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Synthesis of $HC[(CBu^t)(NAr)]_2Al$ ($Ar = 2,6\text{-}Pr^i{}_2C_6H_3$) and Its Reaction with Isocyanides, a Bulky Azide, and H_2O

Xiaofei Li, Xiaoyan Cheng, Haibin Song, and Chunming Cui*

State Key Laboratory of Elemento-Organic Chemistry, Nankai University,
Tianjin 300071, People's Republic of China

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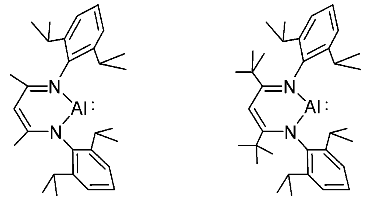
The reaction of $H_2C[(CBu^t)_2(NAr)_2]$ ($Ar = 2,6\text{-}Pr^i{}_2C_6H_3$) with $AlEt_3$ in refluxing toluene gave $HC[(CBu^t)_2(NAr)_2]AlEt_2$ (**1**) in high yield. Treatment of **1** with 2 equiv of iodine in toluene yielded $HC[(CBu^t)_2(NAr)_2]AlI_2$ (**2**). Reduction of **2** with potassium resulted in the formation of the *tert*-butyl-substituted β-diketiminato aluminum(I) compound $HC[(CBu^t)_2(NAr)_2]Al$ (**3**). Reactions of **3** with isocyanides, H_2O, and a bulky terphenyl azide were investigated. **3** reacted with 2 equiv of CNAr to give two C−C coupling products: in dilute solution, the C−C coupling of two CNAr molecules was followed by the C−H activation of one of the $CHMe_2$ groups on the Ar ring of CNAr, while in concentrated solution or in the presence of an excess of the isocyanide, the coupling was accompanied by cleavage of one of the C−N bonds of the ligand backbone. Reaction of **3** with the bulky azide $2,6\text{-}Ar_2C_6H_3N_3$ yielded the C−H activation product **6**. Hydrolysis of **3** in toluene afforded a hydroxyaluminum hydride. Compounds **1** and **3**−**5** were characterized by X-ray single-crystal analysis.

Introduction

The syntheses of the isolable β-diketiminato group 13 element carbene analogues $HC[(CMe)(NAr)]_2M$ (M = Al, Ga, In, Tl; $Ar = 2,6\text{-}Pr^i{}_2C_6H_3$) represent interesting achievements in group 13 chemistry.[1] Experimental and theoretical work indicated that they could act as strong σ-donors, as Lewis acids, and as reducing agents.[2] In addition, easily tunable β-diketiminato ligands may allow access to other members of this series with modified structures and reactivities. A number of reactions of $HC[(CMe)(NAr)]_2Al$ (**3′**; Chart 1) with organic functional groups and Lewis acids have been examined.[2b,3] We are interested in extending this chemistry using the more sterically demanding β-diketiminato ligand $\{HC[(CBu^t)(NAr)]_2\}^-$, in which bulkier *tert*-butyl groups are present on the ligand backbone instead of methyl groups.[4] It has been demonstrated that steric manipulations of the β-diketiminato ligand backbone can have a profound effect on the coordination number and reactivity of the metal complexes.[5] Herein we report the synthesis of the monomeric aluminum(I) species $HC[(CBu^t)(NAr)]_2Al$ (**3**; Chart 1) and its reactions with isocyanides, $2,6\text{-}Ar_2C_6H_3N_3$, and H_2O.

Chart 1



3′ **3**

Coupling reactions of isocyanides can create new C−C and C−N bonds and, hence, have attracted widespread interest.[6] These reactions usually proceed either by reductive coupling of isocyanide complexes of transition metals mediated by a reducing reagent[7] or by consecutive insertion into M−C bonds.[8] However, reductive coupling of isocyanides promoted by heavier main-group-element complexes has been less investigated.[9] It has been shown that bulky isocyanides interact with low-valent heavier main-group-element species to yield donor−acceptor complexes or ketenimine analogues.[10] Insertion of isocyanides

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* To whom correspondence should be addressed. E-mail: cmcui@nankai.edu.cn.

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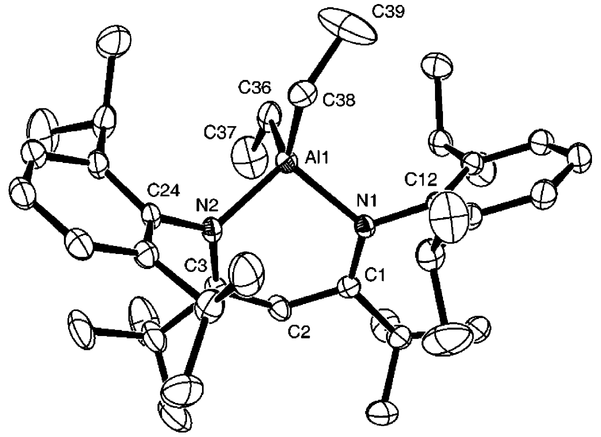


