

Synthesis and Structures of Dinuclear Aluminum Complexes Based on Bis(β -diketiminate) Ligands

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Dedicated to Manfred Scheer on the Occasion of his 65th Birthday

Abstract. A series of ten dinuclear aluminum alkyl complexes based on rigid, semirigid, and flexible bis(β -diketiminate) ligands (NacNac) has been obtained from the reaction of trimethylaluminum and the corresponding bis(β -diketimine)s. All compounds were fully charac-

terized using NMR and IR spectroscopy and elemental analysis. The molecular structures of five compounds have been investigated by means of single-crystal X-ray diffraction analysis.

Introduction

Since the first reports on transition-metal complexes of β -diketiminate ligands, also known as β -diiminate or NacNac ligands, in 1968,^[1] this ligand class has been frequently used to stabilize a variety of elements from all sections of the periodic table and in unusual oxidation states.^[2] Today, β -diketimines belong to the most ubiquitous ligands in coordination chemistry, mostly because their electronic and steric features can readily be altered through variation of the ligand backbone and/or the terminal substituents at the nitrogen atoms, Figure 1a.^[3] However, it has been shown that β -di-

ketimines do not necessarily behave as spectator ligands and their (hidden) non-innocence is an interesting feature in terms of reactivity.^[3,4] Poly(β -diketiminate)s have been recently emerged as useful tools in coordination chemistry,^[5] and the respective bis(β -diketiminate)s grant access to both, mono-^[6] and polynuclear complexes,^[7] not only depending on the respective element and the experimental protocol, but also on the ligand framework. In this regard, three types of bis(β -diketimine)s have to be considered: (i) nitrogen-bridged, (ii) backbone-bridged, and (iii) macrocyclic derivatives (Figure 1b).

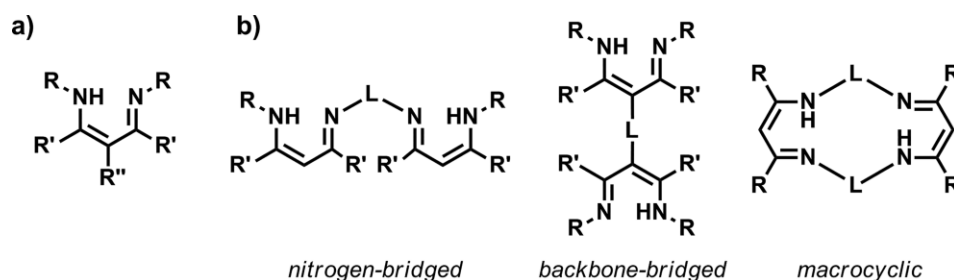


Figure 1. (a) β -diketimines and (b) various types of bis(β -diketimine)s.

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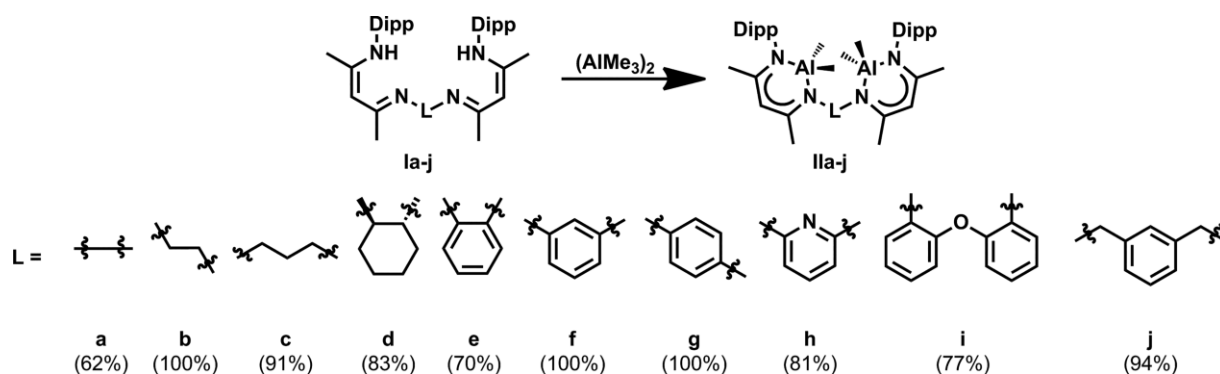
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The steric constraints of the ligand impact both, the element-element separation and the relative orientation of the two elemental centers. These aspects are very relevant in terms of cooperative catalysis, i.e. the concept of utilizing two or more catalytically active centers in one reaction system,^[8] which is one of the most promising concepts in catalysis by main-group elements as it allows promoting chemical transformations that hitherto have been believed to be limited to transition metals. In their seminal work, Normand et al. could prove that a dinuclear aluminum complex excels its mononuclear counterpart in terms of activation free energy giving rise to a 5-to-10 fold increase in activity in the ring-opening polymerization (ROP) of racemic lactide.^[9] Although in the following years various dinuclear aluminum(III) complexes have been probed as cooperative catalysts, mostly in the ROP of lactide,^[10] systematic



Scheme 1. Syntheses of dinuclear organoaluminum complexes **II** starting from bis(β -diketimine)s **I** with different linker (**L**) groups. Dipp = 2,6-diisopropylphenyl.

