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Synthesis and Characterization of the Monomeric Vicinal Dianion $Li_2(THF)_3[ArNC(SiMe_3)_2]$ and the Aluminum and Lithium Derivatives of the Amido Ligand $[ArNCH(SiMe_3)_2]^-$

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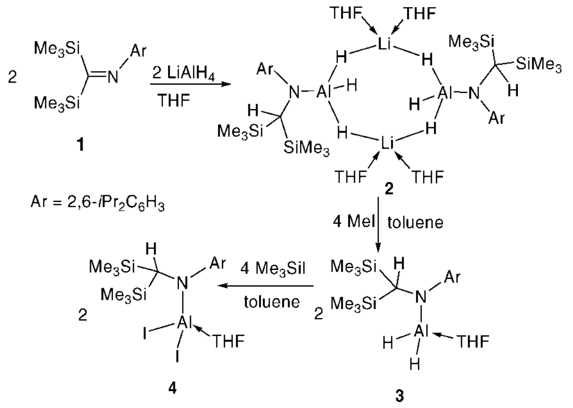
Reaction of the imine $ArNC(SiMe_3)_2$ (**1**; Ar = 2,6-*i*$Pr_2C_6H_3$) with $LiAlH_4$ in THF resulted in the formation of the dimeric hydroaluminate $[(THF)_2LiH_3AlL]_2$ (**2**; L = $[ArNCH(SiMe_3)_2]^-$). **2** reacted with CH_3I to give the monomeric aluminum dihydride $LAlH_2(THF)$ (**3**), which can be converted to the diiodide $LAlI_2(THF)$ (**4**) upon treatment with 2 equiv of Me_3SiI. The quasi two-coordinate lithium amide $Li(OEt_2)L$ (**8**) with an intramolecular CH−Li interaction was obtained by the deprotonation of the corresponding amine LH (**5**) generated from hydrolysis of **2**. Reduction of **1** with lithium in THF resulted in the first structurally characterized monomeric C−N vicinal dianion, $Li_2(THF)_3[ArNC(SiMe_3)_2]$ (**6**), and the monomeric lithium amide $Li(THF)_2L$ (**7**).

Introduction

Reduction of imines by active metals or low-valent metal complexes constitutes a powerful method for the synthesis of vicinal diamines and α-amino alcohols via their homocoupling and cross-coupling reactions.[1] Earlier studies have shown that reduction of imines by alkali metals generated various products, among which the corresponding radical anions and vicinal dianions are the key intermediates.[2] Despite the fundamental importance of these highly reactive intermediates, detailed structural studies of these intermediates have not been achieved, owing to their high reactivity and tendency to form large aggregates in both solution and the solid state.

There has been considerable interest in the synthesis and structural characterization of organolithium species, since they are versatile nucleophiles and ligand transfer reagents in organic and organometallic synthesis.[3] Bulky amide ligands are particularly attractive because of their unusual kinetic stabilizing ability for unusual oxidation state, low-coordinate, and highly reactive metal complexes.[4] Imines with different substituents are readily available and are thus excellent precursors for the preparation of various secondary amines, which can be subsequently converted to lithium amides by deprotonation. Lithium aluminum hydride has been frequently used for the reduction of imines to generate the corresponding amines. The hydroaluminate intermediates may be isolated and fully characterized when imines with bulky substituents are employed.[5] Herein we report on the reduction of the bulky imine $ArNC(SiMe_3)_2$ (**1**; Ar = 2,6-*i*$Pr_2C_6H_3$)[6] with lithium aluminum hydride and lithium and the subsequent isolation and crystal structures of a trihydroaluminate, a monomeric vicinal dianion, and a monomeric lithium amide with an intramolecular CH−Li interaction.

