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Article

Synthesis, Characterization, and Reactivity of Aluminum Alkyl/Amide Complexes Supported by Guanidinate and Monoanionic OCO-Pincer Ligands

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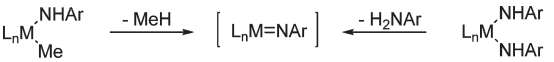
The synthesis and characterization of mixed alkyl/amide Al complexes supported by guanidinate and monoanionic OCO-pincer ligands are described. *In situ* generation of the lithium-guanidinate reagents via reaction of carbodiimides and lithium-amide reagents, followed by reaction with the corresponding $AlMe_xCl_{3-x}$ reagents, resulted in the formation of compounds **1**−**3**. Subsequent reaction with lithium arylamide reagents provided access to mixed alkyl/amide- and bis-amide-substituted complexes **4**−**6**, which were characterized by multinuclear NMR spectroscopy and elemental analysis. Single-crystal X-ray diffraction of compounds **5a** and **6a** confirmed the monomeric nature of these complexes and revealed the influence of the alkyl/amide functionalities on the bonding of the guanidinate ligands. A similar synthetic approach resulted in isolation of an OCO-pincer-supported Al dialkyl complex, which was also fully characterized. In contrast to the guanidinate compounds, complex **8** showed activity toward intramolecular hydroamination of 2,2-diphenylpent-4-en-1-amine.

Introduction

Alkyl- and amide-substituted transition metals show remarkably rich chemistry, ranging from traditional organometallic catalysis to more exotic applications such as precursors for materials chemistry.[1] Main group metals have shown interesting behavior themselves and thus received a comparable amount of attention. Not only can these ligands act as active sites on their own, but careful arrangement of these functional groups allows entry into imide chemistry via α-hydrogen elimination, a reaction pathway mainly observed for transition metals (eq 1).[2−6] Extensive applications of these complexes in organic transformations such as hydroamination catalysis have made metal imides desirable targets for organometallic chemists. Despite obvious similarities of main group metals with early transition metals (e.g., atom size, electronegativity), well-characterized main group 13 metal imides are scarce in the literature.[7,8]



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Although the alkyl/amide functionalities have a significant influence on the reactivity of the metal complex, the supporting ligands play an equally crucial role by providing the appropriate steric protection and electronic support for the metal center. Guanidinate anions have been used extensively in organometallic chemistry since their first appearance as supporting ligands for Zr-amide complexes in 1970 by Lappert et al.[9] Besides their similarity to the widely used cyclopentadienyl (Cp) ligand, the relative ease of steric and electronic tunability via variation of the N-substitution makes these molecules interesting targets for a variety of applications.[10−15] As a result, coordination chemistry involving transition, f-block, and main group metals enjoys extensive presence in the literature.[16−20] Starting in the late 1990s, guanidinate ligands coordinated to group 13 metals

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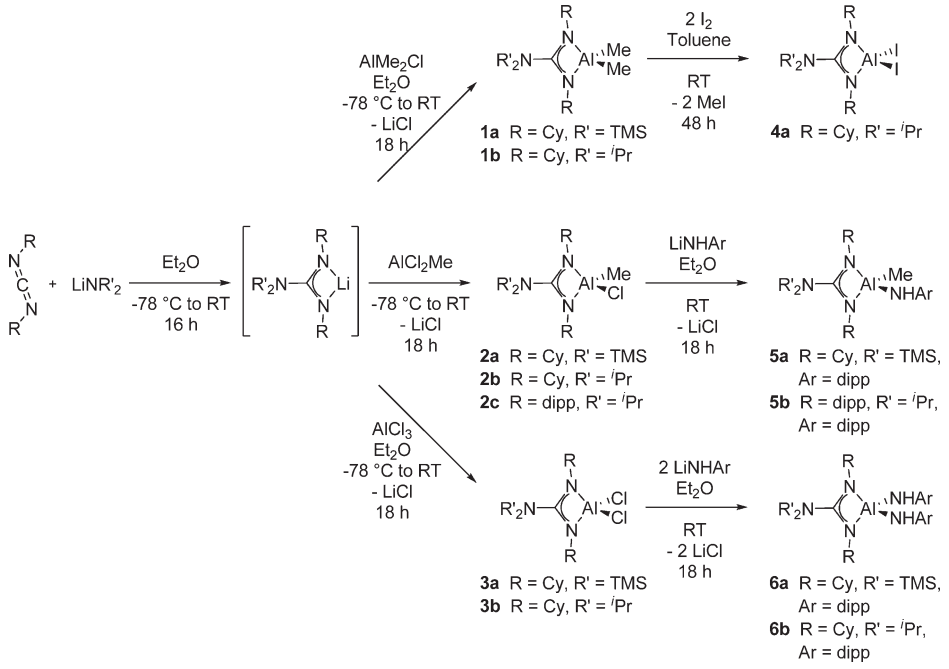
Scheme 1. Synthesis of Compounds 1−6



have received increased attention.[21−23] Similarly, pincer ligands are represented equally well due to their robust nature when coordinated to transition metals.[24,25] Extremely large catalytic turnover numbers and facile tunability of steric and electronic influences of the ligand on the metal center have made these ligands desirable especially in late transition metal catalysis.[26−28] Recent reports of pincer ligands coordinated to group 4 and 13 metals have tempted us to consider these compounds as viable ligands for Al chemistry.[29−31] Herein we would like to present our attempts to mimic the behavior of transition metal complexes such as [Cp*Zr(NHAr)(R)] and [Cp*Zr(NHAr)$_2$] in hydroamination catalysis with cheap and easily prepared group 13 metal complexes supported by a variety of guanidinate and monoanionic OCO-pincer ligands.

Results and Discussion

Synthesis of Aluminum Guanidinate Complexes. The guanidinate ligands were prepared via reaction of lithium-amide reagents with carbodiimides at −78 °C as described in the literature.[12,32,33] The resulting Li salts were not isolated but rather reacted *in situ* with the appropriate aluminum reagents ($AlMe_xCl_{3-x}$) in ethereal solutions at −78 °C (Scheme 1). Following the completion of the salt metathesis reactions by warming the solutions to room temperature and stirring overnight, compounds **1a**−**3b** were isolated as colorless crystalline solids after recrystallization from concentrated toluene, diethyl ether, or pentane solutions at −35 °C depending on their respective solubility characteristics. ^{1}H and ^{13}C NMR spectra of compounds **1a**−**3b** show the equivalence of the substituents on the guanidinate ligands and the equivalence of the alkyl functionalities in complexes **1a** and **1b**, thus suggesting monomeric Al species. The observed ^{13}C NMR resonances in the range 166.23−173.82 ppm are diagnostic for the central guanidinate C atom and further corroborate the structural assignment.

