Facile Cleavage of the Silicon−Oxygen Bond Leading to Unusual Dinuclear Aluminum Complexes

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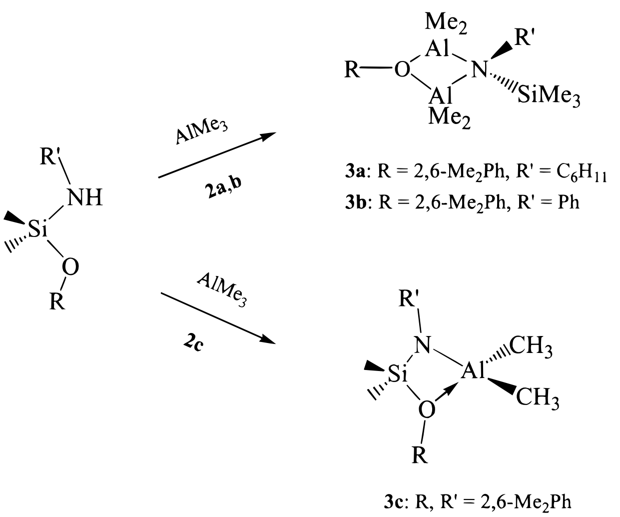
*Summary: Reactions of $Me_2Si(OR)(NHR')$ (R = 2,6-Me_2-Ph; R′ = Cy (**2a**), Ph (**2b**)) with $AlMe_3$ in pentane at room temperature afford unusual dinuclear aluminum complexes $(Me_2Al)_2[(\mu\text{-}OR)(\mu\text{-}NR'SiMe_3)]$ (R = 2,6-Me_2Ph; R′ = Cy (**3a**), Ph (**3b**)) that contain both nitrogen- and oxygen-bridging groups. Meanwhile, the corresponding reaction of $Me_2Si(OR)(NHR')$ (R, R′ = 2,6-Me_2Ph (**2c**)) yields a monomeric N,O-chelated aluminum species $[Me_2Si(OR)(NR')]AlMe_2$ (**3c**). It is most likely that two $AlMe_3$ molecules are associated with the facile cleavage of the Si−O bond to form the stable four-membered (μ-N)Al_2(μ-O) ring of **3a**,**b**, but the analogous reaction does not occur in **2c**, having a bulkier N-substituent. The crystal structure of **3a** is reported.*

Introduction

Recently, there is much attention on neutral aluminum complexes that are chelated by bi- or tridentate anionic ligands.[1] The related efforts have explored a wide range of novel organoaluminum compounds with well-defined structures and chemical reactivity. In particular, N,N′-bidentate amidinate ligands of the type $[RC(NR')_2]^-$ (R, R′ = alkyl, aryl) with a π-delocalized NCN fragment are extensively used to coordinate an electrophilic Al center.[2]

Similarly, N,O-substituted (oxydimethylsilyl)amides of $[Me_2Si(OR)(NR')]^-$ that contain a localized N-anion with a pendant neutral O-donor also act as attractive chelating ligands. It is previously known that the N,O-bis(*tert*-butyl) ligand of $[Me_2Si(O^tBu)(N^tBu)]^-$ is useful for stabilizing main group metals, but not including aluminum.[3] In this regard, we here report bulky N,O-chelate ligands ($Me_2Si(OR)(NHR')$, R = 2,6-Me_2Ph; R′ = C_6H_{11} (**2a**), Ph (**2b**), 2,6-Me_2Ph (**2c**)) for use in organoaluminum chemistry. Interestingly, reactions of **2a**,**b** with $AlMe_3$ undergo a facile cleavage of the silicon−oxygen bond and form unusual dinuclear aluminum complexes $(Me_2Al)_2[(\mu\text{-}OR)(\mu\text{-}NR'SiMe_3)]$ (R = 2,6-Me_2Ph; R′ = Cy (**3a**), Ph (**3b**)).