Figure 1. Thermal-ellipsoid plot (30% probability) of **1**. Only one of the two independent molecules in the unit cell is shown. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−C36 = 1.980(4), Al1−C38 = 1.974(4), Al1−N1 = 1.945, Al1−N2 = 1.936(3); N1−Al1−N2 = 99.03(13), N1−Al1−C36 = 108.43(16), N1−Al1−C38 = 111.47(17), N2−Al1−C36 = 110.60(17), N2−Al1−C38 = 110.77(16), C36−Al1−C38 = 115.3(2).

into Al−C bonds has also been reported.[11] Compound **3** reacts with CNAr, leading to the C−C coupling of the isocyanide molecules accompanied by the respective C−N and C−H bond cleavages. These kinds of isocyanide-coupling reactions mediated by a mononuclear main-group-metal complex that do not contain metal−alkyl groups and carried out without additional reagents are unprecedented.

Results and Discussion

Synthesis of HC[(CBu^t)(NAr)]$_2$Al. Reaction of the free diimine $H_2C[(CBu^t)NAr]]_2$ with $AlEt_3$ in refluxing toluene for 8 h and subsequent crystallization from *n*-hexane afforded HC[(CBu^t)(NAr)]$_2$AlEt$_2$ (**1**) as pale yellow crystals in high yield. The diiodide precursor HC[(CBu^t)(NAr)]$_2$AlI$_2$ (**2**) was prepared in excellent yield by the reaction of **1** with 2 equiv of iodine. Reduction of **2** with 2 equiv of potassium in toluene at room temperature followed by crystallization from toluene gave red crystals of the *tert*-butyl-substituted (*β*-diketiminato)aluminum(I) species HC[(CBu^t)(NAr)]$_2$Al (**3**). Compound **3** has a limited solubility in toluene and is very thermally stable in solution. No decomposition was observed after it had been heated at reflux in toluene for 2 h.

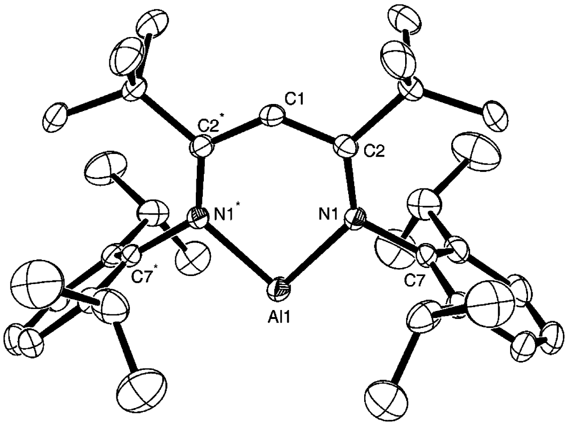
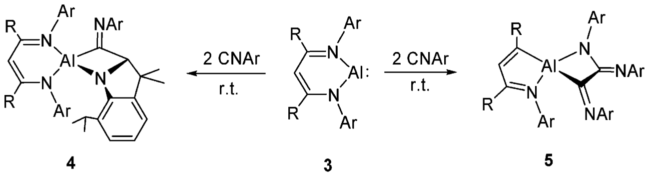


Figure 2. Thermal-ellipsoid plot (30% probability) of **3**. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.9637(15), Al1−N1* = 1.9637(15), N1−C2 = 1.341(2), C1−C2 = 1.393(2), N1−C7 = 1.445(2); N1−Al1−N1* = 91.85(9), C2−N1−C7 = 125.61(14), C2−N1−Al1 = 128.14(12), C7−N1−Al1 = 106.18(10), C2−C1−C* = 131.9(2).

Scheme 1. Reaction of 3 with CNAr



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, R = Bu^t

Compounds **1**−**3** have been characterized by their ^{1}H and ^{13}C NMR and IR spectra and elemental analysis. The NMR spectra of these complexes show the expected patterns. The UV−vis spectrum of **3** in *n*-hexane shows a maximum at 364 nm (ϵ = 13 000 M^{-1} cm^{-1}). The structures of **1** and **3** were determined by X-ray single-crystal analysis (Figures 1 and 2). The structure of **3** (Figure 2) contains a planar AlN$_2$C$_3$ six-membered ring similar to that of HC[(CMe)(NAr)]$_2$Al.[1a] The N−Al−N angle (91.85(9)°) is larger by 2° compared to that found in the methyl-substituted derivative,[1a] probably caused by the increasing repulsion of the two flanking Ar groups in the *tert*-butyl-substituted species.