Roesky and co-workers previously reported that Al dialkyl complexes supported by diketiminate ligands can undergo substitution with I_2 under mild conditions to form the corresponding dihalide species.[34] The Al guanidinate complex **1b** shows similar reactivity under equally mild conditions. Upon stirring a toluene solution of **1b** at room temperature in the presence of I_2 for two days, the bis-iodo complex **4a** was isolated as a yellow crystalline solid. The mixed alkyl/amide complexes **5a** and **5b** were prepared as crystalline solids via reaction of compounds **2a** and **2c** with lithium arylamides at ambient temperature followed by

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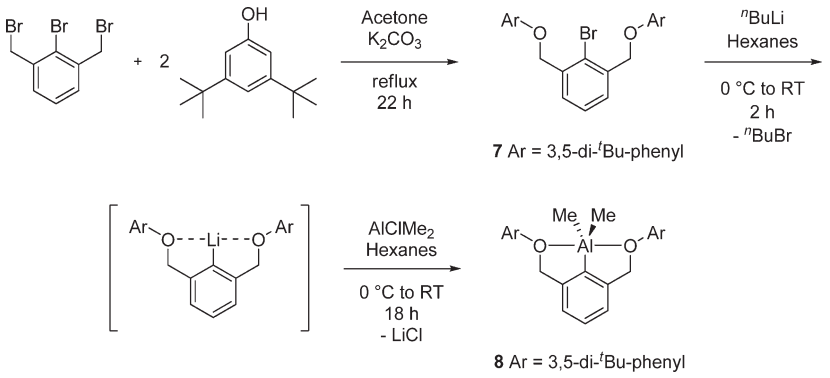
Scheme 2. Synthesis of Compound 8



recrystallization from pentane at −35 °C. Similarly, the bis-amide compounds were prepared by reaction of two equivalents of lithium arylamide with the dichloro-substituted complexes **3a** and **3b** at room temperature. Once again, recrystallization from pentane at −35 °C resulted in the isolation of **6a** and **6b** as colorless crystalline solids.

Synthesis of Aluminum Pincer Complexes. Synthesis of the pincer ligand precursor was achieved by refluxing a mixture of 2,6-bis(bromomethyl)bromobenzene and 3,5-di-*tert*-butylphenol in the presence of anhydrous potassium carbonate (Scheme 2). After workup and crystallization from hexanes, the ligand **7** (2,6-bis(3,5-^{t}Bu-phenoxymethyl)bromobenzene) was isolated on a 10 g scale in 61% yield as a microcrystalline colorless solid. Similar to the synthesis of the Al guanidinate complexes, the lithiated ligand was not isolated but generated *in situ* via activation of the C_{aryl}−Br bond with ^{n}BuLi followed by salt metathesis with $AlClMe_2$ in noncoordinating solvents. Compound **8** was isolated as a white microcrystalline solid in good yield. The ^{1}H and ^{13}C NMR spectra (at 25 °C) both display single resonances for the ^{t}Bu substituents as well as the Al-bound alkyl groups, suggesting a highly symmetric coordination environment around the Al metal center.

Solid-State Structures of Compounds 5a and 6a. To confirm the monomeric nature of the synthesized complexes, single crystals of compounds **5a** and **6a** were grown and their structure was determined via X-ray crystallography. Crystal data and structure refinement for these complexes can be found in Table S1 (Supporting Information). Unsurprisingly, the structural features of **5a** and **6a** are similar to those of previously reported Al complexes supported by guanidinate and closely related amidinate ligands.[23,35] Compound **5a** adopts a distorted tetrahedral coordination sphere, as shown in the ORTEP representation of **5a** (Figure 1). Selected bond lengths and angles for **5a** can be found in Table 1. The sterically demanding bis-trimethylsilyl substitution around N3 of the guanidinate backbone causes the amide functionality to adopt a position almost perpendicular to the metal−ligand plane (torsion angle 76.6°). This twist limits the electron overlap of the N3-based lone pair with the remaining guanidinate ligand, as evidenced by a comparatively long N3−C1 bond (1.402(2) Å). The Al1−C20 bond length (1.949(2) Å) of the Al-bound methyl moiety is within the expected range for Al alkyl complexes.[36,37] The steric

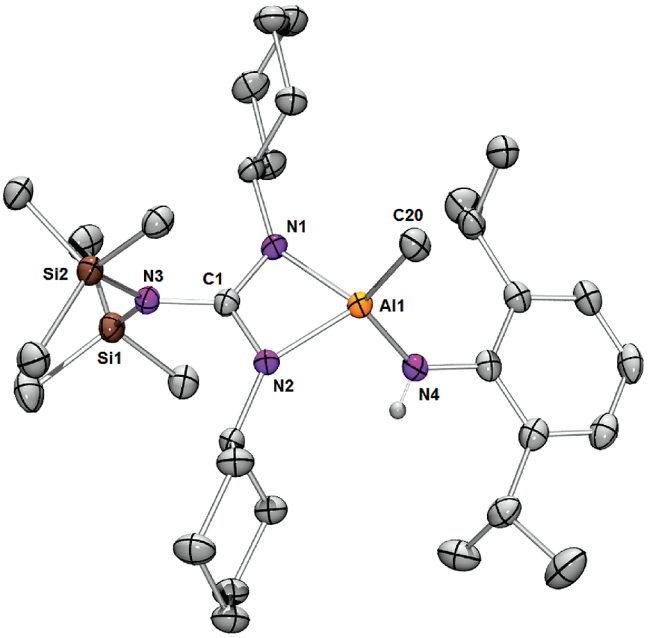


Figure 1. Thermal ellipsoid diagram of the molecular structure of **5a**. Thermal ellipsoids are drawn at 50% probability. H atoms (except H4) are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound 5a

Al1−N1	1.9296(16)	N1−Al1−N2	69.60(7)
Al1−N2	1.9172(16)	N1−C1−N2	109.91(16)
C1−N1	1.336(2)	N1−C1−N3	125.55(16)
C1−N2	1.345(2)	N2−C1−N3	124.54(16)
C1−N3	1.402(2)	C20−Al1−N4	117.61(9)
Al1−C20	1.949(2)		

demand of the 2,6-di-isopropylphenyl substituent on the metal-bound amide moiety slightly distorts the tetrahedral coordination environment around Al toward a square-planar arrangement. Consequently, the larger *trans* influence of the amide ligand is reflected in the elongated Al1−N1 bond (1.9296(16) Å) compared to the Al1−N2 bond (1.9172(16) Å). The noticeably different C1−N1 and C1−N2 bond distances (1.336(2) and 1.345(2) Å, respectively) further corroborate this finding and suggest a more amide-like character of the Al1−N2 bond compared to the more amine-like Al1−N1 bond.