Scheme 1



Results and Discussion

Reactions of (Aryloxydimethylsilyl)amides (2a−c) with Trimethylaluminum. The N,O-ligands (**2a−c**) were prepared from the reaction between 2,6-dimethylphenol and excess dichlorodimethylsilane, followed by treatment with appropriate amines, cyclohexylamine, aniline, and 2,6-dimethylaniline, respectively, in a stepwise fashion.[4]

When **2a** was allowed to react with an equimolar amount of $AlMe_3$ in pentane at room temperature, a white solid precipitated in 12 h (Scheme 1). Surprisingly, X-ray crystallographic (vide infra) and elemental analyses showed that the product is an unprecedented dinuclear species, $(Me_2Al)_2[(\mu\text{-}O\text{-}2,6\text{-}Me_2Ph)(\mu\text{-}NCySiMe_3)]$ (**3a**), in which each aluminum center is connected with both an alkylamide- and an alkoxide-bridging group. Homo- and hetero-2D COSY spectra confirmed that the solid-state structure is maintained in solution as well. Two sets of proton and ^{13}C resonances for Al−Me groups are in harmony with the four-membered cyclic structure.

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[3] Veith, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1, and other references therein.

[4] Preparation of a similar ligand, $Me_2Si(O\text{-}t\text{-}Bu)(NH\text{-}t\text{-}Bu)$, has been reported. Please see: Veith, M.; Rösler, R. *J. Organomet. Chem.* **1982**, *229*, 131.

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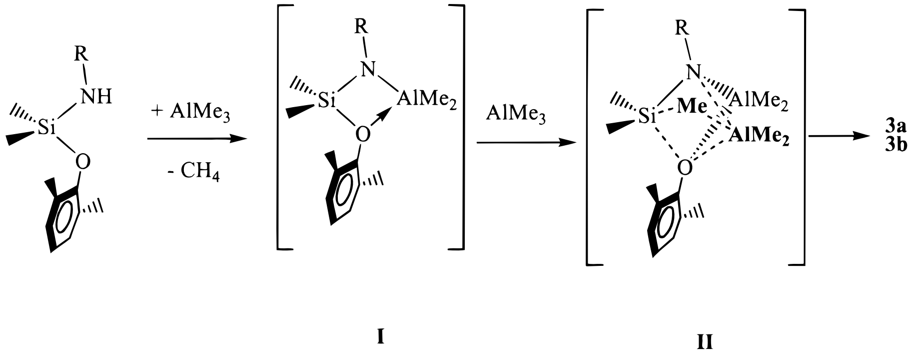
Scheme 2



The same behaviors are also observed for the corresponding reaction of **2b** to give a dinuclear species, $(Me_2Al)_2[(\mu\text{-}O\text{-}2,6\text{-}Me_2Ph)(\mu\text{-}NPhSiMe_3)]$ (**3b**). Elemental analysis and NMR spectra of **3b** at room temperature are consistent with the dinuclear species. In particular, only seven ^{13}C peaks for the aromatic groups were observed in benzene-d_6. However, the expected eight peaks were recorded in $CDCl_3$. A peak at 127.9 ppm must overlap one of the benzene-d_6 peaks. For **3b**, the large difference between chemical shifts (δ −0.24 and −0.43 ppm in ^1H NMR; −3.00 and −5.44 ppm in ^{13}C NMR) of the nonequivalent Al−Me groups is presumably due to the anisotropic environment invoked by the phenyl ring current.

Variable-temperature NMR spectra showed that the four-membered cycle of **3b** is fluxional. As the solution of **3b** in toluene-d_8 was gradually heated, two signals of the Al−Me groups become broadened and finally coalesced at 58 °C, from which $\Delta G^\ddagger$ for exchange of the methyl groups is estimated to be about 16 kcal mol^{-1}.[5] The mechanism could be either unimolecular or bimolecular, and the latter must be associated with two molecules of the binuclear species or extra ligands such as coordinating solvents. To probe the possibility, coalescence temperature (T_c) was measured at several concentrations. It is found that T_c is independent of the concentration of **3b**. Also, tetrahydrofuran was added to find out whether the coordinating solvent assists the exchange process. Almost the same T_c (50 °C) in the presence of a catalytic amount of THF (10 mol %) indicates that the exchange process is not associated with the extra coordinating ligand. Addition of 4 equiv of THF generated four new peaks for the Al−Me group with concurrent disappearance of the original two resonances. When the ^1H NMR spectrum was taken in THF-d_8, only one resonance for the Al−Me group was observed. Therefore, it seems that the dissociation into mononuclear species has occurred in the presence of a large excess of THF, and the final products are labile and/or fluxional enough to show one resonance for the Al−Me group in ^1H NMR.

