Synthesis and Structure of an Amino-Linked N-Heterocyclic Carbene and the Reactivity of its Aluminum Adduct

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Treatment of $[HC{(MES)N(CHCH)N(CH₂CH₂NH$ *t* $Bu}]Br cdot HBr (1) with an excess of NaOH afforded$ $the organic-soluble imidazolium salt 2, <math>[HC{(MES)N(CHCH)N(CH₂CH₂NH$ *t* $Bu}]Br$, the structure of which was confirmed by X-ray crystallography. Deprotonation of 2 by NaN(SiMe₃)₂ yielded the thermally unstable amino-linked free carbene, 3. The molecular structure of 3 was determined by single-crystal X-ray analysis, revealing an unexpectedly close intermolecular contact associated with the carbene and amine through an N-H···C interaction. In contrast to compound 3, the reaction of 2 with LiN(SiMe₃)₂ gave the much more stable LiBr carbene adduct 3-LiBr, which serves as an effective carbene transfer agent for organoaluminum compounds to give the corresponding AlR₃-NHC (4a, Me; 4b, Et) in high yield. X-ray diffraction studies of 4a and 4b confirmed the formation of monomeric distorted tetrahedral Al species, in which the NHC binds via conventional σ -donation of the lone pair to the electrophilic metal center. The reaction of benzaldehyde with 4a resulted in the quantitative formation of a zwitterionic species consisting of a distorted pseudotetrahedral aluminate center covalently linked to imidazolium, 5. The product 5 resulted from insertion of the carbonyl moiety into the Al-carbene group. A similar reactivity with benzaldehyde was observed in compound 6, which was independently synthesized from addition of 1,3-bis(mesityl)imidazol-2-ylidene to AlMe₃.

Introduction

The remarkable discovery of N-heterocyclic carbenes (NHCs) as neutral σ -donating ligand platforms prompted a massive breakthrough in homogeneous transition metal catalysis.¹ More recently, hybrid ligand sets based on the presence of anionic functional pendants linked to NHC, led by Arnold, Fryzuk, Shen, and Kawaguchi, have received much attention.² The interest in these systems is fueled by the simultaneous use of anionic σ -amino or alkoxide groups coupled with the neutral electron-

donor NHC scaffold to provide stability for hard electropositive metal centers, as well as the ability to afford a library of ligands due to their relatively straightforward preparation. Unfortunately, due to their lack of stability in the free form at room temperature, these ligand motifs have found only limited use thus far.



In the case of group 13 elements such as Al, the use of NHCs as good σ -donor molecules to stabilize the trivalent compounds was established with the isolation of the first alane adduct of an imidazol-2-ylidene, **A**.³ When compared to AlH₃•NMe₃, which decomposed above 100 °C,⁴ the stability of **A** is surprisingly high, with a melting point of 246 °C. Therefore, aluminum complexes supported by ligands bearing N-heterocyclic carbene (NHC) groups may have promising and diverse chemical reactivity with potential applications in catalysis. With only a handful of literature references to date,⁵ this area has been neglected, particularly when it comes to understanding the nature of Al–NHC bonding and its reactivity.

It has been extensively documented that aluminum compounds can serve as powerful nucleophilic alkylating reagents in organic transformations.⁶ For example, Schneider et al. reported that phosphine ligands could be used as catalytic Lewis bases for the ring-opening alkylation of epoxides by alkylalu-

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minum reagents.^{6i,j} Furthermore, studies by Nguyen^{6d} and Dorta^{6h} on the use of bulky NHCs have demonstrated the viability of a similar catalytic process. More importantly, the concept of frustrated Lewis pairs, pioneered by Power and Stephan, has generated tsunami-level hype in the use of Lewis pairs of main group elements for hydrogen and other small molecule activation.⁷ With this in mind, we have sought to (a) improve the preparation of functional amino-pendant-linked NHC species and (b) subsequently exploit the potential of this ligand with respect to Al complexes and their reactivity. In this contribution, we report the solid state structure of a thermally unstable amino-carbene and its unusual intermolecular interaction between the carbene center and the amide. We also describe the peculiar example of an Al complex supported by an amino-NHC and its corresponding reactivity with electrophiles.

Results and Discussion

Synthesis and Structural Features of the Amino-Linked Carbene. Imidazolium salts containing a covalently linked ammonium group (1) were first reported by the Arnold group (Scheme 1).^{2b} However, salts such as 1 contain two cationic groups, leading to solubility problems in organic solvents and therefore making it difficult to work with strong organic bases like alkyl lithium. Thus, altering the ionic character in 1 may have a desirable effect on the compound's solubility. Indeed, 1 equiv of HBr can be removed from 1 with a slight excess of NaOH to afford the amine-imidazolium bromide 2 with ease. The identity of 2 is confirmed by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The solid state structure of 2 is illustrated in Figure 1. The ¹H and ¹³C NMR chemical shifts of the N–CH–N fragment for compound 2 (δ

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Figure 1. Molecular diagram of 2 with thermal ellipsoids drawn at the 30% probability level.