Some of the structural features discussed for compound **5a** are also evident in the solid-state structure of **6a**, as depicted in its ORTEP drawing (Figure 2). Selected bond lengths and

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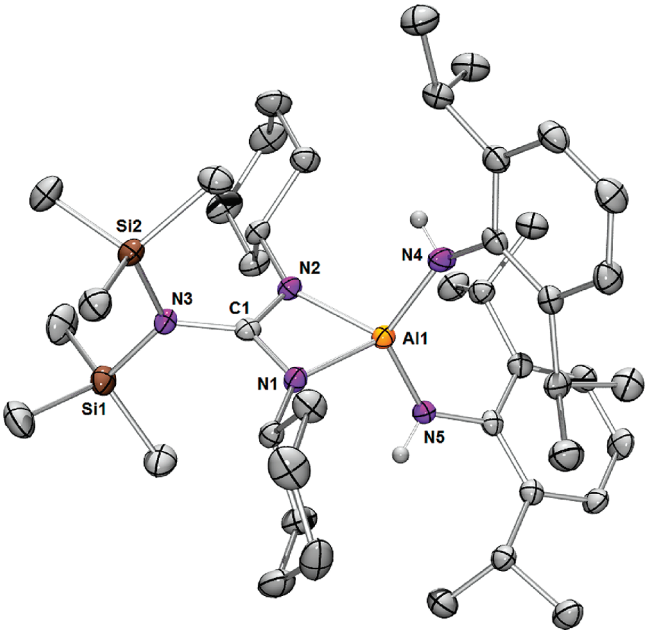


Figure 2. Thermal ellipsoid diagram of the molecular structure of **6a**. Thermal ellipsoids are drawn at 50% probability. H atoms (except H4 and H5) are omitted for clarity.

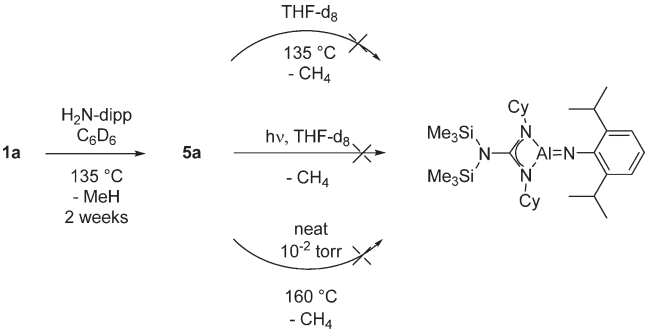
Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 6a

Al1−N1	1.8960(13)	N4−Al1−N5	123.71(7)
Al1−N2	1.9258(13)	N1−Al1−N2	69.75(5)
Al1−N4	1.8119(14)	N1−C1−N2	109.38(13)
Al1−N5	1.8022(14)	N1−C1−N3	125.07(14)
N1−C1	1.336(2)	N2−C1−N3	125.54(14)
N2−C1	1.342(2)		
N3−C1	1.4103(19)		

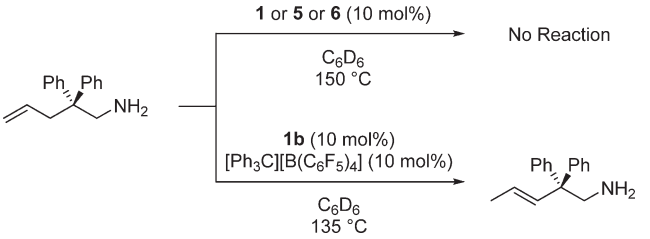
angles can be found in Table 2. Although the bis-amide substitution might suggest a highly symmetric molecule, the steric bulk of the two 2,6-di-isopropylphenyl substituents considerably distorts the tetrahedral coordination environment around Al and renders the two amide functionalities inequivalent. The larger *trans* influence of the amide moiety bound through N5, caused by the shorter Al1−N5 bond (1.8022(14) Å) compared to Al1−N4 (1.8119(14) Å), is reflected in the significantly different Al1−N1 and Al1−N2 bond distances (1.8960(13) and 1.9258(13) Å, respectively). The differences in C1−N1 and C1−N2 bond lengths (1.336(2) and 1.342(2) Å, respectively) further substantiate this finding. Once again, the sterically demanding trimethylsilyl substituents bound to N3 force a perpendicular arrangement of the ligand backbone (torsion angle 88.6°), allowing little electron delocalization, as evidenced by the relatively long C1−N3 bond (1.4103(19) Å).

Reactivity of Aluminum Complexes. To establish the reactivity of these Al compounds with primary amines, **1a** was treated with 2,6-di-isopropylphenylaniline. As expected, the mixed alkyl/amide complex **5a** is formed via the elimination of methane gas (Scheme 3). Surprisingly, however, the reaction requires high temperatures (135 °C in C_6D_6) and extended heating times (two weeks) to reach quantitative conversion, as determined by ^{1}H NMR spectroscopy (see Supporting Information). All attempts to generate an imido species via the elimination of a second equivalent of methane have been unsuccessful thus far, suggesting that these Al

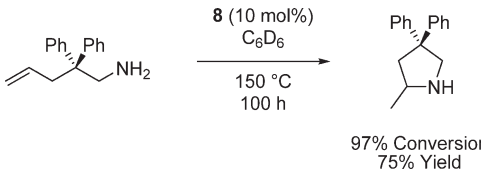
Scheme 3. Reaction of Compound 1a with 2,6-Diisopropylaniline



Scheme 4. Attempted Intramolecular Hydroamination Reactions



Scheme 5. Catalytic Intramolecular Hydroamination of 2,2-Diphenylpent-4-en-1-amine with 8



complexes show significantly different behavior compared to their transition metal analogues.