studies that investigate the role of the bridging unit and hence the metal-metal distance with respect to activity and selectivity are still missing to the best of our knowledge. Hence, the synthesis and structural characterization of a whole set of dinuclear aluminum alkyl complexes is worthy of pursuit as they are suitable pre-catalyst for example in the ROP of cyclic esters.^[11]

Herein we report the synthesis of a library of ten dinuclear aluminum complexes (**II**) based on bis(β -diketimine) ligands (**I**), Scheme 1, and their structural characterization. We choose the β -diketimine framework as the related mononuclear aluminum complexes have been shown to be active catalysts in polymerization reactions^[12] or hydroboration reactions.^[13]

Results and Discussion

The protio-ligands **Ia–j** were synthesized by alkylation of 2-(2,6-diisopropylphenyl)imido-2-penten-4-one using Meerwein's salt ($[\text{O}(\text{C}_2\text{H}_5)_3][\text{BF}_4]$) followed by condensation with various primary diamines as described before.^[6b,6e,7b,7i,7j] The protio-ligands were subsequently converted into the respective dinuclear dimethylaluminum complexes **IIa–j** using trimethylaluminum, Scheme 1. All compounds were isolated in good to quantitative yields using a simple work-up procedure and were obtained as (pale) yellow (**IIa,b,c,e,g,h,i,j**), brown (**IIf**) or colorless (**IId**) powders. The species **IIa–j** were found to be thermally stable and melt without decomposition with values in between 162 °C and 296 °C; notably, melting points above 200 °C were only found for bis(β -diketimine)s containing aryl linker.

Except for **IId**, **IIe**, and **IIIi**, common features observed in the respective ^1H NMR spectra include one singlet for the aluminum methyl groups and one septet for the methine groups (Figure 2) consistent with a symmetrical substitution pattern at aluminum. Notably, for **IIIf** only one doublet ($\delta = 1.29$ ppm) corresponding to the methyl protons of the isopropyl groups is observed, indicating a lower barrier of rotation about the C–N bond. In case of **IIId** and **IIe**, respectively, the ^1H NMR spectrum shows two separated groups of septets and more complex peaks for the respective isopropyl methine and methyl proton resonances of the isopropyl groups, indicating a hindered con-

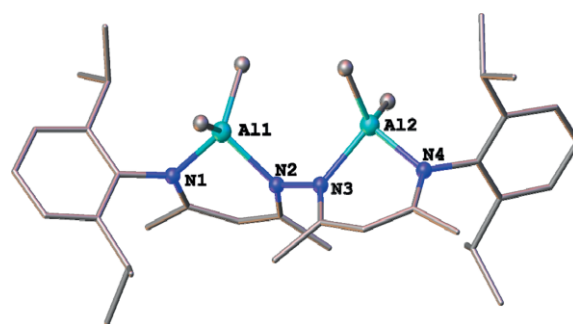


Figure 2. Solid state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths /Å and angles /° of **IIa**: Al1–Al2 3.8866(6), Al1–N1 1.917(1), Al1–N2 1.928(1), Al2–N3 1.929(1), Al2–N4 1.921(1), Al1–C18 1.965(1), Al1–C19 1.962(2), Al2–C25 1.967(2), Al2–C26 1.974(2), N2–N3 1.432(2), N1–Al1–N2 93.64(5), N3–Al2–N4 93.04(5), C18–Al1–C19 117.92(7), C25–Al2–C26 118.52(7).

formational flexibility of both binding sites. A similar pattern has also been observed for the thallium(I)^[7i] and copper(I)^[7j] derivatives of **IIId**.

For the thallium congener of **IIe**, however, a pattern comparable to that of the respective protio-ligand **Ie**, with one isopropyl methine septet and two methyl doublets was observed, demonstrating a symmetric or averaged structure in solution. This difference most likely arises from the increased steric demands of the $\text{Al}(\text{CH}_3)_2$ group in comparison with the “naked” Tl^{I} center bearing a diffuse s-type lone pair of electrons. This argument might also account for the difference in the ^1H NMR spectrum of **IIIi** in comparison to the respective thallium derivative. While for the latter, conformational flexibility has been evidenced, two distinct peaks corresponding to the $\text{Al}(\text{CH}_3)_2$ groups are observed at -0.77 and -1.18 ppm, respectively, and the signals associated with the Dipp methyl and methine group appear as four doublets and two septets, respectively. Variable-temperature ^1H NMR experiments have been conducted in the temperature range of 223–298 K (**IIa–c**, **f**, **g**, **j**) and 223–334 K (**IIId**, **e**, **h**) (Figures S1–S11, Supporting Information) in order to derive information about the rotational dynamics of the complex. Across the investigated temperature range, only a minor dependence of the chemical shifts on temperature were

observed and the absence of a coalescence point indicates small rotational barriers in case of **IIa–c, f, and j**, while the rotation has a significantly higher activation barrier for the species **II d, e, and h**. In case of **II g**, coalescence could be observed between 223 and 233 K but due to the overlap of two singlets we could not extract the relevant data. In addition, ^{27}Al -NMR resonances are only observed in case of **II b, II c, II d, II h, and II j** as broad signals with values in between 150.5 and 154.3 ppm. The IR spectra show characteristic bands associated with C–H stretching in the region between 2800 and 3100 cm^{-1} as well as C–N stretches of the ligand framework between 1500 and 1550 cm^{-1} .

