

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

Hongping Zhu, Jianfang Chai, Vadapalli Chandrasekhar, Herbert W. Roesky,* Jörg Magull,
Denis Vidovic, Hans-Georg Schmidt, Mathias Noltemeyer and Philip P. Power

Supporting Informations (S 1-S 3)

Experimental Section

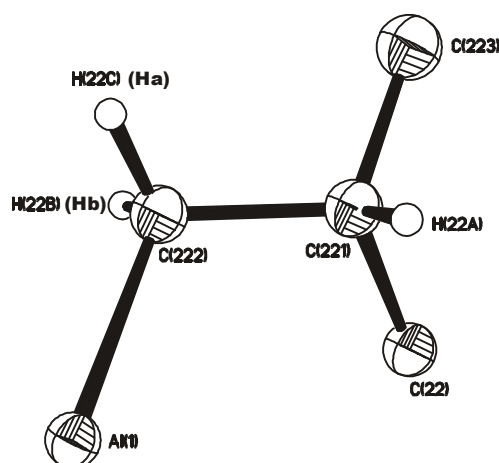
All manipulations were carried out under nitrogen atmosphere using Schlenk line techniques and a glove box.

- 1. Syntheses of 2 and 3.** Pre-cooled toluene (25 mL) was added to a mixture of LAl (0.25 g, 0.56 mmol) and N₃Ar' (0.25 g, 0.56 mmol) at -78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The light yellow solution was concentrated (5 mL), and to it *n*-hexane (10 mL) was added. The solution was kept at 4 °C for three weeks to afford colorless crystals of **3**. Yield: 0.12 g (24%). mp 381-383 °C (> 320 °C, decomp.). ¹H NMR (500.13 MHz, C₆D₆, 298 K): δ -1.75 (t, 1H, ²J_{HH} = -13.8 Hz, ³J_{HH} = 13.8 Hz, Al-CH₂), -0.28 (dd, 1H, ²J_{HH} = 13.8 Hz, ³J_{HH} = 3.0 Hz, Al-CH₂), 0.36, 0.39, 0.50, 0.80, 1.15, 1.22, 1.30 (d, 7 x 3H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 0.93, 0.94, 1.08, 1.11 (d, 4 x 3H, ³J_{HH} = 6.7 Hz, CH(CH₃)₂), 1.25, 1.34 (d, 2 x 3H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.31, 1.53 (d, 2 x 3H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 1.45, 1.50 (s, 2 x 3H, β-CH₃), 2.30 (sept, 1H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 2.41, 2.80, 3.47 (sept, 3 x 1H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 2.99, 3.39 (sept, 2 x 1H, ³J_{HH} = 6.7 Hz, CH(CH₃)₂), 3.07 (sept, 1H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 2.56 (m, 1H, CH(CH₃)(CH₂)), 3.41 (s, 1H, NH), 4.82 (s, 1H, γ-CH), 6.65 (m, 1H, Ph-H), 6.92-7.00 (m, 3 x 1H, Ph-H), 7.04-7.20 (m, 6 x 1H, Ph-H), 7.20-7.32 (m, 4 x 1H, Ph-H), 7.34-7.38 (m, 1H, Ph-H). ¹³C NMR (500.13 MHz, C₆D₆, 298 K): δ 18.50 (br, Al-C), 21.64, 21.68, 22.10,