Despite the absence of an isolable guanidinate-supported Al imide species, we were encouraged by the reactivity of the Al guanidinate complexes with primary amines. Heating solutions of 2,2-diphenylpent-4-en-1-amine (150 °C in C_6D_6) in the presence of catalytic amounts (10 mol %) of compounds **1**, **5**, and **6**, however, did not result in the formation of intramolecular hydroamination products, an observation that further corroborates the stability of these four-coordinate Al guanidinate complexes (Scheme 4). On the basis of recent reports of intramolecular hydroamination of aminoalkenes catalyzed by cationic aminotroponiminate-supported Zn complexes,[38] we attempted the reaction in the presence of $[Ph_3C][B(C_6F_5)_4]$ as a methyl-abstracting reagent in an effort to generate a cationic Al species *in situ*. Upon heating solutions of 2,2-diphenylpent-4-en-1-amine, **1b**, and $[Ph_3C][B(C_6F_5)_4]$ (10 mol % each) at 135 °C, complete isomerization of the terminal olefin to the internal position was observed accompanied by the absence of any observable hydroamination products.

In an attempt to disrupt the preferred tetrahedral coordination sphere of Al and possibly force increased reactivity, complex **8**, bearing a tridentate monoanionic OCO-pincer ligand, was subjected to similar conditions to evaluate its reactivity toward aminoalkenes. Upon heating a solution of

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2,2-diphenylpent-4-en-1-amine (in C_6D_6) in the presence of catalytic amounts of complex **8** (10 mol %), formation of the cyclized hydroamination product (2-methyl-4,4-diphenylpyrrolidine) was observed (Scheme 5). However, high conversion of the aminoalkene to the corresponding hydroamination product was only observed after extended reaction times (~100 h) at relatively high temperature (150 °C), as determined by integration of the reactant/product ^{1}H NMR signals against 1,3,5-trimethoxybenzene as an internal standard (see Supporting Information, Figure S1). For this reason, hydroamination chemistry using this catalyst system was not pursued any further.

Conclusions

In conclusion, we have prepared and fully characterized a series of mixed alkyl/amide Al complexes (**1**−**6**) supported by guanidinate ligands. X-ray crystallographic characterization of compounds **5a** and **6a** allowed comparison of the structural features of these Al guanidinate complexes with varying alkyl/amide substitution. The reactivity of these complexes was determined to be comparable to that of other Al compounds; however, significantly different behavior with regard to their transition metal analogues was observed most likely due to the high stability of four-coordinate Al(III) complexes. Although catalytic hydroamination reactions involving compounds **1**−**6** were unsuccessful, controlled variation of the coordination sphere around Al via the introduction of a monoanionic OCO-pincer ligand (compound **8**) resulted in increased activity toward the intramolecular hydroamination of 2,2-diphenylpent-4-en-1-amine.

Experimental Section

General Procedures. Unless otherwise noted, all reactions and manipulations were performed in an inert atmosphere (N_2) glovebox or using standard Schlenk and high-vacuum-line techniques. Glassware was dried overnight at 150 °C before use. ^{1}H and ^{13}C NMR spectra were recorded at room temperature (except where noted) on Bruker AV 300 MHz, AVQ 400 MHz, or DRX 500 MHz spectrometers using residual protons of deuterated solvents for reference. Elemental analyses were performed at the University of California, Berkeley, Microanalytical Facility, on a Perkin-Elmer 2400 Series II CHNO/S analyzer. X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley. Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock via a Cajon Ultra-Torr reducing union followed by flame-sealing on a vacuum line. Reaction yields were not systematically optimized.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Pentane, diethyl ether, and toluene were purified by passing through a column of activated alumina (type A2, size 12−32, Purifry Co.) under nitrogen pressure and sparged with N_2 prior to use. Deuterated solvents (Cambridge Isotope Laboratories) were degassed by three freeze−pump−thaw cycles and stored over activated 3 Å molecular sieves. 2,6-Diisopropylaniline was distilled from sodium and stored over activated 3 Å molecular sieves. 2,6-Bis(bromomethyl)bromobenzene was prepared according to literature procedures.[39] 2,2-Diphenylpent-4-en-1-amine was prepared according to published literature procedures and distilled from CaH_2 prior to use.[40]

Crystallographic Analysis. Single crystals of **5a** and **6a** were coated in Paratone-N oil, mounted on a Kaptan loop, transferred to a Bruker APEX CCD area detector, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that was previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrixes and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT. Cell dimensions reported were calculated from all reflections with $I > 10\sigma$. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP. An empirical absorption correction based on S3 comparison of redundant and equivalent reflections was applied using SADABS. The structures were solved using SHELXS and refined on all data by full-matrix least-squares with SHELXL-97.[41] Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. Nitrogen-bound H atoms were located on the electron density map and fully refined. For compound **5a**, a total of 356 parameters were refined in the final cycle of refinement using 5279 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 4.16% and 10.07%, respectively. For compound **6a**, a total of 468 parameters were refined in the final cycle of refinement using 9033 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.48% and 8.21%, respectively. Refinement was done using F^2. ORTEP diagrams were created using the ORTEP-3 software package and rendered using Pov-Ray 3.6.

[CyNC(N(SiMe$_3$)$_2$)NCy]AlMe$_2$ (1a). A slurry of LiN(SiMe$_3$)$_2$ (1.51 g, 9.00 mmol) in Et_2O (25 mL) was cooled to −78 °C, and a solution of *N,N′*-dicyclohexylcarbodiimide (1.86 g, 9.00 mmol) in Et_2O (15 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. The resulting suspension was cooled to −78 °C, and $AlClMe_2$ (10 mL, 0.9 M solution in heptane, 9.00 mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 18 h. All volatiles were removed *in vacuo*, and the product was extracted with pentane (2 × 10 mL). The combined extracts were filtered and cooled to −35 °C to yield pure **1a** as colorless crystals, which were isolated by filtration. Yield: 1.11 g (29%, 2.62 mmol). ^{1}H NMR (benzene-d_6): δ 3.18 (m, 2H, NC*H*), 1.79 (m, 4H, CH_2), 1.65 (m, 4H, CH_2), 1.46 (m, 2H, CH_2), 1.23 (m, 8H, CH_2), 1.05 (m, 2H, CH_2), 0.18 (s, 18H, Si(CH_3)$_3$), −0.19 (s, 6H, AlCH_3). ^{13}C NMR (benzene-d_6): δ 166.23 (s, N$_3$*C*), 52.68 (s, N*C*H), 36.95 (s, *C*H$_2$), 26.16 (s, *C*H$_2$), 26.13 (s, *C*H$_2$), 2.36 (s, Si(*C*H$_3$)$_3$), −8.89 (s, Al*C*H$_3$). Anal. Calcd for $C_{21}H_{46}N_3AlSi_2$: C, 59.52; H, 10.94; N, 9.92. Found: C, 59.58; H, 11.07; N, 10.08.