Besides the behavior in solution, we became interested in the solid-state structures of the dinuclear complexes and crystals of **II a, II b, II c, II e, and II i** were grown from toluene solutions at room temperature; their molecular structures are depicted in Figure 2, Figure 3, and Figure 4. All structures feature two distorted tetrahedral aluminum centers that are projected out of the plane of each NacNac unit; the smallest and largest deviation from the least-squares N–C–C–N plane amount to 0.235(1) Å and 0.831(1) Å for **II i** and **II d**, respectively. The N–Al–N bite angles with values between 93.04(5)° and 95.23(4)° are in the range regularly observed for mononuclear alkylaluminum β -diketiminato complexes.^[12,13] The same holds true for the Al–C bond lengths [1.958(1)–1.975(2) Å] and the C–Al–C bond angles [113.22(5)–118.52(7)°] of the $\text{Al}(\text{CH}_3)_2$ group, whose values are comparable to those observed for the mononuclear counterparts.

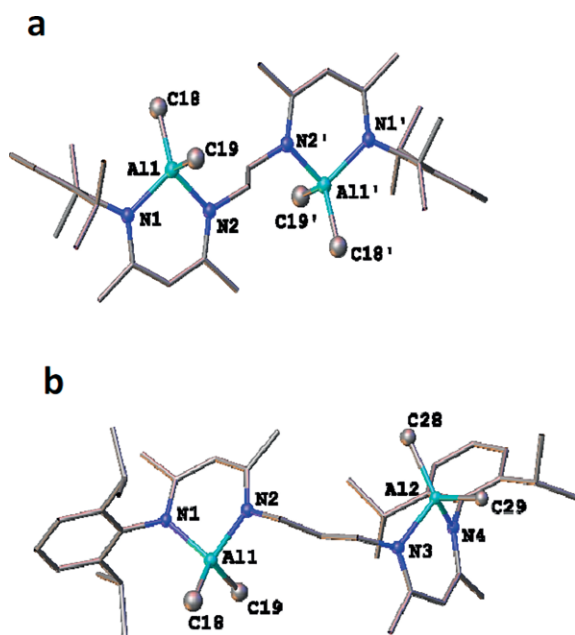


Figure 3. Solid state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths /Å and angles /° of (a) **II b**: Al1–Al1' 6.482(1), Al1–N1 1.918(1), Al1–N2 1.907(1), Al1–C18 1.969(2), Al1–C19 1.975(2), N1–Al1–N2 96.71(6), C18–Al1–C19 113.96(9); (b) **II c**: Al1–Al2 7.3823(4), Al1–N1 1.904(1), Al1–N2 1.915(1), Al2–N3 1.912(1), Al2–N4 1.911(1), Al1–C18 1.963(2), Al1–C19 1.974(2), Al2–C28 1.968(1), Al2–C29 1.967(1), N1–Al1–N2 95.02(5), N3–Al2–N4 94.22(4), C18–Al1–C19 116.53(8), C28–Al2–C29 117.85(6).

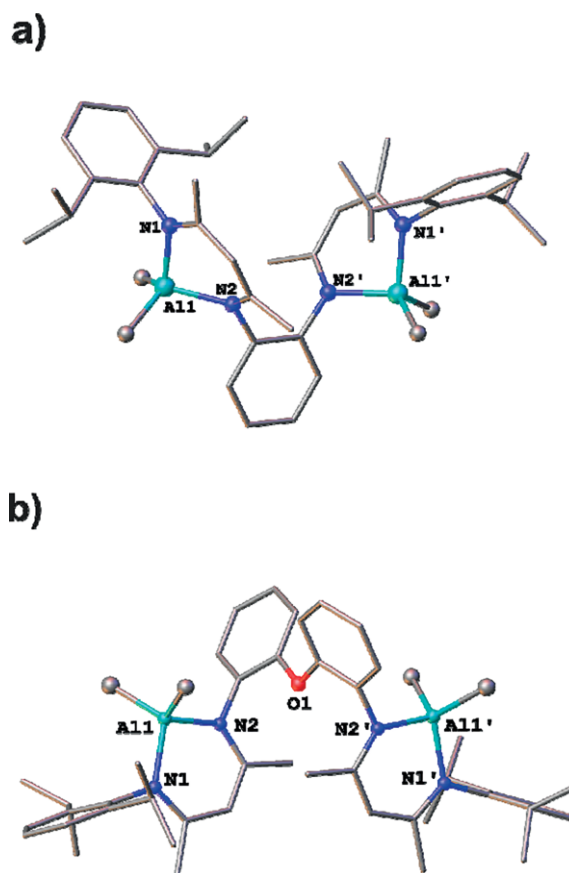


Figure 4. Solid state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths /Å and angles /° of (a) **II e**: Al1–Al1' 6.4023(8), Al1–N1 1.923(1), Al1–N2 1.927(1), Al1–C18 1.958(1), Al1–C19 1.973(1), N1–Al1–N2 95.14(4), C18–Al1–C19 115.14(6); (b) **II i**: Al1–Al1' 7.396(1), Al1–N1 1.930(1), Al1–N2 1.9193(9), Al1–C18 1.970(1), Al1–C19 1.967(1), N1–Al1–N2 95.23(4), C18–Al1–C19 113.22(5).