22.84, 22.98, 23.61, 23.83, 23.93, 24.41, 25.31, 25.45, 25.55, 26.31, 26.92, 26.98, 27.06, 27.25, 27.66, 28.53, 28.57, 29.97, 30.03, 31.23, 31.69, 34.04 (β -CH₃, CH(CH₃)₂, CH(CH₃)(CH₂)), 98.99 (γ -CH), 114.62, 122.23, 122.98, 123.08, 123.64, 124.65, 124.67, 125.06, 125.65, 125.93, 126.55, 126.88, 127.81, 127.92, 128.42, 131.23, 133.84, 138.21, 140.30, 141.50, 142.48, 143.51, 143.82, 145.58, 146.53, 147.62, 148.48, 148.53, 150.68, 150.94 (Ph-C), 169.40, 169.52 (CN). IR (Nujol mull): $\nu_{\text{NH}} = 3298 \text{ cm}^{-1}$. EI-MS: m/z (%): 855 (10, [M⁺ - 1]); 443 (100, [M⁺ - NHAr']). Elemental analysis (%) calcd. for C₅₉H₇₈AlN₃: C 82.76, H 9.18, N 4.91. Found: C 82.60, H 9.28, N 4.98. After the removal of crystals of **3**, the mother liquor was kept at 4 °C for additional three weeks. A crop of yellowish crystals of **2** were obtained and collected by filtration. Yield: 0.21 g (42%). Compound **2** has a similar decomposition temperature and melting point as those of **3**. Its EI mass spectroscopic data is also similar to that of **3**. ¹H NMR (500.13 MHz, C₆D₆, 298 K): δ 0.26, 0.53, 0.54, 1.46 (d, 4 x 3H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 0.81, 0.93, 1.01, 1.06, 1.11, 1.30 (d, 6 x 3H, ³J_{HH} = 6.7 Hz, CH(CH₃)₂), 0.86, 0.88, 1.14, 1.27, 1.39, 1.42 (d, 6 x 3H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 1.30, 1.40 (s, 2 x 3H, β -CH₃), 2.34, 3.33 (sept, 2 x 1H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 2.64, 3.02, 3.18 (sept, 3 x 1H, ³J_{HH} = 6.7 Hz, CH(CH₃)₂), 3.12, 3.33, 3.33 (sept, 3 x 1H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 2.43 (d, 1H, ³J_{HH} = 6.4 Hz, Al-CH), 4.88 (s, 1H, γ -CH), 5.41 (d, 1H, ³J_{HH} = 9.4 Hz, AlCH-CH), 6.08 (dd, 1H, ³J_{HH} = 6.4 Hz, ³J_{HH} = 9.4 Hz, AlCH-CH=CH), 6.86 (m, 2 x 1H, Ph-H), 6.92 (m, 1H, Ph-H), 6.99 (m, 1H, Ph-H), 7.04-7.12 (m, 4 x 1H, Ph-H), 7.28 (m, 2 x 1H, Ph-H), 7.37 (m, 1H, Ph-H), 7.49 (m, 1H, Ph-H). ¹³C NMR (500.13 MHz, C₆D₆, 298 K): δ 14.28, 15.64, 18.58, 20.40, 22.99, 23.46, 23.75, 24.36, 24.47, 24.72, 24.72, 24.84, 24.84, 24.89, 24.96, 25.00, 25.49, 25.63, 26.31, 26.60, 27.40, 28.22, 29.00, 29.10, 29.84, 32.50, 26.93 (β -CH₃, CH(CH₃)₂, CH(CH₃)₂, N-C(*i*Pr), 73.99 (Al-C), 100.93 (γ -CH), 113.08, 118.25, 121.76, 123.88, 124.19, 124.21, 124.52, 124.56, 125.22, 127.05, 127.70, 128.00, 128.10,

128.20, 130.33, 132.06, 134.52, 136.42, 137.18, 141.52, 141.95, 143.21, 143.58, 145.54, 146.09, 146.79, 149.47, 153.54 (Ph-C, CH=CH-C(*i*Pr)=C), 170.21 (CN). Correct elemental analysis. Attempts to recrystallize the yellow crystalline material of **2** by dissolving it in a hot toluene/n-hexane mixture resulted in the formation of colorless solution which was kept at 4 °C for crystallization. Colorless rectangular crystals were obtained and were found by spectroscopic and X-ray crystallographic evidence to be **3**.

2. **The assignment of Al-CH₂ (H_a and H_b) protons in the ¹H NMR spectrum of **3**.** As viewed in the following figure, the different dihedral angles between H(22B)-C(222)-C(221)-H(22A) and H(22C)-C(222)-C(221)-H(22A) give rise to different coupling constants as $^3J_{\text{H}(22\text{B})\text{H}(22\text{A})} = 13.8 \text{ Hz}$ and $^3J_{\text{H}(22\text{C})\text{H}(22\text{A})} = 3.0 \text{ Hz}$ according to the Karplus formula of $^3J_{\text{HH}} = A - B \cdot \cos\phi + C \cdot \cos 2\phi$ ($A = 7, B = -1, C = 5$) ((1) Karplus, *M. J. Am. Chem. Soc.* **1963**, 85, 2870. (2) Lute Fitjer, *NMR-Spektroskopie*). While $^2J_{\text{H}(22\text{B})\text{H}(22\text{C})} = -13.8 \text{ Hz}$, therefore, the resonances at δ -0.28 (dd) and -1.75 (t) are assigned to H(22B) (H_b) and H(22C) (H_a), respectively.



3. **The variable-temperature ¹H NMR kinetic studies of the reaction of LAI with N₃Ar'.** To a mixture of equivalent LAI and N₃Ar' at -78 °C, pre-cooled D₈-toluene was added. At -70 °C, the proton NMR spectrum only presents the features indicated for those of N₃Ar'. This shows the only dissolving of N₃Ar' in D₈-toluene at this

temperature. From -50 to -10 °C, the occurrence of a singlet at δ 5.05-4.60 ppm assigned for that of γ -CH proton in L indicates the starting and proceeding of this reaction, which initiate the dissolving of LAI species. The changes of the chemical shift of this singlet in this area are temperature-dependent. The sample was kept at 50 °C for 1 h and the corresponding proton NMR spectrum showed that there was no remarkable changes of resonances compared to those in the previous one at 50 °C. While for 24 h the measurement on the sample showed the great changes of resonances in the spectrum.