[CyNC(N(*i*Pr)$_2$)NCy]AlMe$_2$ (1b). This compound was prepared by the procedure outlined for **1a**, using 0.96 g of LiN(*i*Pr)$_2$ (9.00 mmol), 1.86 g of *N,N′*-dicyclohexylcarbodiimide (9.00 mmol), and 10 mL of $AlClMe_2$ (0.9 M solution in heptane, 9.00 mmol). The product was isolated as colorless crystals. Yield: 1.84 g (56%, 5.06 mmol). ^{1}H NMR (benzene-d_6): δ 3.25 (sept, 2H, NC*H*(CH$_3$)$_2$), 3.18 (m, 2H, NC*H*), 1.81 (m, 4H, CH_2), 1.67 (m, 4H, CH_2), 1.49 (m, 2H, CH_2), 1.34−1.15 (m, 8H, CH_2), 1.07 (m, 2H, CH_2), 1.02 (d, 12H, J = 6.6 Hz, NCH(CH_3)$_2$). ^{13}C NMR (benzene-d_6): δ 168.05 (s, N$_3$*C*), 53.57 (s, N*C*H), 49.09 (s, *C*H(CH$_3$)$_2$), 36.83 (s, *C*H$_2$), 26.35 (s, *C*H$_2$), 26.31 (s, *C*H$_2$), 23.34 (s, CH(*C*H$_3$)$_2$), −8.51 (s, Al*C*H$_3$). Anal. Calcd for $C_{21}H_{42}N_3Al$: C, 69.38; H, 11.64; N, 11.56. Found: C, 69.58; H, 11.85; N, 11.81.

[CyNC(N(SiMe$_3$)$_2$)NCy]AlMeCl (2a). A slurry of LiN(SiMe$_3$)$_2$ (1.26 g, 7.50 mmol) in Et_2O (25 mL) was cooled to −78 °C, and a solution of *N,N′*-dicyclohexylcarbodiimide

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(40) Crimmin, M. R.; Arrowsmith, M.; Barrett, A. G. M.; Casely, I. J.; Hill, M. S.; Procopiou, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 9670–9685.

(41) *SHELXTL6*; Bruker-AXS: Madison, WI, 2000.

(1.55 g, 7.50 mmol) in Et_2O (15 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. The resulting suspension was cooled to −78 °C, and $AlMeCl_2$ (7.5 mL, 1.0 M solution in hexanes, 7.50 mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 18 h. All volatiles were removed *in vacuo*, and the solid was extracted with diethyl ether (2 × 10 mL). The combined extracts were filtered and cooled to −35 °C to yield pure **2a** as colorless crystals, which were isolated by filtration. Yield: 1.78 g (54%, 4.01 mmol). ^{1}H NMR (benzene-d_6): δ 3.14 (m, 2H, NC*H*), 1.87 (m, 2H, CH_2), 1.71−1.58 (m, 6H, CH_2), 1.49 (m, 4H, CH_2), 1.25−1.08 (m, 6H, CH_2), 1.01 (m, 2H, CH_2), 0.19 (s, 9H, Si(CH_3)$_3$), 0.12 (s, 9H, Si(CH_3)$_3$), −0.06 (s, 3H, AlCH_3). ^{13}C NMR (benzene-d_6): δ 169.93 (s, N_3C), 52.62 (s, N*C*H), 36.75 (s, *C*H_2), 36.39 (s, *C*H_2), 26.01 (s, *C*H_2), 25.95 (s, *C*H_2), 25.92 (s, *C*H_2), 2.36 (s, Si(*C*H_3)$_3$), 2.21 (s, Si(*C*H_3)$_3$), −9.27 (s, Al*C*H_3). Anal. Calcd for $C_{20}H_{43}N_3AlSi_2Cl$: C, 54.08; H, 9.76; N, 9.46. Found: C, 54.32; H, 9.65; N, 9.52.

[CyNC(N(*i*Pr)$_2$)NCy]AlMeCl (2b). This compound was prepared by the procedure outlined for **2a**, using 0.80 g of LiN(*i*Pr)$_2$ (7.50 mmol), 1.55 g of *N,N′*-dicyclohexylcarbodiimide (1.55 g, 7.50 mmol), and $AlClMe_2$ (7.50 mL, 1.0 M solution in hexane, 7.50 mmol). The product was isolated as colorless crystals. Yield: 0.71 g (25%, 1.86 mmol). ^{1}H NMR (benzene-d_6): δ 3.29 (sept, 2H, NC*H*(CH_3)$_2$), 3.10 (m, 2H, NC*H*), 1.92 (m, 2H, CH_2), 1.75−1.61 (m, 6H, CH_2), 1.55−1.44 (m, 4H, CH_2), 1.30−1.03 (m, 8H, CH_2), 0.97 (d, 12H, *J* = 6.6 Hz, NCH(CH_3)$_2$). ^{13}C NMR (benzene-d_6): δ 171.29 (s, N_3C), 53.85 (s, N*C*H), 49.79 (s, N*C*H(CH$_3$)$_2$), 36.59 (s, *C*H_2), 36.21 (s, *C*H_2), 26.32 (s, *C*H_2), 26.25 (s, *C*H_2), 26.07 (s, *C*H_2), 23.35 (s, CH(*C*H$_3$)$_2$), −8.49 (s, Al*C*H_3). Anal. Calcd for $C_{20}H_{39}N_3AlCl$: C, 62.56; H, 10.24; N, 10.94. Found: C, 62.74; H, 10.41; N, 10.68.

