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**Lanthanide Complexes**

# Alkyl Migration and an Unusual Tetramethylaluminate Coordination Mode: Unexpected Reactivity of Organolanthanide Imino–Amido–Pyridine Complexes**

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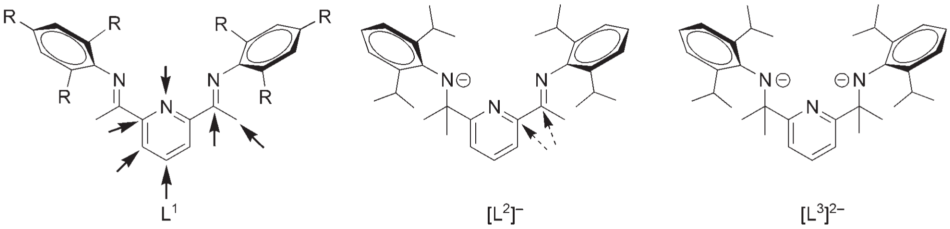
Bis(imino)pyridine compounds provide versatile ancillary ligand sets for efficient Ziegler–Natta catalysts based on the late transition metals iron and cobalt[1] and the earlier transition metals vanadium[2] and chromium.[3] Extended studies have outlined the capability of such conjugated [**N**N**N**] ligands (L$^1$, Scheme 1) to engage in a variety of transformations. In addition to substantial charge-transfer interactions of the ligand π system with the transition-metal center, alkylation proneness at various positions of the ligand framework evidence the chemical non-innocence of these diimino ligands. With diverse alkylating agents, alkyl attack at the imino function[4] or at any position of the pyridine ring,[2,4a,5] even the pyridine N atom,[6] and deprotonation of the methyl sidearms have been reported to occur (Scheme 1).[5b,6b,7] Furthermore, dimerization by C–C bond formation after reduction of the enamine functionality[5b,8] and cycloaddition of the pyridine ring have been observed.[5b]



*Scheme 1.* The chemical non-innocence of [**N**N**N**]$^{n-}$ ($n$ = 0–2) ancillary ligands. Known sites of nucleophilic attack/alkylation are indicated by arrows (broken arrows: this work).

The generally observed decrease of the metal–nitrogen bond energies from late to early transition metals within a given series, combined with the uncharged nature of the bis(imino)pyridine ligand are considered to prevent the formation of stable Group 3 complexes.[9] The only example of a lanthanide complex stabilized by an assumed neutral bis(imino)pyridine ligand turned out to be the product of an internal ligand reduction affording a radical anion; attempts to prepare the $LnCl_3$ (Ln = Nd) adduct of the bis(imino)pyridine were unsuccessful.[8b]

The demonstration of a nucleophilic attack of alkylating reagents or cocatalysts such as $AlMe_3$ on the imino carbon of the ligand backbone has in turn provided a new class of monoanionic imino–amido–pyridine [**N**N**N**]$^-$ ligands (L$^2$, Scheme 1).[4b] These ligands retain the unusual stereoelectronic properties of the bis(imino)pyridine ligand and offer an approach to synthesizing discrete conformationally rigid lanthanide complexes. Starting from $[Lu(CH_2SiMe_3)_3(thf)_2]$ Gordon et al. were able to prepare the first lutetium dialkyl complex stabilized by [L$^2$]$^-$.[10] We have recently shown that homoleptic lanthanide tetramethylaluminates $[Ln(AlMe_4)_3]$ are convenient synthesis precursors for the generation of a variety of heterobimetallic Ln/Al complexes including half-lanthanidocene,[11] lanthanidocene,[12] as well as bis(amido)pyridine-derived [**N**N**N**]$^{2-}$ organolanthanide complexes.[13] Herein we present new [**N**N**N**]$^-$ and [**N**N**N**]$^{2-}$ organolanthanide complexes in which the chemical non-innocence of the imino–amido–pyridine ligand facilitates an unprecedented coordination mode of the tetramethylaluminate ligand.

$[Ln(AlMe_4)_3]$ (Ln = La (**1a**), Nd (**1b**) and Y (**1c**)) react with light yellow HL$^2$ in an alkane elimination reaction (Scheme 2). Instant gas evolution, a color change to dark red and subsequent precipitation of wine-red solid suggested a coordination of the monoanionic imino–amido ligand to a metal center.