Therefore, a unimolecular process is the most probable mechanism. Considering the rather high activation energy to cleave either the aluminum−oxygen bond or the aluminum−nitrogen bond, a concerted mechanism, in which bond breakage and the formation occur simultaneously while the $N(SiMe_3)Ph$ rotates about the N−O vector, must be plausible.

To our knowledge, the dinuclear aluminum species (**3a**,**b**) are very unusual in that most of dinuclear aluminum complexes $[R^1{}_2Al(\mu\text{-}E)]_2$ ($E = NR^2{}_2, OR^2, SR^2$; R^1, R^2 = alkyl, aryl) consist of equivalent monomeric units. Meanwhile, $(Me_2Al)_2[(\mu\text{-}OMe)(\mu\text{-}{}^iPrNC(Me)N^iPr)]$ with a methoxy and an amidinate bridging group has been reported as a rare analogue.[6] **3a**,**b** must originate from the reaction of the intermediates (**I**), $[Me_2Si(OR)(NR')]AlMe_2$ ($R = 2,6\text{-}Me_2Ph$; R' = Cy and Ph, respectively), with the second $AlMe_3$ molecule (Scheme 2). The driving force of the latter reaction must be a large energy gain from the Al−O bond (585 kJ/mol)[7] formation, which is sufficient to compensate for the Si−O bond (439 kJ/mol)[8] cleavage. Similar cleavage in organosiloxanes[9] and tris(trimethylsilyl) phosphate[10] has been observed, but only under rigorous heating conditions. Compared with the previous examples, the cleavage in **2a**,**b** occurs even at 0 °C, showing the kinetic amenability.

To follow the Si−O bond cleavage, an equimolar amount of $AlMe_3$ was added to a C_6D_6 solution of **2a** in an NMR tube at room temperature. Immediately after the mixing, downfield shifts of the silicon−methyl and $N\text{−}C_{ipso}$ protons of **2a** were observed, indicating the transient formation of an adduct, $[Me_2Si(O\text{-}2,6\text{-}Me_2Ph)(NHCy)]\cdot(AlMe_3)_n$ (n = 1 or 2). In 2 h, new proton signals appeared, and the formation of about 40% (NMR yield based on the consumed $AlMe_3$) of **3a** was observed in 24 h. In the NMR reaction of **2b** with an equimolar amount of $AlMe_3$, formation of **3b** is much faster than that observed for **3a**. The conversion is almost quantitative in 2 h, leaving half of the ligand **2b** intact. The remaining ligand can also be transformed into **3b** by the subsequent addition of $AlMe_3$.

To understand these features further, control experiments were carried out and followed by ^1H NMR spectroscopy. $AlMe_3$ was mixed with 2,6-dimethylphenol and cyclohexyltrimethylsilylamine in the ratio of 2:1:1 at room temperature. The reaction afforded a mixture of products, but **3a** was not observed in the mixture. Additionally, heating $2,6\text{-}Me_2PhOSiMe_3$ with excess $AlMe_3$ to 80 °C did not show any sign of cleavage of the Si−O bond in 24 h. These observations confirm that the

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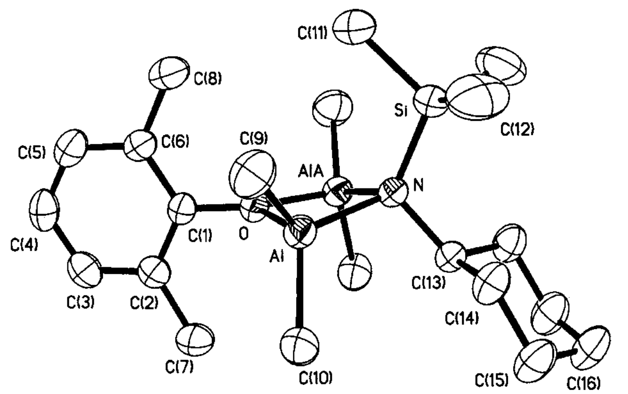

Figure 1. ORTEP diagram of the structure of $(Me_2Al)_2[(\mu\text{-O-2,6-}Me_2Ph)(\mu\text{-NCySi}Me_3)]$ (**3a**)

