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Synthesis and Structural Characterization of Alkaline-Earth-Metal Bis(amido)silane and Lithium Oxobis(aminolato)silane Complexes

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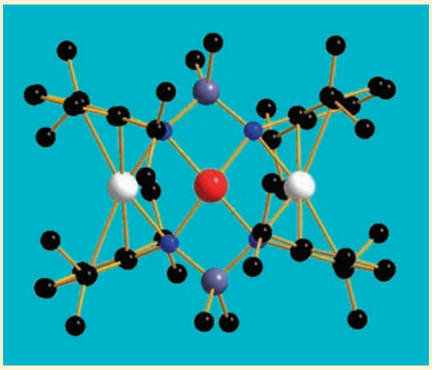
S *Supporting Information*

ABSTRACT: Several of alkaline-earth-metal complexes $[(\eta^2{:}\eta^2{:}\mu(N){:}\mu(N)\text{-Li})^+]_2$-$[\{\eta^2\text{-Me}_2\text{Si(DippN)}_2\}_2\text{Mg}]^{2-}$ (**4**), $[\eta^2(N,N)\text{-Me}_2\text{Si(DippN)}_2\text{Ca}\cdot 3\text{THF}]$ (**5**), $[\eta^2\text{-}(N,N)\text{-Me}_2\text{Si(DippN)}_2\text{Sr}\cdot\text{THF}]$ (**6**), and $[\eta^2(N,N)\text{-Me}_2\text{Si(DippN)}_2\text{Ba}\cdot 4\text{THF}]$ (**7**) of a bulky bis(amido)silane ligand were readily prepared by the metathesis reaction of alkali-metal bis(amido)silane $[\text{Me}_2\text{Si(DippNLi)}_2]$ (Dipp = 2,6-i-$\text{Pr}_2\text{C}_6\text{H}_3$) and alkaline-earth-metal halides MX_2 (M = Mg, X = Br; M = Ca, Sr, Ba, X = I). Alternatively, compounds **5**−**7** were synthesized either by transamination of $\text{M[N(SiMe}_3)_2]_2\cdot 2\text{THF}$ (M = Ca, Sr, Ba) and $[\text{Me}_2\text{Si(DippNH)}_2]$ or by transmetalation of $\text{Sn[N(SiMe}_3)_2]_2$, $[\text{Me}_2\text{Si(DippNH)}_2]$, and metallic calcium, strontium, and barium in situ. The metathesis reaction of dilithium bis(amido)silane $[\text{Me}_2\text{Si(DippNLi)}_2]$ and magnesium bromide in the presence of oxygen afforded, however, an unusual lithium oxo polyhedral complex $\{[(\text{DippN-}(\text{Me}_2\text{Si})_2)(\mu\text{-O})(\text{Me}_2\text{Si})]_2(\mu\text{-Br})_2[(\mu_3\text{-Li})\cdot\text{THF}]_4(\mu_4\text{-O})_4(\mu_3\text{-Li})_2\}$ (**8**) with a square-basket-shaped core $\text{Li}_6\text{Br}_2\text{O}_4$ bearing a bis(aminolato)silane ligand. All complexes were characterized using ^{1}H, ^{13}C, and ^{7}Li NMR and IR spectroscopy, in addition to X-ray crystallography.



INTRODUCTION

There is great interest in the coordination chemistry of alkaline-earth elements (Mg, Ca, Sr, and Ba) over the past decade.[1] Potential applications, from homogeneous catalysis[2−8] to precursor chemistry for high-technology coatings prepared by chemical vapor deposition methods,[9] require prevention of the formation of aggregated species. Much of these work, therefore, has centered on the selection of an array of sterically demanding ligand sets such as the β-diketiminate,[10] triazenido,[2d] tris(imidazolin-2-ylidene-1-yl)borate[11] and bis(3,5-di-*tert*-butylpyrazolyl)borate[12] anions to impose the requisite level of kinetic control over the otherwise ionic and completely labile coordination chemistries of the group 2 elements. While magnesium compounds are likely to maintain their preeminence as the organic chemist's reagents of choice, there is a growing awareness that either greater selectivity or deprotonating power may be achieved through the use of reagents containing both alkali and magnesium atoms. Such bimetallic complexes should encourage modification in the chemical structure, which, in turn, could translate into modification in the chemical reactivity. It has been found that the behaviors of the magnesiates (the mixed alkali magnesium complexes) are neither conventional alkali-metal chemistry nor conventional magnesium chemistry but a unique new synergic chemistry.[13] A few of such complexes have been recently applied to deprotonation of organic or organometallic species such as benzene, toluene, bis(benzene)chromium, and metallocenes,[13a,b] as well as to catalysis in the varied organic transformations.[14] As for the chemistry of heavy alkaline-earth-metal complexes, the potential of their derivatives in fundamental study,[15a−d] catalysis,[15e,f−m] and solid-state applications[15n−p] has intensified the search for suitable reagents and source materials.[15] The large ionic radius of the heavy alkaline-earth metals makes this a challenge, and, generally, the use of sterically demanding ligands, often in conjunction with donor solvents, is required to saturate the coordination sphere of the metals, allow good solubility, and prevent the formation of aggregated species. Particularly, the widespread use of alkaline-earth-metal amide reagents throughout synthetic chemistry provides a major incentive for pursuing this interesting topic,[16] and this has led to a great deal of attention being directed toward elucidating their structures both in solution[17a,b] and in the solid state.[17c,d] Very recently, we have focused on the development of thermally robust, ambient-atmosphere-stable, coordinatively saturated alkaline-earth element compounds with a bulky bis(amido)silane ligand, $[\text{Me}_2\text{Si(DippN)}_2]^{2-}$, and have reported on the first neutral magnesium bis(amido)silane complex $([(\mu\text{-Mg})\{\eta^2{:}\eta^1\text{-Me}_2\text{Si(DippN)}_2\}]_2)$ (**1**) that could be further applied to the preparation of the potassium−magnesium ate complexes (magnesiates) $[(\eta^6{:}\eta^6\text{-K})^+]_2[\text{Mg}\{\eta^2\text{-Me}_2\text{Si(DippN)}_2\}_2]^{2-}$ (**2**)

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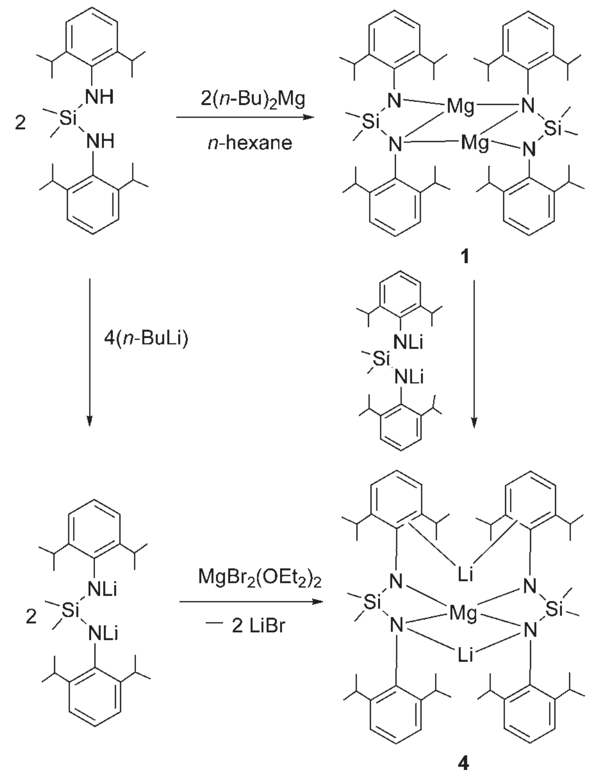
and $[(\eta^6{:}\eta^6\text{-K(THF)})_2]^{2+}[\text{Mg}\{\eta^2\text{-Me}_2\text{Si(DippN)}_2\}_2]^{2-}$ (**3**; THF = tetrahydrofuran).[18] Herein we report the synthesis and structural characterization of a series of alkaline-earth-metal (Mg, Ca, Sr, and Ba) bis(amido)silane complexes as well as an unusual lithium oxobis(aminolato)silane compound. The latter likely arises from a possible peroxide magnesium−lithium ate species.