Separation of the precipitate from the reaction mixture afforded complexes **2** as wine-red powders with yields increasing according to the size of the metal cation (Ln = Y 49 %; Nd 52 %; La 62 %). The IR spectra of complexes **2** show a strong absorption at 1582 cm$^{-1}$ (**2a**, **2c**) and 1588 cm$^{-1}$ (**2b**) attributed to the stretching vibration of a metal-coordinated imino group (HL$^2$: 1644 cm$^{-1}$). Similar shifts were observed in bis(imino)pyridine complexes of titanium.[5a]

The $^1$H NMR spectra of complexes **2** in $C_6D_6$ revealed a rigid L$^2$ coordination at ambient temperature indicating a large rotational barrier for the aryl groups around the N–C$_{ipso}$ bond. Two upfield shifted singlets at $\delta = 1.71$ (3H) and

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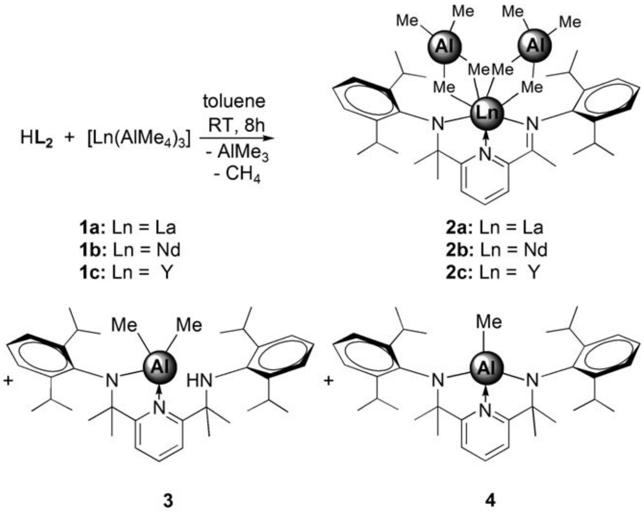


*Scheme 2.* Reaction of imino–amino–pyridine ligand $HL^2$ with $[Ln(AlMe_4)_3]$ (**1**).

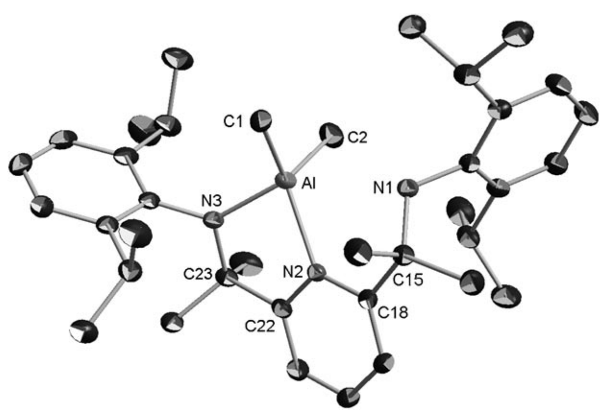


*Figure 1.* Molecular structure of **3** (anisotropic displacement parameters set at 50% probability). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Al···N1 2.8056(13), Al–N2 2.0552(13), Al–N3 1.8568(13), Al–C1 1.9814(17), Al–C2 1.9764(18), N1–C15 1.4954(19), N3–C23 1.4738(19), C15–C18 1.530(2), C22–C23 1.525(2); N2-Al-N3 82.27(5), Al-N3-C23 113.30(10), N3-Al-C1 107.82(7), N3-Al-C2 114.74(7), N2-Al-C1 125.28(7), N2-Al-C2 112.38(7), N1-C15-C18 108.59(12), N3-C23-C22 105.89(12).

1.39 ppm (6H) (**2a**) ($\delta = 1.74$ and 1.35 ppm, **2c**) confirm the maintenance of the imino–amido–pyridine ligand backbone. The $^1$H NMR spectra show only one broad singlet in the methyl alkyl region at $\delta = -0.25$ (**2a**) and $-0.38$ ppm (**2c**), respectively, which can be assigned to the {AlMe$_4$} moieties and indicates a rapid exchange of bridging and terminal methyl groups. These resonances are shifted to lower field compared to the homoleptic precursors ($\delta = -0.20$ (**1a**) and $-0.27$ ppm (**1c**)). The formation of the corresponding paramagnetic neodymium complex **2b** is clearly indicated by elemental analysis, IR data, and a relatively well-resolved $^1$H NMR spectrum ($\delta_{AlCH_3} = 6.30$ ppm).

