# Reactions of the Aluminum(I) Monomer LAl [L = HC{(CMe)(NAr)}$_2$; Ar = 2,6-$i$Pr$_2$C$_6$H$_3$] with Imidazol-2-ylidene and Diphenyldiazomethane. A Hydrogen Transfer from the L Ligand to the Central Aluminum Atom and Formation of the Diiminylaluminum Compound LAl(N=CPh$_2$)$_2$

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*Dedicated to Professor Axel Zeeck on the occasion of his 65th birthday*

**Keywords:** Aluminum / Carbenes / Diazo compounds / Hydrogen transfer / N ligands

The solid-state reaction of LAl and imidazol-2-ylidene at elevated temperature (120 °C) yielded the aluminum monohydride *N*-heterocyclic carbene adduct [{HC[C(CH$_2$)NAr](CMeNAr)}AlH-{CN(R)C$_2$Me$_2$N(R)}] [R = *i*Pr (**1**), Me (**2**)]. Compounds **1** and **2** have been characterized by spectroscopic (IR, and $^1$H and $^{13}$C NMR), mass spectrometric, and elemental analyses, and **1** was further characterized by X-ray structural analysis. These experimental data indicate that the Al–H bond is formed by hydrogen migration from one of the methyl groups of the β-diketiminato ligand backbone. The reaction of LAl with two equivalents of diphenyldiazomethane afforded the diiminylaluminum compound LAl(N=CPh$_2$)$_2$ (**3**), while an excess of diphenyldiazomethane resulted in the formation of Ph$_2$C=N–N=CPh$_2$. This suggests that Ph$_2$C=N–N=CPh$_2$ is initially generated and then reacts further by oxidative addition to yield **3**. The X-ray structural analysis reveals that compound **3** contains the shortest Al–N$_{\text{iminyl}}$ bond among those with a four-coordinate aluminum center.

## Introduction

Monovalent group-13 species are of considerable interest not only for their syntheses, structures, and theoretical investigations,[1] but also for their reactivity.[2] In the last decade, a variety of new reactions has been intensively explored for generating tetrameric aluminum(I) compounds.[3] The compound (Cp*Al)$_4$ has been reported to have a remarkable tendency to dissociate in solution and give a monomeric fragment in the gas phase.[4] Reactions involving such species have also been investigated to some extent and a number of novel compounds have been isolated and structurally characterized.[5] Recently, we have prepared the first monomeric aluminum(I) complex LAl [L = HC{(CMe)(NAr)}$_2$, Ar = 2,6-$i$Pr$_2$C$_6$H$_3$], which is stable at room temperature.[6] Ab initio calculations show that this monomer possesses a nonbonded electron pair at the central two-coordinate Al atom and is isoelectronic with a singlet carbene. Subsequent reaction of LAl with organic azides at low temperature or with P$_4$ at room temperature indicates its reactivity, leading to the formation of a five-membered AlN$_4$ heterocycle [LAl{(NSiMe$_3$)$_2$N$_2$}], a monomeric aluminum imide [LAl($N$-2,6-trip$_2$C$_6$H$_3$)] (trip = 2,4,6-$i$Pr$_3$C$_6$H$_2$), and a sandwich compound [(LAl)$_2$P$_4$] containing a P$_4$$^{4-}$ unit.[7] These results are markedly different from those in which (Cp*Al)$_4$ is used in related reactions. Obviously, the steric and electronic stabilization of the bulky β-diketiminato ligand enables its monomeric nature and therefore its unique chemical behavior, and allows further investigation of its reactivity.

