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A Novel Group of Alkaline Earth Metal Amides: Syntheses and Characterization of $M[N(2,6\text{-}{}^{i}Pr_2C_6H_3)(SiMe_3)]_2(THF)_2$ (M = Mg, Ca, Sr, Ba) and the Linear, Two-Coordinate $Mg[N(2,6\text{-}{}^{i}Pr_2C_6H_3)(SiMe_3)]_2$

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Novel alkaline earth metal aryl-substituted silylamides were prepared using alkane (Mg) and salt elimination reactions (Mg, Ca, Sr, and Ba). The salt elimination regime involved the treatment of the alkaline earth metal iodides with 2 equiv of the respective potassium amide KNDiip(SiMe$_3$), (Diip = 2,6-*i*-Pr$_2$C$_6$H$_3$). The organomagnesium source for the alkane elimination was (^{n}Bu/^{s}Bu)$_2$Mg. All compounds were characterized using ^{1}H, ^{13}C NMR, and IR spectroscopy, in addition to X-ray crystallography (except Mg[NDiip(SiMe$_3$)]$_2$THF$_2$). Crystal data with Mo Kα (λ = 0.710 73 Å) are as follows: Mg[NDiip(SiMe$_3$)]$_2$, 1, a = 9.4687(6) Å, b = 9.6818(6) Å, c = 17.9296(1) Å, α = 96.487(1)°, β = 94.537(1)°, γ = 89.222(1)°, V = 1608.8(2) Å^3, Z = 2 (two independent molecules), triclinic, space group $P\bar{1}$, R1 (all data) = 0.0508; ^{n}BuMg[NDiip(SiMe$_3$)]THF$_2$, **2**, a = 9.5413(1) Å, b = 16.493(2) Å, c = 9.8218(1) Å, β = 108.149(2)°, V = 1468.7(4) Å^3, Z = 2, monoclinic, space group $P2_1$, R1(all data) = 0.1232; Ca[NDiip(SiMe$_3$)]$_2$THF$_2$, **4**, a = 9.7074(1) Å, b = 20.9466(4) Å, c = 21.6242(3) Å, α = 73.573(1)°, β = 78.632(1)°, γ = 89.621(1)°, V = 4129.1(1) Å^3, Z = 4 (two independent molecules), triclinic, space group $P\bar{1}$, R1 (all data) = 0.0902; Sr[NDiip(SiMe$_3$)]$_2$THF$_2$, **5**, a = 20.5874(5) Å, b = 9.8785(2) Å, c = 20.8522(5) Å, β = 102.035(2)°, V = 4147.6(2) Å^3, Z = 4 (two independent molecules), monoclinic, space group $P2/n$, R1 (all data) = 0.0756; Ba[NDiip(SiMe$_3$)]$_2$THF$_2$, **6**, a = 20.5476(2) Å, b = 10.0353(2) Å, c = 20.9020(4) Å, β = 101.657(1)°, V = 4221.0(1) Å^3, Z = 4 (two independent molecules), monoclinic, space group $P2/n$, R1 (all data) = 0.0573.

Introduction

Access to organometallic compounds of the heavy alkaline earth metals has been difficult due to the lack of metal sources with good solubility in a variety of solvents. The recent availability of the bis[bis(trimethylsilyl)]amides of the heavy alkaline earth elements changed this situation by providing a clean, hydrocarbon-soluble starting material. Employment of the amides in transamination schemes resulted in the preparation of several organometallic derivatives of calcium, strontium, and barium.[1] However, under acidic conditions, cleavage of the N−Si bond in the liberated amine under consumption of hydrocarbon educt is frequently observed (eqs 1 and 2), thus limiting possible hydrocarbon substrates to a few within a narrow pK_a range.[2]

$$HN(SiMe_3)_2 + HR \rightarrow H_2NSiMe_3 + Me_3SiR \qquad (1)$$

$$H_2NSiMe_3 + HR \rightarrow H_3N + Me_3SiR \qquad (2)$$

$$R = \text{aryl, alkyl}$$

The chemistry of alkaline earth metal amides has been limited to the bis[bis(trimethylsilyl)]amides, as summarized in a recent review article.[3] In the presence of donors, such as THF, the amido derivatives display monomeric species with two amides and two THF donors bound to the metal centers.[4−7] The THF donors may be removed by applying vacuum, resulting in dimeric solid-state structures with three-coordinate metal centers.[7−10] In solution, temperature-de-

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Table 1. Synthetic Methods toward Alkaline Earth Metal Amides[a]

synthetic route	reaction	ref
salt elimination	$MX_2 + 2AN(SiMe_3)_2 \xrightarrow[\text{donor}]{} M[N(SiMe_3)_2]_2(\text{donor})_2 + 2AX$	16
transmetalation	$M + M'[N(SiMe_3)_2]_2 \xrightarrow[\text{donor}]{} M[N(SiMe_3)_2](\text{donor})_2 + M'$	4, 17
metalation	$M + 2HN(SiMe_3)_2 \xrightarrow[\text{THF/NH}_3]{} M[N(SiMe_3)_2]_2THF_2 + H_2$	18
alkane elimination	$R_2Mg + 2HN(SiMe_3)_2 \rightarrow Mg[N(SiMe_3)_2]_2 + 2R(H)$	14, 24