It is obvious that the Al–Al separations increase in the order **II a** [3.8866(6) Å] < **II e** [6.4023(8) Å] < **II b** [6.482(1) Å] < **II c** [7.3823(4) Å] < **II i** [7.396(1) Å] as a result of the length and the rigidity of the bridging unit. The molecular structures also rationalize the respective ^1H resonance pattern observed in solution. For **II a**, rotation about the N1–N2 is cancelled out due to the repulsion of the backbone CH_3 groups. In contrast, the alkyl bridges of **II b** and **II c** warrant conformational flexibility in agreement with chemically and magnetically equivalent binding sites in solution. For **II e** and **II i**, rotation about the N2–C_{bridge} bond becomes more restricted, which readily explains the diverse pattern of resonance in the ^1H NMR spectrum.

Conclusions

In summary, the synthesis of ten dinuclear methylaluminum complexes based on bis(β -diketiminato) ligands with various alkylene and (hetero)arylene bridges is reported. The molecular structures of five compounds have been elucidated by X-ray diffraction techniques. In future experiment, we will in-

investigate the impact of the metal-metal separation and the flexibility of the bridging unit on the catalytic performance in various reactions such as the ring-opening polymerization of cyclic esters or the hydroboration of unsaturated compounds.

Experimental Section

General Considerations: All preparations were performed under an inert atmosphere of dinitrogen by means of Standard Schlenk-line or glovebox techniques (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3–11 (CuO/MgSiO₃) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P₄O₁₀. Dichloromethane was freshly collected from a Solvent Purification System by M. Braun (MB SPS-800). Toluene was used as p.a. grade and distilled from Na/benzophenone prior to use. CDCl₃ was dried by distillation from calcium hydride. Trimethylaluminum (2 M in Toluene) was purchased from Sigma Aldrich.

Characterization: The NMR spectra were recorded with a Bruker Avance 400 spectrometer (*T* = 300 K) with δ referenced to external tetramethylsilane (¹H, ¹³C and ²⁷Al). ¹H and ¹³C NMR spectra were calibrated by using the solvent residual peak (CHCl₃: δ (¹H) = 7.26) and the solvent peak [CDCl₃: δ (¹³C) = 77.16], respectively. ²⁷Al NMR spectra were calibrated relative to external Al(NO₃)₃·9H₂O. IR spectra were recorded with a Bruker ALPHA spectrometer equipped with a diamond ATR unit **Ib–j** and a Thermo Scientific Nicolet iS5 spectrometer with an ATR-coated diamond crystal **1e** and **IIa**. Elemental analysis was performed with a Vario MICRO cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules was verified by ¹H NMR spectroscopy. Melting points were determined in sealed capillaries with an Apotec melting point apparatus.

Ligand Synthesis: 4-((2,6-Diisopropylphenyl)amino)pent-3-en-2-one,^[6b] triethyloxonium tetrafluoroborate^[14] and the bis(β -diketimine)s **Ia–d**, and **If–j**^[6b,6c,7b,7i,7j] were prepared according to published procedures.

1e: A solution of [Et₃O]⁺[BF₄][−] (14.26 g, 75.0 mmol) in CH₂Cl₂ (40 mL) was added to a solution of 4-((2,6-diisopropylphenyl)amino)pent-3-en-2-one (19.46 g, 75.0 mmol) in CH₂Cl₂ (70 mL) at 0 °C. The orange reaction mixture was stirred for 19 h at room temperature and then Et₃N (7.59 g, 75.0 mmol) was added. After 30 min a solution of *o*-phenylenediamine (4.06 g, 37.5 mmol) in Et₃N (24 g) was added to the mixture. After stirring at room temperature for 1 d all volatiles were removed in vacuo. Toluene (80 mL) was added to extract the product from the oily precipitate of [Et₃NH]⁺[BF₄][−]. Toluene was removed from the extract and the crude product was dissolved in ethanol (3 mL). A yellow solid was obtained. Drying in vacuo gave 10.04 g (45%) of the product. ¹H NMR: (400 MHz, CDCl₃): δ = 1.12 [d, 12 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.21 [d, 12 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.67 [s, 6 H, CMe], 1.83 [s, 6 H, CMe], 3.06 [sept, 4 H, ³J_{HH} = 6.8 Hz, CHMe₂], 4.82 [s, 2 H, CH], 6.87–6.90 [m, 2 H, ArH], 7.00–7.03 [m, 2 H, ArH], 7.14 [br, 6 H, ArH], 12.12 ppm [s, 2 H, NH]. ¹³C{¹H} NMR: (101 MHz, CDCl₃): δ = 20.9 [CMe], 23.0 [CMe], 24.5 [CHMe₂], 28.4 [CHMe₂], 95.3 [β -CH], 123.1 [*m*-C(Dipp)], 124.3 [C(Aryl)], 125.0 [*p*-C(Dipp)], 125.2 [C(Aryl)], 139.6 [*o*-C(Dipp)], 141.0 [*ipso*-C(Dipp)], 142.6 [C(Aryl)], 160.5 [CN], 160.8 ppm [CN]. IR (ATR): $\tilde{\nu}$ = 3066, 2958, 2923, 1622, 1542, 1501, 1439, 1361, 1255, 1175, 1103, 1022, 930, 789, 756, 701 cm^{−1}. Elemental analysis calcd. (found) C₄₀H₅₄N₄: C 81.31 (81.47), H 9.21 (8.97), N 9.48 (9.34). M.p. 135 °C.