Imidazol-2-ylidene is a stable neutral *N*-heterocyclic carbene which has been prepared in recent years.[8] Diphenyldiazomethane can be used as an effective precursor for the generation of transient :CPh$_2$.[9] The reaction of imidazol-2-ylidene with monovalent group-13 compounds has only been reported for InBr; a disproportionation reaction is observed.[10] More recently, a handful of reactions involving treatment of imidazol-2-ylidene with trivalent group-13 species have been investigated; the *N*-heterocyclic carbene functions as a Lewis base.[11] The corresponding reactions of diphenyldiazomethane with monovalent group-13 species have not been described so far. We now report on the reaction of LAl with imdazol-2-ylidene and diphenyldiazome-

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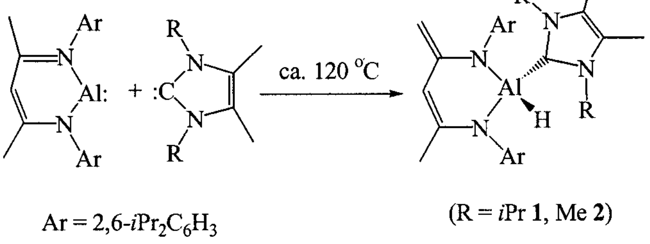
thane. The formation of the aluminum monohydride *N*-heterocyclic carbene adduct of composition [{HC[C(CH$_2$)NAr](CMeNAr)}AlH{CN(R)C$_2$Me$_2$N(R)}] [R = *i*Pr (**1**), Me (**2**)] indicates a hydrogen transfer from the L ligand to the aluminum center. The formation of a diiminylaluminum compound [LAl(N=CPh$_2$)$_2$] (**3**) might proceed through the initial generation of Ph$_2$C=N−N=CPh$_2$ followed by its oxidative addition to LAl.

## Results and Discussion

### Reaction of LAl with Imdazol-2-ylidenes

The initial reaction of LAl with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene was conducted in toluene in the temperature range from 25 to 80 °C. However, due to the low solubility of the *N*-heterocyclic carbene, this reaction was not successful. Therefore both starting materials were mixed in the solid state at 120 °C for 5 h. A softening of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene and a subsequent color change of LAl from red black to light yellow were observed. Extraction of the product with hot toluene and keeping the eluate at room temperature afforded crystalline [{HC[C(CH$_2$)NAr](CMeNAr)}AlH{CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)}] (**1**, Scheme 1).



Scheme 1

Compound **1** is colorless and soluble in hot toluene and benzene while sparingly soluble in *n*-hexane and pentane. It was characterized by spectroscopic and elemental analyses. The mass spectrum exhibits the molecular ion of **1** {*m*/*z* (%) = 624 (5) [M$^+$], 609 (40) [M$^+$ − Me], 581 (100) [M$^+$ − *i*Pr]}. The $^1$H and $^{13}$C NMR spectra recorded in C$_6$D$_6$ are consistent with a pseudo-tetrahedral geometry and $C_s$ symmetry about aluminum, giving rise to six isopropyl C*H* resonances and twelve diastereotopically split isopropyl C*H*$_3$ resonances due to the chiral environment of the Al center. The proton resonance of the β-CH$_3$ group on the L ligand backbone ($\delta$ = 1.72 ppm) integrates for three protons, while two other singlets are observed downfield ($\delta$ = 3.98 and 3.30 ppm) and integrate for one proton each. The former corresponds to the normal terminal C*H*$_3$−C group, and the latter is assigned to the terminal C*H*$_2$=C group which gives rise to two nonequivalent protons due to the restricted rotation about the C=C double bond. One broad proton resonance centered at $\delta$ = 4.80 ppm is characteristic for aluminum hydrides.[12] The IR spectrum exhibits a single band at 1809 cm$^{-1}$ for Al−H absorption.[13]