[a] M = Mg, Ca, Sr, Ba; M′ = Sn, Hg; X = halide; A = alkali metal; donor = THF, pyridine, etc.

pendent fluxional behavior is observed. Monomeric alkaline earth metal amides with a metal coordination number of 2 have only been observed in the solid state if a very cumbersome ligand was utilized, as seen in $Mg[N(SiPh_2Me)_2]_2$.[11] If sterically less demanding ligands are employed, the coordination number 2 can only be observed in the gas phase, as shown in electron diffraction studies for $M[N(SiMe_3)_2]_2$ (M = Be, Mg).[12,13]

Alkaline earth metal amides may be prepared by different synthetic routes, as summarized in Table 1. Alkane/arene elimination reactions, used previously to prepare $Mg[N(SiMe_3)_2]_2OEt_2$[14] and $Mg(N(SiMePh_2)_2)_2$[11] among others, are limited to magnesium, due to the lack of suitable organometallic reagents of the heavier alkaline earth metals. The widely known and easily prepared cyclopentadienide (Cp) complexes[15] as basic substrates are not suitable due to the inherent stability of the Cp^- anion. In addition, the tendency of liberated C_5H_6 to dimerize causes significant difficulties in separation and purification.

Alternative routes are salt elimination[16] and transmetalation chemistry employing zinc or mercury amides in conjunction with freshly distilled alkaline earth metals.[17] A third possibility is metalation, involving the treatment of ammonia activated alkaline earth metals with freshly distilled amine in a THF/NH_3 mixture.[18] Importantly, the metalation route is best suited for the heaviest, most reactive alkaline earth element, barium, while the lighter, less reactive congener strontium requires extensive reaction/reflux conditions. The route is not suited for the preparation of the calcium analogues.

Here, we explore the secondary amide $[NDiip(SiMe_3)]^-$ (Diip = 2,6-$^iPr_2C_6H_3$) in conjunction with the alkaline earth metals magnesium, calcium, strontium, and barium. The motivation for this work was to develop alkaline earth metal amides less prone to bond scission under consumption of educt to serve as starting materials for the preparation of organometallic derivatives via transamination. By replacement of silyl groups by alkyl or aryl substituents, materials with a reduced tendency toward bond cleavage will be obtained. We also aim to increase the further understanding of how ligand bulk influences the coordination chemistry of the heavier alkaline earth metals. An additional goal is the preparation of mononuclear alkaline earth metal amides to be used as precursors for various solid-state materials.

We here report on a group of alkaline earth metal arylsilylamides carrying the $[N(2,6\text{-}^iPr_2C_6H_3)(SiMe_3)]^-$ ligand, specifically THF adducts of the general formula $M[NDiip(SiMe_3)]_2THF_2$, where M represents magnesium (**3**), calcium (**4**), strontium (**5**), and barium (**6**). We also report on the two-coordinate $Mg[NDiip(SiMe_3)]_2$, **1**, and the heteroleptic butylamide $^nBuMg[NDiip(SiMe_3)]THF_2$, **2**. Both **1** and **2** provide important information toward the formation of the amide target materials via alkane elimination chemistry.

Experimental Section

General Procedures. All reactions were performed under a purified nitrogen atmosphere by using modified Schlenk techniques and/or a Braun Labmaster 100 drybox. *n*-Hexanes and tetrahydrofuran (THF) were distilled just prior to use from a Na/K alloy followed by two freeze−pump−thaw cycles. Alkaline earth metal iodides were obtained from commercial sources. The secondary amine $HNDiip(SiMe_3)$ was synthesized according to literature procedures.[19] Commercially available 2,6-diisopropylaniline and $ClSiMe_3$ were dried over CaH_2 and distilled prior to use. Dibutylmagnesium (1 M solution of a statistical mixture of *n*- and *sec*-butylmagnesium ($(^nBu/^sBu)_2Mg$ in heptane) was obtained from a commercial source and used as received. KH in a mineral oil dispersion was washed several times with hexane and dried under reduced pressure. ^1H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 spectrometer. Spectra were recorded in C_6D_6 and referenced to residual solvent resonances. Infrared spectra were recorded as Nujol mulls between NaBr plates on a Perkin-Elmer PE 1600 FI-IR spectrometer. Melting points are uncorrected.

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Reliable elemental analyses could not be obtained, even when glovebox handling was attempted, due to the high moisture and oxygen sensitivity of all compounds reported. This is a well-known problem in alkaline earth metal chemistry.[20]

Mg[NDiip(SiMe$_3$)]$_2$, 1. To a solution of 0.36 mL of HNDiip(SiMe$_3$) (2 mmol) in 40 mL of hexane was added 1 mmol of Bu$_2$Mg (1 mL) by syringe. The resulting clear, colorless solution was refluxed for 3 h, affording a clear, colorless solution, which upon cooling to room temperature was reduced in volume to about 15 mL. After 24 h, storage at −23 °C yielded colorless, block-shaped crystals suitable for X-ray crystallography studies, in 71% yield (0.37 g). Mp: 185−190 °C.