■ RESULTS AND DISCUSSION

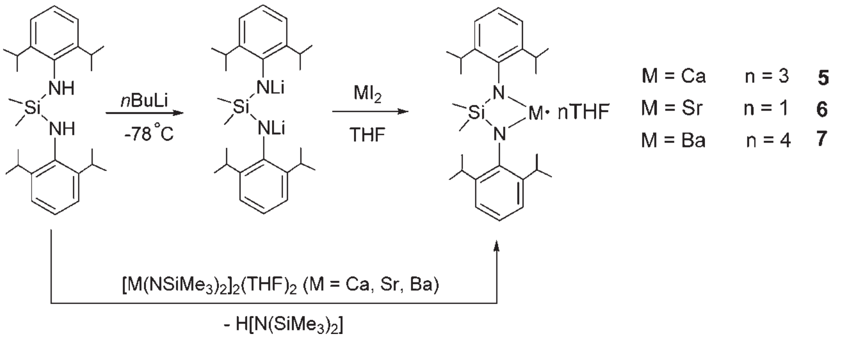
Synthetic Chemistry. Methods for the preparation of organomagnesium compounds are usually based on (a) direct metalation of organic halides with metallic magnesium, (b) deprotonation, (c) transmetalation from other organometallics, or (d) halogen−magnesium exchange. Method c is particularly useful for the preparation of alkali metal−magnesium ate complexes.[13,19,20] In contrast, heavy alkaline-earth-metal complexes may be prepared by the transamination of $\text{M[N(SiMe}_3)_2]_2\text{(THF)}_2$ (M = Ca, Sr, Ba), transmetalation, and metathesis reactions because of the lack of suitable calcium, strontium, and barium organometallics. These methods have been applied to the preparation of the corresponding product molecules, employing a variety of ligand systems.[21] Our previous results on the magnesium as well as the potassium−magnesium ate complexes[18,22] have suggested that alkaline-earth-metal derivatives bearing the bulky bis(amido)silane ligand are likely accessible.

Scheme 1

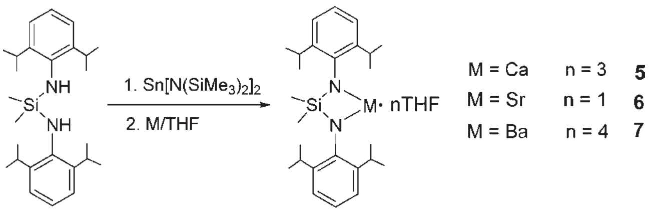


Preparation of Complex $[(\eta^2{:}\eta^2{:}\mu(N){:}\mu(N)\text{-Li})^+]_2[\{\eta^2\text{-Me}_2\text{Si(DippN)}_2\}_2\text{Mg}]^{2-}$ (4). For the preparation of organomagnesium amides, salt elimination of lithium amides and $\text{MgBr}_2\cdot2\text{OEt}_2$ was particularly attractive.[23] Because dilithium bis(diamido)silane $\text{Me}_2\text{Si(DippNLi)}_2$ has been reported previously,[24] a reaction of $\text{Me}_2\text{Si(DippNLi)}_2$ with $\text{MgBr}_2\cdot2\text{Et}_2\text{O}$ was thus carried out in *n*-hexane. Magnesiate complex **4** was, however, obtained as air- and moisture-sensitive white crystals after workup (Scheme 1). Compound **4**, rather than the known dimeric magnesium bis(amido)silane **1**,[18] was the only isolated product even though the reactants were in a molar ratio of 1:1, suggesting high thermodynamic stability. The NMR data supported molecule **4**, which was determined by integration of the ^{1}H NMR spectrum in a dimethyl sulfoxide (DMSO)-d_6 solution. However, two sets of resonances for the nonequivalent $-C\mathit{H}(\text{CH}_3)_2$ groups revealed the molecular asymmetry in the solution. Notably, the resonances of the $-\text{CH}_3$ groups in the ^{1}H NMR (DMSO-d_6) spectrum are slightly overlapped by the signals of the lattice *n*-hexane. In the ^{7}Li NMR (DMSO-d_6, 23 °C) spectrum, only one sharp resonance was observed at $\delta = -1.06$ ppm, suggesting that the centrosymmetric $\text{Si}_2\text{N}_4\text{Li}_2\text{Mg}$ framework of the solid structure remained intact in the solution. The observed significant upfield shift resonance at $\delta = -1.06$ ppm relative to the corresponding signals of PhLi in a THF/ether solution (^{7}Li, $\delta = 1.1$ ppm at −120 °C) and in a 12-crown-4/THF solution (^{7}Li, $\delta = 1.9$ ppm at −105 °C),[25] probably suggests the lower electrophilicity of lithium atoms in **4** relative to that found in PhLi. From the viewpoint of the structure, **4** can be viewed as an adduct of **1** and the corresponding lithium salt $[\text{Me}_2\text{Si(DippNLi)}_2]$.[24] Impetus was provided by this assumption that **4** may be prepared by mixing $[\text{Me}_2\text{Si(DippNLi)}_2]$ and **1**. Indeed, upon the addition of **1** to a *n*-hexane solution of $[\text{Me}_2\text{Si(DippNLi)}_2]$ in a ratio of 1:2, a group of white crystals were, after workup, obtained in good yield (0.58 g, 68.0%). The data in the ^{1}H NMR (DMSO-d_6, 23 °C) spectrum are completely identical with those of **4**. In comparison with **2**, complex **4** is quite stable under an inert atmosphere and well-soluble in THF and DMSO but fairly soluble in *n*-hexane. We believe that the magnesium−lithium ate complex with the bis(amido)silane ligand has not been reported before the present work.[23] Notably, complex **2** was previously synthesized by the reduction of **1** with potassium graphite (C_8K).[18]

Scheme 2



Scheme 3



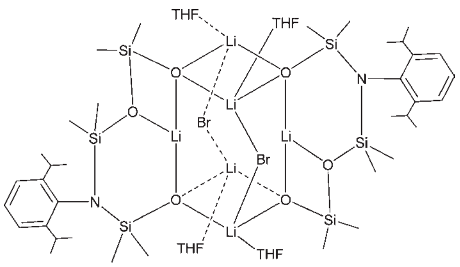
The method is unique, but it takes several days upon isolation only in fair yield. To make it easier, **2** was supposed to be obtained by the metathesis reaction of $Me_2Si(DippNK)_2$[22] and magnesium bromide directly. Unfortunately, the preparation of **2** was not successful by this reaction (molar ratio of the reactants = 1:1) in toluene at room temperature because it resulted in an oily mixture that showed several sets of complicated resonances in the ^1H NMR spectrum.