Complex **1** was also characterized by X-ray structural analysis. The molecular structure of **1** is shown in Figure 1. Due to the poor quality of the crystal data the bond lengths and angles for **1** will not be discussed in detail. The quality of the crystals gave no improvement in the refinement of the structure even after recrystallization from several different solvents. Nonetheless, the structural solution of **1** offers important structural information which is in agreement with its spectral analysis. Compound **1** is monomeric and the central Al atom adopts a distorted tetrahedral geometry. The Al−N bond lengths [1.844(3) and 1.853(2) Å] appear to be shorter than other Al−N$_{\beta\text{-diketiminato}}$ bonds [1.875(4)−1.957(2) Å],[5,14] and are closer to those found in diamidoaluminum monohydride [{ArN(CH$_2$)$_3$NAr}AlH(NMe$_3$)] [1.820(1) and 1.828(1) Å].[13c] In the ligand backbone, the terminal C−C bond lengths [C(4)−C(5): 1.507(4) Å; C(1)−C(2): 1.363(4) Å] are indicative of a single and double bond, respectively, as are the others within the backbone [C(2)−C(3): 1.458(4) Å; C(3)−C(4): 1.351(4) Å]. The adjacent N−C bond lengths [1.411(3) and 1.413(3) Å] are intermediate between N−C double and single bonds.

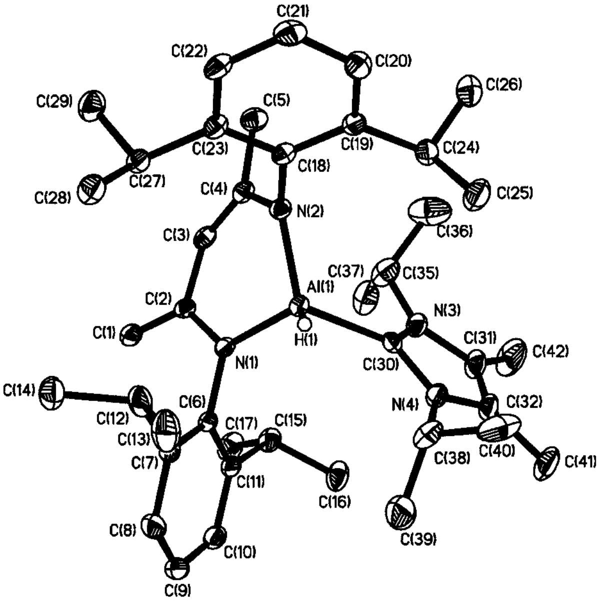


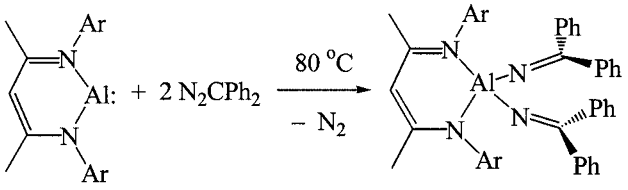
Figure 1. Molecular structure of **1**; H atoms are omitted for clarity except for the Al−H hydrogen atom

Obviously, the Al−H hydrogen comes from one of the terminal methyl groups of the L ligand, although whether this hydrogen transfer occurs via a proton, a hydrogen radical, or a hydride is not clear.

The reaction of LAl with less bulky *N*-substituted 1,3,4,5-tetramethylimidazol-2-ylidene was also performed in a similar manner (method A) to the preparation of **1** in order to investigate the effect of the steric bulk on the reaction product. As a result, [{HC[C(CH$_2$)NAr](CMeNAr)}AlH{CN(Me)C$_2$Me$_2$N(Me)}] (**2**) was obtained in a relatively low yield. All the spectroscopic data (IR, EI mass, and $^1$H and $^{13}$C NMR) confirm a structure analogous to that of **1**.

### Reaction of LAl with $N_2CPh_2$

In the majority of organic and organometallic reactions diphenyldiazomethane is used as a precursor for the generation of transient :$CPh_2$ carbene.[9] Therefore, it was selected as another electron-rich species for the reaction with LAl. However, treatment of LAl with two equivalents of $N_2CPh_2$ under heating unexpectedly afforded [LAl($N{=}CPh_2$)$_2$] (**3**; Scheme 2), the first example of a diiminylaluminum compound. When LAl was treated with an excess of $N_2CPh_2$ under the same conditions $Ph_2C{=}N{-}N{=}CPh_2$ was isolated.[15] Therefore, we assumed that the formation of **3** proceeds by the initial generation of $Ph_2C{=}N{-}N{=}CPh_2$ followed by its oxidative addition to LAl. In order to test this assumption a toluene solution of LAl was heated under reflux with one equivalent of $Ph_2C{=}N{-}N{=}CPh_2$ and complex **3** was formed, as expected, in an almost quantitative yield.[16]



Ar = 2,6-$i$Pr$_2$C$_6$H$_3$ **3**

Scheme 2

Complex **3** is an orange-yellow crystalline solid that is thermally stable, as indicated by its high melting point (344−346 °C). The most intense ion in the EI mass spectrum appears at $m/z$ = 624 [$M^+ - NCPh_2$]; the peak at $m/z$ = 805 (20%) is assigned to the molecular ion [$M^+$].