^{1}H NMR (C$_6$D$_6$) (ppm): 0.124 (s, 18H, $-$CH$_3$), 1.12 (s, 24H), 3.75 (sept., 4H, $-$CH$-$), 6.97 (t, 2H, *p*-H), 7.07 (d, 4H, *m*-H).

^{13}C NMR (C$_6$D$_6$) (ppm): 1.18 (Si(Me)$_3$), 21.5 ($-$CH$-$), 27.9 ($-$(CH$_3$)$_2$), 122.4 (*p*-C), 123.7 (*o*-C) 144.4 (*m*-C), 145.6 (N$-$C).

IR (cm^{-1}) (Nujol): ν = 1377.4 m, 1313.1 m, 1242.1 w, 1295.1 w, 816.2 s, 790.7 s, 743.5 m, 668.1 w.

^{n}BuMg[NDiip(SiMe$_3$)](THF)$_2$, 2. To a solution of 4.43 mL (6.15 mmol) of HNDiip(SiMe$_3$) in 40 mL of hexane were added 6.15 mL of Bu$_2$Mg (6.15 mmol) and 15 mL of THF. The resulting clear, colorless solution was refluxed for 6 h, after which the volume was reduced to about 20 mL. After 24 h of storage at −23 °C colorless, plate-shaped crystals suitable for X-ray crystallography studies were obtained in 65% yield (0.31 g). Mp: 195−200 °C.

^{1}H NMR (C$_6$D$_6$) (ppm): 1.29 (t, 3H, $-$CH$_3$), 1.44 (d, 6H, ($-$CH$_3$)$_2$), 1.46 (m, 2H, ($-$CH$_3$)$_2$), 3.27 (s, 8H, THF), 4.20 (sept., 2H, $-$CH$-$), 7.01 (t, 1H, *p*-H), 7.18 (s, 2H, *m*-H).

^{13}C NMR (C$_6$D$_6$) (ppm): 4.3 (Si(Me)$_3$), 9.40 (Mg$-$CH$_2-$), 14.94 (CH$_3-$), 21.96 ($-$CH$_2-$), 25.38 (THF), 25.67 ($-$(CH$_3$)$_2$), 27.47 ($-$CH$-$), 69.6 (THF), 119.6 (*p*-C), 123.6 (*m*-C), 145.6 (N$-$C).

IR (cm^{-1}) (Nujol): ν = 2789 m, 1422.1 s, 1377.1 s, 1322.8 w, 1309.1 m, 1237.8 s, 1193.2 m, 1022.8 s, 935.4 s, 877.6 m, 835.7 s, 776.7 s, 741.2 m, 662.2 w.

General Procedure for the Synthesis of M[NDiip(SiMe$_3$)]$_2$(THF)$_2$ (M = Mg (3), Ca (4), Sr (5), Ba (6)). In a typical experiment, a Schlenk tube was charged with 5 mmol of KH (0.20 g) and 25−30 mL of tetrahydrofuran. To the resulting suspension, 5 mmol (1.24 g) of HNDiip(SiMe$_3$) was added slowly by syringe, upon which the evolution of hydrogen was observed. This solution was stirred for 2 h at room temperature, during which it became clear and almost colorless. An additional Schlenk tube was charged with 2.5 mmol of the alkaline earth metal iodide and 25 mL of tetrahydrofuran. The resulting suspension was heated briefly to reflux temperature, upon which the KNDiip(SiMe$_3$) solution was added dropwise via cannula. The formation of a white solid was observed immediately. The reaction mixture was stirred for 18 h at room temperature. The solvent was removed under vacuum yielding a gray powdery residue. Upon extraction with hexane and filtration through a Celite padded filter frit, the volume of the filtrate was reduced to 15 mL. Crystallization was initiated by storage of the solutions at −23 °C. After 24 h, colorless block-shaped crystals suitable for X-ray crystallographic studies were obtained in all instances.

Mg[NDiip(SiMe$_3$)]$_2$(THF)$_2$, 3: 0.20 g of KH (5 mmol); 1.26 mL of HNDiip(SiMe$_3$) (5 mmol); 0.74 g of MgI$_2$ (2.5 mmol).

Yield: 63% (0.81 g). Mp: 235−242 °C.

^{1}H NMR (C$_6$D$_6$) (ppm): 0.41 (s, 18H, SiMe$_3$), 1.16 (s, 8H, THF), 1.29 (s, 24H, $-$CH$_3$), 3.31 (s, 8H, THF), 4.22 (sept., 2H, $-$CH$-$),7. 15 (t, 1H, *p*-H), 7.41 (s, 2H, *m*-H).

^{13}C NMR (C$_6$D$_6$) (ppm): 4.85 (Si(Me)$_3$), 24.46 ($-$CH$-$), 25.52 ($-$(CH$_3$)$_2$), 27.85 (THF), 70.24 (THF), 120.85 (*p*-C), 123.13 (*m*-C), 145.54 (*o*-C), 153.08 (N$-$C).

IR (cm^{-1}) (Nujol): ν = 2723.1 w, 1417.5 m, 1306 w, 1237.6 m, 1180.2 w, 1022 w, 915 m, 877.4 w, 838.2 m, 775.6 w, 737.4 w, 661.6 w.