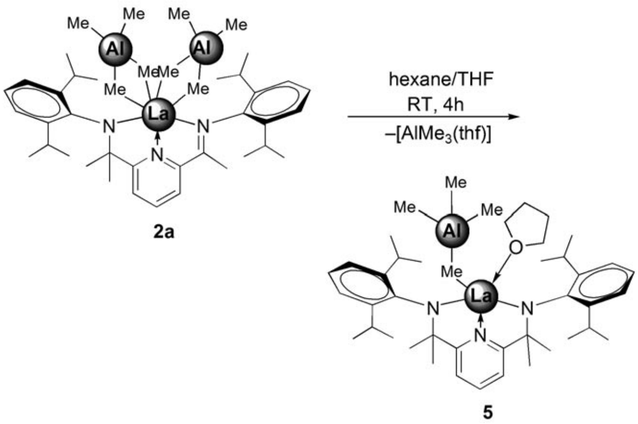
The moderate yields of complexes **2** and the striking red color of the soluble fraction made a closer investigation of the supernatant solution necessary. Apart from residual $[Ln(AlMe_4)_3]$, fractional crystallization from hexane afforded analytically pure orange and red crystals of aluminum complexes **3** and **4**, respectively (Scheme 2).

An X-ray structure analysis of complex **3** revealed the unprecedented alkylation of the imino carbon atom of $[L^2]^-$ (Figure 1). The metal center in **3** is in a distorted tetrahedral coordination environment which features a methylated ancillary ligand, $\eta^2$-coordinated to the metal center. The Al–N bonds and the N2-Al-N3 bite angle are in the expected ranges.[4b,14a,15] Alkylation of the imino carbon atom with the consequent formation of a dianionic bis(amido)pyridine of the [**NNN**]$^{2-}$ type was not anticipated and is in striking contrast with the reactivity of bis(imino)pyridine ligands and complexes derived there from. For example, treatment of bis(imino)pyridines and their late transition-metal complexes even with an excess of $AlMe_3$ exclusively affords the monoalkylation products.[4b,14] Hence, the reactivity observed in our system suggests an alkylation sequence via highly reactive {Ln–Me} moieties rather than alkylation by $AlMe_3$ released in the acid–base reaction of $[Ln(AlMe_4)_3]$ and $HL^2$. At the same time, the Lewis acidic $Al^{3+}$ competes with the lanthanide centers for the [**NNN**]$^{n-}$ ligand coordination—the strong Lewis acid $Al^{3+}$ has a high affinity for nitrogen donors.[16] The competition is evidenced by the dependency of the aluminum complex formation on the size of the $Ln^{3+}$ ion. The 4:1 ratio of **3**:**4** is indicative of a kinetically (**3**) or thermodynamically (**4**, by $CH_4$ elimination from **3**) controlled reaction.

Complexes $[L^2Ln(AlMe_4)_2]$ (**2a–c**; Ln = La, Nd, Y) resemble [(**NNN**)FeMe(AlMe$_4$)] (**NNN** = bis(imino)pyridine) which has been discussed as an active site in highly efficient catalytic systems based on bis(imino)pyridine $Fe^{2+}$ complexes activated by methylaluminoxane (MAO) or trialkylaluminum reagents.[17] Tetramethylaluminate {AlMe$_4$} moieties, also referred to as "alkyls in disguise", offer a commonly used synthesis approach to highly reactive {Ln–Me} derivatives.[18] The donor-induced cleavage of tetramethylaluminates (donor = THF, diethyl ether, pyridine) has been applied to convert heteroleptic lanthanidocene and halflanthanidocene complexes, $[Cp'_2Ln(AlR_4)]$ and $[Cp'Ln(AlR_4)_2]$ (Cp′ = substituted cyclopentadienyl), into complexes $[Cp'_2LnR]$ and $[Cp'LnR_2]$, respectively.[11,18,19]

Addition of an excess of THF to a stirred suspension of the bis(tetramethylaluminate) complex **2a** in hexane (Scheme 3) resulted in instant dissolution of the wine-red solid accompanied by decolorization of the solution.