X-ray quality single crystals of **3** had formed from a 1:1 solvent mixture ($n$-hexane, diethyl ether) at 4 °C after two days. The structural analysis unambiguously ascertains the composition of **3**. The molecular structure is shown in Figure 2 and selected bond lengths and angles are listed in Table 1. The central Al atom is bound to two β-diketiminato nitrogen atoms and two iminyl nitrogen atoms. The $AlN_4$ core exhibits a distorted tetrahedral geometry with *trans*-N−Al−N angles ranging from 97.23(18)° to 117.6(2)°. The Al−N$_{\beta\text{-diketiminato}}$ bond lengths [1.899(4) and 1.901(4) Å] are in the expected range [1.875(4)−1.957(2) Å].[5,14] However, the Al−N$_{\text{iminyl}}$ distances [1.774(4) and 1.785(4) Å] are the shortest yet found in four-coordinate Al−N complexes.[17] Comparable Al−N bond lengths have only been observed in three-coordinate [trip$_2$Al{N(H)dipp}] [1.784(3) Å],[18a] [MeAl(Ndipp)]$_3$ [1.782(4) Å][18b] and Al[N(SiMe$_3$)$_2$]$_3$ [1.78(2) Å].[18c] Surprisingly, the N−C distances of the iminyl group [1.249(6) and 1.269(6) Å] are shorter than that of a C=N bond.[19] The short Al−N$_{\text{iminyl}}$ bond can be considered to be highly ionic, and the shortening of the N=C bond may be due to a charge delocalization over the phenyl groups. The Al(1)−N(4)−C(50) [163.4(5)°] and Al(1)−N(3)−C(30)