Reaction of 3 with Isocyanides. Reactions of **3** with isocyanides were performed with the expectation that a donor−acceptor or an allenic species would result, analogous to the reactions of the isolable silylenes with bulky isocyanides.[10] Reaction of **3** with CNBu^t resulted in the formation of a complicated mixture under various conditions. Many attempts to isolate pure products were unsuccessful. Therefore, we used the sterically more demanding aryl isocyanide CNAr for the reaction. Reaction of CNAr with 1 equiv of **3** was conducted in toluene from −78 °C to room temperature. The proton NMR study of the crude product indicates the formation of multiple products, which could not be identified. Nevertheless, yellow crystals of **4** were obtained in 30% yield by crystallization from *n*-hexane (Scheme 1). Attempts to isolate the other products were unsuccessful. Since **3** is poorly soluble in toluene, the reaction was carried out at room temperature. Upon addition of 2 equiv of CNAr in toluene to a dilute toluene solution of **3**, an immediate color change to dark pink was observed and, surprisingly, compound **5** was isolated in high yield. However, when 2 equiv of neat CNAr (or an excess) was added to a suspension of **3** in a small amount of toluene, compound **4** was obtained selectively in good yield. Compounds **4** and **5** are thermally stable, and rearrangements of one to the other were not observed under various conditions, suggesting that they are very likely generated by different mechanisms.

The X-ray structure of **4** (Figure 3) shows of the presence of an AlC$_2$N four-membered ring and a C$_4$N heterocycle, most likely formed via C−C coupling of the two CNAr molecules and C−H addition of one of the *CH*Me$_2$ groups to the *β*-C of the AlC$_2$N ring. The AlC$_2$N cycle is almost planar (Δ = 0.0363

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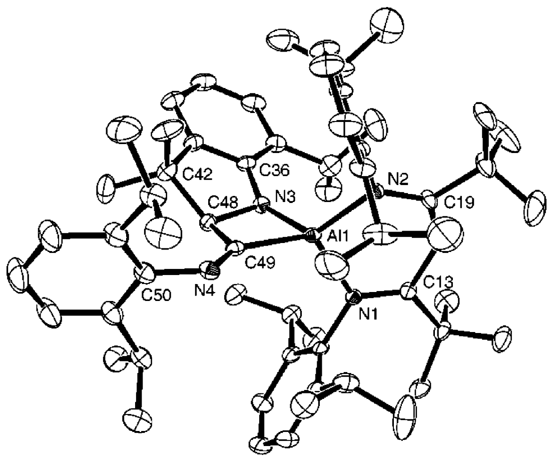
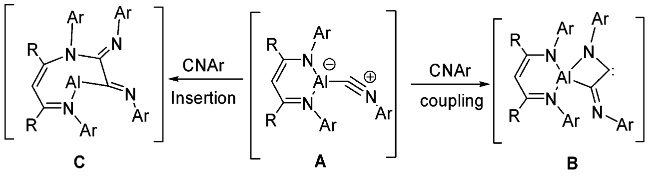


Figure 3. Thermal-ellipsoid plot (30% probability) of **4**. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.909(3), Al1−N2 = 1.899(4), Al1−N3 = 1.818(4), Al1−C49 = 2.003(5), N3−C48 = 1.511(6), N4−C49 = 1.278(5), C48−C49 = 1.556(6): N1−Al1−N2 = 122.27(16), N3−Al−C49 = 75.19(18), N3−C48−C49 = 99.2(3).

Scheme 2. Proposed Mechanisms for CNAr Coupling



Å), while the C_4N ring adopts a puckered conformation with the C24 atom bent out of the C_3N quasi-plane ($\Delta = 0.0595$ Å). The N3−C48 and C48−C49 bond lengths are 1.511(6) and 1.556(16) Å and are typical of C−N and C−C single bonds, respectively. The ^1H NMR spectrum of **4** shows a singlet at δ 3.61 ppm, attributed to the resonance due to the β-C*H* in the AlC_2N ring, and the ^{13}C resonance appears at δ 85.9 ppm. We reason that the reaction may proceed by way of reductive coupling of two CNAr molecules to form a four-membered AlC_2N carbene intermediate (Scheme 2; **B**), which subsequently undergoes intramolecular C−H addition[13] to yield **4**. However, we were unable to isolate the intermediate or to trap it with alkynes and alkenes.

Deep pink crystals of **5** suitable for an X-ray diffraction study were obtained from diethyl ether at −20 °C. The molecular structure of **5** is shown in Figure 4. The molecular array shows that one of the C−N bonds in the ligand backbone has been cleaved and a new C−N bond has been formed. This kind of cleavage has been reported for divalent (β-diketiminato)-zirconium intermediates and postulated to be a reductive process.[14] The Al1−C3 (1.969(2) Å) and Al1−C25 (2.020(2) Å) bond lengths are in the reported range for Al−C single bonds. The Al−N3 bond distance (1.8559(17) Å) is consistent with a Al−N single bond, while the Al1−N1 bond distance (1.9795-(18) Å) is slightly longer than those found in trivalent (β-diketiminato)aluminum compounds.[15] The C24−C25 bond length (1.528(3) Å) is indicative of a C−C single bond. The NMR spectra of **5** are in agreement with the structure. The proton resonance of the γ-C*H* for the β-diketiminato ligand does not appear in the ^1H NMR spectrum. The ^{13}C NMR spectrum shows two broad singlets at δ 204.66 and 197.26 ppm, attributed to the resonances of the two carbon atoms attached to the aluminum atom, respectively.