Colorless single crystals of **5** suitable for X-ray diffraction were grown from a hexane solution and revealed the product of an unexpected "incomplete" donor-induced tetramethylaluminate cleavage (Figure 2).[15] Contrary to an anticipated organoaluminum-free methyl derivative, lanthanum complex **5** features an intact tetramethylaluminate ligand in a novel (μ-Me){AlMe$_3$} coordination mode. To our knowledge, this is the first example of a structurally authenticated $\eta^1$-coordinated {AlMe$_4$} moiety—the missing tetramethylaluminate coordination mode to complete the series, the $\eta^2$ and $\eta^3$ modes have been reported.[20] Moreover, complex **5** features the cleaving agent THF and a tetramethylaluminate in the same molecule. The only comparable structures reported are $[(C_5Me_5)_2Sm$-



*Scheme 3.* Donor-induced cleavage of one tetramethylaluminate ligand from **2a** with THF.

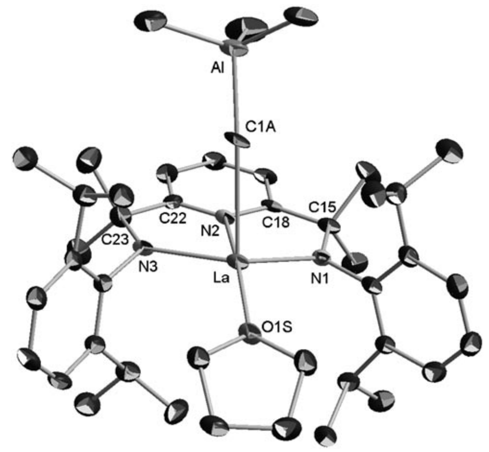


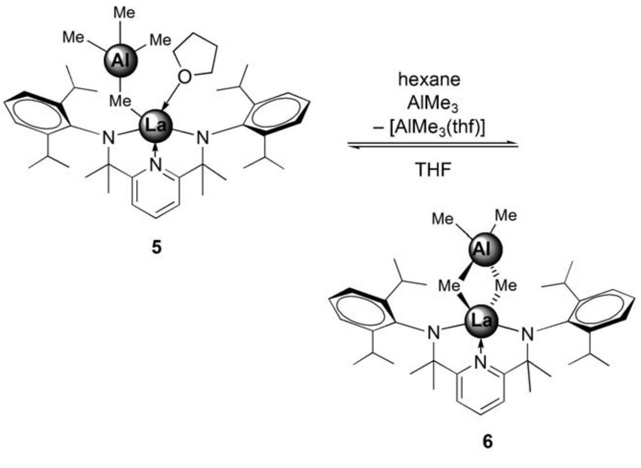
*Figure 2.* Molecular structure of **5** (anisotropic displacement parameters set at 50% probability). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: La–N1 2.294(5), La–N2 2.516(5), La–N3 2.246(6), La–O1S 2.538(4), La–C1A 2.825(7), Al–C1A 2.024(7), Al–C2A 1.980(9), Al–C3A 1.980(9), Al–C4A 1.963(9), N3–C23 1.475(8), C22–C23 1.511(9), N1–C15 1.475(8), C15–C18 1.481(10); N1-La-N3 127.82(18), N1-La-N2 64.96(18), N2-La-N3 64.15(17), N1-La-O1S 111.86(17), N3-La-O1S 114.68(16), N1-La-C1A 97.85(2), N3-La-C1A 87.56(2), O1S-La-C1A 109.95(2), La-C1A-Al 165.0(4), N1-C15-C18 108.2(5), N3-C23-C22 106.1(5).

(thf)($\mu$-$\eta^2$-Et)AlEt$_3$][21] and [(C$_5$Me$_5$)$_2$Yb($\eta^2$-Et)AlEt$_2$(thf)][22] which involve $\eta^2$-ethyl ligands.[23] The five-coordinate La center in **5** is further surrounded by the three N atoms of the ancillary ligand which has undergone alkylation in similarity to **3** and **4**. The coordination geometry of the La center is best described as a distorted trigonal bipyramidal with the THF oxygen and the pyridine nitrogen (N2) atoms occupying the apical positions (O1S-La-N2, 166.3°) while the amido nitrogen atoms (N1 and N3) and a tetramethylaluminate carbon atom (C1A) form the equatorial plane.[15]