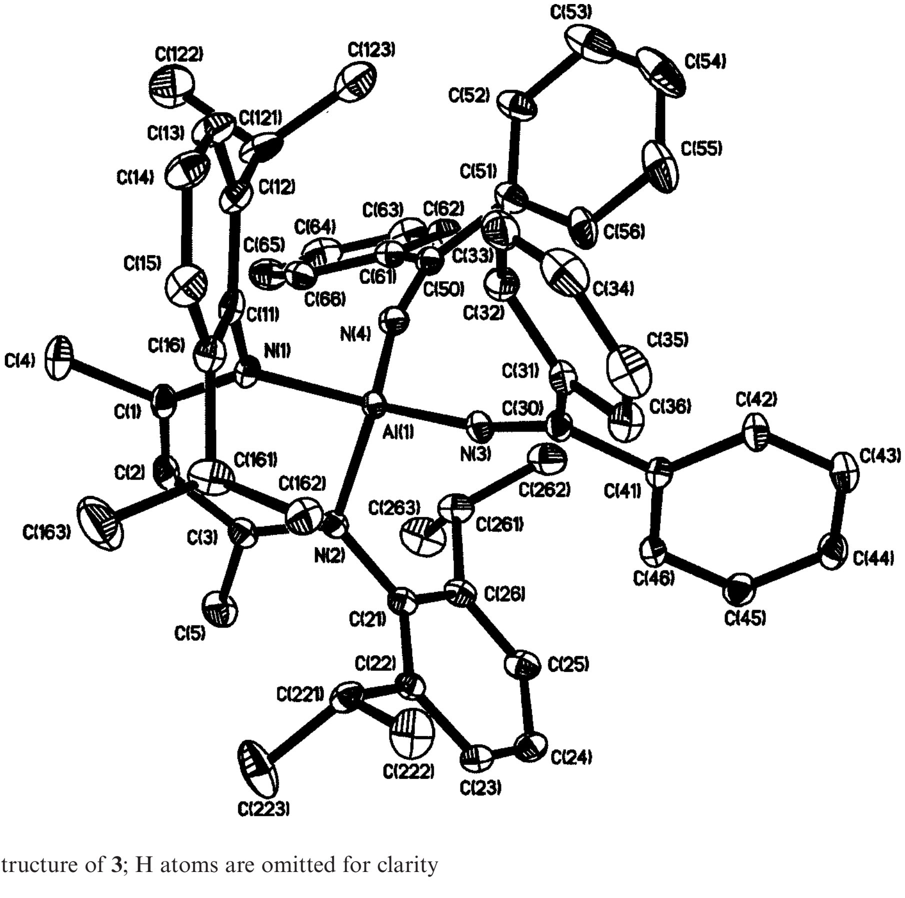


Figure 2. Molecular structure of **3**; H atoms are omitted for clarity

[169.4(4)°] angles show a less-bent arrangement of the Al−N=C group. The observation of two sets of resonances for the iminyl phenyl rings in the $^{1}$H and $^{13}$C NMR spectra suggests a restricted rotation of the phenyl rings around the N=C bond. This was confirmed by a high-temperature proton NMR spectral analysis (40, 60, and 80 °C), where two corresponding sets of resonances are always observed.

Table 1. Selected bond lengths (Å) and angles (deg) for compound **3**

| | | | |
|---|---|---|---|
| Al(1)−N(1) | 1.901(4) | Al(1)−N(2) | 1.899(4) |
| Al(1)−N(3) | 1.774(4) | Al(1)−N(4) | 1.785(4) |
| N(3)−C(30) | 1.249(6) | N(4)−C(50) | 1.269(6) |
| N(1)−Al(1)−N(2) | 97.23(18) | N(3)−Al(1)−N(4) | 116.1(2) |
| N(1)−Al(1)−N(3) | 117.6(2) | N(1)−Al(1)−N(4) | 107.4(2) |
| N(2)−Al(1)−N(3) | 109.5(2) | N(2)−Al(1)−N(4) | 106.9(2) |
| C(30)−N(3)−Al(1) | 169.4(4) | C(50)−N(4)−Al(1) | 163.4(5) |

## Conclusions

In summary, we have reacted the aluminum(I) monomer LAl with imidazol-2-ylidene and diphenyldiazomethane and obtained the new compounds [{HC[C($CH_2$)NAr](CMeNAr)}AlH{CN(R)$C_2Me_2$N(R)}] [R = *i*Pr (**1**), Me (**2**)] and [LAl(N=$CPh_2$)$_2$] (**3**). This further shows the unique reaction behavior of LAl, and exhibits its properties as a carbene analog. Inspired by these results, we are now exploring the reaction of LAl with metal carbonyl complexes to compare the electronic equivalence of LAl with CO.

## Experimental Section

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques. The solvents were dried by standard methods. Chemicals were purchased from Aldrich or Fluka and used as received. LAl,[6] [CN(R)$C_2Me_2$N(R)] (R = Me, *i*Pr),[8] and $N_2CPh_2$ [9a] were prepared as described in the literature.

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. $^{1}$H (300.13 MHz), $^{13}$C (125.76 MHz) and $^{27}$Al NMR (65.17 MHz) spectra were recorded on a Bruker AM 200 or a Bruker AM 250 spectrometer and IR spectra on a Bio-Rad Digilab FTS-7 spectrometer. EI mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes and are not corrected.