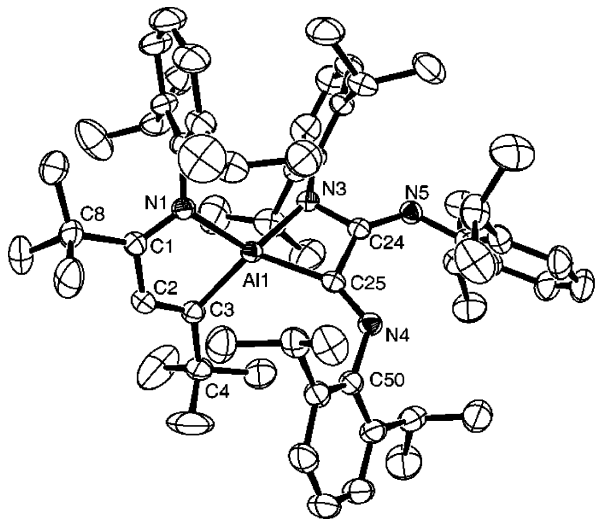


Figure 4. Thermal-ellipsoid plot (30% probability) of **5**. Selected bond lengths and angles (deg): Al1−N1 = 1.9795(18), Al1−N3 = 1.8559(17), Al1−C3 = 1.969(2), Al1−C25 = 2.020(2), N1−C1 = 1.313(3), C1−C2 = 1.471(3), C2−C3 = 1.342(3), N3−C24 = 1.412(2), C24−C25 = 1.528(3); N1−Al1−C3 = 86.71(8), N1−Al1−N3 = 112.69(7), N3−Al1−C25 = 72.38(7), N3−C24−C25 = 102.37(16).

Because the reactions proceed instantaneously, the mechanisms are subject to speculation. The reactions might involve initial coordination of the isocyanide to **3** to form a donor−acceptor or zwitterionic species (**A**), which could either undergo migration−insertion of CNAr into one of the Al−N bonds or couple with another molecule of CNAr. In the dilute solution, the former pathway might dominate and subsequent double insertion and reductive cleavage of the C−N bond[14] by the aluminum atom would lead to the formation of **5**. However, high concentration or an excess of CNAr in the system may favor isocyanide coupling prior to the insertion followed by the C−H addition to yield **4** (Scheme 2).

Reaction of 3 with $2,6\text{-}Ar_2C_6H_3N_3$. It has been shown that reaction of the methyl-substituted (β-diketiminato)aluminum-(I) species $HC[(CMe)(NAr)]_2Al$ with a bulky terphenyl azide gives two types of intramolecular addition products, and an aluminum imide species was assumed as an intermediate.[2b] We reason that the *tert*-butyl-substituted β-diketiminato ligand would provide more efficient protection and thus stabilize the monomeric imide species. Therefore, the reaction of **3** with $2,6\text{-}Ar_2C_6H_3N_3$ was performed analogously as reported. The isolable yellow crystalline product was identified as **6** on the basis of the ^1H and ^{13}C NMR and IR spectra and elemental analysis (Scheme 3). The ^1H NMR spectrum showed a broad singlet at δ 3.37 ppm, and the IR spectrum displayed an absorption centered at 3238 cm^{-1}, suggesting the presence of an N−H group. The spectroscopic data of **6** are similar to those of one of the two products generated by the reaction of HC[(CMe)-(NAr)]$_2$Al with $2,6\text{-}Ar_2C_6H_3N_3$. The formation of **6** may also result from an monomeric imide species, as proposed.[2b]

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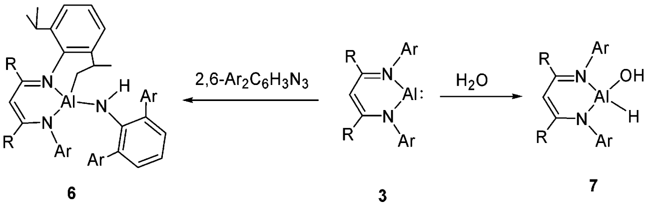
Scheme 3. Reaction of 3 with 2,6-Ar$_2$C$_6$H$_3$N$_3$ and H$_2$O



Hydrolysis of 3. Since aluminum hydroxides are important precursors for the preparation of oxo-bridged bimetallic systems,[16] we were interested in the reaction of **3** with H$_2$O, expecting to generate a hydroxyaluminum hydride. Indeed, reaction of **3** with 1 equiv of H$_2$O in toluene afforded colorless crystals of **7** in high yield (Scheme 3). The ^{1}H NMR spectrum of **7** showed a singlet at δ 0.37 ppm, attributed to the resonance arising from the hydroxy proton. The OH absorption is also observed in the IR spectrum as a sharp band at 3715 cm^{-1}.[17] The IR spectrum also showed a strong absorption at 1857 cm^{-1}, indicating the presence of an Al$-$H moiety.[18] Unfortunately, we were unable to obtain single crystals of **7** suitable for X-ray analysis, since it is not stable in solution and slowly underwent ligand cleavage even at low temperature.