The formation of **5** is assumed to originate from fast sequential processes involving initial donor-induced cleavage of one tetramethylaluminate ligand in complex **2a** to produce a highly reactive terminal methyl group. The transient {Ln–Me} species can undergo methyl migration from the metal center to the imino carbon atom. Such an intramolecular nucleophilic attack on the imino functionality implies additional anionization of the ligand and concomitant quaternization of the former imino carbon atom.[24] Comparatively short bonds between the lanthanum and the amido nitrogen atoms (La–N1 2.294(5), La–N3 2.246(6) Å) and pyridine nitrogen (N2–La 2.516(5) Å) indicate a strong interaction of the newly formed [**NNN**]$^{2-}$ ligand with the low-coordinate metal center.[8b,13] The heterobimetallic {La($\mu$-Me)Al} moiety features a markedly obtuse La-C1A-Al angle of 165.0(5)° with a La–C bond length of 2.825(7) Å which is in the upper range of $\eta^2$-coordinated tetramethylaluminates (2.694(3) Å–2.802(4) Å).[11]

The symmetric environment around the metal center imparted by the [**NNN**]$^{2-}$ ligand is also in accordance with the $^1$H NMR spectrum of **5**. In C$_6$D$_6$, only one set of signals was observed for the bis(amido)pyridine ligand comprising one multiplet at $\delta = 3.47$ ppm for the methine protons and two duplets at $\delta = 1.18$ and 1.15 ppm for the methyl protons of the isopropyl groups. A relatively sharp singlet at $\delta = -0.15$ ppm is assigned to the {AlMe$_4$} unit indicating a rapid exchange of the bridging and the terminal methyl groups. Moreover, the significantly upfield shifted multiplets at $\delta = 2.74$ and 0.98 ppm assigned to the THF ligand are in agreement with a strongly bonded THF molecule.

Nevertheless, displacement of the strongly coordinating donor solvent can be achieved by addition of AlMe$_3$ to a solution of **5** in hexane (Scheme 4). Formation of the donor-free tetramethylaluminate complex **6** is quantitative and affords an analytically pure white solid that is sparingly soluble in hexane, [AlMe$_3$(thf)] is the only byproduct. This displacement of THF is fully reversible and complex **5** can be quantitatively recovered by adding THF to a hexane solution of **6**. Owing to the steric unsaturation of the lanthanum center a $\eta^2$-coordination of the tetramethylaluminate ligand is assumed for compound **6**. However, variable-temperature (VT) NMR spectroscopy could not give final proof, as no



*Scheme 4.* THF displacement/coordination equilibrium between **5** and **6**.

decoalescence of the aluminate signal was observed in the accessible temperature range (−90–25 °C).

Compared to the high degree of delocalization in bis(imino)pyridine ligands, the conjugation in the imino–amido–pyridine system is restrained. However, it still allows significant internal charge-transfer processes resulting in exceptional reaction pathways, coordination modes, and complex stabilization. The observed reactivity of the imino–amido–pyridine lanthanide complexes not only emphasizes the non-innocence of this ligand system but also the enhanced alkylation capability of {Ln–Me} moieties. The new $\eta^1$-tetramethylaluminate coordination substantiates the coordinative flexibility of anionic cocatalysts in Ziegler–Natta-type catalysts and the unpredictable nature of so-called dormant species.