Preparation of Complexes [Ca{η^2(*N,N*)-$Me_2Si(DippN)_2$}]·3THF (5), [Sr{η^2(*N,N*)-$Me_2Si(DippN)_2$}]·THF (6), and [Ba{η^2-(*N,N*)-$Me_2Si(DippN)_2$}]·4THF (7). By slightly altering the reaction conditions of the preparation of **2**, such as the use of mixed THF and *n*-hexane as the solvent, we were able to cleanly prepare in good purity bis(amido)silane compounds **5** (58.0%), **6** (72.0%), and **7** (70.0%) as air- and moisture-sensitive white (**5** and **7**) or yellow (**6**) crystals by the metathesis reaction of $Me_2Si(DippNLi)_2$ and anhydrous CaI_2, SrI_2, and BaI_2 in a 1:1 molar ratio, respectively (Scheme 2). All complexes present fair solubility in *n*-hexane, benzene, and toluene but are well-soluble in THF and DMSO. In the ^1H NMR (C_6D_6) spectra, the solid structures of **5**−**7** (in DMSO-d_6) are maintained in the solution, as is evident from the two very close sharp resonances for the $-SiCH_3$ groups ($\delta = 0.52$ and 0.53 ppm) and two sets of very close coupled doublets for the $-C(CH_3)_2$ groups ($^1J_{H-H} = 8.0$ Hz) (**5**), from only one sharp resonance for the $-SiCH_3$ groups ($\delta = 0.31$ ppm), three sets of coupled doublets for the $-CH(CH_3)_2$ groups ($^1J_{H-H} = 66.0$ Hz), and one set of multiple resonances ($\delta = 4.10$ ppm) for $-CH(CH_3)_2$ groups (**6**), and from one sharp resonance for the $-SiCH_3$ groups ($\delta = -0.11$ ppm) and two sets of very closely coupled doublets for the $-C(CH_3)_2$ groups ($^1J_{H-H} = 6.60$ and 7.20 Hz) (**7**). The two sets of resonances for the nonequivalent $-C(CH_3)_2$ groups in complexes **5**−**7** reveal the molecular asymmetry in the solution. These are similar to the observation in the analogous neutral dimeric magnesium complex **1**.[18] Two multiple resonances in ^1H NMR spectra are assigned to the solvated THF molecules in **5** (at $\delta = 1.29$ and 3.44 ppm) and **6** (at $\delta = 1.42$ and 3.21 ppm), supporting the determination of the ratio of THF molecules to bis(amido)silane ligands. Similarly, the multiple resonances at $\delta = 1.78$ and 3.62 ppm are also assigned to the solvated THF molecules in **7**; however, integration of the ratio of THF to bis(amido)silane ligands reveals only three solvated THF molecules, negating the determination of the ratio (4:1) of THF molecules to $[Me_2Si(DippN)_2]^{2-}$ ligands by X-ray crystallographic analysis, suggesting that **7** is prone to solvent loss as the sample dried under high vacuum during the NMR determination. The solvated THF molecule loss in the barium amide complex has been known previously, where solvated barium amide transformed from a monomer into its corresponding dimer in the solid state.[26] However, we did not observe solvent loss even though complexes **5** and **6** were dried in high vacuum. Because **6** was only obtained from *n*-hexane and was not able to be recrystallized from a THF solution with its high solubility, the finding with only one THF coordination in **6** probably arises from a shortage of the solvated molecules in the system. Alternatively, complexes **5**−**7** can be readily prepared by transamination of $M[N(SiMe_3)_2]_2(THF)_2$ (M = Ca, Sr, Ba) and $Me_2Si(DippNH)_2$ in THF at room temperature in good yield (70.7% for **5**, 77.5% for **6**, and 82.7% for **7**; Scheme 2) or by transmetalation of $Sn[N(SiMe_3)_2]_2$, $Me_2Si(DippNH)_2$, and metallic calcium, strontium, and barium in situ (vide infra).

Preparation of Complexes 5−7 by Transmetalation with Metallic Calcium, Strontium, and Barium in Situ. In addition to preparing complexes **5**−**7** by salt elimination or by transamination of $M[N(SiMe_3)_2]_2(THF)_2$ (M = Ca, Sr, Ba; Scheme 2), we also studied the reactions with $Me_2Si(DippNH)_2$, $Sn[N(SiMe_3)_2]_2$, and corresponding metallic calcium, strontium, and barium in situ (Scheme 3). We were able to obtain complexes **5**−**7** in high yields in this way (see the Experimental Section). It seems that the formation of the target derivatives **5**−**7** occurs via a two-step process, where transamination of $Me_2Si(DippNH)_2$ with $Sn[N(SiMe_3)_2]_2$ initially afforded an intermediate $\{Sn[Me_2Si(DippN)_2]\}$,[27] which reacted further with metallic calcium, strontium, and barium via transmetalation to give the corresponding products **5**−**7** as isolated crystals.

Preparation of Complex {[(DippN($Me_2Si)_2$)(μ-O)(Me_2Si)]$_2$-(μ-Br)$_2$[(μ_3-Li)·THF]$_4$(μ_4-O)$_4$(μ_3-Li)$_2$} (8). As mentioned above, the reaction of $Me_2Si(DippNLi)_2$[23] with $MgBr_2 \cdot 2Et_2O$ smoothly afforded **4** in good yield. We found that, when the mother liquor was further concentrated, however, it enabled isolation of an additional group of white crystals in low yield. The X-ray diffraction analysis revealed a lithium oxo polyhedron **8** with bromide bridges, containing one set of unusual organic units [(DippN($Me_2Si)_2$)(μ-O)(Me_2Si)], suggesting that the reaction was contaminated by free oxygen (vide infra). Oxygen incorporation in lithium compounds has been known for a long time.[28] For example, lithium amide oxo complexes $[\{(c\text{-}C_5H_9)N(H)Li\}_{12}Li_2O]$[28a] and $[\{PhC(NSiMe_3)_2\}_4Li_4Mg(O)$,[28b] octadecalithium phosphanediide $[\{[iPr_2(Mes)Si]P\}_8Li_{16} \cdot Li_2O]$,[28c] and octalithium−dipotassium mixed oxide−alkoxide $[Li_8K_2(O)(tBuO)_8 \cdot 2TMEDA]$[28d] have been structurally characterized. These complexes all arose from the contamination of traces of oxygen. However, no lithium oxo species such as **8** has been reported. Because the interaction of organometallic complexes with oxygen was generally poorly understood, particularly when there was insufficient oxygen present to ultimately produce the stoichiometric metal oxide, it was interesting for us to verify the reproduction of **8**. To check its reproducibility, an excess of dried air or a small amount of water was deliberately introduced into the reaction system under what we believed to be strictly anhydrous conditions, respectively. Three batches of the above reaction were carried out following the same in situ procedure in the presence of water or dry oxygen. As expected, **8** could be obtained only with oxygen in fair yield (Scheme 4) and distinguished both from their oxygen-free counterpart **4** by melting point analysis and from the unit cell parameters of several crystals by X-ray diffraction. The NMR data supported molecule **8**, which was determined by integration of the ^1H NMR spectrum, but the overlapping resonances for the nonequivalent $-CH(CH_3)_2$ and $-Si(CH_3)_2$ groups reveal the possible molecular asymmetry and a hindered rotation about the C−N bond in the solution. In the ^7Li NMR (DMSO-d_6, 23 °C) spectrum, two very close resonances were observed at $\delta = 0.96$ and 0.82 ppm for **8**, assigned with two sets of chemical environments of lithium ions, indicative of the retained $Li_4O_4Br_2$ core of the solid structure in the solution. The chemical shift at δ = 0.96 and 0.82 ppm in the ^{7}Li NMR spectrum are comparable to those at δ = 2.97 ppm found in the lithium complex $[\{(Me_3Si)_2N\}_4Li_2Mg_2(O_2)_x(O)_y]$ and at δ = 3.20 ppm found in the lithium−magnesium ate compound $[\{(Me_3Si)_2N\}_3LiMg]\}$,[29a] suggesting the possible ionic bonding character. The mechanism of formation is currently unknown, probably via an oxygen (O−O)-centered magnesium−lithium intermediate followed by decomposition of the O−O and Si−N bonds,[29a] similar to $[\{(Me_3Si)_2N\}_4Li_2Mg_2(O_2)_x(O)_y]$ reported by Mulvey and co-workers.[29b] This also suggests that the Si−N bond of the bis(amido)silane ligand is easily cleaved when the reaction system is not strictly under oxygen-free conditions.