Scheme 1



Results and Discussion

The reaction of $ArNC(SiMe_3)_2$ (**1**; Ar = 2,6-*i*$Pr_2C_6H_3$) with $LiAlH_4$ in refuxing THF afforded the hydroaluminate $[(THF)_2LiH_3AlL]_2$ (**2**; L = $[ArNCH(SiMe_3)_2]^-$) (Scheme 1). Crystals of **2** could be obtained from toluene at low temperature. The X-ray crystal structure of **2** (Figure 1) disclosed that **2** is a dimer with a hydride-bridged eight-membered ring. The structure is similar to those of several structurally characterized trihydroalu-

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(1) For examples: (a) Roskamp, E. J.; Pederson, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551. (b) Jones, D. S.; Srinivasan, A.; Kasina, S.; Fritzgerg, A. R.; Wilkening, D. W. *J. Org. Chem.* **1989**, *54*, 1940. (c) Liao, P.; Huang, Y.; Zhang, Y. *Synth. Commun.* **1997**, *27*, 1483. (d) Talukdar, S.; Banerji, A. *J. Org. Chem.* **1998**, *63*, 3468. (e) Jin, W.; Makioka, Y.; Kitamura, T.; Fujiwara, Y. *J. Org. Chem.* **2001**, *66*, 514. (f) Kim, M.; Knettle, B. W.; Dahlen, A.; Himersson, G.; Flowers, R. A., II *Tetrahedron* **2003**, *59*, 10397.

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(5) (a) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1999**, *38*, 4467. (b) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4652. (c) Cole, M. L.; Jones, C.; Junk, P. C.; Kloth, M.; Stasch, A. *Chem. Eur. J.* **2005**, *11*, 4482.

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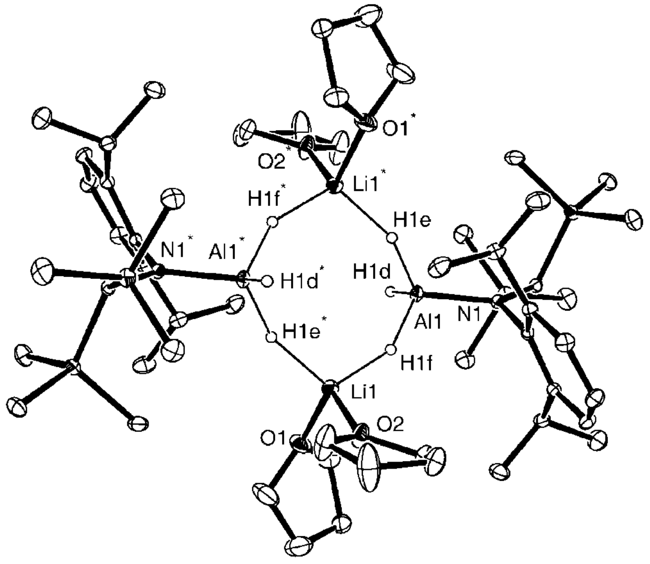

Figure 1. Ortep drawing of **2** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.8473(16), Li1−O1 = 1.927(4), Li1−O2 = 1.916(4), Al1−H1d = 1.53(3), Al1−H1e = 1.58(3); O1−Li1−O2 = 107.86(18).

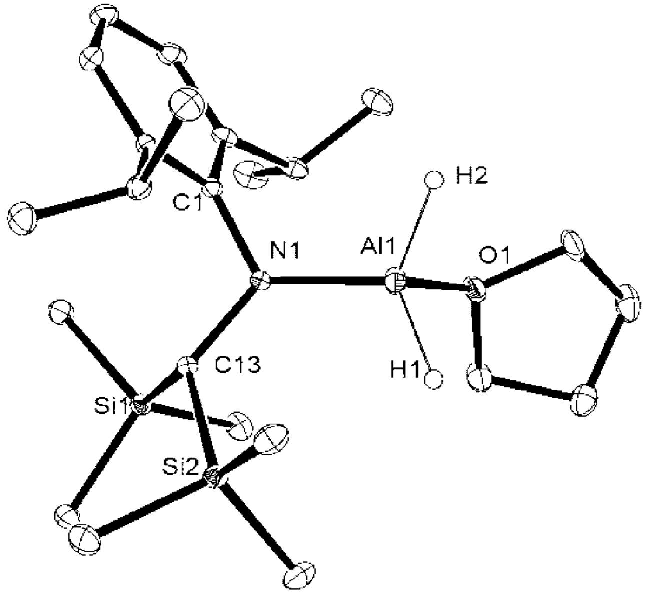

Figure 2. Ortep drawing of **3** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): N1−Al1 = 1.8251(13), O1−Al1 = 1.9404(13), N1−C1 = 1.4334(18), N1−C13 = 1.5161(17), Al1−H1 = 1.518(17), Al1−H2 = 1.50(2); N1−Al1−O1 = 114.89(5).