General Procedure for the Synthesis Employing Trimethylaluminum: Trimethylaluminum (2.8 mL, 5.5 mmol, 2 M in Toluene) was added dropwise to a solution of the respective bis(β -diketimine) (2.5 mmol) in Toluene (20 mL). The reaction solution was stirred for 16 h at 90 °C. The volatile substances were removed in vacuo and the residue was washed with pentane (3 × 10 mL). The residue was then extracted with toluene (20 mL) and the concentration of the filtered extract yielded the products. **IIc** has already reported in the literature.^[15]

Colorless crystals suitable for an X-ray diffraction analysis were obtained from concentrated toluene solutions of **IIa**, **IIb**, **IIc**, **IIe**, and **IIi** at room temperature.

IIa: Pale yellow powder, 0.97 g (62%). ¹H NMR: (400 MHz, CDCl₃): δ = −0.97 [s, 6 H, AlMe₂], −0.73 [s, 6 H, AlMe₂], 1.08 [d, 6 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.17–1.21 [m, 18 H, CHMe₂], 1.75 [s, 6 H, CMe], 2.06 [s, 6 H, CMe], 3.05 [sept, 2 H, ³J_{HH} = 6.8 Hz, CHMe₂], 3.19 [sept, 2 H, ³J_{HH} = 6.8 Hz, CHMe₂], 4.95 [s, 2 H, CH], 7.13–7.15 [m, 2 H, ArH], 7.18–7.20 [m, 2 H, ArH], 7.22–7.27 ppm [m, 2 H, ArH]. ¹³C{¹H} NMR: (101 MHz, CDCl₃): δ = −11.2 [AlMe₂], −8.6 [AlMe₂], 21.3 [CMe], 23.7 [CMe], 24.3 [CHMe₂], 24.6 [CHMe₂], 24.9 [CHMe₂], 25.9 [CHMe₂], 27.7 [CHMe₂], 28.0 [CHMe₂], 94.9 [β -CH], 124.1 [*m*-C(Dipp)], 124.3 [*m*-C(Dipp)], 126.7 [*p*-C(Dipp)], 140.8 [*o*-C(Dipp)], 143.6 [*o*-C(Dipp)], 144.8 [*ipso*-C(Dipp)], 168.0 [CN], 169.3 ppm [CN]. IR (ATR): $\tilde{\nu}$ = 2964, 2926, 2868, 1524, 1443, 1357, 1318, 1254, 1184, 1104, 1020, 925, 800, 764, 731, 676 cm^{−1}. Elemental analysis calcd. (found) C₃₈H₆₀Al₂N₄·0.2C₇H₈: C 73.33 (73.47), H 9.62 (9.79), N 8.68 (8.57). M.p. 201 °C.

IIb: Yellow powder, 1.64 g (100%). ¹H NMR: (400 MHz, CDCl₃): δ = −0.94 [s, 12 H, AlMe₂], 1.12 [d, 12 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.18 [d, 12 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.68 [s, 6 H, CMe], 2.16 [s, 6 H, CMe], 3.01 [sept, 4 H, ³J_{HH} = 6.8 Hz, CHMe₂], 3.43 [s, 4 H, CH₂], 4.97 [s, 2 H, CH], 7.13–7.15 [m, 4 H, ArH], 7.19–7.23 ppm [m, 2 H, ArH]. ¹³C{¹H} NMR: (101 MHz, CDCl₃): δ = −10.5 [AlMe₂], 21.7 [CMe], 23.3 [CMe], 24.6 [CHMe₂], 24.9 [CHMe₂], 27.9 [CHMe₂], 48.1 [CH₂], 98.3 [β -CH], 123.9 [*m*-C(Dipp)], 126.4 [*p*-C(Dipp)], 140.9 [*o*-C(Dipp)], 144.2 [*ipso*-C(Dipp)], 168.3 [CN], 168.9 ppm [CN]. ²⁷Al{¹H} NMR: (104 MHz, CDCl₃): δ = 154.0 ppm [AlMe₂]. IR (ATR): $\tilde{\nu}$ = 2963, 2925, 2869, 1552, 1522, 1441, 1380, 1312, 1294, 1261, 1184, 1098, 1014, 871, 798, 760, 668, 576 cm^{−1}. Elemental analysis calcd. (found) C₄₀H₆₄Al₂N₄: C 73.36 (73.25), H 9.85 (9.48), N 8.55 (8.36). M.p. 199 °C.