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $(Me_2Al)_2[(\mu\text{-O-2,6-}Me_2Ph)(\mu\text{-NCySi}Me_3)]$ (3a)[a]

bond distances		bond angles	
Al−N	2.0035(16)	N−Al−O	85.07(6)
Al−O	1.8731(13)	C(9)−Al−C(10)	112.40(13)
Al−C(9)	1.949(3)	N−Al−C(9)	119.96(12)
Al−C(10)	1.959(2)	O−Al−C(9)	112.59(11)
N−Si	1.804(2)	Al−N−AlA	89.58(9)
O−C(1)	1.410(3)	Al−N−C(13)	108.09(12)
N−C(13)	1.539(3)	Si−N−C(13)	115.32(17)
Al−AlA	2.8229(12)	Al−N−Si	116.37(8)
		Al−O−AlA	97.80(9)
		Al−O−C(1)	130.87(5)

[a] Symmetry transformation used to generate equivalent atoms: A, *x*, −*y*, *z*.

formation of two separate fragments, the aluminum alkoxide and the aluminum alkylamide, is not on the reaction pathway, and the chelation leading to the four-membered metallacycle is important for the facile cleavage.

In contrast, when **2c** reacted with 1 equiv of $AlMe_3$, the four-coordinate aluminum complex $[Me_2Si(O\text{-2,6-}Me_2Ph)(N\text{-2,6-}Me_2Ph)]AlMe_2$ (**3c**) was immediately observed as a white solid. The proton and carbon NMR spectra of **3c** display the singlets of the $AlMe_2$ moiety at −0.31 and −5.54 ppm, respectively. Integration of the proton resonances clearly showed that the 1:1 complex was formed, and the singlet resonance in the NMR spectra is in harmony with the resulting symmetric molecular structure. The stability of the mononuclear complex **3c** against $AlMe_3$ should be associated with the larger N-substituent, which might inhibit the formation of the transition state like **II**.

Structures of $(Me_2Al)_2[(\mu\text{-O-2,6-}Me_2Ph)(\mu\text{-NCySi}Me_3)]$ (3a). The structure of **3a** was determined by X-ray crystallography. The molecular structure is shown in Figure 1, and selected bond lengths and angles are summarized in Table 1. **3a** is a dinuclear aluminum species with the two molecular units of $Me_2AlO(2,6\text{-}Me_2Ph)$ and $Me_2AlN(Cy)(SiMe_3)$ being associated with each other. The molecule has crystallographic *m* symmetry with a mirror plane passing through the N, O, C(11), and C(16) atoms and the 2,6-dimethylphenyl group. The four-membered Al_2NO ring is planar within 0.10 Å. Each aluminum center is 1.411(2) Å away from the mirror plane and adopts a distorted tetrahedral geometry with an N−Al−O angle of 85.07(6)°. The geometry of nitrogen and oxygen atoms is distorted tetrahedral and nearly trigonal planar, respectively. As expected, the Al−N−AlA angle (89.58(9)°) is more acute than the Al−O−AlA angle (97.80(9)°), and the angles are comparable to those found in the dimeric aluminum compounds $[R^1{}_2Al(\mu\text{-E})]_2$ (E = $NR^2{}_2$, OR^2; R^1, R^2 = alkyl, aryl). The Al−N (2.0035(16) Å) and Al−O (1.8731(13) Å) bond lengths are close to the standard values (1.95 and 1.85 Å, respectively)[11] of Al−E (E = N, O) bonds featuring similar bonding character.

Summary

We observed the facile cleavage of the Si−O bond promoted by two molecules of $AlMe_3$ to form unusual dinuclear aluminum complexes $(Me_2Al)_2[(\mu\text{-OR})(\mu\text{-NR}'\text{-Si}Me_3)]$ (R = 2,6-Me_2Ph; R′ = Cy, Ph) that contain both an alkoxide and an alkylamide bridge. Meanwhile, a bulkier substituent on the nitrogen atom gives a N,O-chelated mononuclear aluminum species, instead. The above approach seems to be quite useful for the formation of hetero-bridged dinuclear aluminum complexes as long as the steric bulkiness on the nitrogen atom can be avoided.

Experimental Section

General Procedure. All manipulation of air- and/or moisture-sensitive compounds was carried out with use of standard Schlenk or vacuum-line techniques. Argon was purified by passing through columns of Ridox oxygen scavenger (R31-3, Fisher) and Linde 4-Å molecular sieves. Solids were transferred and stored in an N_2-filled Vacuum Atmospheres glovebox equipped with a HE-493 Dri-Train, a CS-40 Dri-Cold, and an oxygen analyzer (model 315, Teledyne Analytical Instruments).