minates stabilized by bulky ligands.[7] Treatment of **2** with neat MeI in toluene yielded the neutral aluminum dihydride $LAlH_2(THF)$ (**3**) in good yield.[8] Attempts to remove the coordinated THF molecule in **3** at elevated temperatures were unsuccessful, due to its low thermal stability. The structure of **3** is shown in Figure 2 along with selected bond parameters. **3** is a monomer, and the central aluminum atom adopts a distorted-tetrahedral geometry. Treatment of **3** with 2 equiv of Me_3SiI gave the expected aluminum diiodide $LAlI_2(THF)$ (**4**) in excellent yield. Crystals of **4** from *n*-hexane at 4 °C are suitable for X-ray investigation, and the results of a structural analysis are presented in Figure 3. **4** is a monomer, and the molecular geometry is very similar to that of **3** (Figure 3). The aluminum atom, bound to two iodide ligands, a THF donor, and a bulky amido ligand, is four-coordinate. The Al−N bond length (1.8063(19) Å) of **4** is slightly longer than that in $(Ar(SiMe_3)NAlI_2)_2$(1.784(6) Å).[9] The Al−I bond lengths (2.5418(7) and 2.5710(7) Å) in **4** are comparable to those observed in the reported alumiunm diiodides.[10]

Reduction of the imine **1** with an excess of lithium in dry THF at room temperature for 6 h yielded a deep red solution, from which dark red crystals of **6** were isolated. Similar reduction with 1 equiv of lithium gave **7** as orange crystals in modest yield. **7** was presumably formed via the abstraction of a hydrogen atom from the solvent by the highly reactive radical anion $[ArNC(SiMe_3)_2]^-$ Reaction of **1** with $LiAlH_4$ in refluxing THF followed by hydrolysis yielded the amine **5**, which can be deprotonated in THF and diethyl ether to give **7** and **8**, respectively, in high yield (Scheme 2). All of the lithium salts are extremely air and moisture sensitive.

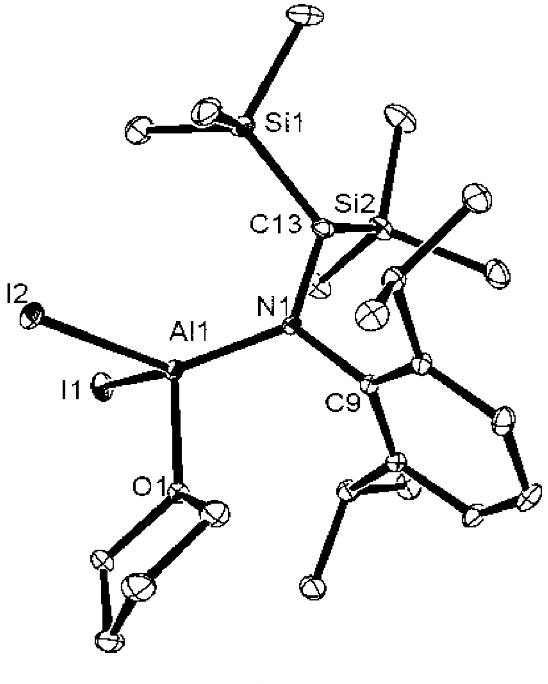

Figure 3. Ortep drawing of **4** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.8063(19), Al1−O1 = 1.8682(16), Al1−I1 = 2.5418(7), Al1−I2 = 2.5710(7), N1−C9 = 1.452(3), N1−C13 = 1.530(3); N1−Al1−O1 = 106.13(8), N1−Al1−I1 = 119.37(7), O1−Al1−I1 = 104.10(6), N1−Al1−I2 = 124.28(7), O1−Al1−I2 = 95.30(6), I1−Al1−I2 = 103.33(3).