Ca[NDiip(SiMe$_3$)]$_2$(THF)$_2$, 4: 0.20 g of KH (5 mmol); 1.26 mL of HNDiip(SiMe$_3$) (5 mmol); 0.74 g of CaI$_2$ (2.5 mmol).

Yield: 46% (0.73 g). Mp: 184−186 °C.

^{1}H NMR (C$_6$D$_6$) (ppm): 0.71 (s, 18H, SiMe$_3$), 1.40 (s, 8H, THF), 1.54 (s, 24H, $-$CH$_3$), 3.40 (s, 8H, THF), 4.27 (sept, 2H, $-$CH$-$),7. 15 (t, 1H, *p*-H), 7.41 (s, 2H, *m*-H).

^{13}C NMR(C$_6$D$_6$) (ppm): 4.95 (Si(Me)$_3$), 24.21 ($-$CH$-$), 25.35 ($-$(CH$_3$)$_2$), 26.09 (THF), 27.64, 69.60 (THF), 118.85 (*p*-C), 123.71 (*m*-C), 144.23 (*o*-C), 153.72 (N$-$C).

IR (cm^{-1}) (Nujol): ν = 2853.4 s, 1594.1 w, 1557.9 w, 1412.4 w, 1326 w, 1265.1 w, 1234.3 w, 1107 w, 1033.9 w, 665.4 w.

Sr[NDiip(SiMe$_3$)]$_2$(THF)$_2$, 5: 0.25 g of KH (6 mmol); 1.51 mL of HNDiip(SiMe$_3$) (6 mmol); 1.02 g of SrI$_2$ (3 mmol).

Yield: 63% (1.38 g). Mp: 185−190 °C.

^{1}H NMR (C$_6$D$_6$) (ppm): 0.46 (s, 18H, SiMe$_3$), 1.13 (s, 8H, THF), 1.20 (s, 24H,$-$CH$_3$), 3.03 (s, 8H, THF), 3.98 (sept, 2H, $-$CH$-$), 6.82 (t, 1H, *p*-H), 7.08 (s, 2H, *m*-H).

^{13}C NMR (C$_6$D$_6$) (ppm): 4.93 (Si(Me)$_3$), 25.48 ($-$CH$-$), 26.06 ($-$(CH$_3$)$_2$), 27.53 (THF), 69.16 (THF), 118.12 (*p*-C), 123.97 (*m*-C), 144.17 (*o*-C), 152.33 (N$-$C).

IR (cm^{-1}) (Nujol): ν = 3033.8 m, 1411.5 s, 1359.5 m, 1315.9 s, 1253.8 s, 1198 m, 1140.5 m, 1105.6 m, 1026.6 s, 875.2 s, 829.4 s, 770.5 s, 601.2 m.

Ba[NDiip(SiMe$_3$)]$_2$(THF)$_2$, 6: 0.13 g of KH (3 mmol); 0.75 mL of HNDiip(SiMe$_3$) (3 mmol); 0.75 g of BaI$_2$ (1.5 mmol).

Yield: 40% (0.47 g). Mp: 172−175 °C.

^{1}H NMR (C$_6$D$_6$) (ppm): 0.45 (s, 18H, SiMe$_3$), 1.25 (s, 8H, THF), 1.35 (s, 24H, $-$CH$_3$), 3.10 (s, 8H, THF), 3.85 (sept., 2H, $-$CH$-$), 6.80 (t, 1H, *p*-H), 7.05 (s, 2H, *m*-H).

^{13}C NMR (ppm): 4.96 (Si(Me)$_3$), 25.67 ($-$CH$-$), 26.16 ($-$(CH$_3$)$_2$), 27.48 (THF), 68.49 (THF), 124.39 (*p*-C), 145.03 (*o*-C), 153.90 (N$-$C).

IR (cm^{-1}) (Nujol): ν = 2943.4 s, 1602.1 w, 1550.9 w, 1402.4 w, 1300 w, 1273.2 w, 1225.2 w, 1107 w, 1025.2 w, 664.5 w.

X-ray Crystallographic Studies. X-ray-quality crystals for all compounds were grown as described above. The crystals were removed from the Schlenk tube under a stream of N$_2$ and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature N$_2$ stream of the diffractometer.[21] The intensity data sets for all compounds were collected using a Siemens SMART system, complete with 3-circle goniometer and CCD detector operating at −54 °C. Data for compounds **1**, **2**, and **4−6** were collected at 96, 89, 90, 95, and 92 K, respectively, using a custom-built low-temperature device from Professor H. Hope (UC Davis). In all cases graphite-monochromated Mo Kα radiation (=0.710 73 Å) was employed. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different angle, and each exposure covering 0.3° in ϕ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. In all cases, no decay was observed. An absorption correction was applied for all compounds

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by utilizing the program SADABS.[22] The crystal structures of all compounds were solved by Direct Methods as included in the SHELXTL-Plus program package.[23] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F (SHELX-93). Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C−C bonds for methyl groups with U(iso) constrained at 1.2 for nonmethyl groups and 1.5 for methyl groups times U(eq) of the carrier C atom. The crystallographic programs used for structure refinement and solution were installed on a Silicon Graphics Indigo2 R10000 Solid Impact or a PC clone. Scattering factors were those provided with the SHELX program system. All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Severe disorder was detected in compound **2**; the affected positions were refined using split positions.