IIc: Pale yellow powder, 1.53 g (91%). The analytic data are in agreement with published data.^[15] ¹H NMR: (400 MHz, CDCl₃): δ = −0.98 [s, 12 H, AlMe₂], 1.12 [d, 12 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.16 [d, 12 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.66 [s, 6 H, CMe], 1.73–1.81 [m, 2 H, CH₂], 2.09 [s, 6 H, CMe], 3.01 [sept, 4 H, ³J_{HH} = 6.8 Hz, CHMe₂], 3.33 [t, 4 H, ³J_{HH} = 8.1 Hz, CH₂], 4.94 [s, 2 H, CH], 7.11–7.13 [m, 4 H, ArH], 7.18–7.21 ppm [m, 2 H, ArH]. ¹³C{¹H} NMR: (101 MHz, CDCl₃): δ = −10.8 [AlMe₂], 20.8 [CMe], 23.3 [CMe], 24.5 [CHMe₂], 24.9 [CHMe₂], 27.9 [CHMe₂], 32.7 [CH₂], 45.5 [CH₂], 98.0 [β -CH], 123.9 [*m*-C(Dipp)], 126.3 [*p*-C(Dipp)], 141.1 [*o*-C(Dipp)], 144.4 [*ipso*-C(Dipp)], 167.8 [CN], 168.3 ppm [CN]. ²⁷Al{¹H} NMR: (104 MHz, CDCl₃): δ = 152.5 ppm [AlMe₂]. IR (ATR): $\tilde{\nu}$ = 2961, 2927, 2868, 1559, 1515, 1399, 1355, 1317, 1253, 1186, 1094, 1016, 800, 754, 670, 574 cm^{−1}. Elemental analysis calcd. (found) C₄₁H₆₆Al₂N₄: C 73.61 (73.42), H 9.94 (9.56), N 8.38 (8.07). M.p. 195 °C.

IIId: Colorless powder, 1.47 g (83%). ¹H NMR: (400 MHz, CDCl₃): δ = −0.85 [s, 6 H, AlMe₂], 0.82 [s, 6 H, AlMe₂], 1.04 [d, 6 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.15 [d, 6 H, ³J_{HH} = 6.8 Hz, CHMe₂], 1.17 [d, 6 H,

$^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 1.19 [d, 6 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 1.30 [br, 2 H, ring- CH_2], 1.58 [br, 2 H, ring- CH_2], 1.66 [s, 6 H, CMe], 1.72 [br, 4 H, ring- CH_2], 2.24 [s, 6 H, CMe], 2.84 [sept, 2 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 3.23 [sept, 2 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 4.24 [br, 2 H, ring- CH], 5.05 [s, 2 H, CH], 7.09–7.11 [m, 2 H, ArH], 7.15–7.23 ppm [m, 4 H, ArH]. $^{13}\text{C}\{^1\text{H}\}$ NMR: (101 MHz, CDCl_3): $\delta = -9.8$ [AlMe_2], -6.7 [AlMe_2], 23.4 [CMe], 24.2 [CMe], 24.3 [CHMe_2], 24.7 [CHMe_2], 25.4 [ring- CH_2], 25.5 [CHMe_2], 27.8 [CHMe_2], 27.9 [CHMe_2], 35.5 [ring- CH_2], 62.0 [ring- CH], 100.1 [β -CH], 123.6 [m -C(Dipp)], 123.7 [m -C(Dipp)], 126.1 [p -C(Dipp)], 141.7 [o -C(Dipp)], 144.1 [o -C(Dipp)], 145.1 [$ipso$ -C(Dipp)], 166.9 [CN], 168.7 ppm [CN]. $^{27}\text{Al}\{^1\text{H}\}$ NMR: (104 MHz, CDCl_3): $\delta = 153.9$ ppm [AlMe_2]. IR (ATR): $\tilde{\nu} = 2965$, 2926, 2868, 1546, 1526, 1459, 1382, 1316, 1251, 1189, 1091, 1021, 949, 800, 763, 673, 572 cm^{-1} . Elemental analysis calcd. (found) $\text{C}_{44}\text{H}_{70}\text{Al}_2\text{N}_4$: C 74.54 (74.17), H 9.95 (10.16), N 7.90 (7.64). M.p. 217 °C.

IIe: Pale yellow powder, 1.23 g (70%). ^1H NMR: (400 MHz, CDCl_3): $\delta = -1.17$ [s, 6 H, AlMe_2], -0.81 [s, 6 H, AlMe_2], 1.14–1.23 [m, 24 H, CHMe_2], 1.76 [s, 6 H, CMe], 1.88 [s, 6 H, CMe], 2.98 [sept, 2 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 3.25 [sept, 2 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 5.21 [s, 2 H, CH], 6.87–6.93 [m, 2 H, ArH], 7.11–7.22 ppm [m, 8 H, ArH]. $^{13}\text{C}\{^1\text{H}\}$ NMR: (101 MHz, CDCl_3): $\delta = -10.0$ [AlMe_2], -9.6 [AlMe_2], 23.7 [CMe], 24.6 [CMe], 24.6 [CHMe_2], 24.7 [CHMe_2], 25.4 [CHMe_2], 25.5 [CHMe_2], 27.9 [CHMe_2], 28.1 [CHMe_2], 99.2 [β -CH], 124.0 [m -C(Dipp)], 124.0 [m -C(Dipp)], 126.5 [$\text{C}(\text{Aryl})$], 127.0 [p -C(Dipp)], 128.7 [$\text{C}(\text{Aryl})$], 141.2 [o -C(Dipp)], 143.2 [o -C(Dipp)], 144.0 [$ipso$ -C(Dipp)], 144.7 [$\text{C}(\text{Aryl})$], 169.2 [CN], 169.8 ppm [CN]. IR (ATR): $\tilde{\nu} = 2962$, 2923, 1542, 1521, 1448, 1364, 1318, 1185, 1109, 1042, 1021, 869, 802, 763, 750, 673, 583, 482, 440 cm^{-1} . Elemental analysis calcd. (found) $\text{C}_{44}\text{H}_{64}\text{Al}_2\text{N}_4$: C 75.18 (74.19), H 9.18 (8.73), N 7.97 (7.95) + silicon grease, shown in the NMR. M.p. 296 °C.