The ^1H and ^{13}C NMR spectra of **6** only show two broad resonances for the three coordinated THF molecules, indicating rapid exchange of the two lithium ions on the NMR time scale at ambient temperature. Thus, the ^7Li NMR spectrum displays one signal, appearing at −1.40 ppm. The ^{13}C signal of the anionic carbon is observed at 5.80 ppm, which is a marked shift

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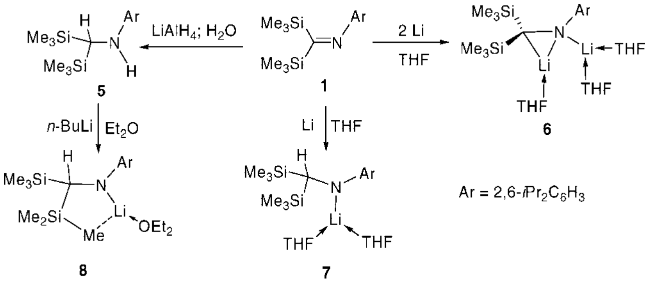
Scheme 2



to upper field relative to that of **1** (ca. δ 218 ppm) due to the location of the negative charge.[6] The ^{29}Si NMR resonance of the trimethylsilyl groups also appeared at high field (δ −15.7 ppm). The molecular structure of **6** was finally confirmed by X-ray single-crystal analysis.

Single crystals of **6** suitable for X-ray analysis were obtained from THF at −40 °C, and crystallographic analysis revealed a monomeric structure (Figure 4). The most notable structural feature is that the Li2 ion is coordinated to both the central C1 and N1 atoms with the formation of the unique lithiaazacyclopropane structure, while the Li1 ion is coordinated to the N1 atom. Both the lithium ions are three-coordinate with the normal Li2−C1 bond length of 2.072(5) Å and Li−N distances of 1.907(5) and 1.908(5) Å.[11] The Li1−Li2 separation is 2.637 Å. The C1−Li2−N1 angle (44.86(16)°) is acute. The C1−N1 bond length (1.526(4) Å) is significantly longer than those found in structurally characterized transition-metal η^2-imine complexes (1.41–1.45 Å),[12] indicating the strong vicinal dianonic character of **6**. The geometry around the C1 atom is almost planar (mean derivation from the plane 0.0381 Å), while that of the N1 atom is pyramidal.

Although the dianion species $(Ph_2CNPh)^{2-}$ is known and has served as a model compound in studying the chemical behavior of such anions, the isolation and structural characterization of this type of alkali-metal species has not been realized to date.[2] It is noted that a handful of metal η^2-imine complexes, including those of calcium and lanthanides, have been structurally characterized.[12] To the best of our knowledge, compound **6** represents the first well-characterized vicinal dianion generated by reduction of an imine with alkali metals.

The lithium amides **7** and **8** were characterized by ^{1}H, ^{7}Li, ^{13}C, and ^{29}Si NMR spectroscopy. The ^{1}H NMR spectrum of **7** indicates that two THF molecules are coordinated to the lithium ion. The lithium resonance in the ^{7}Li NMR spectrum of **7** appears at −2.25 ppm. The spectroscopic data support the monomeric lithium amide structure with the three-coordinate lithium atom. The ^{1}H NMR spectrum of **8** disclosed that only one diethyl ether molecule is solvated. In order to disclose the coordination environment of the lithium ion, an X-ray single-crystal analysis was carried out.