Scheme 4



Single Crystal and Molecular Structures. The crystallographic data of complexes **4**−**8** are given in Table 1.

Complex 4. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences uniquely corresponding to the monoclinic space group *P*2(1)/*c*. The subsequent solution and refinement of the structure confirmed this choice. The crystals were sealed in the capillary and mounted nearly equidimensional. In spite of air and moisture sensitivity, the diffraction properties of the sample were excellent. The structure elucidation of **4** revealed a monomeric mixed lithium−magnesium ate complex in which the central magnesium atom is $\eta^2(N,N)$-coordinated by two bis(amido)silane ligands, whereas each of two lithium ions is π-bonded to two carbon atoms of the arene groups and σ-bonded to two nitrogen atoms of the ligands (Figure 1). The geometry of magnesium is distorted tetrahedral, while the lithium atom is distorted bipyramidal, giving the magnesium metal center a coordination number of four. Interestingly, the dispositions of the metals are close to linearity [the angle value of Li(1)−Mg(1)−Li(2) is 166.0°]. The Mg−N bond lengths are almost identical [Mg(1)−N(1) 2.048 Å; Mg(1)−N(2) 2.050 Å], suggesting perfect η^2-coordination, but are significantly longer than those found in **1** [Mg−N 1.963(3) Å].[18] The longer Mg−N bond lengths found in **4** are likely due to the coordinated lithium ions, the higher coordination number at the magnesium center (4 vs 3), and repulsion of the bulky diamido groups. The

Table 1. Crystal and Data Collection Parameters of Complexes 4−8

	4	5	6	7	8
formula	$C_{58}H_{94}Li_2MgN_4Si_2$	$C_{38}H_{64}CaN_2O_3Si$	$C_{30}H_{48}SrN_2OSi$	$C_{42}H_{72}BaN_2O_4Si$	$C_{52}H_{102}Br_2Li_6N_8O_4Si_6$
fw	898.66	665.08	568.41	834.44	1273.38
cryst size (mm)	0.25 × 0.16 × 0.10	0.15 × 0.20 × 0.25	0.15 × 0.12 × 0.08	0.23 × 0.18 × 0.15	0.55 × 0.36 × 0.29
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*P*2(1)/*c*	*C*/*c*	*P*2(1)/*c*	*P*2/*c*	$P\bar{1}$
a (Å)	13.288(10)	22.773(3)	8.831(3)	10.606(3)	12.9987(12)
b (Å)	20.967(17)	10.1659(12)	22.700(7)	10.127(3)	14.2883(13)
c (Å)	20.419(16)	19.218(2)	16.076(5)	22.487(6)	19.3868(18)
α (deg)	90	90	90	90	100.6800(10)
β (deg)	99.613(10)	113.359(2)	91.455(4)	108.854(12)	101.0620(10)
γ (deg)	90	90	90	90	96.1460(10)
V (Å^3)	5609(8)	4084.4(8)	3221.5(17)	2285.7(12)	3434.4(5)
Z	4	4	4	4	2
D_c (g cm^{-3})	1.064	1.082	1.172	1.212	1.243
abs coeff (mm^{-1})	0.111	0.217	1.733	0.932	1.334
F (000)	1964	1456	1208	880	1360
T (K)	293	296	293	293	296
range (deg)	1.40−25.01	2.23−25.77	2.975−29.996	1.91−23.29	1.09−25.01
reflns measd	22 956	12 635	14 439	7792	24 321
unique reflns	9866	7399	6268	3294	11 959
θ_{max} (deg)	25.01	25.77	29.996	23.29	25.01
R_{int}	0.0748	0.0349	0.0416	0.0481	0.0195
max and min transmn	0.9890 and 0.9728	0.9682 and 0.9478	0.8738 and 0.7811	0.8728 and 0.8141	0.6984 and 0.5275
R1, wR2 $[I > 2\sigma(I)]$[a]	0.0639, 0.1629	0.0566, 0.1338	0.0596, 0.1724	0.0434, 0.1026	0.0282, 0.0727
R1, wR2 (all data)[b]	0.1342, 0.1920	0.0969, 0.1601	0.0825, 0.1875	0.0530, 0.1068	0.0377, 0.0790
GOF	0.92	1.038	0.939	0.975	1.041
Δ(max) (e Å^{-3})	0.327	0.242	1.39	1.003	0.464
Δ(min) (e Å^{-3})	−0.294	−0.391	−1	−0.422	−0.358

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

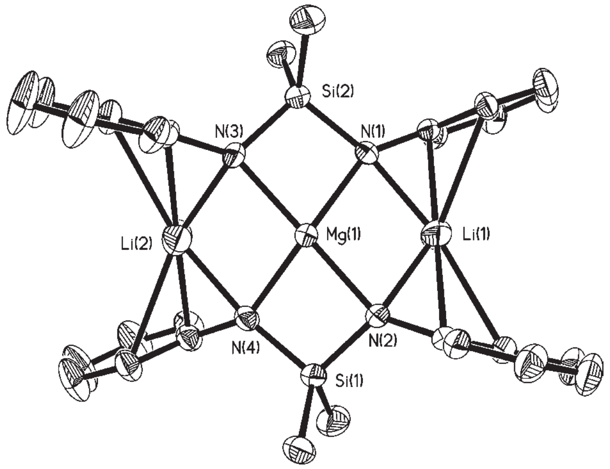


Figure 1. Molecular structure of **4** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Mg(1)−N(1) 2.048(3), Mg(1)−N(4) 2.050(3), Mg(1)−N(2) 2.055(3), Mg(1)−N(3) 2.061(3), Li(1)−N(1) 2.084(8), Li(1)−N(2) 1.993(8), Li(1)−C(1) 2.217(8), Li(1)−C(13), 2.262(8), Si(1)−N(4) 1.724(3), Si(1)−N(2) 1.746(3); N(1)−Mg(1)−N(4) 151.56(12), N(1)−Mg(1)−N(2) 103.65(12), N(1)−Mg(1)−N(3) 79.93(12), N(2)−Si(1)−N(4) 98.76(14), N(1)−Li(1)−N(2) 104.6(3), Mg(1)−N(1)−Li(1) 75.0(2), Li(1)−N(2)−Mg(1) 76.8(2).