Results and Discussion

Synthetic Aspects. The donor-free magnesium amide **1** was obtained in high yield and purity by alkane elimination chemistry in hexane (eq 3).

$$(Bu)_2Mg + 2HNDiip(SiMe_3) \xrightarrow[HEX]{reflux} Mg[NDiip(SiMe_3)]_2 + 2Bu(H) \quad (3)$$

If instead, the reaction is carried out in a mixture of hexane and tetrahydrofuran (1:1), the heteroleptic amide **2** is reproducibly isolated. Compound **2** can be obtained rationally if Bu_2Mg is treated with only 1 equiv of $HNDiip(SiMe_3)$ (eq 4).

$$(Bu)_2Mg + HNDiip(SiMe_3) \xrightarrow[HEX/THF]{reflux} BuMg[NDiip(SiMe_3)](THF)_2 + Bu(H) \quad (4)$$

Accordingly, alkane elimination does not allow for the direct preparation of $Mg[NDiip(SiMe_3)]_2THF_2$, **3**. This compound may be obtained by dissolving **1** in a hexane/tetrahydrofuran solution or by salt elimination (eqs 5 and 6), also utilized to prepare the heavier alkaline earth metal congeners **4**−**6**.

$$HNDiip(SiMe_3) + KH \xrightarrow[THF]{} KNDiip(SiMe_3) + H_2 \quad (5)$$

$$2KNDiip(SiMe_3) + MI_2 \xrightarrow[THF]{} M[NDiip(SiMe_3)]_2(THF)_2 + 2KI \quad (6)$$

$$M= Mg, Ca, Sr, Ba$$

An earlier report involving the reaction of $BaCl_2$ with 2 equiv of $NaN(SiMe_3)_2$ in diethyl ether describes the synthesis of barium amide by salt elimination.[16] The low solubility of $BaCl_2$ in etheral solvents results in heterogeneous reaction conditions, long reaction times, and low yields and product purity. If instead, alkaline earth metal iodides are treated with potassium amides in THF, homogeneous reaction conditions, the clean precipitation of potassium iodide, and excellent yields and product purity are observed. Direct metalation (eq 7) is a convenient route to the heaviest alkaline earth metal amides as shown previously with the preparation of $Ba(N(SiMe_3)_2)_2(donor)_n$.[18] The method requires the activation of the metals with dry, liquid ammonia. The metal with the highest reactivity, barium, reacts smoothly, while the less reactive strontium requires extended reflux in a NH_3(l)/THF solvent mixture. Calcium amides cannot be prepared by metalation due to lack of reactivity. Direct metalation also critically requires the presence of THF. If the metals are dissolved solely in liquid ammonia followed by treatment with amine, no reaction is observed.

$$2HNDiip(SiMe_3) + Ba \xrightarrow[NH_3/THF]{} Ba[NDiip(SiMe_3)]_2(THF)_2 + H_2 \quad (7)$$

All compounds were obtained in good yield and purity by metathesis reactions, either by alkane elimination as utilized for the preparation of compounds **1** and **2** or by salt elimination as used for compounds **3**−**6**. The donor-free **1** is only available if the alkane elimination is performed in hexane. In the presence of THF, the heteroleptic **2** is reproducibly isolated, even under reflux conditions. It is conceivable that THF coordination to the metal center results in steric shielding and, thus, kinetically protects the heteroleptic **2** from further reaction with amine.

Indications of why different products are obtained in the two solvent systems are obtained by comparing the literature procedures for the preparation of $[Mg(N(SiMe_3)_2]_2$.[14,24] The heteroleptic organomagnesium amide $[^sBuMgN(SiMe_3)_2]_2$ was obtained by treating $(^nBu/^sBu)_2Mg$ with 1 equiv of $HN(SiMe_3)_2$ in heptane.[24] The addition of a second 1 equiv of amine, followed by the removal of all volatiles, resulted in the clean formation of homoleptic magnesium amide. In contrast, Wannagat et al. reported on the synthesis of $Mg[N(SiMe_3)_2]_2(OEt_2)$ by alkane elimination from Et_2Mg and $HN(SiMe_3)_2$ in diethyl ether.[14] In our hands, predominantly heteroleptic organomagnesium amide was obtained, as evidenced by NMR studies. If however the reaction mixture is heated to reflux temperature, clean homoleptic amide is obtained in excellent yields and purity,[25] indicating that in the presence of ether a higher reaction temperature is required. It is conceivable that similar reaction tendencies are observed for the sterically more demanding $[NDiip(SiMe_3)]^-$ amide. Its increased steric bulk however renders higher reaction temperatures, as achieved in refluxing THF, not sufficient for complete alkane elimination.