Single crystals of **8** were obtained from *n*-hexane at −25 °C. The structure is shown in Figure 5, along with selected bond parameters. Compound **8** is monomeric, with a formally two-coordinate lithium ion. It is noted that two-coordinated lithium ions have been found in dimeric and oligomeic lithium amides.[13] The Li−N bond length (1.853(3) Å) is relatively shorter compared to those found in the known monomeric lithium amides, due to the low-coordinate lithium atom of **8**. There are only a few structurally characterized monomeric lithium amides,

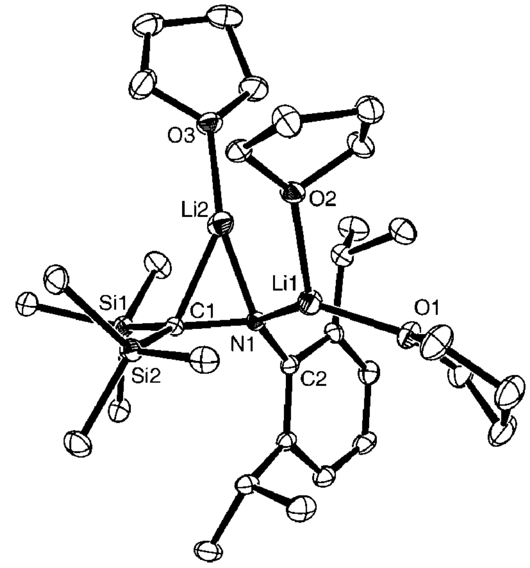


Figure 4. Ortep drawing of **6** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Li1−N1 = 1.908(5), Li1−O1 = 1.907(6), Li1−O2 = 2.024(4), C1−Li2 = 2.072(5), N1−Li2 = 1.907(5), Li2−O3 = 1.957(5), C1−N1 = 1.526(4); C1−N1−Li2 = 73.3(2), N1−C1−Li2 = 61.8(2), N1−Li2−C1 = 44.86(16), Si1−C1−Si2 = 120.58(19).

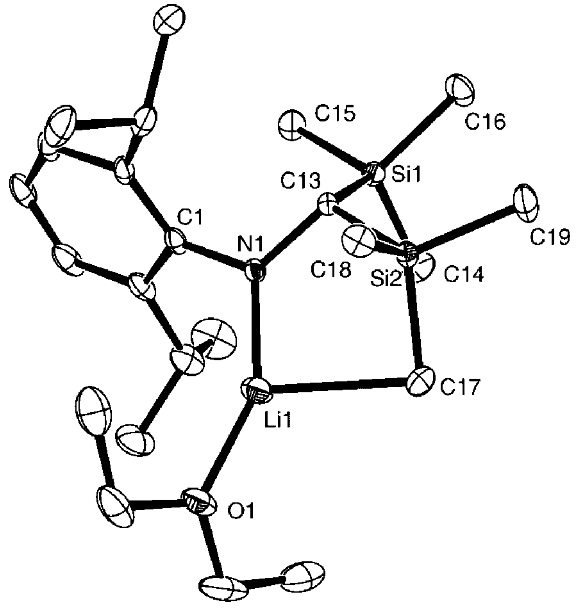


Figure 5. Ortep drawing of **8** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): N1−C1 = 1.3956(18), N1−Li1 = 1.853(3), N1−C13 = 1.4999(18), Li1−O1 = 1.900(3), Si2−C17 = 1.8836(17); C1−N1−C13 = 118.88(12), C1−N1−Li1 = 115.11(13), C13−N1−Li1 = 125.65(13), N1−Li1−O1 = 152.08(19).

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in which the lithium ions are three- and four-coordinate with Li−N bond lengths ranging from 1.895 to 1.957 Å.[14] The geometry of the N1 atom is almost planar (mean derivation from the plane 0.0200 Å). The most striking feature of **8** is the close Li1−C17 interaction (2.511 Å) due to the coordination unsaturation of the lithium ion. This kind of interaction is not common for solvated alkali-metal species. However, it has been observed in bulky silyl- and germyllithium and alkyllithium species.[15]

In conclusion, hydroalumination of the bulky imine **1** yielded the well-defined hydroaluminate **2**, which could be easily converted to the neutral aluminum dihydride and diiodide **3** and **4**. The monomeric vicinal dianionic species **6** has been isolated and structurally characterized. The lithium amide **8** is a monomer with the shortest Li−N bond length observed in the solid state. These results indicate that the bulky amido ligand L could support monomeric metal complexes.