IIf: Pale brown powder, 1.76 g (100%). ^1H NMR: (400 MHz, CDCl_3): $\delta = -0.94$ [s, 12 H, AlMe_2], 1.28 [d, 24 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 1.87 [s, 6 H, CMe], 2.00 [s, 6 H, CMe], 3.19 [sept, 4 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 5.26 [s, 2 H, CH], 6.69 [t, 1 H, $^3J_{\text{HH}} = 2.0$ Hz, ArH], 6.92 [d, 1 H, $^3J_{\text{HH}} = 2.0$ Hz, ArH], 6.94 [d, 1 H, $^3J_{\text{HH}} = 2.0$ Hz, ArH], 7.24–7.25 [m, 4 H, ArH], 7.29–7.35 ppm [m, 2 H, ArH]. $^{13}\text{C}\{^1\text{H}\}$ NMR: (101 MHz, CDCl_3): $\delta = -10.9$ [AlMe_2], 23.0 [CMe], 23.5 [CMe], 24.5 [CHMe_2], 24.8 [CHMe_2], 28.0 [CHMe_2], 98.5 [β -CH], 122.9 [m -C(Dipp)], 123.2 [m -C(Dipp)], 124.0 [$\text{C}(\text{Aryl})$], 126.5 [p -C(Dipp)], 129.8 [$\text{C}(\text{Aryl})$], 141.0 [o -C(Dipp)], 144.1 [$ipso$ -C(Dipp)], 147.0 [$\text{C}(\text{Aryl})$], 167.1 [CN], 169.6 ppm [CN]. IR (ATR): $\tilde{\nu} = 2962$, 2928, 2868, 1551, 1521, 1441, 1376, 1317, 1252, 1185, 1106, 1018, 899, 798, 757, 674, 578, 443 cm^{-1} . Elemental analysis calcd. (found) $\text{C}_{44}\text{H}_{64}\text{Al}_2\text{N}_4$: C 75.18 (75.15), H 9.18 (9.12), N 7.97 (7.78). M.p. 199 °C.

IIg: Pale yellow powder, 1.76 g (100%). ^1H NMR: (400 MHz, CDCl_3): $\delta = -1.06$ [s, 12 H, AlMe_2], 1.17 [d, 12 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 1.18 [d, 12 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 1.76 [s, 6 H, CMe], 1.91 [s, 6 H, CMe], 3.08 [sept, 4 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 5.15 [s, 2 H, CH], 6.94 [s, 4 H, ArH], 7.13–7.15 [m, 4 H, ArH], 7.19–7.23 ppm [m, 2 H, ArH]. $^{13}\text{C}\{^1\text{H}\}$ NMR: (101 MHz, CDCl_3): $\delta = -11.2$ [AlMe_2], 22.8 [CMe], 23.4 [CMe], 24.4 [CHMe_2], 24.7 [CHMe_2], 27.9 [CHMe_2], 98.3 [β -CH], 123.8 [m -C(Dipp)], 126.2 [$\text{C}(\text{Aryl})$], 126.3 [p -C(Dipp)], 140.9 [o -C(Dipp)], 143.2 [$ipso$ -C(Dipp)], 144.0 [$\text{C}(\text{Aryl})$], 167.1 [CN], 169.2 ppm [CN]. IR (ATR): $\tilde{\nu} = 2964$, 2927, 2866, 1552, 1526, 1491, 1440, 1380, 1316, 1258, 1180, 1016, 893, 800, 759, 673, 577, 445 cm^{-1} . Elemental analysis calcd. (found) $\text{C}_{44}\text{H}_{64}\text{Al}_2\text{N}_4$: C 75.18 (75.20), H 9.18 (8.91), N 7.97 (7.74). M.p. 279 °C.

IIh: Pale yellow powder, 1.43 g (81%). ^1H NMR: (400 MHz, CDCl_3): $\delta = -0.87$ [s, 12 H, AlMe_2], 1.25 [$^{\text{u}}$], 24 H, $^3J_{\text{HH}} = 6.5$, $^3J_{\text{HH}} = 6.6$ Hz,

