reaction of LAlI with N₃Ar' was carried out at –78 °C and allowed to warm to room temperature. Partial removal of toluene and addition of *n*-hexane led to crystallization of compounds **3** (colorless crystals in 24% yield) and **2** (yellowish crystals in 42% yield), one after the other. Crystals of **2** are of X-ray quality, while single crystals of **3** were obtained when **2** was treated by dissolving in a hot toluene/*n*-hexane mixture and then kept at 4 °C to allow crystallization. This suggests that a thermal conversion of **2** to **3** is occurring.

The LAlI reacting with N₃Ar' may proceed through an intermediate LAlNAr' (**1**) with elimination of N₂. A similar reaction of LM (M = Al, Ga) with N₃L' has been reported to afford LMNL' containing a M=N multiple bond.^{3b} The ¹H NMR kinetic study also suggests the existence of **1** at low temperature. Compound **2** is formed as a result of a [2 + 2] cycloaddition of a phenyl ring of the Ar' substituent on nitrogen (route b, Scheme 1), while the formation of **3** might occur by an intramolecular C–H activated addition involving the methyl group of the isopropyl substituent on the β-diketiminato ligand (route a).

Compounds **2** and **3** are thermally stable. They change with color at ~320 °C and finally melt at 381–382 °C. Both of them show

Scheme 1. Proposed Formation of **2** and **3** from the Reaction of LAlI with N₃Ar'



the molecular ion [M⁺ – 1] at *m/z* 855. They have been characterized by spectroscopic, analytical, and X-ray crystal measurements.

The structure of **2**^{5a} (Figure 1) exhibits a [2 + 2] cycloaddition product. The four-membered AlNC₂ ring is quasi-planar (Δ = 0.0680 Å) with Al–N bond length (1.876(2) Å) longer than those in the AlN₄ ring complex (1.851(2), 1.8152(15) Å)⁴ and Al–C distance (1.998(3) Å) similar to that in the AlC₃O ring compound (1.9852(16) Å).⁶ The phenyl ring involved in the [2 + 2] cycloaddition becomes nonplanar, where C(50), C(51), C(52), and C(53) are in-plane (Δ = 0.0430 Å) and C(48) and C(49) are away from this plane by 0.1813 and –0.2827 Å. The C–C bond lengths for C(50)–C(51) and C(52)–C(53) are respectively 1.348(4) and 1.336(4) Å and are typical of C=C double bonds,⁷ while the remaining four C–C distances are in the range (1.469(4)–1.536(4) Å) and are indicative of C–C single bonds.⁷ The structural features of this phenyl ring are in good agreement with the proton NMR spectrum. The resonances at δ 6.08 (dd), 5.41 (d), and 2.43 (d) ppm are assigned to H_e, H_f, and H_d, respectively, reflecting the extent of (un)saturation at the carbons where these protons are attached.

The X-ray crystal structure of **3** is shown in Figure 2. Compound **3** is monomeric^{5b} and contains a tetracoordinate Al (3N, 1C) center. The Al atom is involved as part of two fused six-membered rings (AlN₂C₃ and AlNC₄). The Al(1)–C(222) (1.961(3) Å) and C(222)–C(221) (1.556(3) Å) bond lengths are consistent with experimental values observed for Al–C⁸ and C–C⁷ single bonds. This suggests the absence of strain within the AlNC₄ ring formed as a result of Al–C ligation. The Al–NH(Ar') bond length (1.858(2) Å) falls within the range (1.75–1.85 Å) of terminal Al–N single bonds⁸ and is a little shorter than that of Al(1)–N(3) in **2**. The NH and the CH₂ protons (H_a and H_b) resonate at δ 3.41 (s), –0.28 (dd), and –1.75 (t), respectively. The characteristic absorption at 3298 cm^{–1} is assignable to ν_{NH} in the IR spectrum of **3**.

Now we gain further insight into the reaction process between LAlI and N₃Ar' carried out by a variable-temperature ¹H NMR study

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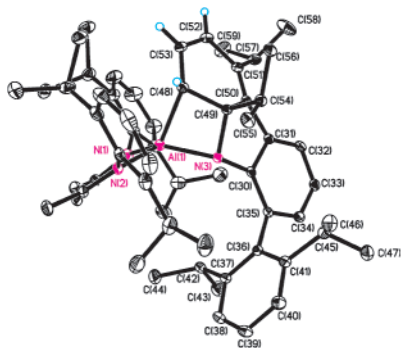


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.915(2), Al(1)–N(2) 1.926(2), Al(1)–N(3) 1.876(2), Al(1)–C(48) 1.998(3), C(48)–C(49) 1.536(4), C(49)–C(50) 1.520(4), C(50)–C(51) 1.348(4), C(51)–C(52) 1.469(4), C(52)–C(53) 1.336(4), C(53)–C(48) 1.475(4), N(3)–C(49) 1.537(3), N(1)–Al(1)–N(2) 96.92(10), N(3)–Al(1)–N(1) 127.76(10), N(3)–Al(1)–N(2) 117.99(10), N(3)–Al(1)–C(48) 78.53(10), Al(1)–N(3)–C(30) 138.71(17).