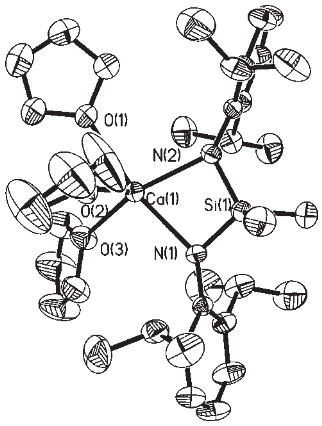


Figure 2. Molecular structure of **5** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ca(1)−N(1) 2.313(3), Ca(1)−N(2) 2.288(3), Ca(1)−O(1) 2.463(3), Ca(1)−O(2) 2.358(4), Ca(1)−O(3) 2.389(3), Si(1)−N(1) 1.702(3), Si(1)−N(2) 1.708(3); N(1)−Ca(1)−N(2) 70.17(11), N(1)−Si(1)−N(2) 101.66(15), N(1)−Ca(1)−O(1) 167.30(12), N(1)−Ca(1)−O(2) 105.52(13), N(1)−Ca(1)−O(3) 152.39(13), O(1)−Ca(1)−O(2) 83.17(15), O(1)−Ca(1)−O(3) 89.08(13), O(2)−Ca(1)−O(3) 103.41(14).

Li(1)−C(Ar) distances in **4** vary between 2.217(8) and 2.650(9) Å, versus the Li−C π bond lengths [2.533(16) and 2.729(16) Å] found in an ionic associate species lithium tetrkis(pentafluorophenyl)-borate−benzene[30] and the Li−C σ bond length [2.317(4) Å] found in $[(PhLi\cdot Et_2O)_4]$,[31] clearly indicating the slipped η^2-coordination (π-bonded).

Complexes 5−7. The molecular structures of **5**−**7** are monomeric in the solid state and actually isostructural without considering the solvated THF molecules (Figures 2−4). The molecular structure of **5** has a distorted trigonal-bipyramidal geometry about the calcium center and exhibits five-coordination with one bis(amido)silane $[Me_2Si(Dipp)_2]^{2-}$ and three solvated THF ligands (Figure 2). The Ca−N bond lengths are 2.288(3) and 2.313(3) Å, respectively, which are slightly shorter than those found in the amidinate calcium complex [[{ArNC(Me)CHCN(Me)Ar}Ca{*i*PrN)$_2$CC≡C(4-MeC$_6$H$_4$)]}(THF)] [2.3918(14) and 2.4294(14) Å][32] and the phosphaguanidinate complex [[{ArNC(Me)CHCN(Me)Ar}Ca{*i*PrN)$_2$C(PPh$_2$)]}(THF)] [2.3934(15) and 2.4410(15) Å],[33] suggesting η^2-coordination of the bis(amido)silane ligand. The N−Ca−N bite angle of the η^2-terminal bis(amido)silane ligand is 70.14(11)°, significantly less acute than those found in [[{ArNC(Me)CHCN(Me)Ar}Ca{*i*PrN)$_2$CC≡C(4-MeC$_6$H$_4$)]}(THF)] [N(4)−Ca−N(3) 56.65(5)°][32] and in [[{ArNC(Me)CHCN(Me)Ar}Ca{*i*PrN)$_2$C(PPh$_2$)]}(THF)] [55.83(5)°].[33] The molecular structure of **6** has a distorted tripod geometry about the strontium center, with one η^2-bis(amido)silane $[Me_2Si(Dipp)_2]^{2-}$ and one solvated THF ligand (Figure 3). The Sr−N bond lengths are 2.095(5) and 2.103(4) Å, respectively, which are significantly shorter than those found in the strontium guanidinate complex [(η^2-{(*i*PrN=C(N(*i*Pr)$_2$N*i*Pr))}$_2$Sr{μ^2, η^2:η^2-(*i*PrN=C(N(*i*Pr)$_2$N*i*Pr)$_2$)}$_2$Sr{η^2-(*i*PrN=C(N(*i*Pr)$_2$N*i*Pr)$_2$)}$_2$] [2.562(2) and 2.568(2) Å].[34a] The bis(amido)silane ligand N−Sr−N bite angle is 73.08(18)°, significantly larger than that found in [(η^2-{(*i*PrN=C(N(*i*Pr)$_2$N*i*Pr))}$_2$Sr{μ^2, η^2:η^2-(*i*PrN=C(N(*i*Pr)$_2$N*i*Pr)$_2$)}$_2$Sr{η^2-(*i*PrN=C(N(*i*Pr)$_2$N*i*Pr)$_2$)}$_2$] [N(1)−Sr(1)−N(2) 52.56(8)°].[34a] Notably, it is quite remarkable that the calcium and barium analogues have large coordination numbers, whereas the strontium compound bonds only to one THF molecule. However, it seems that this feature is not a reflection of the crystal packing effect. The molecular structure of **7** was found to share common features with **5** and **6** without considering the THF ligands. The barium atom displays coordination at the six-coordinate, trigonal-bipyramidal complex with one η^2-bis(amido)silane $[Me_2Si(Dipp)_2]^{2-}$ and four THF molecules (Figure 4). The Ba−N bis(amido)silane bond lengths are 2.582(4) Å, which indicate the perfect η^2-coordination. The bond lengths are slightly shorter than

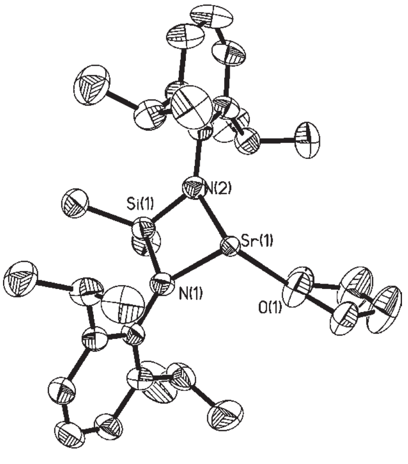


Figure 3. Molecular structure of **6** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sr(1)−N(1) 2.095(5), Sr(1)−N(2) 2.103(4), Sr(1)−O(1) 2.506(5), Sr(1)−Si(1) 2.8648(17), Si(1)−N(1) 1.718(5), Si(1)−N(2) 1.718(5); N(1)−Sr(1)−N(2) 73.08(18), N(1)−Sr(1)−O(1) 92.89(18), N(2)−Sr(1)−O(1) 99.93(17), N(1)−Si(1)−N(2) 93.3(2).

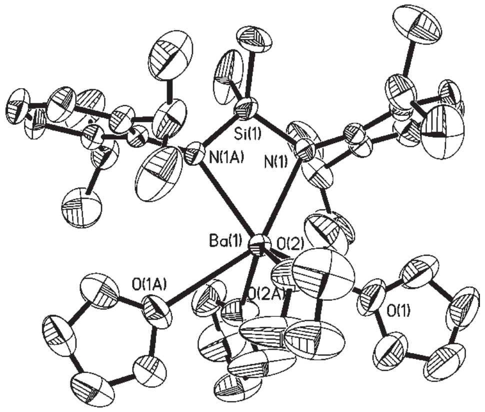


Figure 4. Molecular structure of **7** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ba(1)−N(1) 2.582(4), Ba(1)−N(1A) 2.582(4), Si(1)−N(1) 1.687(4), Si(1)−N(1A) 1.687(4), Ba(1)−O(1) 2.863(4), Ba(1)−O(1A) 2.863(4), Ba(1)−O(2) 2.774(4), Ba(1)−O(2A) 2.774(4); N(1A)−Ba(1)−N(1) 61.93(15), O(1A)−Ba(1)−O(1) 122.6(2), O(2A)−Ba(1)−O(2) 130.67(19), O(1A)−Ba(1)−O(2A) 77.17(16), O(1)−Ba(1)−O(2) 77.17(16).