**Synthesis of [{HC[C($CH_2$)NAr](CMeNAr)}AlH{CN(*i*Pr)$C_2Me_2$N(*i*Pr)}] (1). Method A:** A suspension of $LAlI_2$ (2.08 g, 3.0 mmol) and finely divided potassium (0.25 g, 6.3 mmol) in toluene (50 mL) was stirred vigorously for 3 d at room temperature until all the potassium had disappeared. After filtration the dark-red filtrate was slowly dried in vacuo and some red microcrystals of LAl were observed to deposit on the walls of the flask. [CN(*i*Pr)$C_2Me_2$N(*i*Pr)] (0.36 g, 2 mmol) was added to the resulting solid. The mixture was heated slowly to about 120 °C and kept for 5 h. After cooling to room temperature, the yellow product was extracted with hot toluene (30 mL) and the extract was kept at room temperature for 24 h to afford X-ray quality colorless block crystals, which were collected by filtration (0.42 g). The mother liquor was concentrated (ca. 5 mL) and kept at 4 °C for 24 h to give another crop of colorless crystals (0.25 g). Total yield of **1**: 0.67 g {47%, based on [CN(*i*Pr)$C_2Me_2$N(*i*Pr)]}. M.p. 298−300 °C (>250 °C decomp.). $^{1}$H NMR ($C_6D_6$, 300 K): $\delta$ = 0.38, 0.50, 0.76, 0.82, 1.19, 1.32, 1.46, 1.50, 1.53, 1.55, 1.57, 1.59 [d, 12 × 3 H, CH*Me*$_2$ and N(CH*Me*$_2$)], 1.38, 1.62 (s, 2 × 3 H, $C_2$*Me*$_2$), 1.72 (s, 3 H, β-C*H*$_3$), 3.30, 3.98 (s, 2 × 1 H, β-C*H*$_2$), 3.28, 3.62, 4.18, 4.26 (sept, 4 × 1 H, C*H*Me$_2$), 4.80 (br., 1 H, Al-*H*), 5.60 (s, 1 H, γ-C*H*), 5.44, 5.62 [sept, 2 × 1 H, N(C*H*Me$_2$)], 7.10−7.38 (m, 6 H, *Ar*) ppm. $^{13}$C NMR ($C_6D_6$, 300 K): $\delta$ = 9.9, 10.0 ($C_2$*Me*$_2$), 20.7, 21.1, 21.4, 22.0, 23.3, 23.7, 23.8, 24.4, 24.5, 24.7, 25.6, 25.7, 26.4, 27.1, 27.7, 28.4, 28.9 [N(CH*Me*$_2$), *C*HMe$_2$, CH*Me*$_2$ and β-*C*H$_3$], 50.9, 53.0 [N(*C*HMe$_2$)], 80.8 (β-*C*H$_2$), 106.6 (γ-*C*), 123.0, 124.5, 124.7, 124.9, 125.6, 126.6, 127.8, 128.5, 129.3, 143.4, 144.7, 145.6, 146.1, 147.2, 148.4, 149.0 (*Ar*, *C*N and *C*$_2$Me$_2$), 154.5 (Al-*C*) ppm. $^{27}$Al NMR ([D$_8$]toluene, 300 K): no resonances were observed. IR (Nujol): $\nu_{Al-H}$ = 1809 cm$^{-1}$ (m), $\nu_{C=C}$ = 1619 (m). MS (EI): *m*/*z* (%) = 624 (5) [M$^+$], 609 (40) [M$^+$ − Me], 581 (100) [M$^+$ − *i*Pr]. $C_{40}H_{61}AlN_4$ (624.94): calcd. C 76.87, H 9.84, N 8.97; found C 77.07, H 9.55, N 8.86.

**Method B:** A suspension of $LAlI_2$ (2.08 g, 3.0 mmol), [CN(*i*Pr)$C_2Me_2$N(*i*Pr)] (0.54 g, 3 mmol) and finely divided potassium (0.25 g, 6.3 mmol) in toluene (50 mL) was stirred vigorously for 3 d at room temperature until all the potassium had disappeared. After filtration the orange filtrate was concentrated (ca. 20 mL) and *n*-hexane (20 mL) was added. The solution was kept at 4 °C for one week to afford colorless block crystals (0.72 g). The mother liquor was further concentrated (ca. 5 mL) and kept at 4 °C for 2 d to give another crop of colorless crystals (0.32 g). Total yield of **1**·toluene: 1.04 g (48%). The IR, $^{1}$H and $^{13}$C NMR spectroscopic data are essentially the same as those of **1** except for one extra molecule of toluene.