¹H 9.70 ppm, δ ¹³C 141.0 ppm) are in the range observed for imidazolium salts. The structural parameters within the cation are unremarkable and consistent with those observed previously in other salts,⁸ having a typical large internal N(1)–C(10)–N(2) angle of 109.1(2)° and short carbenium–nitrogen distances of 1.337(3) and 1.325(3) Å. Of more interest is the close contact between the ion pairs, associated through C–H····Br (2.915 Å, 3.786 Å, 155.1°) and N–H····Br(2.859 Å, 3.677 Å, 155.9°) interactions.⁹

Compound 2 is much more soluble in THF than compound 1 and can be deprotonated by $NaN(TMS)_2$ to afford free carbene 3 under mild conditions. The ${}^{13}C$ NMR spectrum of 3 in C_6D_6 shows a carbenic signature peak at δ 216.3, and the structural identity of 3 is unambiguously established by single-crystal X-ray diffraction (Figure 2). Compound 3 represents a rare example of a structurally characterized N-heterocyclic carbene possessing a covalently linked functionalized pendant moiety. Crystallographic data for this type of free carbene species remain sparse. Recently, Fryzuk et al. have isolated the first stable free carbene featuring a mesityl substituent on an amino pendant arm, (mesityl)NHCH₂CH₂-[NC(CHCH)N(mesityl)]. Unfortunately, details concerning its structural characterization and stability are not fully discussed in the paper.¹⁰ The structural parameters of 3 are comparable to both the free carbene isolated by Arduengo,8 and Fryzuk's (mesityl)NHCH2CH2-[NC-

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Figure 2. Molecular diagram of **3** with thermal ellipsoids drawn at the 30% probability level. Atom H3 was located from the difference map and refined with a riding model. All other hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(10)-N(1) 1.3702(14), C(10)-N(2) 1.3613(15), C(11)-C(12) 1.3421(17), N(2)-C(10)-N(1) 101.51(10).



Figure 3. View of a one-dimensional chain of NHC **3** formed by two N(3)–H(3)····C(10) interactions (blue dotted lines) and two π - π interactions between the imidazole moiety and the mesityl ring (red dotted lines).

(CHCH)N(mesityl)]. Specifically, **3** possesses almost statistically equal bond lengths for both carbene–nitrogen bonds (N(2)–C-(10)_{alkyl} = 1.3613(1) Å, N(1)–C(10)_{aryl} = 1.370(1) Å, and N(1)–C(10)–N(2) = 101.51(10)°). The slightly different bond lengths in the N(1)–C(10)–N(2) moiety may exemplify the prospect of irregular π donation of N_{aryl} and N_{alkyl} toward carbenic center.

Notably, compound **3** is thermally unstable. Heating a solution of **3** in C_6D_6 at 60 °C results in the product's decomposition within a few minutes. In addition, decomposition occurs slowly at room temperature under a nitrogen atmosphere over several hours to intractable products. Although the lack of sufficient steric protection is a major contributor toward the overall stability of carbene **3**, we speculate that uneven aromatic conjugation may further aggravate this situation.¹¹ Careful inspection of the crystal packing of **3** (Figure 3) reveals an unexpectedly close intermolecular contact associated with the carbenic carbon and the amine through a N–H ··· C interaction (N(3)–H(3)···C(10), 2.507 Å, 3.404 Å, 170°).⁹ The intermolecular interaction is somewhat longer than that reported in a similar case between cocrystallized 1,3-dimethylimidazol-2-



Figure 4. Molecular diagram of **3-LiBr** with thermal ellipsoids drawn at the 30% probability level, showing two symmetry-independent, but chemically similar molecules. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Br(1)–Li(1) 2.514(7), Li(1)–O(1) 1.977(7), Li(1)–C(7) 2.125(7), Li(1)–N(1) 2.186(8), Br(2)–Li(2) 2.488(8), Li(2)–O(2) 1.975(8), Li(2)–C(29) 2.144(8), N(2)–C(7) 1.360(5), N(3)–C(7) 1.367(5),N(5)–C(29)1.355(5),N(6)–C(29)1.368(5),N(2)–C(7)–N(3) 101.8(3), N(5)–C(29)–N(6) 102.3(3).

ylidene and diphenylamine.¹² The slightly longer interaction in **3** may be a consequence of the unfavorable steric crowding incurred by the close proximity between the *tert*-butyl group and mesityl sidearm. Regardless, this is an unusual circumstance involving a nontraditional hydrogen bond between a more electronegative nitrogen and a carbon atom. In this case, the nonbonded *tert*-butyl amine of the carbene may donate its lone pair into the empty p_{π} orbital of the carbenic center of another molecule, which may further disrupt the rather weak aromatic conjugation of **3** from the irregular π donation of N_{aryl} and N_{alkyl}, and hence it downgrades the overall stability of the compound.