[(2,6-*i*Pr$_2$C$_6$H$_3$)NC(N(*i*Pr)$_2$)N(2,6-*i*Pr$_2$C$_6$H$_3$)]AlMeCl (2c). This compound was prepared by the procedure outlined for **2a**, using 0.54 g of LiN(*i*Pr)$_2$ (5.00 mmol), 1.81 g of *N,N′*-bis(2,6-diisopropylphenyl)carbodiimide (5.00 mmol), and $AlMeCl_2$ (5.00 mL, 1.0 M solution in hexanes, 5.00 mmol). The product was isolated as colorless crystals. Yield: 0.98 g (36%, 1.81 mmol). ^{1}H NMR (benzene-d_6): δ 7.11−7.03 (m, 6H, Ph), 3.99 (sept, 2H, NC*H*(CH$_3$)$_2$), 3.90 (sept, 2H, C*H*(CH$_3$)$_2$), 3.57 (sept, 2H, C*H*(CH$_3$)$_2$), 1.52 (d, 6H, *J* = 6.6 Hz, CH(CH_3)$_2$), 1.32 (d, 6H, *J* = 6.9 Hz, CH(CH_3)$_2$), 1.26 (d, 6H, *J* = 6.8 Hz, CH-(CH_3)$_2$), 1.18 (d, 6H, *J* = 6.7 Hz, CH(CH_3)$_2$), 0.77 (d, 12H, *J* = 7.1 Hz, NCH(CH_3)$_2$), −0.03 (s, 3H, AlCH_3). ^{13}C NMR (benzene-d_6): δ 167.70 (s, N_3C), 146.45 (s, Ph), 145.33 (s, Ph), 138.30 (s, Ph), 126.79 (s, Ph), 125.14 (s, Ph), 124.43 (s, Ph), 50.51 (s, N*C*H(CH$_3$)$_2$), 28.89 (s, *C*H(CH$_3$)$_2$), 28.86 (s, *C*H(CH$_3$)$_2$), 28.17 (s, CH(*C*H$_3$)$_2$), 27.28 (s, CH(*C*H$_3$)$_2$), 24.35 (s, CH(*C*H$_3$)$_2$), 24.02 (s, CH(*C*H$_3$)$_2$), 23.77 (s, NCH(*C*H$_3$)$_2$), −7.55 (s, Al*C*H_3). Anal. Calcd for $C_{32}H_{51}N_3AlCl$: C, 71.15; H, 9.52; N, 7.78. Found: C, 71.32; H, 9.33; N, 7.83.

[CyNC(N(SiMe$_3$)$_2$)NCy]AlCl$_2$ (3a). A slurry of LiN(SiMe$_3$)$_2$ (1.26 g, 7.50 mmol) in Et_2O (25 mL) was cooled to −78 °C, and a solution of *N,N′*-dicyclohexylcarbodiimide (1.55 g, 7.50 mmol) in Et_2O (15 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. The resulting suspension was cooled to −78 °C, and a solution of $AlCl_3$ (1.00 g, 7.50 mmol) in Et_2O (15 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 18 h. The solution was filtered through a pad of Celite, and all volatiles were removed *in vacuo* to yield the crude product as an off-white solid. Pure **3a** was obtained via recrystallization from toluene (10 mL) at −35 °C as colorless crystals, which were isolated by filtration. Yield: 0.54 g (16%, 1.16 mmol). ^{1}H NMR (benzene-d_6): δ 3.13 (m, 2H, NC*H*), 1.78 (m, 4H, CH_2), 1.58 (m, 4H, CH_2), 1.36 (m, 6H, CH_2), 1.07 (m, 4H, CH_2), 0.94 (m, 2H, CH_2), 0.12 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 172.38 (s, N_3C), 52.71 (s, N*C*H), 36.22 (s, *C*H_2), 25.85 (s, *C*H_2), 25.66 (s, *C*H_2), 2.21 (s, Si(*C*H_3)$_3$). Anal. Calcd for $C_{19}H_{40}N_3AlSi_2Cl_2$: C, 49.12; H, 8.68; N, 9.04. Found: C, 49.17; H, 8.71; N, 8.92.

[CyNC(N(*i*Pr)$_2$)NCy]AlCl$_2$ (3b). This compound was prepared by the procedure outlined for **3a**, using 0.80 g of LiN(*i*Pr)$_2$ (7.50 mmol), 1.55 g of *N,N′*-dicyclohexylcarbodiimide (7.50 mmol), and 1.00 g of $AlCl_3$ (7.50 mmol). The product was isolated as colorless crystals. Yield: 0.65 g (22%, 1.61 mmol). ^{1}H NMR (benzene-d_6): δ 3.34 (sept, 2H, NC*H*(CH$_3$)$_2$), 3.03 (m, 2H, NC*H*), 1.85 (m, 4H, CH_2), 1.61 (m, 4H, CH_2), 1.51−1.40 (m, 6H, CH_2), 1.12−0.98 (m, 6H, CH_2), 0.93 (d, 12H, *J* = 6.8 Hz, NCH(CH_3)$_2$). ^{13}C NMR (benzene-d_6): δ 172.65 (s, N_3C), 52.27 (s, N*C*H), 50.55 (s, *C*H(CH$_3$)$_2$), 35.99 (s, *C*H_2), 26.22 (s, *C*H_2), 25.85 (s, *C*H_2), 23.33 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{19}H_{36}N_3AlCl_2$: C, 56.43; H, 8.97; N, 10.39. Found: C, 56.81; H, 9.17; N, 10.39.

[CyNC(N(*i*Pr)$_2$)NCy]AlI$_2$ (4a). A Schlenk flask was charged with I_2 (1.40 g, 5.50 mmol), and subsequently, a solution of compound **1b** (1.00 g, 2.75 mmol) in 15 mL of toluene was added at room temperature. The mixture was stirred for 48 h at room temperature, during which time a color change from deep purple to yellow and the precipitation of a yellow solid was observed. The precipitation was completed by cooling the suspension to −20 °C for 24 h. The crude product was collected by filtration and dried *in vacuo*. Recrystallization from toluene (10 mL) afforded pure **4a** as yellow needles. Yield: 0.46 g (0.78 mmol, 29%). ^{1}H NMR (benzene-d_6): δ 3.26 (sept, 2H, NC*H*(CH$_3$)$_2$), 3.18 (m, 2H, NC*H*), 1.91 (m, 4H, CH_2), 1.67−1.60 (m, 8H, CH_2), 1.42 (m, 2H, CH_2), 1.10−0.97 (m, 6H, CH_2), 0.91 (d, 12H, *J* = 6.7 Hz, NCH(CH_3)$_2$). ^{13}C NMR (benzene-d_6): δ 171.55 (s, N_3C), 54.71 (s, N*C*H), 50.30 (s, *C*H(CH$_3$)$_2$), 36.19 (s, *C*H_2), 26.29 (s, *C*H_2), 25.86 (s, *C*H_2), 23.13 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{19}H_{36}N_3AlI_2$: C, 38.86; H, 6.18; N, 7.15. Found: C, 38.96; H, 5.99; N, 6.77.