Experimental Section

General Remarks. All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately before use. The chemicals used in this study were purchased from Aldrich and Acros and used as received. $ArNC(SiMe_3)_2$ (Ar = 2,6-iPrC_6H_3) was prepared as described in the literature.[6] The ^1H, ^7Li, ^{13}C, and ^{29}Si NMR spectroscopic data were recorded on Varian Mercury Plus 300, 400, and 600 M NMR spectrometers.

Synthesis of $[(THF)_2LiH_3AlL]_2$ (2). A solution of imine **1** (1.765 g, 5.0 mmol) in THF was added to $LiAlH_4$ (0.209 g, 5.5 mmol) in THF at room temperature. The mixture was refluxed for 10 h. The solvent was removed under vacuum, and the remaining yellow-white solid was washed with *n*-hexane and recrystallized from toluene at −40 °C to give colorless crystals of **2** (1.80 g, 70%). Mp: 147–149 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 7.07–7.10 (m, 3H, Ar *H*), 4.07 (sept, *J* = 6.8 Hz, 2H, C*H*Me$_2$), 3.47 (t, *J* = 6.0 Hz, 8H, OC*H*$_2$), 2.59 (s, 1H, C*H*(SiMe$_3$)$_2$), 1.52 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.38 (m, *J* = 6.0 Hz, 8H, OCH$_2$C*H*$_2$), 1.30 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.44 (s, 18H, Si*Me*$_3$). ^{13}C NMR (400 MHz, C_6D_6): δ 157.22, 146.28, 124.22, 121.58 (Ar *C*), 68.40 (O*C*H$_2$), 50.77 (*C*H(SiMe$_3$)$_2$), 27.72, 27.62 (*C*H(CH$_3$)$_2$), 25.54 (O*C*H$_2$CH$_2$), 24.56 (CH(*Me*$_3$)$_2$), 2.79 (Si*Me*$_3$).

Synthesis of $LAlH_2(THF)$ (3). To a solution of **2** (0.52 g, 1.0 mmol) in toluene was added CH_3I (0.06 mL, 1.2 mmol) at room temperature. The mixture was then stirred at room temperature for 12 h. The solvent was removed under vacuum, and the remaining yellow-white solid was recrystallized from toluene to give colorless crystals of **3** (0.32 g, 73%). Mp: 100–102 °C dec. ^1H NMR (300 MHz, C_6D_6): δ 7.0–7.15 (m, 3H, Ar *H*), 4.0 (sept, *J* = 6.6 Hz, 2H, C*H*Me$_2$), 3.46 (t, *J* = 6.3 Hz, OC*H*$_2$), 2.65 (s, 1H, C*H*(SiMe$_3$)$_2$), 1.51 (d, *J* = 6.6 Hz, 6H, CH*Me*$_2$), 1.28 (d, *J* = 6.6 Hz, 6H, CH*Me*$_2$), 0.92 (m, *J* = 6.3 Hz, OCH$_2$C*H*$_2$), 0.40 (s, 18H, Si*Me*$_3$) ppm. ^{13}C NMR (300 MHz, C_6D_6): δ 153.35, 145.42, 125.11, 122.85 (Ar *C*), 71.84 (O*C*H$_2$), 50.15 (*C*H(SiMe$_3$)$_2$), 27.80, 27.02 (*C*HMe$_2$), 25.41 (OCH$_2$*C*H$_2$), 24.61 (CH*Me*$_2$), 2.42 (Si*Me*$_3$).

Synthesis of $LAlI_2(THF)$ (4). To a solution of **3** (0.44 g, 1.0 mmol) in toluene was added Me_3SiI (0.28 mL, 2.0 mmol) at room temperature. The mixture was then stirred at room temperature for 12 h. The solvent was removed under vacuum, and the remaining white solid was recrystallized from *n*-hexane at 4 °C to give colorless crystals of **4** (0.62 g, 90%). Mp: 126–128 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 6.94–7.02 (m, 3H, Ar *H*), 4.03 (sept, *J* = 6.4 Hz, 2H, C*H*Me$_2$), 3.42 (br s, 4H, OC*H*$_2$), 3.27 (s, 1H, C*H*(SiMe$_3$)$_2$), 1.37 (d, *J* = 6.4 Hz, 6H, CH*Me*$_2$), 1.29 (d, *J* = 6.4 Hz, 6H, CH*Me*$_2$), 0.84 (br s, 4H, OC*H*$_2$CH$_2$), 0.34 (s, 18H, Si*Me*$_3$). ^{13}C NMR (400 MHz, C_6D_6): δ 150.18, 149.42, 126.50, 125.10 (Ar *C*), 75.34 (O*C*H$_2$), 47.12 (*C*H(SiMe$_3$)$_2$), 28.13, 26.67 (*C*HMe$_2$), 25.53 (O*C*H$_2$CH$_2$), 24.39 (CH*Me*$_2$), 4.98 (Si*Me*$_3$).