that found in the barium guanidinate complex $[(\eta^2\text{-}\{(i\text{PrN}{=}\text{C}(\text{N}(i\text{Pr})_2\text{N}i\text{Pr}))\}\text{Ba}\{\mu^2, \eta^2{:}\eta^2\text{-}(i\text{PrN}{=}\text{C}(\text{N}(i\text{Pr})_2\text{N}i\text{Pr})_2)\}_2\text{Ba}\{\eta^2\text{-}(i\text{PrN}{=}\text{C}(\text{N}(i\text{Pr})_2\text{N}i\text{Pr})_2)\}]$ [2.735(2) Å].[34a] The bis(amido)silane ligand N−Ba−N bite angle is 61.93(15)°, significantly larger than that found in $[(\eta^2\text{-}\{(i\text{PrN}{=}\text{C}(\text{N}(i\text{Pr})_2\text{N}i\text{Pr}))\}\text{Ba}\{\mu^2 \text{ and } \eta^2{:}\eta^2\text{-}(i\text{PrN}{=}\text{C}(\text{N}(i\text{Pr})_2\text{N}i\text{Pr})_2)\}_2\text{Ba}\{\eta^2\text{-}(i\text{PrN}{=}\text{C}(\text{N}(i\text{Pr})_2\text{N}i\text{Pr})_2)\}]$ [N(1)−Ba(1)−N(1A) 49.42(10)°].[34a] The reason is probably similar to those of **5** and **6**. The Ae−O bond lengths are about 2.358(4) Å in **5**, 2.506(5) Å in **6**, and 2.863(4) Å in **7**, respectively, comparable with those found in amide complexes $\text{Ae}[\text{NSiMe}_3]_2\text{THF}_2$ [Ca−O 2.377(6) Å, Sr−O 2.534(1) Å, and Ba−O 2.731(1) Å].[34b] The observed shorter Ae−N bond lengths in **5**−**7** compared with those in the corresponding guanidinate complexes are apparently due to an increased electrostatic attraction of the dianionic bis(diamido)silane ligand.

Complex 8. Even though the resonances of compound **8** in the ^{1}H NMR spectrum are somewhat overlapped, we report the structure now because the X-ray data are of good quality and there are few previous examples of derivatives containing the $\text{Li}_6\text{Br}_2\text{O}_4$ core with the unusual decomposed bis(amido)silane ligands (Figure 5). The structure of **8** displays a lithium oxo polyhedral complex with a square-basket-shaped core $\text{Li}_6\text{Br}_2\text{O}_4$ bearing two different bis(aminolato)silane ligands, in which two bromide ions are bridged between two of the lithium atoms and four oxygen atoms are linked to four of the lithium atoms. The $\text{Li}_6\text{Br}_2\text{O}_4$ core of **8**, consisting of 10 faces formed by two four-membered Li_2O_2 and eight four-membered Li_2OBr quadrilateral rings, is stabilized with four solvated THF molecules and two tridentate bis(aminolato)silane ligands $[(\text{DippN}(\text{Me}_2\text{Si})_2)(\mu\text{-O})(\text{Me}_2\text{Si})]$. Two of the lithium ions are four-coordinated by exclusive oxide atoms, while the others are four-coordinated by oxide and bromide atoms, respectively. The geometries of both lithium and oxygen atoms are slightly distorted tetrahedral. The Li−O bond lengths are within the range of 1.874(4)−2.340(4) Å, longer than those found in complex $[\{\text{PhC}(\text{NSiMe}_3)_2\}_4\text{Li}_4\text{Mg}(\text{O})]$ [1.799(11)−1.919(11) Å],[29a] while the Li−Br bond lengths are 2.522(4)−2.546(4) Å, slightly shorter than those found in complexes $[\text{LiBr}\{\text{Li}(\text{THF})\}_2\{\text{CoBr}(\text{OSiMe}_3)_3\}]_2$ [2.634(5) Å][35] and $[\text{LiBr}\cdot\text{LiN}(\text{SiMe}_3)_2\cdot\{\text{LiOC}(t\text{Bu}{=}\text{CH}_2)_2\cdot 2\text{TMEDA}\}$ [2.604(7) and 2.613(6) Å].[36] The bis(aminolato)silane ligands $[(\text{DippN}(\text{Me}_2\text{Si})_2)(\mu\text{-O})(\text{Me}_2\text{Si})]$ in **8** obviously arise from the imposition of oxygen upon the $\text{Me}_2\text{Si}(\text{Dipp})_2$ unit. Presumably, decomposition of a peroxide-coordinated magnesium−lithium intermediate leads to Si−N bond cleavage.[29b]

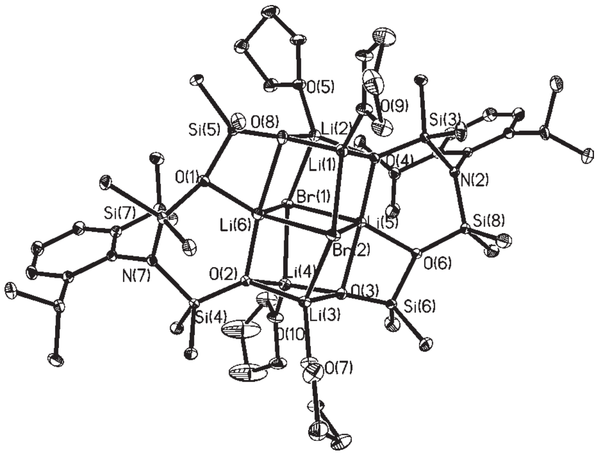


Figure 5. Molecular structure of **8** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Br(1)−Li(1) 2.794(4), Br(1)−Li(2) 2.546(4), Br(1)−Li(3) 2.507(4), Br(1)−Li(4) 2.644(4), Br(2)−Li(1) 2.946(4), Br(2)−Li(3) 2.507(4), Br(2)−Li(4) 2.969(4), Br(2)−Li(6) 2.522(4), Si(1)−O(1) 1.6073(14), Si(1)−N(8) 1.7696(17), Si(1)−C(2) 1.867(2), Si(1)−C(1) 1.880(2), Si(2)−O(2) 1.6457(14), Si(2)−N(8) 1.7310(17), Si(2)−C(16) 1.846(2), Si(3)−O(2) 1.6780(15), Si(3)−O(3) 1.5909(15), Si(3)−C(18) 1.854(2), Li(1)−O(1) 1.933(4), Li(1)−O(2) 2.020(4), Li(1)−O(3) 2.180(4), Li(3)−O(6) 1.878(4), Li(3)−O(1) 1.945(4), Li(3)−O(7) 1.956(4), Li(5)−O(3) 1.895(4), Li(5)−O(9) 1.929(4), Li(5)−O(4) 1.959(4); Li(6)−Br(1)−Li(2) 128.05(11), Li(6)−Br(1)−Li(4) 67.07(11), Li(2)−Br(1)−Li(4) 72.45(11), Li(6)−Br(1)−Li(1) 70.14(11), Li(2)−Br(1)−Li(1) 65.86(11), Li(4)−Br(1)−Li(1) 69.18(11), Li(5)−Br(2)−Li(3) 124.95(11), Li(5)−Br(2)−Li(1) 69.64(11), Li(3)−Br(2)−Li(1) 63.15(11), Li(5)−Br(2)−Li(4) 63.37(11), Li(3)−Br(2)−Li(4) 70.84(11), Li(1)−Br(2)−Li(4) 62.97(10), O(1)−Li(1)−O(2) 108.95(17), O(1)−Li(1)−O(3) 173.8(2), O(2)−Li(1)−O(3) 75.37(13), O(1)−Li(1)−Br(1) 123.42(17), O(3)−Li(1)−Br(1) 87.34(13), O(6)−Li(3)−O(1) 98.21(17), O(6)−Li(3)−O(7) 116.46(19), O(1)−Li(3)−O(7) 124.65(19), O(6)−Li(3)−Br(2) 103.67(15), O(1)−Li(1)−Br(2) 105.44(16), O(7)−Li(3)−Br(2) 106.27(15), O(3)−Li(5)−O(9) 117.82(19), O(3)−Li(5)−O(9) 117.82(19), O(3)−Li(5)−O(4) 98.40(17), O(9)−Li(5)−O(4) 120.88(19), O(3)−Li(5)−Br(2) 102.36(15), O(9)−Li(5)−Br(2) 109.41(16), O(4)−Li(5)−Br(2) 105.82(15).