Preparation of a Thermally Stable Lithium Bromide Carbene Adduct as a Potential Carbene Transfer Agent. To validate our thoughts with respect to the instability of 3, we attempted to cap the tBu-amino pendant arm and prevent it from interacting with another carbene molecule by generating a lithium halide carbene adduct. Deprotonation of 2 with LiN-(SiMe₃)₂ at 0 °C in THF afforded the carbene species 3-LiBr in high yield (Scheme 1). The ¹H NMR resonances demonstrate that **3-LiBr** is uniquely different from **3**. Due to ${}^{13}C-{}^{7}Li$ spin coupling, a rather broad signature peak for the carbon of 3-LiBr appears at 201 ppm in the ¹³C NMR spectrum, signaling the possible formation of a lithium-carbene adduct. A single-crystal X-ray diffraction study was undertaken to determine the connectivity in **3-LiBr**, and a structural model is presented in Figure 4. There are two independent units in the asymmetric unit, in which both lithium atoms exhibit pseudotetrahedral geometry by forming three dative bonds with NHC, amine, and THF. The Li-C distances (Li(1)-C(7) 2.125(7) and Li(2)-C(29) 2.144(8) Å) are the shortest reported for a lithiumcarbene adduct. For comparison, [Li{C₅H₂(SiMe₃)₃{C(NtBu-CH)₂] has a Li-C bond length of 2.155 Å,¹³ while the dimer $[tBuNHCH_2CH_2[C{tBuN(CHCH)N}] \cdot Li-Br]_2$, prepared by the

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Arnold group, has a much longer Li–C distance of 2.196 Å.^{2b} The molecular structure of **3-LiBr** also reveals that the amine function is bonded to the Li⁺ center rather than demonstrating any noticeable interaction with the carbene carbon and thus preventing any possible interruption of π -conjugation within the carbene ring system. **3-LiBr** can be stored in its crystalline state at room temperature for indefinite periods of time without any signs of decomposition. To our delight, when a toluene solution of **3-LiBr** was heated to 100 °C for several hours, there was also no indication of decomposition.

Preparation and Characterization of Organoaluminum Complexes Supported by an Amino-Linked Carbene. The excellent thermal stability displayed by **3-LiBr** prompted an examination of its effectiveness as a carbene transfer agent, similar to the well-known silver NHC species. Amino-pendantlinked NHC **3-LiBr** was readily introduced to AIR_3 (R = Me (a), Et (b)) in THF to produce 4a and 4b, respectively, in good yield (Scheme 2). The ¹H NMR spectroscopic features of 4a are notably different than 3-LiBr, displaying a new singlet integrating to 9 H at -0.48 ppm for the Al-Me protons and a sharp triplet (${}^{3}J = 8.0 \text{ Hz}$) integrating to 1 H at 0.26 ppm for the amine proton. 4b also exhibits a similar proton NMR pattern to 4a, with one singlet for the amino-*tert*-butyl group at 0.85 ppm integrating to 9 protons and two more singlets for the mesityl groups at 2.06 and 1.90 ppm integrating to a total of 9 protons. With the exception of the high-field resonances, the aluminum ethyl groups of 4b are observed at 1.45 (t, 9H) and 0.09 ppm (q, 6H). The shift in the high-field ¹³C resonance at 177 and 176 ppm in 4a and 4b, respectively, compared to that in 3-LiBr (207 ppm) and 3 (216 ppm), is attributed to the depletion of the NHC's electron density by the strong Lewis acidity of the Al center.

Single crystals of 4a suitable for X-ray analysis were grown from a concentrated ether solution at -20 °C and represent the first isolated organoaluminum complex supported by an aminopendant-linked NHC (Figure 5). The structure consists of a tetrahedrally distorted Al center bearing a dangling nonbonded amino sidearm with an Al(1)–N(3) distance of 5.40 Å. The nonbonding nature of the amine may be due to the coordination of the electron-rich carbene and its saturation of the Al center. To a lesser extent, steric repulsion may also play a role in discouraging such an Al-amino interaction. The Al-carbene bond length is 2.074(2) Å, in line with reported AlMe₃-1,3diisopropyl-4,5-dmethylimidazol-2-ylidene B (2.082(3) Å). However, the independent Al-Me bond distances in 4a (1.980(2), 1.985(3), and 1.995(2) Å) are slightly shorter than those in B (2.062(7) and 1.940 (5) Å).^{5f} The bond lengths (1.365(3) and 1.360(2)Å) and bond angle (103.13(18)°) in the N(1)-C(10)-N(2) moiety of 4a are not significantly different from those of the free carbene, 3.

Reactivity of Al-NHCs with Benzaldehyde. Nguyen et al. reported the high-yield synthesis of alcohols from the ring-opening reaction of epoxides with triethylaluminum using

catalytic amounts of either NHC or imidazolium salts.^{6d} The authors believe NHC-AlR₃ to be the active catalytic species for this process, but no subsequent mechanistic studies concerning this catalyst system have been reported. In addition, no specific reactivity experiments have been undertaken to explore the nature of the Al-carbene bonding, despite the significant focus in recent chemistry on the use of boron-carbene or phosphine Lewis base pairs with respect to small molecule activation.7b-h On the basis of this finding, we should anticipate reactivity between an electrophile and compound 4. Exposure of a solution of 4a in C_6D_6 to benzaldehyde resulted in the quantitative formation of a new species, 5, over a period of 5 min. The 1 H NMR spectrum of 5 indicates the incorporation of a single equivalent of benzaldehyde, whereas the integration of the Al-CH₃ signal remains unchanged at 9H. The disappearance of the carbenium carbon at δ 177.0 ppm in the ¹³C NMR spectrum of 5, corresponding to the rise of a new signal at 153.2 ppm, strongly suggests that the NHC is acting as a noninnocent ligand. An X-ray diffraction study of a white crystal of complex 5 confirmed a somewhat surprising outcome for this reaction, as presented in Figure 6.