Structural Aspects. Crystallographic data and data collection parameters for compounds **1**, **2**, and **4**−**6** are summarized in Table 2. A summary of selected geometrical parameters for compounds **1** and **4**−**6** is provided in Table 3, while Table 4 contains pertinent data for compound **2.**

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Table 2. Crystallographic Data for Compounds **1**, **2**, and **4**−**6**[a]

param	**1**	**2**	**4**	**5**	**6**
formula	$C_{30}H_{52}MgN_2Si_2Si_2$	$C_{27}H_{51}MgNO_2Si_2O_2SiO_2Si$	$C_{38}H_{68}CaN_2O_2Si_2$	$C_{38}H_{68}SrN_2O_2Si_2$	$C_{38}H_{68}BaN_2O_2Si_2$
fw	521.23	474.09	681.20	728.74	778.46
a (Å)	9.4687(6)	9.5413(1)	9.7074(1)	20.5874(5)	20.5476(2)
b (Å)	9.6818(6)	16.4930(2)	20.9466(4)	9.8785(2)	10.0353(2)
c (Å)	17.9296(1)	9.8218(1)	21.6242(3)	20.8522(5)	20.9020(4)
α (deg)	96.487(1)		73.573(1)		
β (deg)	94.537(1)	108.149(2)	78.632(1)	102.035(2)	101.67(1)
γ (deg)	98.222(1)		89.621(1)		
V (Å^3)	1608.77(2)	1468.7(4)	4129.13(1)	4147.56(2)	4220.97(1)
Z	2	2	4	4	4
space group	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P2/n$	$P2/n$
d_{calc} (g/cm^3)	1.076	1.072	1.096	1.167	1.225
linear abs coeff (mm^{-1})	0.149	0.123	0.242	1.389	1.029
T (K)	96	89	90	95	92
2*θ* range (deg)	2.3−56.5	4.4−50.0	2.0−56.7	2.5−56.7	2.5−56.6
indep reflcns	10 438	7993	19 229	35 420	25 994
no. of params	319	344	811	408	407
R1, wR2 (all data)	0.0508, 0.1417	0.1232, 0.2069	0.0902, 0.1376	0.0756, 0.1306	0.0573, 0.0725
R1, wR2 (>2*σ*)	0.0476, 0.1382	0.0828, 0.1891	0.0533, 0.1210	0.0509, 0.1245	0.0364, 0.0671

[a] Radiation: Mo Kα ($\lambda = 0.710\,73$ Å). $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^{2)}2]^{1/2}$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**, **4**−**6**, and Related Compounds[a]

compd	M−N	M−O	N−Si	N−C	N−M−N	O−M−O	ref
1	1.919(2)		1.712(2)	1.426(4)	180.00		b
$Mg[NR_2]_2$	1.966(6)		1.707(1)		162.8(3)		11
4	2.326(8)	2.356(8)	1.703(8)	1.412(1)	128.16(1)	87.94(1)	b
$Ca[NR'_2]_2THF_2$	2.301(6)	2.377(6)	1.686(1)		121.25(1)	81.43(1)	5
5	2.480(6)	2.511(4)	1.692(6)	1.402(8)	123.61(2)	82.99(2)	b
$Sr[NR'_2]_2THF_2$	2.458(1)	2.534(1)	1.674(2)		120.6(2)	84.7(2)	6
6	2.635(4)	2.693(3)	1.688(4)	1.394(6)	123.55(2)	78.56(2)	b
$Ba[NR'_2]_2THF_2$	2.592(1)	2.731(1)	1.682(1)		116.77(2)	91.4(2)	7

[a] R = $SiPh_2Me$; R′ = $SiMe_3$. [b] This work.

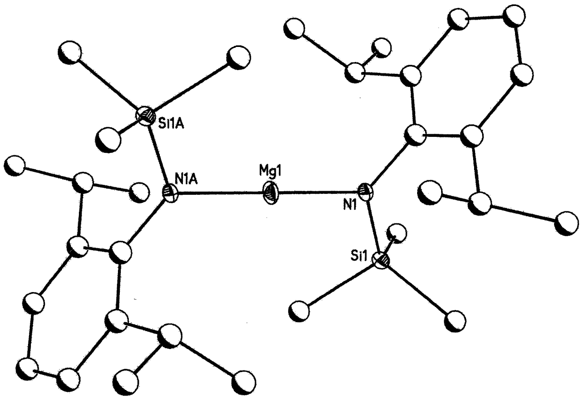

Figure 1. Computer-generated plot of **1** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms. The hydrogen atoms have been omitted for clarity.