Anhydrous toluene, tetrahydrofuran, and diethyl ether were purchased from Aldrich and transferred to sodium/benzophenone ketyl without prior treatment. Pentane were stirred over concentrated H_2SO_4, dried over CaH_2, and then transferred to sodium/benzophenone ketyl. Dried deoxygenated solvents were vacuum-transferred to dry glass vessels equipped with a J-Young valve and stored under argon. Benzene-d_6 was transferred from purple sodium/benzophenone ketyl. $CDCl_3$ was predried under CaH_2 and vacuum-transferred. Cl_2SiMe_2 and $AlMe_3$ were used as received from Aldrich. 2,6-Dimethylaniline, aniline, and cyclohexylamine were dried under KOH and distilled. 2,6-Dimethylphenol was purified through vacuum sublimation.

NMR spectra were recorded on Bruker DPX300 (300 MHz, ^1H) spectrometers. Chemical shifts are reported in δ, referenced to residual solvent signals. Elemental analyses were performed at Pohang University of Science and Technology (Elementar Vario-EL). High-resolution mass spectral analyses were preformed at Korea Basic Science Institute (JEOL SX102). Melting points were measured in sealed glass tubes and were not corrected.

Preparation of 2,6-Me_2PhOSiMe_2Cl (1). *n*-BuLi (97.0 mL, 1.32 M in hexane, 128 mmol) was slowly added to sublimed 2,6-dimethylphenol (15.6 g, 128 mmol) dissolved in diethyl ether (100 mL) at −45 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The solution was cooled again to −45 °C, and Cl_2SiMe_2 (54.0 mL, 445 mmol) was slowly added. Immediately white precipitates were formed. The mixture was warmed to room temperature and stirred overnight. The solution was filtered, and the filtrate was evacuated to afford pale yellow oil. Colorless oil **1** (22.1 g,

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[11] Robinson, G. H. *Coordination Chemistry of Aluminum*; VCH: New York, 1993; Chapter 1.

80.4%) was obtained by vacuum distillation (30 mTorr, 40 °C). ^{1}H NMR (CDCl$_3$): δ 7.04 (d, 2H), 6.90 (t, 1H), 2.28 (s, 6H), 0.63 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 153.2, 128.9, 122.1, 121.5, 50.9, 38.9, 26.0, 18.4, −0.71.

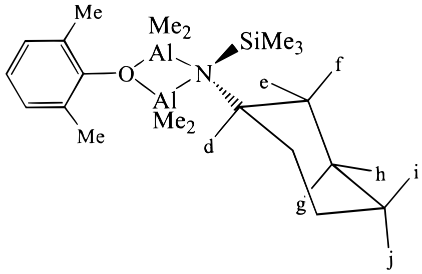
Preparation of Me$_2$Si(O-2,6-Me$_2$Ph)(NHCy) (2a). Cyclohexylamine (6.50 mL, 56.8 mmol) was slowly added to an ether (200 mL) solution of compound **1** (6.10 g, 28.4 mmol) at 0 °C. Immediately, white precipitates were formed, and the mixture was stirred overnight at room temperature. The solution was filtered, and a pale yellow oil was obtained by evacuating the filtrate. Colorless oil **2a** (5.6 g, 71%) was isolated by vacuum distillation (85 °C, 30 mTorr). ^{1}H NMR (C$_6$D$_6$): δ 6.96 (d, 2H), 6.81 (t, 1H), 2.62 (m, 1H), 2.25 (s, 6H), 1.69 (m, 2H), 1.56 (m, 2H), 1.41 (m, NH), 1.14−0.82 (m, 6H), 0.20 (s, 6H). ^{13}C NMR (C$_6$D$_6$): δ 153.3, 128.8, 128.7, 121.6, 50.7, 38.7, 26.0, 25.9, 18.3, −0.95. MS (EI, 70 eV): *m/z* 105 (21), 178 (63), 234 (61), 253 (100), 277 (M$^+$, 13). HRMS (EI, 70 eV): calcd for C$_{16}$H$_{27}$NOSi 277.1862, found 277.1848.