Rather than undergoing alkyl addition, compound **5** displays insertion of the carbonyl moiety into the Al-carbene group. Complex **5** is a zwitterionic species consisting of a distorted pseudotetrahedral aluminate center covalently linked to imidazolium. To the best of our knowledge, there are no reported structures of imidazolium-linked aluminate species, the closest example resembling **5** being the imidazolium tetraphenoxyaluminate salts [IMeMe \cdot H][Al(OPh)₄] (IMeMe = tetramethylimi-



Figure 5. Molecular diagram of **4a** with thermal ellipsoids drawn at the 30% probability level. Atom H3 was located from the difference map and refined with a riding model. All other hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): AI-C(21) 1.980(2), AI-C(19) 1.985(3), AI-C(20) 1.995(2), AI-C(10) 2.074(2), N(1)-C(10) 1.365(3), N(2)-C(10) 1.360(2), C(21)-AI-C(19)111.37(12), C(21)-AI-C(20)111.50(12), C(19)-AI-C(20) 116.08(11), C(21)-AI-C(10) 109.00(10), (19)-AI-C(10) 108.34(11), C(20)-AI-C(10) 99.70(10), N(2)-C(10)-N(1) 103.13(18).



Figure 6. Molecular diagram of **5** with thermal ellipsoids drawn at the 30% probability level. Atom H3 was located from the difference map and refined with a riding model. All other hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)-O(1) 1.8030(12), Al(1)-C(1) 1.988(2), Al(1)-C(3) 1.9960(19), Al(1)-C(2) 1.999(2), N(1)-C(11) 1.348(2), N(2)-C(11) 1.341(2), O(1)-C(10) 1.381(2), C(9)-C(10) 1.529(2), C(10)-C(11) 1.517(2), O(1)-Al(1)-C(1) 104.16(8), O(1)-Al(1)-C(3) 107.52(7), C(1)-Al(1)-C(3) 111.26(9), O(1)-Al(1)-C(2) 108.81(7), C(1)-Al(1)-C(2) 111.78(9), C(3)-Al(1)-C(2) 112.82(8), N(2)-C(11)-N(1) 107.16(14).

dazol-2-ylidene).¹⁴ The Al–O distance of 1.803(1) Å in **5** is slightly longer than those reported for the Al-OPh analogues (1.730(3), 1.742(3), 1.709(3), 1.736(3) Å), whereas the average Al–CH₃ distance for **5** (\sim 1.994 Å) is very similar to that of **4a**. The cationic component of **5** has intra-ring parameters consistent with typical imidazolium salts, where the N(1)–C(11)–N(2) angle of 107.1(1)° is larger than its parent carbene **3** (101.51(10)°), indicating a significant enhancement in electronic delocalization about the heterocycle.

Recent literature shows that NHC-transition metal bonds are not inert and NHC ligands are able to participate in various inter- and intramolecular reactions.^{15,16} However, thus far, there have been no reports of experimental work with regard to the reactivity of Al-NHC. One of our hypotheses suggests the ability of the dangling amino group on the Al complex to serve as a directing group for the nucleophilic attack by the carbene via intermolecular hydrogen bonding with the carbonyl group, as shown in Scheme 3, pathway A. We sought additional evidence for this pathway by further preparing the separate compound AlMe₃-NHC, 6, independently synthesized by the addition of 1,3-bis(mesityl)imidazol-2-ylidene to AlMe₃ (Scheme 4). Interestingly, the crystal structure determination of 6, analogous to the reported AlMe₃-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, B, has not been reported to date in the literature. The structure of product $\mathbf{6}$ is confirmed by singlecrystal X-ray diffraction (Figure 7). The bond distances of Al-C_{methyl} in **6** (1.975(2), 1.987 (2), 1.987(2) Å) are no different from the amino-linked NHC of 4a. However, the presence of a slightly longer Al-carbenic bond of 2.097(2) Å, compared to 4a, indicates that 1,3-bis(mesityl)imidazol-2-ylidene is a less electron rich carbene than the amino-linked NHC of 4a.

In the presence of benzophenone, compound **6** undergoes a similar chemical transformation to that of **5** to afford **7**, as observed by ¹H NMR spectroscopy (Scheme 4). The atom connectivity in **7** was further confirmed by single-crystal X-ray diffraction (Figure 8). Although the free amino pincer arm did play a role in the carbene stability of **3** (*vide supra*), the control experiment failed to support the hypothesis that the dangling amino arm helps to mediate the insertion of carbonyl into the Al–carbene bond. Thus, an alternative pathway to afford **5** and **7** has also been considered, involving intermolecular nucleophilic attack of the NHC ligand via a five-coordinate Al complex (pathway B). Considering the fact that there are several cases of isolated five-coordinate organoaluminum complexes supported by a structurally rigid multidentate framework,¹⁷ the latter pathway is the more likely of the two.