[CyNC(N(SiMe$_3$)$_2$)NCy]AlMe[NH(2,6-*i*Pr$_2$C$_6$H$_3$)] (5a). Method A. A 20 mL scintillation vial was charged with LiNH(2,6-*i*Pr$_2$C$_6$H$_3$) (206 mg, 1.13 mmol) and 10 mL of diethyl ether. A solution of **2a** (500 mg, 1.13 mmol) in 5 mL of diethyl ether was added via pipet. The resulting mixture was stirred for 18 h at ambient temperature. LiCl was filtered off and the solvent removed *in vacuo*. The resulting solid was extracted with pentane (2 × 4 mL). The combined extracts were filtered and subsequently cooled to −35 °C to yield pure **5a** as colorless crystals, which were isolated by filtration. Yield: 468 mg. (71%, 0.80 mmol). ^{1}H NMR (benzene-d_6): δ 7.25 (d, 2H, Ph), 7.03 (m, 1H, Ph), 3.56 (sept, 2H, C*H*(CH$_3$)$_2$), 3.23 (bs, 1H, N*H*), 3.19 (m, 2H, NC*H*), 1.85 (m, 4H, CH_2), 1.68 (m, 4H, CH_2), 1.52 (m, 4H, CH_2), 1.44 (d, 12H, *J* = 6.8 Hz, CH(CH_3)$_2$), 1.37 (m, 2H, CH_2), 1.14 (m, 8H, CH_2), 0.21 (s, 9H, Si(CH_3)$_3$), 0.17 (s, 9H, Si(CH_3)$_3$), −0.26 (s, 2H, AlCH_3). ^{13}C NMR (benzene-d_6): δ 169.05 (s, N_3C), 146.46 (s, Ph), 137.28 (s, Ph), 123.62 (s, Ph), 118.77 (s, Ph), 53.01 (s, N*C*H), 36.97 (s, *C*H_2), 36.74 (s, *C*H_2), 29.88 (s, *C*H(CH$_3$)$_2$), 26.45 (s, *C*H_2), 26.33 (s, *C*H_2), 26.30 (s, *C*H_2), 24.43 (s, CH(*C*H$_3$)$_2$), 2.47 (s, Si(*C*H_3)$_3$), 2.34 (s, Si(*C*H_3)$_3$), −7.94 (s, Al*C*H_3). Anal. Calcd for $C_{32}H_{61}N_4AlSi_2$: C, 65.70; H, 10.51; N, 9.58. Found: C, 65.38; H, 10.39; N, 9.27.

Method B. Compound **1a** (10 mg, 0.024 mmol) and 2,6-diisopropylaniline (4.5 μL, 0.024 mmol) were dissolved in 1 mL of C_6D_6 and charged into a J-Young NMR tube. The sealed tube was subsequently heated at 135 °C for two weeks. Compound **5a** was formed in near-quantitative NMR yield. ^{1}H NMR signals were identical to those described in method A (Supporting Information, Figure S2).

[(2,6-*i*Pr$_2$C$_6$H$_3$)NC(N(*i*Pr)$_2$)N(2,6-*i*Pr$_2$C$_6$H$_3$)]AlMe[NH-(2,6-*i*Pr$_2$C$_6$H$_3$)] (5b). This compound was prepared by the procedure outlined for **5a**, using 85 mg of LiNH(2,6-*i*Pr$_2$C$_6$H$_3$) (0.46 mmol) and 250 mg of **2c** (0.46 mmol). The product was isolated as colorless crystals. Yield: 155 mg (49%, 0.23 mmol). ^{1}H NMR (benzene-d_6): δ 7.13−7.09 (m, 8H, Ph), 6.97 (m, 1H, Ph), 4.05 (sept, 2H, NC*H*(CH$_3$)$_2$), 3.73 (sept, 2H, C*H*(CH$_3$)$_2$), 3.68 (sept, 2H, NC*H*(CH$_3$)$_2$), 3.20 (sept, 2H, C*H*(CH$_3$)$_2$), 3.04

(bs, 1H, NH), 1.49 (d, 6H, J = 6.7 Hz, CH(CH_3)$_2$), 1.34 (d, 6H, J = 6.9 Hz, CH(CH_3)$_2$), 1.32 (d, 6H, J = 6.7 Hz, CH(CH_3)$_2$), 1.27 (d, 6H, J = 6.8 Hz, CH(CH_3)$_2$), 1.12 (d, 12H, J = 6.7 Hz, CH(CH_3)$_2$), 0.80 (d, 12H, J = 7.0 Hz, NCH(CH_3)$_2$), −0.20 (s, 3H, AlCH_3). ^{13}C NMR (benzene-d_6): δ 167.68 (s, N_3C), 145.48 (s, Ph), 145.34 (s, Ph), 145.17 (s, Ph), 139.87 (s, Ph), 139.42 (s, Ph), 126.30 (s, Ph), 124.98 (s, Ph), 124.63 (s, Ph), 123.63 (s, Ph), 120.00 (s, Ph), 50.61 (s, NCH(CH_3)$_2$), 29.46 (s, CH(CH_3)$_2$), 29.20 (s, CH(CH_3)$_2$), 28.70 (s, CH(CH_3)$_2$), 27.43 (s, CH(CH_3)$_2$), 26.73 (s, CH(CH_3)$_2$), 24.61 (s, CH(CH_3)$_2$), 24.53 (s, CH(CH_3)$_2$), 24.03 (s, NCH(CH_3)$_2$). Anal. Calcd for $C_{44}H_{69}N_4Al$: C, 77.60; H, 10.21; N, 8.23. Found: C, 77.31; H, 10.03; N, 8.02. [Note: ^{13}C NMR resonance for Al-CH_3 could not be observed even after extended acquisition times.]

[CyNC(N(SiMe$_3$)$_2$)NCy]Al[NH(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$ (6a). A 20 mL scintillation vial was charged with LiNH(2,6-^{i}Pr$_2$C$_6$H$_3$) (78.9 mg, 0.43 mmol) and 5 mL of diethyl ether. A solution of **3a** (100 mg, 0.22 mmol) in 5 mL of diethyl ether was added via pipet. The resulting mixture was stirred for 18 h at ambient temperature. LiCl was filtered off and the solvent removed *in vacuo*. The resulting solid was extracted with pentane (2 × 6 mL). The combined extracts were filtered and subsequently cooled to −35 °C to yield pure **6a** as colorless crystals, which were isolated by filtration. Yield: 159 mg (99%, 0.21 mmol). ^{1}H NMR (benzene-d_6): δ 7.15 (d, 4H, Ph), 6.95 (m, 2H, Ph), 3.49 (sept, 4H, CH(CH_3)$_2$), 3.34 (bs, 2H, NH), 3.19 (m, 2H, NCH), 1.85 (m, 4H, CH_2), 1.66 (m, 4H, CH_2), 1.48 (m, 6H, CH_2), 1.32 (d, 24H, J = 6.5 Hz, CH(CH_3)$_2$), 1.14 (m, 8H, CH_2), 0.20 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 171.33 (s, N_3C), 145.99 (s, Ph), 136.86 (s, Ph), 123.65 (s, Ph), 118.87 (s, Ph), 53.19 (s, NCH), 36.43 (s, CH$_2$), 29.80 (s, CH(CH_3)$_2$), 26.39 (s, CH$_2$), 26.04 (s, CH$_2$), 24.48 (s, CH(CH_3)$_2$), 2.49 (s, Si(CH_3)$_3$). Anal. Calcd for $C_{43}H_{76}N_5AlSi_2$: C, 69.21; H, 10.27; N, 9.38. Found: C, 69.06; H, 9.88; N, 9.55.