■ CONCLUSIONS

This work has demonstrated that several alkaline-earth-metal (diamido)silane compounds were readily prepared either by the metathesis reaction of dilithium bis(amido)silane $[\text{Me}_2\text{Si}(\text{DippNLi})_2]$ (Dipp = 2,6-i-$\text{Pr}_2\text{C}_6\text{H}_3$) and alkaline-earth-metal halides MX_2 (M = Mg, X = Br; Ca, Sr, Ba, X = I), by the transamination of $\text{M}[\text{N}(\text{SiMe}_3)_2]_2\cdot 2\text{THF}$ (M = Ca, Sr, Ba) and $[\text{Me}_2\text{Si}(\text{DippNH})_2]$, or by the transmetalation of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, $[\text{Me}_2\text{Si}(\text{DippNH})_2]$, and metallic calcium, strontium, and barium in situ, respectively. In the presence of oxygen, the metathesis reaction of dilithium bis(amido)silane and magnesium bromide gives, however, an unusual lithium oxo polyhedral complex **8** with a square-basket-shaped core $Li_6Br_2O_4$ bearing a bis(aminolato)silane ligand. The X-ray structure analyses of bis(amido)silane complexes have shown comparable features. Compound **4** is revealed as a remarkable magnesium−lithium ate species versus the monomeric compounds **5**−**7** and is a rare example of structurally elucidated "alkaline-rich" compounds with a stoichiometry of lithium and magnesium ions in a ratio of 2:1 despite a previously known example with Na/Mg (2:1), K/Mg (2:1), and Li/Mg (2:1).[18,37] The N−M bond distances (M = Mg, Ca, Ba) increase upon going down from the group but for Sr−N [average values: Mg 2.065(3) Å, Ca 2.300(3) Å, and Ba 2.582(4) Å]. The steric factors and less solvated THF molecules may be responsible for the bond length of Sr−N being outside the row [2.099(5) Å]. Complexes **4**−**7** are highly potential as precursors in catalysis and materials chemistry. Work is proceeding along these lines.

■ EXPERIMENTAL SECTION

All manipulations were carried out in an argon atmosphere under anaerobic conditions using standard Schlenk-line, vacuum-line, and glovebox techniques. The solvents were thoroughly dried, deoxygenated, and distilled in an argon atmosphere prior to use. DMSO-d_6 was degassed and dried over molecular sieves for 24 h before use. C_6D_6 was dried with metallic sodium before use. The ^{1}H NMR, ^{13}C NMR, and ^{7}Li NMR spectra were recorded with a Bruker DRX-600 spectrometer. IR measurements were carried out on a Nicolet 360 Fourier transform IR spectrometer from Nujol mulls prepared in a drybox. Melting points were measured in sealed argon-filled capillaries without temperature correction with a XT4-100A apparatus (Electronic and Optical Instruments, Beijing, China). Reliable elemental analyses could not be obtained, even when a glovebox handling was attempted, likely because of the high moisture and oxygen sensitivity of all compounds reported. This is a well-known problem in alkaline-earth-metal chemistry.[38] Therefore, analysis is limited to NMR and IR spectroscopic investigations, supplemented by single-crystal X-ray diffraction studies in the cases of **4**−**8**. *n*BuLi, $MgBr_2 \cdot 2Et_2O$, CaI_2, SrI_2, BaI_2, calcium, strontium, and barium (99.7%) were purchased from Aldrich. $Me_2Si(DippNH)_2$,[24] $Me_2Si(DippNLi)_2$,[24] and $M[N(SiMe_3)_2]_2(THF)_2$ (M = Ca, Sr, Ba)[39] were prepared according to the literatures.

Synthesis of Complex 4. To a mixture of $Me_2Si(DippNLi)_2$ (0.422 g, 1.00 mmol) and $MgBr_2 \cdot Et_2O$ (0.166 g, 0.5 mmol), *n*-hexane (30 mL) was added at 0 °C via a syringe. After the solution was stirred for 18 h at room temperature, the light-yellow solution was filtered through Celite. The solvent of the filtrate was concentrated to about 5 mL under reduced pressure and then was kept at −30 °C to afford **4** as colorless crystals (0.62 g, 73.0%). Mp: >270 °C (dec). ^{1}H NMR (DMSO-d_6, 23 °C): δ −0.07 (s, 12 H, $\mathrm{SiC}H_3$), 6.54−6.86 (br, 12 H, Ph), 3.00 (sept, 2 H, $\mathrm{Me_2C}H$), 3.56 (sept, 6 H, $\mathrm{Me_2C}H$), 1.05 (d, 36 H, $(\mathrm{C}H_3)_2\mathrm{C}$), 1.12 (d, 12 H, $(\mathrm{C}H_3)_2\mathrm{C}$). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C): δ 121 (br, *C* for [Ph]), 122.6 (s, *C* for [Ph]), 131.7 (s, *C* for [Ph]), 31.4 (s, $(CH_3)_2C$), 27.7 (s, $(CH_3)_2C$), 27.1 (s, $(CH_3)_2C$), 24.1 (s, $(CH_3)_2C$), 14.4 (s, $(CH_3)_2Si$). ^{7}Li{^{1}H} NMR (DMSO-d_6, 23 °C): δ −1.06 (s). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2922(s), 2582(s), 2726(w), 1640(s), 1376(s), 1304(s), 1154(w), 722(s), 911(w). Single crystals suitable for X-ray diffraction analysis were obtained from recrystallization at room temperature in *n*-hexane.

Synthesis of Complex 5. To a mixture of $Me_2Si(DippNLi)_2$ (0.422 g, 1.00 mmol) and CaI_2 (0.167 g, 1.0 mmol) in a Schlenk flask (100 mL), a mixed solvent of THF (10 mL) and *n*-hexane (20 mL) was added via a syringe at 0 °C. After the suspension was stirred for 18 h at room temperature, the solution was filtered through Celite. The filtrate was concentrated to about 5 mL to afford **5** as colorless solid at −30 °C for several days (0.38 g, 58.0%). Alternatively, to a mixture of $Me_2Si(DippNH)_2$ (0.410 g, 1.0 mmol) and $Ca[N(SiMe_3)_2]_2(THF)_2$ (0.510 g, 1.0 mmol), THF (30 mL) was added via a syringe and the solution was stirred for 18 h. After the orange solution was filtered, the volatile components were removed under reduced pressure. The solid was recrystallized in the mixed solvents of THF (10 mL) and *n*-hexane (20 mL) to afford **5** as colorless crystals at −30 °C after several days (0.47 g, 70.7%). Mp = 173 °C. ^{1}H NMR ($CDCl_3$, 23 °C): δ = 0.52, 0.53 (2s, 6 H, $\mathrm{Si}(\mathrm{C}H_3)$), 7.36 (d, 1 H, Ph), 7.04 (m 1 H, Ph), 7.17 (m 4 H, Ph), 4.63 (sept, 4 H, $\mathrm{Me_2C}H$), 3.44 (d, 12 H, THF), 1.46, 1.52 (2d, 24 H, $(\mathrm{C}H_3)_2\mathrm{C}$), 1.34 (d, 12 H, THF); ^{13}C{1H}NMR (C_6D_6, 23 °C): δ = 155.1, 142.0, 122.7,122.6, 115 (5s, C for [Ph]), 68.9, 25.3 (2s, C for THF), 25.4 (s, C for $(CH_3)_2C$), 27.1 (s, C for $(CH_3)_2C$), 5.5 (s, C for $(CH_3)_2Si$); IR(Nujol Mull, cm^{-1}): $\tilde{\nu}$ = 2855 (s), 2725(s), 2673(w), 2031(w), 1653(w), 1461(s), 1376(s), 1306(w), 1258(w), 1153(s), 1075(s), 1028(w), 932(w), 722(s). Single crystals suitable for X-ray diffraction analysis were obtained from recrystallization at room temperature in a mixed solvent of *n*-hexane and THF (1:1).