Conclusion

In conclusion, a soluble amino-linked imidazolium salt, 2, has been synthesized. Deprotonation of 2 with $NaN(TMS)_2$ produced the marginally stable compound 3, whose crystal structure suggests that the instability is the consequence of a detrimental effect arising from the interaction of the amino sidearm with the free carbene center. The rare example of an amino-linked NHC-Al complex, 4, was obtained, and its solid state structure is consistent with the formation of monomeric distorted tetrahedral Al species in which the NHC binds via donation of the lone pair to the electrophilic metal center, without coordinating to the dangling arm of *tert*-butylamine. Benzaldehyde readily inserts into the Al-carbene bond of 4, affording a zwitterionic complex consisting of a distorted pseudotetrahedral aluminate center covalently linked to imidazolium, 5. A similar chemical transformation with benzaldehyde was observed for compound 6, [C{(MES)N(CHCH)N-(MES)}]•AlMe₃, suggesting that the dangling amino arm of NHC is not responsible for mediating the insertion of carbonyl into the Al-carbene bond. We hope that these observations with regard to amino-pendant-linked NHC and their Al complexes will open up new avenues for chemical reactivity with other main group elements. Further experimental and theoretical studies on Al complexes supported by amino-linked NHC are now underway.

Experimental Section

General Procedures. All air-sensitive manipulations were performed under an atmosphere of nitrogen using Schlenk techniques and/or a glovebox. Toluene, hexane, THF, and ether were purified by passage through a column of activated alumina using a solvent purification system purchased from Innovative Technology, Inc. Deuterated benzene and toluene were dried by vacuum transfer from activated molecular sieves. LiN(SiMe₃)₂, AlMe₃ (2.0 M in toluene), and AlEt₃ (1.0 M in hexane) were purchased from Aldrich and used without further purification. NaN(SiMe₃)₂ was obtained from Alfa Aesar. ¹H and ¹³C NMR spectra were recorded on Bruker 300 MHz, Bruker 400 MHz, and Bruker 500 MHz spectrometers using the residual proton signal in the deuterated solvent for reference.Compound1,^{2b}[HC{(MES)N(CHCH)N(CH₂CH₂NH*t*Bu}]-HBr₂, and 1,3-bis(mesityl)imidazol-2-ylidene¹⁸ were prepared as previously reported.

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Preparation of [HC{(MES)N(CHCH)N(CH₂CH₂NHtBu]]Br (2). To a solution of 1.0 M sodium hydroxide was added compound **1** (4.000 g, 8.90 mmol). The mixture was stirred at room temperature for 4 h. The resulting solution was extracted with CH₂Cl₂, and the organic layer was dried over MgSO₄. The solvent was removed *in vacuo* to afford a white residue, which was dissolved in 50 mL of acetone/CH₂Cl₂ (50:50 by volume) and cooled to -10 °C to afford pure white microcrystals. Yield: 85% (2.790 g). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 9.70 (br, 1H, NCHN), 8.01 (s, 1H,CH), 7.05 (s, 1H, CH), 6.85 (s, 2H, C₆H₂), 4.64 (t, ³J_{H-H} = 6 Hz, 2H, CH₂), 2.88 (t, ³J_{H-H} = 6 Hz, 2H, CH₂), 2.20 (s, 3H, CH₃), 1.93 (s, 6H, CH₃), 0.85 (s, 9H, tBu). ¹³C NMR (CDCl₃, 100 MHz, 20 °C): δ 141.0 (NCHN), 138.2 (Ar), 134.2 (Ar), 130.7 (Ar), 129.6 (Ar), 123.6 (NCH), 122.1 (NCH₂), 50.6 (NCH₂), 49.9 (NCMe₃), 42.1 (NCH₂),



Figure 7. Molecular diagram of 6 with the thermal ellipsoids drawn at the 30% probability level. All other hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): AI-C(1) 1.9750(19), AI-C(2) 1.9870(15), AI-C(2A) 1.9870(15), AI-C(3) 2.0965(16), N(1)-C(3) 1.359(2), N(2)-C(3) 1.365(2), N(1)-C(3)-N(2) 103.44(13).

Table 1. Crystallographic Data and Refinement for 2, 3, and 3-LiBr

2	3	3-LiBr
$C_{18}H_{28}BrN_3$	$C_{18}H_{27}N_3$	C22H35BrLiN3O
366.34	285.43	444.38
monoclinic	triclinic	triclinic
P2(1)/n	$P\overline{1}$	$P\overline{1}$
8.7287(3)	9.3823(3)	12.1381(5)
17.7547(5)	9.6495(4)	14.1671(5)
12.5192(4)	10.0070(4)	14.4333(5)
90	83.027(2)	91.415(2)
105.4620(10)	88.846(2)	106.716(2)
90	74.717(2)	95.938(2)
4	2	4
1.301	1.093	1.250
15687/3289	14210/3903	59612/8257
0.0358	0.0219	0.0462
1.027	1.029	1.042
0.0338/0.0759	0.0443/0.1261	0.0503/0.1294
	$\begin{array}{c} \textbf{2} \\ \hline \textbf{C}_{18}\textbf{H}_{28}\textbf{BrN}_3 \\ 366.34 \\ monoclinic \\ P2(1)/n \\ 8.7287(3) \\ 17.7547(5) \\ 12.5192(4) \\ 90 \\ 105.4620(10) \\ 90 \\ 4 \\ 1.301 \\ 15687/3289 \\ 0.0358 \\ 1.027 \\ 0.0338/0.0759 \end{array}$	$\begin{array}{cccc} 2 & 3 \\ \hline C_{18}H_{28}BrN_3 & C_{18}H_{27}N_3 \\ 366.34 & 285.43 \\ monoclinic & triclinic \\ P2(1)/n & P\bar{1} \\ 8.7287(3) & 9.3823(3) \\ 17.7547(5) & 9.6495(4) \\ 12.5192(4) & 10.0070(4) \\ 90 & 83.027(2) \\ 105.4620(10) & 88.846(2) \\ 90 & 74.717(2) \\ 4 & 2 \\ 1.301 & 1.093 \\ 15687/3289 & 14210/3903 \\ 0.0358 & 0.0219 \\ 1.027 & 1.029 \\ 0.0338/0.0759 & 0.0443/0.1261 \\ \end{array}$