Experimental Section

All experiments were carried out under an argon atmosphere using Schlenk line and glovebox techniques. Solvents were dried over sodium and freshly distilled and degassed prior to use. The NMR spectra were recorded at room temperature on a Bruker AMX 400 spectrometer. Infrared spectra were recorded on a Bio-Rad FTS 6000 FT IR spectrophotometer. UV$-$vis spectra were measured with a Shimadzu UV-2401PC spectrometer. The free ligand H$_2$C[(CBu^t)(NAr)]$_2$ was prepared as described in the literature.[4]

Synthesis of HC[(CBu^t)(NAr)]$_2$AlEt$_2$ (1). A solution of AlEt$_3$ (2.8 g, 24.0 mol) in *n*-hexane (12 mL) was added with rapid stirring to a solution of H$_2$C[(CBu^t)(NAr)]$_2$ (10.0 g, 20.0 mmol) in *n*-hexane (70 mL). The colorless solution was heated at reflux for 24 h to yield a yellow solution. This was concentrated (to ca. 25 mL) and kept at -25 °C overnight. Yellow crystals of **1** formed (11.1 g, 94.7%). Mp: 169 °C. Anal. Calcd for C$_{39}$H$_{63}$AlN$_2$ (586.89): C, 79.81; H, 10.82; N, 4.77. Found: C, 79.54; H, 11.07; N, 4.62. ^{1}H NMR (CDCl$_3$): δ 0.27 (br s, 4H, Al$-$C*H*$_2$), 0.73 (br, 6H, Al$-$CH$_2$C*H*$_3$), 1.13 (s, 18H, CMe$_3$), 1.26 (d, 12H, CH*Me*$_2$), 1.32 (d, 12H, CH*Me*$_2$), 3.34 (sept, 4H, C*H*Me$_2$), 5.66 (s, 1H, γ-C*H*), 7.09 (d, 4H, Ar *H*), 7.17 (m, 2H, Ar *H*). ^{13}C NMR (CDCl$_3$): δ 9.67 (Al$-$*C*), 24.69 (CH$_3$), 26.66 (CHMe$_2$), 27.87 (CH), 32.66 (*C*H$_3$), 43.21 (*C*Me$_3$), 100.60 (γ-C), 124.00, 126.02, 142.44, 144.42 (Ar *C*), 179.10 (CN). IR (cm^{-1}): 3061, 2980, 2855, 1536, 1490, 1387, 1359, 1312, 1270, 1218, 1182, 1134, 1102, 990, 933, 787, 758, 691, 626.

Synthesis of HC[(CBu^t)(NAr)]$_2$AlI$_2$ (2). A hot (80 °C) solution of LAlEt$_2$ (11.1 g, 18.9 mmol) in toluene (60 mL) was added rapidly to a stirred solution of iodine (12.1 g, 47.3 mmol) in toluene (20 mL) at 80 °C. The mixture turned from purple to bright yellow after the addition was complete. The solution was stirred for 2 h at room temperature and then concentrated (to 25 mL). The solution was kept at -25 °C overnight to yield light yellow crystals of **2** (12.3 g, 83.0%). Mp: 252 °C. Anal. Calcd for C$_{35}$H$_{53}$AlI$_2$N$_2$ (782.58): C, 53.72: H, 6.83; N, 3.58. Found: C, 53.95; H, 6.70; N 3.65. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.16 (s, 18H, C*Me*$_3$), 1.28 (d, 24H, CH*Me*$_2$), 3.53 (sept, 4H, C*H*Me$_2$), 6.25 (s, 1H, γ-C*H*), 7.13 (d, 4H, Ar *H*), 7.23 (d, 2H, Ar *H*). ^{13}C NMR (CDCl$_3$): δ 24.24 (*C*H$_3$), 27.31 (CH*Me*$_2$), 28.97 (*C*H), 32.00 (*C*H$_3$), 43.79 (*C*Me$_3$), 103.04 (γ-C), 124.48, 127.43, 140.36, 145.12 (Ar *C*), 181.66 (*C*N). IR (cm^{-1}): 2968, 2868, 1655, 1622, 1498, 1466, 1352, 1314, 1260, 1180, 1103, 1018, 934, 795, 757, 599.