**Synthesis of [{HC[C($CH_2$)NAr](CMeNAr)}AlH{CN(Me)$C_2Me_2$N(Me)}] (2):** Compound **2** was prepared in a similar manner (method A) as **1**. $LAlI_2$ (2.08 g, 3.0 mmol), finely divided potassium (0.25 g, 6.3 mmol) and [CN(Me)$C_2Me_2$N(Me)] (0.24 g, 2.0 mmol) were used. The extract (10 mL) was added to *n*-hexane (10 mL) and kept at −26 °C for 48 h to afford colorless crystals of **2** {yield: 0.42 g, 25%, based on [CN(Me)$C_2Me_2$N(Me)]}. M.p. 252−253 °C. $^{1}$H NMR ([D$_8$]toluene, 300 K): $\delta$ = 1.45, 1.47 (s, 2 × 3 H, $C_2$*Me*$_2$), 0.29, 0.30, 1.16, 1.46, 1.58, 1.60, 1.61, 1.62 (d, 8 × 3 H, CH*Me*$_2$), 1.69 (s, 3 H, β-C*H*$_3$), 3.70, 3.75 (s, 2 × 3 H, N(*Me*)), 3.10, 3.85 (s, 2 × 1 H, β-C*H*$_2$), 3.21, 3.25, 4.15, 4.21 (sept, 4 × 1 H, C*H*Me$_2$), 4.80 (br., 1 H, Al-*H*), 5.39 (s, 1 H, γ-C*H*), 7.04−7.38 (m, 6 H, *Ar*) ppm. $^{13}$C NMR ([D$_8$]toluene, 300 K): $\delta$ = 7.9, 8.0 ($C_2$*Me*$_2$), 23.6, 24.0, 24.2, 24.3, 24.8, 24.9, 25.4, 25.8, 26.0, 26.4, 26.5, 27.1, 27.8, 28.7, 29.0 [N(*Me*), *C*HMe$_2$, CH*Me*$_2$ and β-*C*H$_3$), 80.1 (β-*C*H$_2$), 102.3 (γ-*C*), 122.9, 123.7, 124.2, 124.6, 124.9, 125.1, 125.3, 127.7, 128.0, 143.2, 143.8, 145.4, 146.3, 147.4, 148.2, 149.0 (*Ar*, *C*N and *C*$_2$Me$_2$), 155.2 (Al-*C*) ppm. MS (EI): *m*/*z* (%) = 568 (15) [M$^+$], 553 (100) [M$^+$ − Me]. IR (Nujol): $\nu_{Al-H}$ = 1810 cm$^{-1}$ (m), $\nu_{C=C}$ = 1616 (m). $C_{36}H_{53}AlN_4$ (568.83): calcd. C 76.01, H 9.29, N 9.85; found C 76.50, H 9.60, N 9.40.