## Experimental Section

Representative synthesis of **2a**: In a glovebox, [La(AlMe$_4$)$_3$] (**1a**, 241 mg, 0.60 mmol) was dissolved in toluene (3 mL) and added to a stirred solution of HL$^2$ (300 mg, 0.60 mmol) in toluene (4 mL). The resulting mixture immediately turned red and gas evolution was observed. The reaction mixture was stirred for another 8 h at ambient temperature while the formation of a wine-red precipitate was observed. The product was separated by centrifugation, washed with hexane (4 × 5 mL) and dried under vacuum to yield **2a** as a powdery wine-red solid (303 mg, 0.37 mmol, 62 %). $^1$H NMR (600 MHz, C$_6$D$_6$, 25 °C): $\delta = 7.18$–7.10 (m, 6H, ar), 7.04 (t, $^3J = 7.8$ Hz, 1H, C$_5$H$_3$N-*p*-proton), 6.86 (d, $^3J = 7.8$ Hz, 1H, C$_5$H$_3$N-*m*-proton), 6.85 (d, $^3J = 7.8$ Hz, 1H, C$_5$H$_3$N-*m*-proton), 3.26 (sept, $^3J = 6.6$ Hz, 2H, ar-CH), 2.62 (sept, $^3J = 6.6$ Hz, 2H, ar-CH), 1.71 (s, 3H, N=CCH$_3$), 1.39 (s, 6H, NCCH$_3$), 1.30 (d, $^3J = 6.6$ Hz, 6H, CH$_3$), 1.26 (d, $^3J = 6.6$ Hz, 6H, CH$_3$), 1.00 (d, $^3J = 6.6$ Hz, 6H, CH$_3$), 0.88 (d, $^3J = 6.6$ Hz, 6H, CH$_3$), −0.25 ppm (s, 24H, Al(CH$_3$)$_4$). $^{13}$C NMR (126 MHz, C$_6$D$_6$, 25 °C): $\delta = 175.1$, 158.7, 149.4, 140.7, 139.1, 138.4, 125.5, 125.3, 124.9, 117.3, 69.9, 33.7, 29.1, 28.6, 28.1, 26.3, 26.1, 25.5, 25.1, 20.3, 3.1 ppm (s br, Al(CH$_3$)$_4$). VT-NMR was unsuccessful due to low solubility of complex **2a** in [D$_8$]toluene. IR (nujol): $\tilde{\nu} = 1582$ (s, C=N), 1468 (vs, nujol), 1375 (vs, nujol), 1303 (s), 1261 (m), 1220 (w), 1214 (w), 1173 (s), 1095 (w), 1007 (w), 971 (w), 950 (w), 888 (w), 847 (w), 821 (w), 785 (m), 769 (m), 723 (vs), 593 (w), 578 (w), 516 cm$^{-1}$ (w). Elemental analysis (%) calcd for C$_{42}$H$_{70}$N$_3$Al$_2$La (809.910 g mol$^{-1}$): C 62.29, H 8.71, N 5.19; found: C 62.21, H 8.77, N 5.13.

**5**: THF (3 mL) was added dropwise to a stirred suspension of **2a** (126 mg, 0.16 mmol) in hexane (3 mL). The wine-red solid dissolved immediately accompanied by decolorization of the reaction mixture. After stirring for 4 h at ambient temperature the solvent was removed in vacuo to give a white solid which was washed with hexane (3 × 2 mL) and dried under vacuum to yield **5** as a powdery white solid (117 mg, 0.14 mmol, 90 %). $^1$H NMR (600 MHz, C$_6$D$_6$, 25 °C): $\delta = 7.20$–7.11 (m, 6H, ar), 7.06 (t, $^3J = 7.8$ Hz, 1H, C$_5$H$_3$N-*p*-proton), 6.81 (d, $^3J = 7.8$ Hz, 2H, C$_5$H$_3$N-*m*-protons), 3.47 (sept, $^3J = 6.6$ Hz, 4H, ar-CH), 2.74 (m, 4H, THF), 1.40 (s, 12H, NCCH$_3$), 1.18 (d, $^3J = 6.6$ Hz, 12H, CH$_3$), 1.15 (d, $^3J = 6.6$ Hz, 12H, CH$_3$), 0.98 (m, 4H, THF), −0.15 ppm (s, 12H, Al(CH$_3$)$_4$). $^{13}$C NMR (151 MHz, C$_6$D$_6$, 25 °C): $\delta = 174.3$, 150.3, 141.3, 139.0, 125.6, 125.0, 117.8, 70.8 (THF), 69.1, 32.8, 31.9, 28.2, 28.0, 25.1, 23.0, 1.7 ppm (s, Al(CH$_3$)$_4$). IR (nujol): $\tilde{\nu} = 1572$ (w), 1468 (vs, nujol), 1375 (vs, nujol), 1303 (s), 1256 (w), 1220 (w), 1194 (m), 1158 (m), 1126 (w), 1101 (w), 1044 (w), 1013 (w), 982 (w), 930 (w), 852 (m), 816 (w), 785 (m), 764 (m), 723 (vs), 692 (w), 583 (w), 562 (w), 536 (w), 516 cm$^{-1}$ (w). Elemental analysis (%) calcd for C$_{43}$H$_{69}$N$_3$OAlLa (809.930 g mol$^{-1}$): C 63.77, H 8.59, N 5.19; found: C 63.37, H 8.58, N 5.02.