28.9 (*tBu*), 20.9 (Ar-*Me*), 17.2 (Ar-*Me*). Anal. Calcd for $C_{18}H_{28}BrN_3$: C, 59.01; H, 7.70; N, 11.47. Found: C, 58.64; H, 8.05 N, 11.50.

Preparation of [C{(MES)N(CHCH)N(CH₂CH₂NH*t***Bu}] (3). To the suspension of 3 (3.680 g, 10.0 mmol) in 40 mL of THF was added a THF solution of NaN(TMS)₂ (1.830 g, 10.0 mmol) at -**



Figure 8. Molecular diagram of **7** with the thermal ellipsoids drawn at the 30% probability level. All other hydrogen atoms are omitted for clarity.

Table 2. Crystallographic Data and Refinement for 4a, 5, 6, and 7

	4a	5	6	7
formula	C ₂₁ H ₃₆ AlN ₃	C ₂₈ H ₄₂ AlN ₃ O	C22H27AlCl2N2	C31H39AlN2O
fw	357.51	463.63	417.34	482.62
cryst syst	orthorhombic	triclinic	orthorhombic	monoclinic
space group	Pbca	$P\overline{1}$	Pnma	P2(1)/n
a (Å)	8.4077(17)	9.6323(3)	23.0321(9)	9.5070(2)
b (Å)	16.499(3)	12.5350(4)	12.1449(5)	15.8593(4)
<i>c</i> (Å)	32.626(7)	13.8141(7)	7.9660(3)	19.3497(5)
α (deg)	90	108.364(2)	90	90
β (deg)	90	108.548(2)	90	92.5880(10)
γ (deg)	90	103.3880(10)	90	90
Z	8	2	4	4
$D_{\text{calcd}} \text{ (mg/m}^3)$	1.049	1.104	1.244	1.100
reflns collected	15 914/3972	17 488/4881	18 391/2577	26 403/6678
indep reflns (R_{int})	0.0473	0.0330	0.0277	0.0693
goodness-of-fit on F^2	1.082	1.077	1.057	1.022
$\mathbf{R}1, \mathbf{wR}2 \ [I > 2\sigma(I)]$	0.0534/0.1411	0.0439/0.1049	0.0737/0.2406	0.0549/0.1257

20 °C. After stirring for 10 min, the insoluble salt was removed from the reaction mixture by filtering through Celite to afford a light yellowish solution. The volatiles were removed under vacuum, and the product was further purified by crystallization from a concentrated ether solution at -30 °C. Yield: 67% (1.910 g). ¹H NMR (C₆D₆, 500 MHz, 25 °C): δ 6.75 (s, 2H, C₆H₂), 6.64 (d, ³J_{H-H} = 1.5 Hz, 1H, CH), 6.39 (d, ³J_{H-H} = 1.5 Hz, 1H, CH), 4.00 (t, ³J_{H-H} = 6.0 Hz, 2H, CH₂), 2.83 (dt, 2H, CH₂), 2.11 (s, 3H, CH₃), 2.07 (s, 6H, CH₃), 1.35 (t, ³J_{H-H} = 7.2 Hz, H, NH), 0.98 (s, 9H, *tBu*). ¹³C NMR (C₆D₆, 125 MHz, 25 °C): 216.3 (*C*_{carbene}), 139.3 (*Ar*), 137.0 (*Ar*), 135.4 (*Ar*), 129.0 (*Ar*), 120.2 (NCH), 119.5 (NCH), 52.3 (NCH₂), 49.9 (NCMe₃), 44.2 (NCH₂), 29.2 (*tBu*), 20.9 (Ar-*Me*), 18.1 (Ar-*Me*). HR-MS (FAB): *m*/*z* [(M + H)⁺] calculated for C₁₈H₂₈N₃ 286.2278, found 286.2287.