Synthesis of HC[(CBu^t)(NAr)]$_2$Al (3). A solution of LAlI$_2$ (3.2 g, 6.0 mmol) in 50 mL of toluene was added to a suspension of finely divided potassium (0.56 g, 14.4 mmol) in toluene (10 mL). The mixture was vigorously stirred at room temperature for 5 days. The solution became red, and all of the potassium appeared to be consumed. The solution was filtered, and the residue was extracted with toluene (80 mL). The red-brown filtrate was concentrated (to 15 mL) and stored at -35 °C overnight, affording red crystals of **3** (0.62 g, 20%). The remaining solid could not be identified, due to its poor solubility in organic solvents. Mp: 172 °C dec. Anal. Calcd for C$_{35}$H$_{53}$AlN$_2$ (528.77): C, 79.50; H, 10.10; N, 5.30. Found: C, 79.32; H, 10.23; N, 5.52. ^{1}H NMR (C$_6$D$_6$): δ 1.13 (s, 18H, C*Me*$_3$), 1.26 (d, 12H, CH*Me*$_2$), 1.43 (d, 12H, CH*Me*$_2$), 3.21 (sept, 4H, C*H*Me$_2$), 5.88 (s, 1H, γ-C*H*), 6.95 (br s, 1H), 7.06 (d, 4H, Ar H), 7.34 (br s, 1H, Ar H). ^{13}C NMR (CDCl$_3$): δ 23.40 (CH$_3$), 25.68 (CHMe$_2$), 28.96 (CH), 32.96 (CH$_3$), 42.61 (*C*Me$_3$), 100.57 (γ-C), 123.76, 127.11, 143.74, 144.26 (Ar C), 173.36 (CN). UV$-$vis (*n*-hexane; $\lambda_{\max}$ (nm) (ϵ (mol^{-1} L cm^{-1}))): 285 (2900), 364 (13 000). IR (cm^{-1}): 3061, 2977, 2867, 1624, 1547, 1501, 1392, 1358, 1304, 1273, 1217, 1100, 759.

Synthesis of 4. To a suspension of **3** (0.21 g, 0.40 mmol) in toluene (2 mL) was added 2,6-diisopropylphenyl isocyanide (0.16 g, 0.82 mmol) at room temperature. The originally red solution became black immediately. The solution was stirred at room temperature for 15 min, and then all volatiles were removed under vacuum. The residue was extracted with *n*-hexane (20 mL). The extract was filtered, and the black filtrate was concentrated (to ca. 3 mL). After it stood overnight at -35 °C, the solution afforded yellow crystals of **4** (0.26 g, 72%). Mp: 80 °C dec. Anal. Calcd for C$_{61}$H$_{87}$AlN$_4$: C, 81.10; H, 9.71; N, 6.20. Found: C, 80.97; H, 9.57; N, 6.08. ^{1}H NMR (CDCl$_3$): δ 0.01, 0.08 (s, 6H, C*Me*$_2$), 0.33, 0.59, 0.78, 0.87, 0.90, 1.04, 1.15, 1.25, 1.27, 1.28, 1.30, 1.35, 1.61 (d, 42H, CH*Me*$_2$), 1.21, 1.24 (s, 18H, C*Me*$_3$), 2.29, 3.02, 3.19, 3.66 (sept, 7H, CHMe$_2$), 3.61 (s, 1H, C*H*), 5.89 (s, 1H, γ-C*H*), 6.36 (m, 1H, Ar *H*), 6.45 (m, 1H, Ar *H*), 6.79$-$6.85 (m, 2H, Ar *H*), 6.98 (m, 1H, Ar *H*), 7.15$-$7.21 (m, 4H, Ar *H*), 7.21$-$7.28 (m, 2H, Ar *H*). ^{13}C NMR (CDCl$_3$): δ 14.12, 20.59, 22.18, 22.66, 23.00, 23.37, 24.41, 24.75, 25.06, 25.29, 25.80, 25.85, 25.92, 26.63, 26.69, 26.84, 27.18, 27.35, 27.73, 28.23, 28.54, 28.62, 29.44, 29.80, 31.60 (CH*Me*$_2$, C*Me*$_2$), 32.47, 32.87 (CMe$_3$), 43.46, 43.76, 45.01 (*C*Me$_3$, *C*Me$_2$), 85.95 (*C*H), 99.20 (γ-*C*), 116.98, 119.40, 121.11, 123.09, 123.75, 123.96, 124.50, 124.59, 125.23, 126.92, 127.56, 129.41, 133.73, 138.54, 140.31, 140.77, 143.97, 144.14, 145.08, 145.80, 149.88, 151.60 (Ar *C*), 179.60, 180.58 (*C*N). UV$-$vis (*n*-hexane; $\lambda_{\max}$ (nm) (ϵ (mol^{-1} L cm^{-1}))): 354 (shoulder). IR (cm^{-1}): 3059, 2964, 2867, 1621, 1538, 1492, 1435, 1387, 1359, 1311, 1265, 1189, 1103, 1030, 927, 792, 749.

Synthesis of 5. To a solution of **3** (0.21 g, 0.40 mmol) in toluene (40 mL) was slowly added a solution of 2,6-diisopropylphenyl isocyanide (0.15 g, 0.80 mmol) in toluene (10 mL) at room temperature. Upon addition, the solution turned from red to purple. After the addition was complete in 15 min, the solution was stirred for an additional 2 h. The solution was concentrated (to ca. 10 mL) and then kept at -35 °C overnight to give purple crystals of **5** (0.22 g, 61%). Mp: 208 °C dec. Anal. Calcd for C$_{61}$H$_{87}$AlN$_4$: C, 81.10; H, 9.71; N, 6.20. Found: C, 80.92; H, 9.92; N, 5.98. ^{1}H NMR (CDCl$_3$): δ 0.03, 0.07, 0.46, 1.01, 1.03, 1.08, 1.43, 1.54 (d,

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[16] For examples, see: (a) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449. (b) Jancik, V.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2005**, *44*, 6016.