Synthesis of $Li_2(THF)_3[ArNC(SiMe_3)_2]$ (6). A solution of imine **1** (1.77 g, 5.0 mmol) in THF (50 mL) was added to finely divided lithium turnings (0.074 g, 10.5 mmol) at room temperature. After the mixture was stirred for 6 h, all volatiles were removed. The remaining brown-red solid was recrystallized from THF at −40 °C to give dark red crystals of **6** (1.7 g, 60%). Mp: 109 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 6.69–7.20 (m, 3H, Ar *H*), 4.75 (sept, *J* = 6.80 Hz, 2H, C*H*Me$_2$), 3.32 (br s, 12H, OC*H*$_2$), 1.41 (d, *J* = 6.80 Hz, 12H, CH*Me*$_2$), 1.27 (br s, 12H, OCH$_2$C*H*$_2$), 0.42 (s, 18H, Si*Me*$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 158.6, 139.5, 123.7, 111.4 (Ar *C*), 70.2, 70.0 (O*C*H$_2$), 48.2 (*C*HMe$_2$), 26.2 (OCH$_2$*C*H$_2$), 25.7, 25.6 (CH*Me*$_2$), 5.8 (*C*(SiMe$_3$)$_2$), 0.87 (Si*Me*$_3$). ^7Li NMR (116.6 MHz, C_6D_6): δ −1.40. ^{29}Si NMR (59.6 MHz, C_6D_6, TMS): δ −15.73. UV/vis (hexane): λ_{max} (nm) 215, 244. UV/vis (THF): λ_{max} (nm) 247, 253, 259.

Synthesis of $Li(THF)_2L$ (7). This compound was prepared by the reduction of the imine **1** with 1 equiv of lithium (yield 50%) in THF or deprotonation of **5** with *n*-BuLi in THF at room temperature (yield 90%). Mp: 122 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 6.76–7.15 (m, 3H, Ar *H*), 4.21 (sept, *J* = 6.80 Hz, 1H, C*H*Me$_2$), 3.62 (sept, *J* = 6.80 Hz, 1H, C*H*Me$_2$), 3.33 (br s, 8H, OC*H*$_2$), 3.29 (s, 1H, C*H*(SiMe$_3$)$_2$), 1.50 (d, *J* = 6.80 Hz, 6H, CH*Me*$_2$), 1.31 (d, *J* = 6.80 Hz, 6H, CH*Me*$_2$), 1.23 (br s, 8H, OCH$_2$C*H*$_2$), 0.27 (s, 18H, Si*Me*$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 134.4, 125.9, 123.0, 112.5 (Ar *C*), 68.5 (O*C*H$_2$), 46.2 (*C*H(SiMe$_3$)$_2$), 29.0 (*C*HMe$_2$), 26.0 (CH*Me*$_2$), 25.9 (CH*Me*$_2$), 25.8 (CH*Me*$_2$), 25.3 (OCH$_2$*C*H$_2$), 0.71 (Si*Me*$_3$). ^7Li NMR (116.6 MHz, C_6D_6, 1 M LiCl in D_2O): δ −2.25. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 4.02.