CHMe_2], 1.89 [s, 6 H, CMe], 2.22 [s, 6 H, CMe], 3.15 [sept, 4 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 5.33 [s, 2 H, CH], 6.82 [d, 2 H, $^3J_{\text{HH}} = 7.8$ Hz, ArH], 7.24–7.26 [m, 4 H, ArH], 7.30–7.35 [m, 2 H, ArH], 7.69 ppm [t, 1 H, $^3J_{\text{HH}} = 7.8$ Hz, ArH]. $^{13}\text{C}\{^1\text{H}\}$ NMR: (101 MHz, CDCl_3): $\delta = -11.6$ [AlMe_2], 22.5 [CMe], 22.6 [CMe], 23.5 [CHMe_2], 23.7 [CHMe_2], 27.0 [CHMe_2], 99.4 [β -CH], 113.8 [$\text{C}(\text{Aryl})$], 123.0 [m -C(Dipp)], 125.6 [p -C(Dipp)], 137.7 [$\text{C}(\text{Aryl})$], 140.1 [o -C(Dipp)], 142.7 [$ipso$ -C(Dipp)], 156.6 [$\text{C}(\text{Aryl})$], 165.0 [CN], 169.7 ppm [CN]. $^{27}\text{Al}\{^1\text{H}\}$ NMR: (104 MHz, CDCl_3): $\delta = 154.3$ ppm [AlMe_2]. IR (ATR): $\tilde{\nu} = 2966$, 2927, 2868, 1549, 1530, 1447, 1430, 1370, 1317, 1257, 1179, 1108, 1019, 934, 797, 759, 671, 583, 467 cm^{-1} . Elemental analysis calcd. (found) $\text{C}_{43}\text{H}_{63}\text{Al}_2\text{N}_5$: C 73.37 (73.27), H 9.02 (8.99), N 9.95 (9.66). M.p. 197 °C.

IIi: Pale yellow powder, 1.54 g (77%). ^1H NMR: (400 MHz, CDCl_3): $\delta = -1.18$ [s, 6 H, AlMe_2], -0.77 [s, 6 H, AlMe_2], 0.77 [d, 6 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 0.89 [d, 6 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 1.20 [d, 6 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2], 1.22 [d, 6 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2], 1.73 [s, 6 H, CMe], 2.00 [s, 6 H, CMe], 2.86 [sept, 2 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 3.15 [sept, 2 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 5.17 [s, 2 H, CH], 6.81–6.83 [m, 2 H, ArH], 7.05–7.21 ppm [m, 12 H, ArH]. $^{13}\text{C}\{^1\text{H}\}$ NMR: (101 MHz, CDCl_3): $\delta = -11.2$ [AlMe_2], -8.9 [AlMe_2], 23.2 [CMe], 23.5 [CMe], 24.3 [CHMe_2], 24.7 [CHMe_2], 24.9 [CHMe_2], 25.7 [CHMe_2], 27.8 [CHMe_2], 27.8 [CHMe_2], 97.8 [β -CH], 120.0 [$\text{C}(\text{Aryl})$], 123.8 [m -C(Dipp)], 124.1 [m -C(Dipp)], 126.6 [p -C(Dipp)], 126.9 [$\text{C}(\text{Aryl})$], 127.3 [$\text{C}(\text{Aryl})$], 137.0 [$\text{C}(\text{Aryl})$], 140.6 [$\text{C}(\text{Aryl})$], 143.9 [o -C(Dipp)], 144.3 [$ipso$ -C(Dipp)], 151.5 [$\text{C}(\text{Aryl})$], 169.3 [CN], 169.8 ppm [CN]. IR (ATR): $\tilde{\nu} = 3062$, 2965, 2934, 2925, 2866, 1551, 1530, 1486, 1439, 1389, 1317, 1260, 1178, 1108, 1019, 796, 758, 671, 586, 467 cm^{-1} . Elemental analysis calcd. (found) $\text{C}_{50}\text{H}_{68}\text{Al}_2\text{N}_4\text{O}$: C 75.53 (75.43), H 8.62 (8.63), N 7.05 (7.00). M.p. 267 °C.

IIj: Yellow powder, 1.72 g (94%). ^1H NMR: (400 MHz, CDCl_3): $\delta = -1.03$ [s, 12 H, AlMe_2], 1.14 [d, 24 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2], 1.70 [s, 6 H, CMe], 2.00 [s, 6 H, CMe], 3.09 [sept, 4 H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2], 4.58 [s, 4 H, CH_2], 4.99 [s, 2 H, CH], 7.07–7.14 [m, 7 H, ArH], 7.18–7.21 [m, 2 H, ArH], 7.24–7.28 ppm [m, 1 H, ArH]. $^{13}\text{C}\{^1\text{H}\}$ NMR: (101 MHz, CDCl_3): $\delta = -10.8$ [AlMe_2], 22.0 [CMe], 23.4 [CMe], 24.7 [CHMe_2], 24.9 [CHMe_2], 27.9 [CHMe_2], 50.9 [CH_2], 98.0 [β -CH], 123.9 [m -C(Dipp)], 125.0 [m -C(Dipp)], 125.5 [$\text{C}(\text{Aryl})$], 126.4 [p -C(Dipp)], 128.9 [$\text{C}(\text{Aryl})$], 140.0 [o -C(Dipp)], 141.0 [$ipso$ -C(Dipp)], 144.3 [$\text{C}(\text{Aryl})$], 168.6 [CN], 170.0 ppm [CN]. $^{27}\text{Al}\{^1\text{H}\}$ NMR: (104 MHz, CDCl_3): $\delta = 150.5$ ppm [AlMe_2]. IR (ATR): $\tilde{\nu} = 2962$, 2928, 2868, 1555, 1520, 1466, 1439, 1389, 1319, 1258, 1184, 1099, 1015, 800, 763, 672, 441 cm^{-1} . Elemental analysis calcd. (found) $\text{C}_{46}\text{H}_{68}\text{Al}_2\text{N}_4$: C 75.58 (75.72), H 9.38 (9.50), N 7.66 (7.59). M.p. 162 °C.

Supporting Information (see footnote on the first page of this article): Crystallographic details, NMR and IR spectra are found in the SI.

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