[CyNC(N(^{i}Pr)$_2$)NCy]Al[NH(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$ (6b). This compound was prepared by the procedure outlined for **6a**, using 100 mg of **3b** (0.25 mmol) and 91 mg of LiNH(2,6-^{i}Pr$_2$C$_6$H$_3$) (0.50 mmol). **6b** was isolated as colorless crystals. Yield: 35 mg (22%, 0.051 mmol). ^{1}H NMR (benzene-d_6): δ 7.18 (d, 4H, Ph), 7.00 (m, 2H, Ph), 3.57 (sept, 4H, CH(CH_3)$_2$), 3.51 (sept, 2H, NCH(CH_3)$_2$), 3.04 (m, 2H, NCH), 2.92 (bs, 2H, NH), 1.78 (m, 4H, CH_2), 1.67 (m, 4H, CH_2), 1.50 (m, 2H, CH_2), 1.39 (m, 4H, CH_2), 1.32 (d, 24H, J = 6.8 Hz, CH(CH_3)$_2$), 1.15−1.08 (m, 6H, CH_2), 1.06 (d, 12H, J = 6.8 Hz, NCH(CH_3)$_2$). ^{13}C NMR (benzene-d_6): δ 173.82 (s, N_3C), 146.09 (s, Ph), 139.19 (s, Ph), 123.48 (s, Ph), 119.90 (s, Ph), 54.29 (s, NCH), 51.11 (s, NCH(CH_3)$_2$), 36.04 (s, CH$_2$), 29.26 (s, CH(CH_3)$_2$), 26.74 (s, CH$_2$), 26.22 (s, CH$_2$), 24.19 (s, CH(CH_3)$_2$), 23.96 (NCH(CH_3)$_2$). Anal. Calcd for $C_{43}H_{72}N_5Al$: C, 75.28; H, 10.58; N, 10.21. Found: C, 75.36; H, 10.83; N, 10.50.

2,6-Bis(3,5-^{t}Bu-phenoxymethyl)bromobenzene (7). A mixture of 2,6-bis(bromomethyl)bromobenzene (9.86 g, 28.8 mmol), 3,5-di-*tert*-butylphenol (12.8 g, 61.8 mmol), and anhydrous potassium carbonate (9.94 g, 71.9 mmol) in acetone (100 mL) was heated at reflux for 22 h. The resulting suspension was cooled to room temperature and then quenched with water (200 mL). The product was extracted with methylene chloride (2 × 100 mL), and the combined organic fractions were washed with saturated $NaHCO_3$ (200 mL) and brine (200 mL). The organic phase was then dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo* to yield the crude product as an off-white solid. Pure **6** was obtained as a colorless microcrystalline solid, which was isolated via filtration after recrystallization from hexane (150 mL) at −20 °C. Reduction of the volume of the mother liquor to 75 mL followed by crystallization at −20 °C yielded a second crop of product. Combined yields: 10.3 g (17.4 mmol, 61%). ^{1}H NMR (benzene-d_6): δ 7.48 (d, 2H, Ph), 7.21 (m, 2H, Ph), 7.06 (d, 4H, Ph), 6.99 (m, 1H, Ph), 5.13 (s, 4H, CH_2), 1.30 (s, 36H, C(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 159.44 (s, Ph), 152.90 (s, Ph), 138.14 (s, Ph), 129.12 (s, Ph), 123.18 (s, Ph), 115.91 (s, Ph), 110.29 (s, Ph), 70.26 (s, CH$_2$), 35.45 (s, C(CH_3)$_3$), 31.96 (s, C(CH_3)$_3$). Anal. Calcd for $C_{36}H_{49}BrO_2$: C, 72.83; H, 8.32. Found: C, 72.64; H, 8.21.

{[(3,5-^{t}BuC$_6$H$_3$)OCH$_2$]$_2$C$_6$H$_3$}AlMe$_2$ (8). A Schlenk flask was charged with a solution of 2,6-bis(3,5-^{t}Bu-phenoxymethyl)bromobenzene (2.00 g, 3.37 mmol) in hexanes (40 mL). The solution was cooled to 0 °C, and ^{n}BuLi (2.10 mL, 3.37 mmol, 1.6 M solution in hexanes) was added dropwise via syringe. The solution was allowed to warm to room temperature and was stirred for another 2 h. The solution was then recooled to 0 °C, and $AlClMe_2$ (3.74 mL, 3.37 mmol, 0.9 M solution in heptane) was added dropwise via syringe. The solution was slowly warmed to room temperature and stirred for another 18 h. LiCl was filtered off, and the solvent was removed *in vacuo* to yield the crude product as a white solid. Pure **8** was obtained as colorless crystals via recrystallization from a mixture of toluene/pentane (1:1, 10 mL) at −35 °C. Yield: 1.61 g (2.82 mmol, 84%). ^{1}H NMR (benzene-d_6): δ 7.33 (s, 6H, Ph), 7.29 (m, 1H, Ph), 6.88 (m, 2H, Ph), 5.15 (s, 4H, CH_2), 1.29 (s, 36H, C(CH_3)$_3$), 0.02 (s, 6H, AlCH_3). ^{13}C NMR (benzene-d_6): δ 157.07 (s, Ph), 153.19 (s, Ph), 143.99 (s, Ph), 127.77 (s, Ph), 121.32 (s, Ph), 118.51 (s, Ph), 114.06 (s, Ph), 77.62 (s, CH$_2$), 35.55 (s, C(CH_3)$_3$), 31.88 (s, C(CH_3)$_3$), −6.84 (s, AlCH_3). Anal. Calcd for $C_{38}H_{55}AlO_2$: C, 79.96; H, 9.71. Found: C, 79.63; H, 9.64.

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Supporting Information Available: X-ray data are available as crystallographic information files (CIF) for compounds **5a** and **6a**. ^{1}H NMR data of NMR-scale reactions as pdf files. This material is available free of charge via the Internet at http://pubs.acs.org.