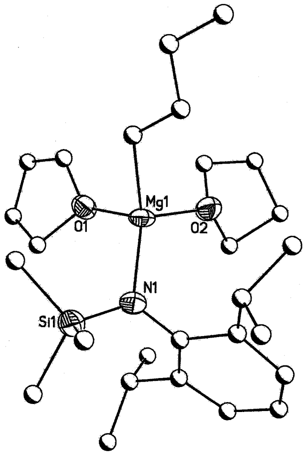

Figure 2. Computer-generated plot of **2** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms. The hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound **2**

Mg(1)−O(1)	2.058(4)	Mg(1)−C(16)	2.189(7)
Mg(1)−O(2)	2.029(5)	Si(1)−N(1)	1.704(5)
Mg(1)−N(1)	2.027(4)	C(1)−N(1)	1.371(7)
O(1)−Mg−O(2)	93.60(2)	Si(1)−N(1)−C(1)	118.10(3)
O(1)−Mg−N(1)	106.00(2)	O(2)−Mg−N(16)	108.30(3)
O(1)−Mg−C(16)	103.50(2)	Mg(1)−N(1)−C(1)	117.30(4)
O(2)−Mg−N(1)	111.80(3)	Mg(1)−N(1)−Si(1)	118.10(3)

$Mg[NDiip(SiMe_3)]_2$, 1. Compound **1**, depicted in Figure 1, crystallizes as a monomeric unit with a two-coordinate metal center. There are two independent molecules/asymmetric unit, of which only one is shown. The central magnesium atom is located on a center of symmetry inducing linear N−Mg−N geometry. The Mg−N distances are 1.919(2) Å, and nitrogen−silicon and nitrogen−carbon bond lengths are 1.712(2) and 1.426(4) Å. The shortest Mg−C distances are observed at 2.861(1) Å for C1 and C16. The C−N−Si angle in the ligand is 125.39(2)°.

$^nBuMg[NDiip(SiMe_3)](THF)_2$, 2. Compound **2 (Figure 2)** displays a four-coordinate metal center bound to one amido and one *n*-butyl group, in addition to two THF donors. The Mg−N and Mg−C distances are 2.027(4) and 2.189(7) Å, and Mg−O contacts are 2.058(4) and 2.029(5) Å. The N−Mg−C angle is observed at 127.70(3)°, and the N−Mg−O

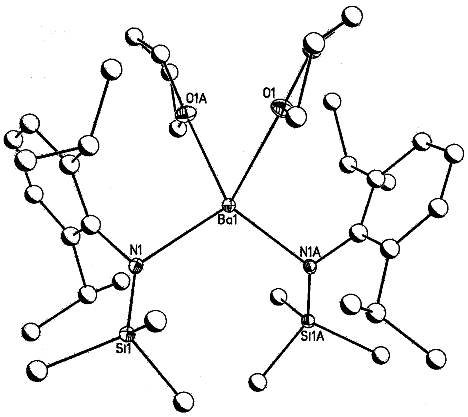

Figure 3. Computer-generated plot of **6** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms. The hydrogen atoms have been omitted for clarity.

angles are on average 108.90(2)°, while the O−Mg−O bond angle is 93.60(2)°.

M[NDiip(SiMe$_3$)]$_2$(THF)$_2$ (M = Ca (4), Sr (5), Ba (6)). Compounds **4**−**6** are isomorphous and will be described together. For all compounds two independent molecules are found in each asymmetric unit. Figure 3 represents one of the two independent molecules in compound **6**. The metal centers are located on a center of symmetry. Besides the two amido groups, two THF molecules are coordinated to the metal center, resulting in a series of monomeric four-coordinated compounds. The geometry around the metal centers is distorted tetrahedral. M−N distances are on average 2.326(8) Å for **4**, 2.480(6) Å for **5**, and 2.635(4) Å for **6**. M−O distances are observed at (average) 2.356(8) Å for **4**, 2.511(4) Å for **5**, and 2.693(3) Å for **6**. The N−M−N angles are observed at (average) 128.16(1)° for **4**, 123.61(2)° for **5**, and 123.55(2)° for **6**, while O−M−O angles are 87.94(1)° for **4**, 82.99(2)° for **5**, and 78.56(2)° for **6**.

Compound **1** displays a rare two-coordinate magnesium center. Other examples involving a similar magnesium coordination include Mg[C(SiMe$_3$)$_3$]$_2$[26] and Mg[N(SiMePh$_2$)$_2$]$_2$[10] in addition to the vapor phase structures of Mg[CH$_2$(^{t}Bu)]$_2$[27] and Mg[N(SiMe$_3$)$_2$]$_2$,[13] as determined by electron diffraction studies. A comparison of **1** with the closely related Mg[N(SiMePh$_2$)$_2$]$_2$[11] shows a distinctly different N−Mg−N angle, which is linear in **1** but bent with an angle of 162.8° in the latter. The bent was attributed to a dipolar interaction between the metal center and the aromatic rings in the ligand, with Mg−C contacts of 2.65 Å. Indeed, the shortest Mg−C distances in **1** are significantly longer (2.86 Å).

Magnesium nitrogen distances in **1** and Mg[N(SiPh$_2$Me)$_2$]$_2$[11] agree well (1.919 versus 1.963 Å), indicating a reduced degree of steric bulk for the [NDiip(SiMe$_3$)]$^-$ ligand. This trend is also observed in the lithium salts of the [N(SiPh$_2$Me)$_2$]$^-$ and [NDiip(SiMe$_3$)]$^-$ systems. A bis-THF adduct is observed for the more cumbersome ligand,[28] in contrast to a tris-THF adduct, namely Li(THF)$_3$NDiip(SiMe$_3$) for the sterically less demanding ligand.[29] The comparison of Mg−N bond lengths in **1** and electron diffraction data for Mg[N(SiMe$_3$)$_2$]$_2$ (1.911(3) Å)[13] indicate that the steric bulk for the [NDiip(SiMe$_3$)]$^-$ ligand lies between that of [N(SiPh$_2$Me)$_2$]$^-$ and [N(SiMe$_3$)$_2$]$^-$.