**Synthesis of LAl(NCPh$_2$)$_2$ (3):** A solution of $N_2CPh_2$ (0.37 g, 1.90 mmol) in toluene (15 mL) was added to a solution of LAl (0.42 g, 0.94 mmol) in toluene (25 mL) at room temperature. The mixture was slowly heated to 60 °C and kept for 12 h; a yellow solution developed. All volatiles were then removed in vacuo and the residue was washed with *n*-hexane (5 mL) to afford an orange-yellow crystalline solid of **3** (0.36 g, 48%). M.p. 344−346 °C. $^{1}$H NMR ($C_6D_6$, 300 K): $\delta$ = 0.82, 1.02 (d, 8 × 3 H, CH*Me*$_2$), 1.64 (s, 2 × 3 H, β-C*H*$_3$), 3.21 (sept, 4 × 1 H, C*H*Me$_2$), 5.28 (s, 1 H, γ-C*H*), 6.92−7.00 (m, 2 × 5 H, *Ph*), 7.00−7.08 (m, 2 × 5 H, *Ph*), 7.18−7.32 (m, 6 H, *Ar*) ppm. $^{13}$C NMR ($C_6D_6$, 300 K): $\delta$ = 23.8, 24.4, 24.9, 28.5 (*C*HMe$_2$, CH*Me*$_2$, β-*C*H$_3$), 98.8 (γ-*C*), 124.5, 126.9, 127.6, 127.6, 127.9, 128.1, 128.3, 128.3, 129.4, 142.4, 143.1, 144.7 (*Ar*, *Ph*), 166.9 (N*C*Ph$_2$), 171.0 (*C*N) ppm. MS (EI): *m/z* (%) = 805 (20) [M$^+$], 790 (30) [M$^+$ − Me], 624 (100) [M$^+$ − NCPh$_2$]. IR (Nujol): $\nu_{C=C}$ = 1667 cm$^{-1}$ (w), $\nu_{C=N}$ = 1624, 1554 (w). $C_{55}H_{61}AlN_4$ (805.10): calcd. C 82.05, H 7.64, N 6.96; found C 82.11, H 7.74, N 7.05. X-ray quality crystals were obtained by recrystallization from a 1:1 *n*-hexane/diethyl ether solution at 4 °C for one week.

**X-ray Structure Determination and Refinement:** The crystallographic data for compound **1** were collected on a Stoe IPDS II-array detector system and for **3** on a Stoe−Siemens−Huber four-circle-diffractometer coupled to a Siemens CCD area-detector. In both cases graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) was used. Both structures were solved by direct methods (SHELXS-96) and refined against $F^2$ using SHELXL-97.[20,21] All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with $U_{iso}$ tied to the $U_{iso}$ of the parent atoms, except for the Al−H hydrogen atom, which was located by difference Fourier synthesis and refined isotropically. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 2.
CCDC-231677 (for **1**) and -231678 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data for compounds **1** and **3**

| | **1** | **3** |
|---|---|---|
| Empirical formula | $C_{40}H_{61}AlN_4$ | $C_{55}H_{61}AlN_4$ |
| Formula mass | 624.91 | 805.06 |
| Temp. (K) | 133(2) | 203(2) |
| Crystal system | monoclinic | orthorhombic |
| Space group | $P2_1/c$ | $P2(1)2(1)2(1)$ |
| $a$ (Å) | 10.161(2) | 12.285(2) |
| $b$ (Å) | 17.380(4) | 12.981(2) |
| $c$ (Å) | 22.274(5) | 30.001(6) |
| $\alpha$ (°) | | |
| $\beta$ (°) | 101.89(3) | |
| $\gamma$ (°) | | |
| $V$ (Å$^3$) | 3849.1(13) | 4784.4(16) |
| Z | 4 | 4 |
| $\rho_c$ (Mg/m$^3$) | 1.078 | 1.118 |
| $\mu$ (mm$^{-1}$) | 0.084 | 0.082 |
| $F$(000) | 1386 | 1728 |
| θ range (°) | 1.87−24.71 | 3.55−25.01 |
| Index ranges | $-11 \le h \le 11$ | $0 \le h \le 14$ |
| | $-20 \le k \le 20$ | $-1 \le k \le 15$ |
| | $-26 \le l \le 24$ | $-35 \le l \le 35$ |
| No. of reflections collected | 33356 | 4675 |
| No. of independent reflns. ($R_{int}$) | 6560 (0.1511) | 4658 (0.0188) |
| No. of data/restraints/parameters | 6560/0/424 | 4658/0/555 |
| $GoF/F^2$ | 0.911 | 1.096 |
| $R1$,[a] $wR2$[b] $[I > 2\sigma(I)]$ | 0.0541, 0.0974 | 0.0614, 0.1530 |
| $R1$,[a] $wR2$[b] (all data) | 0.1198, 0.1096 | 0.0848, 0.1740 |
| largest difference peak/hole (e·Å$^{-3}$) | 0.313/−0.271 | 0.271/−0.282 |

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$.

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