Preparation of Me$_2$Si(O-2,6-Me$_2$Ph)(NHPh) (2b). 2b was obtained using compound **1** (6.10 g, 28.4 mmol) and aniline (5.20 mL, 57.1 mmol) with a similar procedure for **2a**. Vacuum distillation (105 °C, 30 mTorr) of the crude product afforded pure colorless oil (5.2 g, 68%). ^{1}H NMR (C$_6$D$_6$): δ 7.10 (t, 2H), 6.93 (d, 2H), 6.83−6.73 (m, 4H), 3.46 (br s, NH), 2.19 (s, 6H), 0.17 (s, 6H). ^{13}C NMR (C$_6$D$_6$): δ 152.6, 146.0, 129.5, 129.0, 128.8, 122.2, 119.2, 117.5, 17.7, −1.78. MS (EI, 70 eV): *m/z* 150 (18), 163 (18), 178 (100), 271 (M$^+$, 57). HRMS (EI, 70 eV): calcd for C$_{16}$H$_{21}$NOSi 271.1385, found 271.1392.

Preparation of Me$_2$Si(O-2,6-Me$_2$Ph)(NH-2,6-Me$_2$Ph) (2c). *n*-BuLi (15.2 mL, 1.6 M in hexane, 24.3 mmol) was slowly added to a THF (20 mL) solution of 2,6-dimethylaniline (3.0 mL, 24.4 mmol) at −40 °C. The resulting yellowish white suspension was warmed to room temperature and stirred for 1 h. The solution was again cooled to 0 °C, and compound **1** (5.0 g, 23.3 mmol) was added. The mixture was stirred overnight at room temperature. The solution was condensed under vacuum and extracted with pentane. The filtrate was evaporated to afford pale yellow crude oil. Colorless viscous oil **2c** (6.0 g, 82%) was obtained by vacuum distillation (20 mTorr, 115 °C). ^{1}H NMR (CDCl$_3$): δ 7.11 (m, 4H), 6.95 (m, 2H), 3.14 (br s, NH), 2.39 (s, 6H), 2.36 (s, 6H), 0.34 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 153.0, 142.6, 132.4, 129.1, 129.0, 128.8, 122.7, 122.1, 20.1, 18.4, −0.32. MS (EI, 70 eV): *m/z* 121 (79), 163 (26), 178 (100), 196 (20), 299 (M$^+$, 92). HRMS (EI, 70 eV): calcd for C$_{18}$H$_{25}$NOSi 299.1697, found 299.1705.

Preparation of (Me$_2$Al)$_2$[(μ-O-2,6-Me$_2$Ph)(μ-NCySiMe$_3$)] (3a). AlMe$_3$ (1.05 mL, 11.0 mmol) was added dropwise to a pentane (50 mL) solution of **2a** (3.00 g, 10.8 mmol) at room temperature. The resulting pale yellow solution was stirred overnight. Formation of white precipitate was observed. White solid of **3a** (1.3 g, 59% based on the consumed chelate) was obtained by filtration and washing with pentane. Meanwhile, addition of AlMe$_3$ (0.72 mL, 7.51 mmol) into the solution of **2a** (1.00 g, 3.60 mmol) gave 1.10 g of **3a** (yield = 75%). Analytically pure and X-ray suitable colorless crystals could be obtained from toluene solution stored at −45 °C. Melting point: 136 °C. ^{1}H NMR (C$_6$D$_6$): δ 6.86 (d, 2H), 6.82 (t, 1H), 3.50 (m, 1H, cyclohexyl axial d), 2.40 (s, 6H, benzylic), 1.86 (br d, 2H, cyclohexyl equatorial e), 1.55 (br d, 2H, cyclohexyl equatorial h), 1.45 (m, 3H, cyclohexyl axial f and equatorial i), 1.20 (m, 2H, cyclohexyl axial g), 1.02 (m, 1H, cyclohexyl axial j), 0.39 (s, 9H, Si*Me$_3$*), −0.35 (s, 6H, Al*Me*), −0.36 (s, 6H, Al*Me*). ^{13}C NMR (C$_6$D$_6$): δ 148.9 (phenylic, ipso), 130.1 (phenylic, ortho), 129.9 (phenylic, meta), 124.4 (phenylic, para), 61.6 (N*C*H), 38.7 (NCH*C*H$_2$), 27.4 (NCHCH$_2$*C*H$_2$), 25.8 (NCHCH$_2$-CH$_2$*C*H$_2$), 18.7 (benzylic *C*H$_3$), 7.07 (Si*Me$_3$*), −4.80 (Al*Me*), −5.80 (Al*Me*). Anal. Calcd for C$_{21}$H$_{41}$NOSiAl$_2$: C, 62.18; H, 10.19; N, 3.45. Found: C, 62.16; H, 9.77; N, 3.30.