[17] (a) Li, X.; Song, H.; Duan, L.; Cui, C.; Roesky, H. W. *Inorg. Chem.* **2006**, *45*, 1912. (b) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5502. (c) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1017.

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3H, CH*Me*$_2$), 0.24 (br, 3H, CHMe$_2$), 1.02, 1.14, 1.24 (d, 42H, CH*Me*$_2$), 0.76, 0.97 (s, 18H, C*Me*$_3$), 2.32, 2.51, 2.72, 2.88, 3.13, 3.23, 3.43, 3.48 (sept, 8H, C*H*Me$_2$), 6.61−7.26 (m, 13H, CC*H*CN and Ar *H*). ^{13}C NMR (CDCl$_3$): δ 14.12, 21.20, 22.23, 23.01, 23.62, 23.84, 24.21, 24.34, 24.78, 25.22, 25.31, 25.47, 25.67, 26.08, 27.46, 28.07, 28.35, 28.45, 28.67, 28.96, 29.32 (CH*Me*$_2$), 29.03, 31.29 (C*Me*$_3$), 36.83, 42.85 (*C*Me$_3$), 119.49, 121.33, 121.98, 122.15, 122.43, 122.77, 123.08, 123.26, 123.52, 123.80, 124.43, 124.58, 124.71, 128.59, 133.76, 136.44, 138.01, 138.57, 139.94, 140.98, 141.68, 142.52, 143.75, 146.26, 146.68, 146.99 (Ar C), 157.62 (C*CH*═C), 194.21 (N*C*Bu^t), 197.26 (ArN═*C*Al), 204.66 (Bu^t*C*Al). UV−vis (*n*-hexane; λ_{max} (nm) (ϵ (mol^{-1} L cm^{-1}))): 274 (10 800), 352 (2500). IR (cm^{-1}): 3381, 2963, 2867, 1642, 1615, 1465, 1322, 1261, 1184, 757.

Reaction of 3 with 2,6-$Ar_2C_6H_3N_3$. To solution of **3** (0.21 g, 0.40 mmol) in toluene (20 mL) at −78 °C was slowly added a solution of 2,6-$Ar_2C_6H_3N_3$ (0.18 g, 0.40 mmol) in toluene (10 mL) at −78 °C. The color changed from red to black immediately. The mixture was slowly warmed to room temperature, during which time the color changed from black to bright yellow. After all volatiles were removed under vacuum, the residue was extracted with *n*-hexane (20 mL). The extract was concentrated (to 10 mL) and stored at −20 °C for 2 days to give yellow crystals of **6** (0.21 g, 55%). Mp: 148−151 °C dec. Anal. Calcd for $C_{65}H_{97}AlN_3$: C, 82.93; H, 9.74; N, 4.46. Found: C, 82.85; H, 9.69; N, 4.40. ^{1}H NMR (C$_6$D$_6$): δ −0.17 (m, 2H, AlC*H*$_2$), 0.60, 0.86 (s, 18H, C*Me*$_3$), 0.73, 0.79, 0.90 (d, 3 × 3H, CH*Me*$_2$), 1.03 (m, 12H, CH*Me*$_2$), 1.17, 1.19 (d, 2 × 3H, CH*Me*$_2$), 1.27 (d, 3H, CH*Me*$_2$), 1.34 (d, 3H, CH*Me*$_2$), 1.42 (t, 6H, CH*Me*$_2$), 1.49, 1.52 (d, 2 × 3H, CH*Me*$_2$), 2.41, 2.82, 2.95, 3.05, 3.13, 3.17, 3.86 (sept, 7 × 1H, C*H*Me$_2$), 2.66 (m, 1H, C*H*MeCH$_2$), 3.37 (s, 1H, N*H*), 5.90 (s, 1H, γ-C*H*), 6.59 (m, 1H, Ar *H*), 6.92 (m, 1H, Ar *H*), 6.99 (m, 1H, Ar *H*), 7.02−7.10 (m, 2H, Ar *H*), 7.18−7.21 (m, 2H, Ar *H*), 7.28 (m, 1H, Ar *H*). ^{13}C NMR (C$_6$D$_6$): δ 22.12, 23.44, 23.54, 23.63, 24.09, 24.26, 25.24, 25.44, 25.91, 26.05, 26.25, 26.33, 26.51, 26.72, 26.87, 27.04, 27.22, 27.61, 28.60, 30.04, 30.22, 30.32, 30.57, 30.67, 31.00, 32.69 (AlCH$_2$, CHMe$_2$, CHMeCH$_2$), 30.81, 31.59, 41.73, 41.92 (CMe$_3$), 107.55 (γ-*C*), 114.40, 122.62, 022.88, 123.08, 123.31, 123.79, 124.80, 127.20, 128.30, 128.37, 129.07, 132.71, 136.29, 139.71, 141.07, 142.94, 144.04, 144.32, 145.46, 146.77, 147.51, 147.82, 148.28, 148.71, 150.80 (Ar *C*), 172.59 (*C*N). UV−vis (*n*-hexane; λ_{max} (nm) (ϵ (mol^{-1} L cm^{-1}))): 302 (580), 390 (1177). IR (cm^{-1}): 3238 (N−H), 3058, 2963, 2868, 1923, 1698, 1575, 1542, 1461, 1435, 1403, 1386, 1362, 1321, 1253, 1203, 1101, 1030, 931, 867, 804, 758, 730, 692, 663, 556, 506, 447.