Preparation of [C{(MES)N(CHCH)N(CH2CH2NHtBu}]·LiBr-(THF) (3-LiBr). To a suspension of 2 (3.680 g, 10.0 mmol) in 40 mL of THF was added a solution of LiN(TMS)₂ (1.670 g, 10.0 mmol) in THF at -20 °C. After stirring for 10 min, the solvent was removed in vacuo to afford a white powdery solid, which was further purified by crystallization from toluene/THF (70:30 by volume) at -30 °C to afford clear colorless crystals. Yield: 83% (3.100 g). ¹H NMR (C₆D₆, 500 MHz, 25 °C): δ 6.77 (s, 2H, C₆H₂), 6.44 (s, 1H, CH), 6.19 (s, 1H, CH), 4.00 (br, 2H, CH₂), 3.54 (t, ${}^{3}J_{H-H} = 6.0 \text{ Hz}, 4\text{H}, THF$), 2.62 (br, 2H, CH₂), 2.12 (s, 3H, CH₃), 2.08 (s, 6H, CH₃), 1.81 (br, 1H, NH), 1.39 (t, ${}^{3}J_{H-H} = 6.0$ Hz, 4H, *THF*), 1.06 (s, 9H, *tBu*). ¹³C NMR (C₆D₆, 125 MHz, 25 °C): 206.5 (br, C_{carbene}), 139.5 (Ar), 137.3 (Ar), 135.6 (Ar), 129.0 (Ar), 120.0 (NCH), 119.0 (NCH), 67.8 (THF), 51.5 (NCH₂), 50.4 (NCMe₃), 44.4 (NCH₂), 29.1 (tBu), 25.7 (THF), 21.4 (Ar-Me), 18.2 (Ar-Me). Mp: 122 °C. Anal. Calcd for C₂₂H₃₅BrLiN₃O: C, 59.46; H, 7.94; N, 9.46. Found: C, 59.45; H, 7.56; N, 9.40.

Preparation of [C{(MES)N(CHCH)N(CH2CH2NHtBu}] · AlMe3 (4a). To a THF solution of 3-LiBr (10.0 mmol, 4.430 g) was added 2.0 M AlMe₃ in toluene (10.0 mmol, 5 mL) at room temperature. After stirring for 12 h, the solvent was removed in vacuo to afford a white solid. The crude solid was extracted with toluene (30 mL), and the white insoluble precipitate was removed by filtration. The filtrate was dried in vacuo to afford a white solid, which was further purified by recrystallization from ether/hexane (50:50 volume) at −30 °C. Yield: 75% (2.68 g). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 6.69 (s, 2H, C₆H₂), 6.67 (d, ³J_{H-H} = 1.5 Hz, 1H, CH), 5.91 (d, ${}^{3}J_{H-H} = 1.5$ Hz, 1H, CH), 4.00 (t, ${}^{3}J_{H-H} = 5.8$ Hz, 2H, CH₂), 2.62 (m, 2H, CH₂), 2.05 (s, 3H, CH₃), 1.90 (s, 6 H, CH₃), 0.84 (s, 9H, tBu), 0.26 (t, ${}^{3}J_{H-H} = 8.0$ Hz, 1H, NH), -0.48 (s, 9H, CH₃). ${}^{13}C$ NMR (C₆D₆, 125 MHz, 25 °C): 177.0 (br, C_{carbene}), 139.2 (Ar), 135.3 (Ar), 135.3 (Ar), 129.2 (Ar), 122.2 (NCH), 121.0 (NCH), 50.9 (NCH₂), 50.1 (NCMe₃), 43.7 (NCH₂), 28.9 (tBu), 21.0 (Ar-Me), 15.5 (Ar-Me), -7.2 (AlMe₃). Mp: 59 °C. Anal. Calcd for C21H36AlN3: C, 70.55; H, 10.15; N, 11.75. Found: C, 70.12; H, 10.30; N, 11.59.

Preparation of [C{(MES)N(CHCH)N(CH₂CH₂NHtBu}] · AlEt₃ (4b). To a THF solution of 3-LiBr (10.0 mmol, 4.430 g) was added 1.0 M AlEt₃ in hexane (10.0 mmol, 10 mL) at room temperature. After stirring for 12 h, the solvent was removed in vacuo to afford a white powdered solid. The crude solid was extracted with toluene (30 mL), and the white insoluble precipitate was removed by filtration. The filtrate was dried *in vacuo* to afford a white solid, which was further purified by recrystallization from ether/hexane (50:50 volume) at -30 °C. Yield: 70% (2.80 g). ¹H NMR (C₆D₆, 500 MHz, 25 °C): δ 6.79 (d, ${}^{3}J_{H-H} = 1.5$ Hz, 1H, CH), 6.69 (s, 2H, C₆ H_2), 5.90 (d, ${}^{3}J_{H-H} = 1.5$ Hz, 1H, CH), 4.04 (t, ${}^{3}J_{H-H} = 5.5$ Hz, 2H, CH₂), 2.64 (m, 2H, CH₂), 2.06 (s, 3H, CH₃), 1.90 (s, 6 H, CH_3), 1.45 (t, ${}^{3}J_{H-H} = 8$ Hz, 9H, Al CH_2CH_3), 0.85 (s, 9H, tBu), 0.27 (t, ${}^{3}J_{H-H} = 8.0$ Hz, 1H, NH), 0.09 (q, ${}^{3}J_{H-H} = 8$ Hz, 6H, AlCH₂). ¹³C NMR (C₆D₆, 125 MHz, 25 °C): 176.1 (br, C_{carbene}), 139.2 (Ar), 135.8 (Ar), 135.1 (Ar), 129.3 (Ar), 122.2 (NCH), 121.4 (NCH), 50.8 (NCH₂), 50.1 (NCMe₃), 43.6 (NCH₂), 28.9 (tBu), 21.0 (Ar-Me), 17.5 (Ar-Me), 11.5 (CH₂CH₃), 0.8 (CH₂). HR-MS (EI): m/z [(M - Et)⁺] calculated for C₂₂H₃₇AlN₃ 370.2803, found 370.2798.