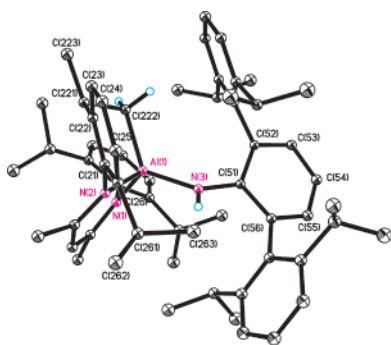


Figure 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.940(2), Al(1)–N(2) 1.913(2), Al(1)–N(3) 1.858(2), Al(1)–C(222) 1.961(3), C(222)–C(221) 1.556(3), N(1)–Al(1)–N(2) 95.69(10), N(3)–Al(1)–N(1) 115.78(9), N(3)–Al(1)–N(2) 103.44(10), N(3)–Al(1)–C(222) 122.34(10), Al(1)–N(3)–C(51) 138.72(16).

(Figure 3). The γ -CH of the starting material LAI resonates at ~ 5.10 ppm,⁹ and its change is a good indicator for the progress of the reaction. Thus in I, from -50 to -10 °C, the occurrence of one singlet may indicate the formation of **1**. From -10 to 50 °C, this singlet was gradually transformed into two other singlets, suggesting the further reaction of **1** and the concomitant formation of compounds **2** and **3**. This is further evidenced by the corresponding presence of the characteristic proton resonances in II indicative for **2** and **3**, respectively. The almost same integral intensity of **2** and **3** shows the equiponderance of the intramolecular addition of **1** via routes a and b. Keeping this reaction at 50 °C for 24 h, the final spectrum shows the disappearance of the characteristic resonances for **2** and the growing in of those for **3**. This experiment confirms the result of recrystallization of **2** from a hot solution to yield **3**.

The strained structure of **2** (torsional AlC_2N and C_6 rings) compared to that of **3** may energetically favor this thermal rearrangement, while the deliberate ^1H NMR kinetic studies of this reaction unambiguously reveal the thermal stability of these three isomers in the order of $\mathbf{1} < \mathbf{2} < \mathbf{3}$.

In summary, we have shown an unprecedented reaction, which occurs by an intramolecular addition to an Al-N multiple bonded species LAlNAr' and furthermore by rearrangement of **2** to **3** without changing the monomeric nature of the products. Presently, we are involved in the low-temperature synthesis of **1** and especially its X-ray structural analysis.

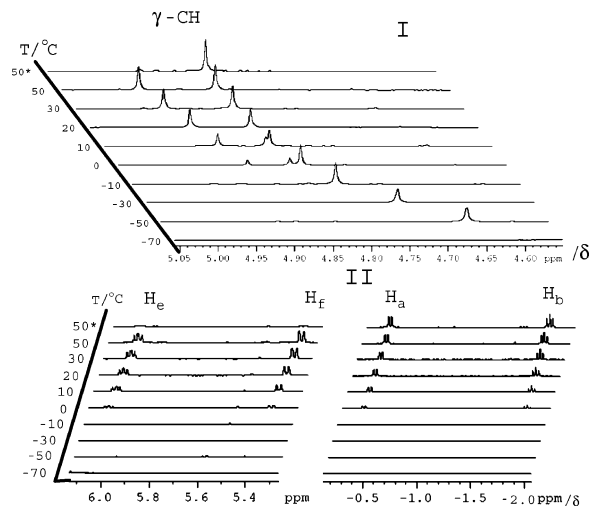


Figure 3. Variable-temperature ^1H NMR kinetic studies of the reaction of LAI with $\text{N}_3\text{Ar}'$ in $[\text{D}_8]\text{toluene}$. (I) records the resonances of γ -CH proton (δ 5.05–4.60 ppm) which correlate with changes of LAI moiety, and (II) shows those of **2** (H_f and H_g , δ 6.20–5.20 ppm) and **1** (H_a and H_b , δ 0.00–2.00 ppm). 50* means the available ^1H NMR data by keeping the sample at 50 °C for 24 h.

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Supporting Information Available: The Experimental Section including the detailed synthetic procedures, analytical and spectral characterization data; CIF data for **2** and **3**. This material is available free of charge via the Internet <http://pubs.acs.org>.

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- (a) Crystallographic data for **2** with Mo $\text{K}\alpha$ ($\lambda = 0.01073$ Å) radiation at 133(2) K. $a = 12.3496(6)$ Å, $b = 26.2644(15)$ Å, $c = 16.0109(7)$ Å, $\beta = 104.051(4)^\circ$, monoclinic, space group $P2(1)/n$, $Z = 4$, $R_1 = 0.0633$, $wR_2 = 0.1360$ for 5709 ($I > 2\sigma(I)$) data, and $R_1 = 0.1059$, $wR_2 = 0.1551$ for all (8626) data. (b) Crystallographic data for **3** with Mo $\text{K}\alpha$ ($\lambda = 0.01073$ Å) radiation at 133(2) K. $a = 11.806(8)$ Å, $b = 12.765(5)$ Å, $c = 19.718(8)$ Å, $\alpha = 76.04(3)^\circ$, $\beta = 74.54(4)^\circ$, $\gamma = 64.63(4)^\circ$, triclinic, space group $P-1$, $Z = 2$, $R_1 = 0.0595$, $wR_2 = 0.1415$ for 6992 ($I > 2\sigma(I)$) data, and $R_1 = 0.0751$, $wR_2 = 0.1496$ for all (8758) data.
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- The low-temperature ^1H NMR spectrum of the starting material LAI was measured as a reference. The resonances of γ -CH at δ 5.11, 5.13, 5.14, and 5.15 ppm respectively correspond to -50 , -30 , -10 , 25 °C.

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