Reaction of 3 with H_2O. To a solution of **3** (0.21 g, 0.40 mmol) in toluene (20 mL) cooled to −78 °C was slowly added a solution of H_2O (0.007 g, 0.40 mmol) in toluene (10 mL). The mixture was slowly warmed to room temperature, during which time the color changed from red to bright yellow. After all volatiles were removed under vacuum, a yellow solid remained. The residue was extracted with *n*-hexane (20 mL). The extract was concentrated (to ca. 10 mL) and stored at −20 °C for 2 days to give white crystals of **7** (0.17 g, 78%). Mp: 108 °C dec. ^{1}H NMR (CDCl$_3$): δ 0.38 (s, 1H, OH), 1.13 (s, 18H, C*Me*$_3$), 1.24, 1.29 (d, 24H, CH*Me*$_2$), 3.41 (sept, 4H, C*H*Me$_2$), 5.80 (s, 1H, γ-C*H*), 7.10 (m, 4H, Ar *H*), 7.18 (m, 2H, Ar *H*). ^{13}C NMR (CDCl$_3$): δ 24.10, 26.53, 28.08 (CH*Me*$_2$, C*Me*$_3$), 32.38, 43.09 (*C*Me$_3$, *C*HMe$_2$), 98.73 (γ-*C*), 124.03, 126.62, 140.57, 144.66 (Ar *C*), 197.59 (*C*N). IR (cm^{-1}): 3744, 3715 (AlO−H), 3055, 2963, 2869, 1857 (Al−H), 1538, 1506, 1465, 1437, 1389, 1364, 1316, 1277, 1262, 1219, 1197, 1157, 1101, 1028, 933, 851, 820, 792, 758, 693, 448.

X-ray Structural Determination. Data were collected at 294(2) K on a Bruker Smart-Apex II diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. All structures were solved by direct methods (SHELXS-97)[12a] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by a riding model (SHELXL-97).[12b] Crystallographic data for **1**: $C_{39}H_{63}AlN_2$, M_r = 586.89, triclinic, space group $P\bar{1}$, a = 12.511(3) Å, b = 18.267(4) Å, c = 18.810(4) Å, α = 77.870(4)°, β = 70.988(3)°, γ = 70.924(3)°, V = 3815.4(13) Å^3, Z = 4, D_c = 1.022 g cm^{-3}, F(000) = 1296, 19 416 reflections measured (13 332 unique). R1 = 0.0628 ($I > 2\sigma(I)$), wR2 = 0.1968 (all data), GOF = 1.009 for 757 parameters and 0 restraints. Crystallographic data for **3**: $C_{35}H_{53}AlN_2$, M_r = 528.77, monoclinic, space group $C2/c$, a = 23.748(4) Å, b = 8.5153(15) Å, c = 17.376(3) Å, β = 108.731(3)°, V = 3327.7(10) Å^3, Z = 4, D_c = 1.055 g cm^{-3}, F(000) = 1160, 8178 reflections measured (2910 unique). R1 = 0.0438 ($I > 2\sigma(I)$), wR2 = 0.1435 (all data), GOF = 1.042 for 180 parameters and 0 restraints. Crystallographic data for **4**: $C_{61}H_{87}AlN_4$, M_r = 903.33, triclinic, space group $P\bar{1}$, a = 12.544(2) Å, b = 14.444(3) Å, c = 18.624(3) Å, α = 73.795(3)°, β = 108.731(3)°, γ = 83.397(3)°, V = 3218.6(9) Å^3, Z = 2, D_c = 0.932 g cm^{-3}, F(000) = 988, 16 271 reflections measured (11 213 unique). R1 = 0.0909 ($I > 2\sigma(I)$), wR2 = 0.2997 (all data), GOF = 1.041 for 621 parameters and 1 restraint. Crystallographic data for **5**: $C_{61}H_{87}AlN_4$, M_r = 903.33, monoclinic, space group $P2_1/n$, a = 14.255(2) Å, b = 18.737(3) Å, c = 21.076(3) Å, β = 91.189(2)°, V = 5628.2(13) Å^3, Z = 4, D_c = 1.066 g cm^{-3}, F(000) = 19 076, 46 034 reflections measured (11 046 unique). R1 = 0.0673 ($I > 2\sigma(I)$), wR2 = 0.1878 (all data), GOF = 1.085 for 619 parameters and 0 restraints.

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Supporting Information Available: CIF files giving X-ray crystallographic data files for compounds **1** and **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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