Preparation of (Me₃Al-OCHPh)[C{(MES)N(CHCH)N(CH₂CH₂-NHtBu}] (5). To a THF solution of 4 (0.28 mmol, 0.100 g) was added benzaldehyde (0.28 mmol, 0.030 g) at room temperature. After stirring for 2 h, the solvent was removed in vacuo to afford a yellow residue, which was further purified by recrystallization from ether at -30 °C to afford colorless crystals. Yield: 61.8% (0.073 g). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 7.26–6.99 (m, 5H, Ph), 6.64 (s, 1H, CH), 6.53 (s, 1H, C₆H₂), 6.50 (s, 1H, C₆H₂), 6.18 (s, 1H, CH), 5.62 (s, 1H, PhCH), 4.91 (m, 1H, CH₂), 3.81 (m, 1H, CH₂), 2.76 (m, 1H, CH₂), 2.44 (m, 1H, CH₂), 2.06 (s, 3H, CH₃), 1.98 (s, 3H, CH₃), 1.35 (s, 3H, CH₃), 0.88 (s, 9H, tBu), 0.63 $(dd, {}^{3}J_{H-H} = 8.4 \text{ Hz}, 1\text{H}, \text{N}H), -0.31 (s, 9\text{H}, \text{Al}Me_{3}).$ ${}^{13}\text{C}$ NMR (C₆D₆, 100 MHz, 25 °C): 152.9 (NCN), 143.8 (Ar), 141.3 (Ar), 135.8 (Ar), 135.2 (Ar), 131.3 (Ar), 130.4 (Ar), 130.0 (Ar), 128.8 (Ar), 128.3 (Ar), 128.1 (PhCO), 127.7 (Ar), 123.2 (NCH), 119.8 (NCH), 72.0 (NCMe₃), 50.5 (NCH₂), 42.7 (NCH₂), 29.4 (tBu), 21.3 (Ar-Me), 18.3 (Ar-Me), 17.6 (Ar-Me), -5.4 (AlMe₃). Mp: 93 °C. Anal. Calcd for C₂₈H₄₂AlN₃O: C 72.54, H 9.13, N 9.06. Found: C 72.37, H 9.06, N 8.99.

Preparation of [C{(MES)N(CHCH)N(MES)}] · **AlMe**₃ (6). To a THF solution of 1,3-bis(mesityl)imidazol-2-ylidene (10 mmol, 3.04 g) was added AlMe₃ in toluene (10.0 mmol, 5 mL) at room temperature. After stirring for 12 h, the solvent was removed *in vacuo* to afford a white powdered solid, which was further purified by recrystallization from toluene/THF (70:30 by volume) at -30 °C. Yield: 75% (2.82 g). ¹H NMR (C₆D₆, 500 MHz, 25 °C): δ

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6.82 (s, 4H, C₆ H_2), 6.06 (s, 2H, CH), 2.15 (s, 6H, CH₃), 2.07 (s, 12H, CH₃), -0.75 (s, 9H, Me). ¹³C NMR (C₆D₆, 125 MHz, 25 °C): 178.2 (br, C_{carbene}), 139.4 (Ar), 135.5 (Ar), 135.3(Ar), 129.3 (Ar), 122.7 (NCH), 21.0 (Ar-Me), 17.6 (Ar-Me), -7.6 (Me).

Preparation of (Me₃Al-OCHPh)[C{(MES)N(CHCH)N(MES)}] (7). To a THF solution of **6** (1 mmol, 0.376 g) was added benzaldehyde (1.1 mmol, 0.111 g) at room temperature. After stirring for 2 h, the solvent was removed *in vacuo* to afford a yellow residue, which was further purified by recrystallization from toluene/ THF (70:30 by volume) at -30 °C to afford yellow crystals. Yield: 50% (0.241 g). Suitable crystals for crystallographic determination were grown from a hexane diffusion into a THF solution. ¹H NMR (d_8 -THF, 500 MHz, 25 °C): δ 7.56 (s, 2H, C₆H₂), 7.15 (s, 2H, CH), 7.02 (dd, $^3J_{H-H} = 7.0 H_Z$, 2H, Ph), 6.94–6.91 (m, 2H, Ph), 6.93 (s, 2H, C₆H₂), 6.78 (d, $^3J_{H-H} = 7.5 H_Z$, 2H, Ph), 5.83 (s, 1H, PhCH), 2.38 (s, 6H, CH₃), 2.30 (s, 6H, CH₃), 1.71 (s, 6H, CH₃), -1.47 (s, 9H, Me). ¹³C NMR (d_8 -THF, 125 MHz, 25 °C): 153.3 (NCN), 142.6 (Ar), 141.6 (Ar), 136.8 (Ar), 136.6 (Ar), 132.5 (Ar), 130.3 (NCH), 130.1 (Ar), 128.1 (Ar), 127.94 (Ar), 127.90 (Ar), 124.1 (Ar), 70.5 (PhCO), 21.3 (Ar-*Me*), 18.6 (Ar-*Me*), 17.7 (Ar-*Me*), -6.8 (*Me*). HR-MS (EI): [(M – Me)⁺] calculated for C₃₀H₃₆AlN₂O 467.2643; found 467.2643.

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Supporting Information Available: Crystal data are also available as CIF files for compounds **2**, **3**, **3-LiBr**, **4a**, **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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