Synthesis of $Li(OEt_2)L$ (8). A solution of *n*-BuLi (2.5 mL, 2.5 M in *n*-hexane) was added to a solution of **5** (0.34 g, 1.0 mmol) in Et_2O (40 mL) at room temperature. The mixture was stirred at room temperature for 15 h. The solvent was removed under vacuum to afford a yellow powder, which was recrystallized from *n*-hexane at −25 °C to give yellow crystals of **8** (0.39 g, 95%). Mp: 53−55 °C. ^1H NMR (400 MHz, C_6D_6): δ 6.80–7.12 (m, 3H, Ar *H*), 3.97 (br s, 1H, CHMe$_2$), 3.65 (br s, 1H, CHMe$_2$), 3.19 (s, 1H, CH(SiMe$_3$)$_2$), 2.74 (q, *J* = 7.20 Hz, 4H, OC*H*$_2$), 1.43 (d, *J* = 4.40 Hz, 6H, CH*Me*$_2$), 1.26 (d, *J* = 4.40 Hz, 6H, CH*Me*$_2$), 0.66 (t, *J* = 7.2 Hz, 6H, OCH$_2$C*H*$_3$), 0.21 (s, 18H, SiMe$_3$). ^{13}C NMR (400 MHz, C_6D_6): δ 156.8, 125.7, 123.0, 114.0 (Ar *C*), 66.3 (OCH$_2$), 45.0 (CH(SiMe$_3$)$_2$), 28.8 (CHMe$_2$), 26.7 (CHMe$_2$), 25.6 (CHMe$_2$), 25.3 (CHMe$_2$), 14.2 (OCH$_2$CH$_3$), 0.59 (SiMe$_3$). ^7Li NMR (116.6 MHz, C_6D_5−CD_3): δ −1.80. ^{29}Si NMR (59.6 MHz, C_6D_5−CD_3): δ −3.53.

X-ray Structure Determination. Data were collected on a Bruker Smart-Apex II diffractometer using graphite-monochromated Mo Kα (λ = 0.710 70 Å) radiation. All structures were solved by direct methods (SHELXS-97)[16] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by a riding model (SHELXL-

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97).[16] Crystallographic data for **2**: T = 113(2) K, monoclinic, space group $P2_1/n$, a = 13.225(2) Å, b = 17.355(3) Å, c = 14.270(3) Å, β = 95.577(2)°, V = 3259.7(10) Å^{3,} Z = 4, R1 = 0.0483, wR2 = 0.1312 for 7782 independent reflections; $R1$ = 0.0689, $wR2$ = 0.1392 for all data. Crystallographic data for **3**: T = 113(2) K, monoclinic, space group $P2_1$, a = 9.447(2) Å, b = 12.565(3) Å, c = 11.380(3) Å, β = 91.994(4)°, V = 1349.9(6) Å^{3,} Z = 2, R1 = 0.0323, wR2 = 0.0690 for 6853 independent reflections; R1 = 0.0398, wR2 = 0.0724 for all data. Crystallographic data for **4**: T = 113(2) K, monoclinic, space group $P2_1/c$, a = 10.4567(6) Å, b = 14.0978(8) Å, c = 20.6210(14) Å, β = 99.981(3)°, V = 2993.9(3) Å^{3,} Z = 4, R1 = 0.0386, wR2 = 0.0636 for 7136 independent reflections; R1 =0.0341, wR2 = 0.0662 for all data. Crystallographic data for **6**: T = 173(2) K, monoclinic, space group $P2_1$, a = 10.134(4) Å, b = 17.794(7) Å, c = 10.376(4) Å, β = 112.011(6)°, Z = 2, R1 = 0.0763, wR2 = 0.1093 for 6818 independent reflections; R1 = 0.0764, wR2 = 0.1192 for all data. Crystallographic data for **8**: T = 113(2) K, monoclinic, space group $P2_1/n$, a = 9.9324(12) Å, b = 17.397(2) Å, c = 16.0983(18) Å, β = 101.203(2)°. V = 2728.7(5) Å^3, Z = 4, R1 = 0.0483, wR2 = 0.1104 for 6488 independent reflections; R1 = 0.0658, wR2 = 0.1179 for all data.

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Supporting Information Available: CIF files for the structures of **2**–**4**, **6**, and **8**. This material is available free at charge at the Internet at http://pubs.acs.org.

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