Preparation of (Me$_2$Al)$_2$[(μ-O-2,6-Me$_2$Ph)(μ-NPhSiMe$_3$)] (3b). AlMe$_3$ (0.58 mL, 6.0 mmol) was added dropwise to a pentane (20 mL) solution of **2b** (1.52 g, 5.60 mmol) at room temperature. Formation of a white precipitate was observed in 1 h. The resulting solution was reduced to 5 mL, and a white solid of **3b** (0.90 g, 80% based on the consumed chelate) was obtained by filtration and washing with pentane. Meanwhile, addition of AlMe$_3$ (0.74 mL, 7.72 mmol) into the solution of **2b** (1.00 g, 3.68 mmol) produced 1.25 g of **3b** (yield = 85%). Melting point: 139 °C. ^{1}H NMR (C$_6$D$_6$): δ 6.97−6.80 (m, 8H, aromatic), 2.31 (br s, 6H, benzylic), 0.22 (s, 9H, Si*Me$_3$*), −0.24 (s, 6H, Al*Me*), −0.43 (s, 6H, Al*Me*). ^{13}C NMR (C$_6$D$_6$): δ 148.9, 143.0, 131.6, 130.1, 129.9, 125.0, 124.6, 18.8 (benzylic), 2.46 (Si*Me$_3$*), −3.00 (Al*Me*), −5.44 (Al*Me*). ^{13}C NMR (CDCl$_3$): 149.0, 143.3, 131.8, 130.4, 130.1, 127.9, 125.1, 124.4, 19.1 (benzylic), 2.98 (Si*Me$_3$*), −3.00 (Al*Me*), −5.23(Al*Me*). Anal. Calcd for C$_{21}$H$_{35}$NOSiAl$_2$: C, 63.12; H, 8.83; N, 3.51. Found: C, 63.38; H, 8.72; N, 3.35.



Preparation of [Me$_2$Si(O-2,6-Me$_2$Ph)(N-2,6-Me$_2$Ph)]-AlMe$_2$ (3c). AlMe$_3$ (0.97 mL, 10 mmol) was added dropwise to a pentane (30 mL) solution of **2c** (3.0 g, 10 mmol) at room temperature. After the addition, a white precipitate started to appear. The mixture was stirred overnight. The volume of the solution was reduced, and the white precipitate of **3c** (3.2 g, 90%) was filtered. Analytically pure colorless crystals could be isolated from the saturated pentane solution at −20 °C. Melting point: 178 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.17 (d, 2H), 6.95 (t, 1H), 6.78 (s, 3H), 2.55 (s, 6H), 2.27 (s, 6H), 0.09 (s, 6H), −0.31 (s, 6H). ^{13}C NMR (C$_6$D$_6$): δ 147.3, 143.7, 135.1, 130.4, 130.0, 128.7, 125.6, 122.3, 20.5, 17.9, 3.49, −5.54. Anal. Calcd for C$_{20}$H$_{30}$NOSiAl: C, 67.56; H, 8.51; N, 3.94. Found: C, 67.28; H, 8.51; N, 3.94.

X-ray Crystallographic Determination for 3a. A crystal sealed in a capillary tube was mounted on a Siemens SMART diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD detector. Fifteen frames of two-dimensional diffraction images were collected and processed to deduce a cell parameter and orientation matrix. Data collection was performed at 293 K. A total of 1271 frames of two-dimensional diffraction images were collected, and each of which was measured for 20 s. The frame data were processed to produce conventional intensity data by the program SAINT. The intensity data were corrected for Lorentz and polarization effects. An absorption correction was also applied based on ψ scans. The structures were solved by a combination of Patterson and difference Fourier methods provided by the program package SHELXTL. All the non-hydrogen atoms were refined anisotropically.

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Supporting Information Available: Tables S1−S4 listing full experimental details for data collection and refinement, atomic coordinates, bond distances and bond angles, and anisotropic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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