Synthesis of Complex 6. In a fashion similar to the preparation of complex **5**, $Me_2Si(DippNLi)_2$ (0.422 g, 1.00 mmol) and SrI_2 (0.22 g, 1.0 mmol) in a mixed solvent of THF (0.1 mL) and *n*-hexane (30 mL) afford **6** as yellow crystals (0.41 g, 72.0%). Alternatively, to a mixture of $Me_2Si(DippNH)_2$ (0.41 g, 1.0 mmol) and $Sr[N(SiMe_3)_2]_2(THF)_2$ (0.55 g, 1.0 mmol) was added via a syringe THF (30 mL) was added via a syringe, and the solution was stirred for 18 h. After the orange solution was filtered, the volatile components were removed under reduced pressure. The solid was recrystallized in *n*-hexane to afford **6** as orange crystals at −30 °C after several days (0.44 g, 77.5%). Mp: 152−154 °C. ^{1}H NMR (C_6D_6, 23 °C): δ 0.31 (s, 6 H, $\mathrm{Si}(\mathrm{C}H_3)$), 7.05−7.22 (d, 6 H, Ph), 3.56 (m, 4 H, THF), 1.40 (m, 4 H, THF), 4.02 (m, 4 H, $\mathrm{Me_2C}H$), 1.31 (d, 24 H, $(\mathrm{C}H_3)_2\mathrm{C}$). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C): δ 147.0, 144.6, 144.0, 124.5, 123.4, 122.6 (6s, *C* for [Ph]), 67.8, 25.6 (2s, *C* for THF), 27.9 (s, C for $(CH_3)_2C$), 5.2 (s, C for $(CH_3)_2C$), 3.7 (s, C for $(CH_3)_2Si$). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2853(s), 2715(s), 2670(w), 650(w), 1462(s), 1374(s), 1152(w), 1028(w), 928(w), 721(s). Single crystals suitable for X-ray diffraction analysis were obtained from recrystallization at −30 °C in *n*-hexane.

Synthesis of Complex 7. In a fashion similar to the preparation of complex **4**, $Me_2Si(DippNLi)_2$ (0.422 g, 1.00 mmol) and BaI_2 (0.27 g, 1.0 mmol) in a mixed solvent of THF (20 mL) and *n*-hexane (10 mL) afford **7** as a colorless solid at −30 °C for several days (0.52 g, 62.3%). Alternatively, to a mixture of $Me_2Si(DippNH)_2$ (0.41 g, 1.0 mmol) and $Ba[N(SiMe_3)_2]_2(THF)_2$ (0.60 g, 1.0 mmol) was added via a syringe THF (30 mL) was added via a syringe, and the solution was stirred for 18 h. After the solution was filtered, the volatile components were removed under reduced pressure. The solid was recrystallized in a mixed solvent of *n*-hexane and THF (1:1) to afford 7 as colorless crystals at −30 °C for several days (0.69 g, 82.7%). Mp: 136 °C (dec). ^{1}H NMR (DMSO-d_6, 23 °C): δ −0.11 (s, 6 H, $\mathrm{Si}(\mathrm{C}H_3)$), 6.57−6.92 (m, 6 H, Ph), 3.65, 1.75 (2s, 32 H, THF), 3.03 (sept, 4 H, $\mathrm{Me_2C}H$), 1.10, 1.09 (2d, 24 H, $(\mathrm{C}H_3)_2\mathrm{C}$). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C): δ 131.1, 122.0, 116.5 (3s, *C* for [Ph]), 67.0, 25.1 (2s, *C* for THF), 26.6 (s, $(CH_3)_2C$), 23.6 (s, $(CH_3)_2C$), 22.5 (s, $(CH_3)_2Si$). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2853(s), 2720(s), 2031(w), 1462(s), 1375(s), 1311(w), 1152(w), 1028(w), 920(s), 722(s). Single crystals suitable for X-ray diffraction analysis were obtained from recrystallization at −30 °C in a mixed solvent of *n*-hexane and THF (1:1).

Syntheses of Complexes 5−7 in Situ. To a mixture of $Me_2Si(DippNH)_2$ (0.41 g, 1.0 mmol) and $Sn[N(SiMe_3)_2]_2$ (0.44 g, 1.0 mmol) in 100 mL Schlenk flask was added via a syringe THF (20 mL) was added via a syringe. After the orange-yellow solution was stirred at ambient temperature for 5 h, a slight excess of metallic metal (1.2 mmol) was added. The gray suspension was stirred for an additional 24 h, and the solution was filtered through Celite. The volatile components of the filtrate were removed under reduced pressure. The solid residue was dissolved in a mixed solvent of *n*-hexane and THF to give **5** (0.47 g, 70.7%), **6** (0.44 g, 77.5%), and **7**

(0.69 g, 82.7%) as air- and moisture-sensitive crystals at −30 °C for several days. The ^{1}H NMR data are identical with those mentioned above.

Synthesis of Complex 8. To a mixture of $Me_2Si(DippNLi)_2$ (0.422 g, 1.00 mmol) and $MgBr_2 \cdot Et_2O$ (0.166 g, 0.5 mmol) in the presence of dry oxygen was added THF (40 mL) at room temperature via a syringe. After the solution was stirred for 48 h, the solution was filtered through Celite. The solvent of the filtrate was concentrated to about 5 mL under reduced pressure. *n*-Hexane (15 mL) was then added and the solution kept at −30 °C to give **5** as colorless crystals (0.62 g, 73.0%). Mp: 204−207 °C. The resonances in the ^{1}H NMR ($CDCl_3$, 23 °C) spectrum are heavily overlapped. ^{7}Li{^{1}H} NMR (C_6D_6, 23 °C): δ 0.96, 0.82 (2s, overlapped). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2922(s), 2582(s), 2726(w), 1640(s), 1376(s), 1304(s), 1154(w), 722(s), 911(w). Accurate microanalytical data could not be obtained for this compound because of the facile loss of THF molecules.

X-ray Structure Determinations. Suitable single crystals were sealed under argon in thin-walled glass capillaries. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo Kα radiation, $\varphi-\omega$ scan technique, λ = 0.710 73 Å). The intensity data were integrated by means of the *SAINT* program.[40] *SADABS*[41] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the *SHELXTL* package.[42] All non-hydrogen atoms in **4**−**8** were refined anisotropically. The hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker *SMART* program. Crystallographic parameters for compounds **4**−**8**, along with details of the data collection and refinement, are collected in Table 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic files for **4**−**8** in CIF format and ^{1}H, ^{7}Li, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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