**6**: AlMe$_3$ (6 mg, 0.09 mmol) was added dropwise to a stirred solution of **5** (71 mg, 0.09 mmol) in toluene (3 mL). After stirring the colorless reaction mixture for 4 h at ambient temperature the solvent was removed in vacuo to form a white solid which was washed with hexane (3 × 2 mL) and dried under vacuum to yield **6** as a powdery white solid (63 mg, 0.09 mmol, 98 %). $^1$H NMR (600 MHz, C$_6$D$_6$, 25 °C): $\delta = 7.20$–7.16 (m, 6H, ar), 7.14 (t, $^3J = 7.8$ Hz, 1H, C$_5$H$_3$N-*p*-proton), 6.78 (d, $^3J = 7.8$ Hz, 2H, C$_5$H$_3$N-*m*-protons), 3.28 (sept, $^3J = 6.6$ Hz, 4H, ar-CH), 1.41 (s, 12H, NCCH$_3$), 1.31 (d, $^3J = 6.6$ Hz, 12H, CH$_3$), 1.05 (d, $^3J = 6.6$ Hz, 12H, CH$_3$), −0.40 ppm (s, 12H, Al(CH$_3$)$_4$). $^{13}$C NMR (151 MHz, C$_6$D$_6$, 25 °C): $\delta = 175.1$, 149.4, 141.5, 139.1, 126.1, 125.3, 117.3, 69.9, 33.7, 28.1, 26.3, 26.1, 2.83 ppm (s, Al(CH$_3$)$_4$). IR (nujol): $\tilde{\nu} = 1577$ (w), 1468 (vs, nujol), 1375 (vs, nujol), 1303 (s), 1251 (w), 1240 (w), 1194 (w), 1168 (m), 1095 (w), 1044 (w), 997 (w), 971 (m), 852 (w), 816 (w), 790 (w), 764 (m), 723 (vs), 609 (w), 567 (w), 562 (w), 536 (w), 516 cm$^{-1}$ (w). Elemental analysis (%) calcd for C$_{39}$H$_{61}$N$_3$AlLa (737.824 g mol$^{-1}$): C 63.49, H 8.33, N 5.70; found: C 63.54, H 8.35, N 5.44.

Full experimental and analytical details for complexes **2**–**6** are available in the Supporting Information.

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[15] Compound **3** ($C_{37}H_{56}N_3Al$, $M_r = 569.83$) crystallizes from hexane in the monoclinic space group $P2_1/n$ with $a = 9.4690(3)$, $b = 17.0926(6)$, $c = 21.1610(8)$ Å, $\beta = 91.874(1)°$, $V = 3423.1$ Å$^3$, and $\rho_{calcd} = 1.106\ g\,cm^{-3}$ for $Z = 4$. Data were collected at 123 K on a BRUKER-AXS 2 K CCD system. The structure was solved by direct methods, and least-square refinement of the model based on 6775 (all data) and 5378 reflections ($I > 2\sigma(I)$) converged to final $wR2 = 0.1116$ and $R1 = 0.0396$. Compound **5** ($C_{43}H_{69}N_3AlOLa$, $M_r = 809.90$) crystallizes from hexane in the triclinic space group $P\bar{1}$ with $a = 11.8063(13)$, $b = 12.4658(13)$, $c = 17.1461(18)$ Å, $\alpha = 76.170(2)$, $\beta = 70.824(2)$, $\gamma = 62.452(2)°$, $V = 2101.8(4)$ Å$^3$, and $\rho_{calcd} = 1.280\ g\,cm^{-3}$ for $Z = 2$. Data were collected at 123 K on a BRUKER-AXS 2 K CCD system. The structure was solved by direct methods, and least-square refinement of the model based on 7302 (all data) and 5723 reflections ($I > 2.0\sigma(I)$) converged to final $wR2 = 0.1723$ and $R1 = 0.0617$. CCDC-627911 and CCDC-627912 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[24] Complex **5** is the only alkylation product under the reaction conditions described in the Experimental Section isolable as an analytically pure white solid in very high yields. Nevertheless, when stirring a hexane solution of **5** for 4 days at 40 °C traces of the pyridine *ortho*-alkylation product were found indicating an alkyl migration from the imino carbon to the pyridine *ortho* position.