Compound **2** joins a small group of heteroleptic organomagnesium amides. All structurally characterized heteroleptic organomagnesium amides are oligomeric, as observed for the aforementioned [^{s}BuMgN(SiMe$_3$)$_2$]$_2$[24] and [^{t}BuMgNH(^{t}Bu)THF]$_2$[30] and the dodecamer [EtMgNHDiip]$_{12}$.[30] As such, no compounds are available for direct comparison with **2**. The Mg−N distance in **2** is, as expected, significantly shorter than in the other heteroleptic organomagnesium amides, due to the bridging nature of their Mg−N moiety. The Mg−N distances in **2** (2.027(4) Å) agree well with the four-coordinate Mg[N(SiMe$_3$)$_2$]$_2$(4-picoline)$_2$ (2.030(4) Å (average))[31] or Mg[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (2.02(1) Å (average)).[4] Magnesium carbon distances in **2** (2.187(7) Å) closely resemble those in the four-coordinate [^{t}BuMgN(H)^{t}Bu(THF)]$_2$ (2.194(4) Å).[30] The influence of coordination number on bond length is demonstrated by the significantly shorter M−C distance in the three-coordinate dimer [^{s}BuMgN(SiMe$_3$)$_2$]$_2$ (2.08(1) Å).[24]

The comparison of M−N distances in **3**−**6** nicely illuminates the effect of ligand bulk. Compared with the bis-THF adducts of the bis[bis(trimethylsilyl)]amides, compounds **3**−**6** display longer M−N bond lengths but shorter M−O contacts. As an example, the Ba−N bonds in **6** are 2.635(4) Å versus 2.592(1) Å for Ba[N(SiMe$_3$)$_2$]$_2$THF$_2$, indicating the increased steric demand of the aryl-substituted ligand. Table 3 compares pertinent bond lengths in the two groups of amido derivatives. Analogous trends as mentioned above for **6** are observed for the lighter congeners **4** and **5**.

Ligand bulk is also influencing the geometry about the metal center with a slight decrease in N−M−N angles upon descending the group of alkaline earth metals. The sterically demanding amido ligands are responsible for the widening of the N−M−N tetrahedral angle to 128.16(1)° in **4**, 123.61(2)° in **5**, and 123.55(2)° in **6**. Since the effective steric bulk of the ligand decreases upon descending the group due to bond elongation, the distortion from regular tetrahedral geometry becomes less severe. This trend is in agreement with calculations indicating that the degree of bending on the metal should increase for the heavier alkaline earth elements due to d-orbital involvement in the small covalent bonding contribution.[32] However, the insignificant decrease in N−M−N angle suggests that the change in geometry is mainly influenced by ligand bulk.

Interestingly, the increase in ionic radii of the alkaline earth metals does not result in an increase of the coordination

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number in the heavier alkaline earth metal amides, and bis-THF adducts are observed for all compounds (**3**−**6**). This result is in direct agreement with data for the $[N(SiMe_3)_2]^-$ ligand, where bis-THF derivatives are observed for all heavy alkaline earth metal derivatives.[4−7] In a similar fashion, no change in coordination number is detected in the absence of donor, and three-coordinate dimers are observed for all heavy metal derivatives.[7−10] The lack of change in metal environment in both in the $[N(SiMe_3)_2]^-$ and the $[NDiip(SiMe_3)]^-$ series indicates the limited influence of the metal center other than size (as demonstrated by comparing M−N distances and N−M−N angles), supporting the view that the geometry about the alkaline earth metals is mainly influenced by ligand characteristics. We are currently performing DFT calculations on a large selection of alkaline earth metal derivatives to shed further light onto the question of M−(p-block element) bonding characteristics.

Conclusion

The aryl-substituted silylamide ligand $[NDiip(SiMe_3]^-$ was used to prepare a family of novel alkaline earth metal amides. The ligands' increased steric demand as compared to the well-explored $[N(SiMe_3)_2]^-$ system allowed the preparation and structural characterization of a rare, two-coordinate monomeric magnesium amide. The heavier alkaline earth metal derivatives were isolated as four-coordinated bis-THF adducts, whose longer M−N and shorter M−O distances as compared to the $[N(SiMe_3)_2]^-$ amides indicate the increased steric demand of the aryl-substituted ligand. The large N−M−N angle is also an indication of the large steric demand of the ligand system. The large deviation form regular tetrahedral geometry is most prevalent for the calcium compound, whose shorter Ca−N distances increase the effective steric bulk of the ligand as compared to strontium or barium. This trend is in agreement with earlier calculations indicating an increased amount of bending (or narrower N−M−N angle) for the heavier alkaline earth metal derivatives. Owing to the small variation in the N−M−N angle in **4**−**6**, we conclude that the change in geometry is mainly due to steric reasoning.

We also gained insight into alkane elimination chemistry for the preparation of $Mg[NDiip(SiMe_3)]_2$ by investigating the solvent dependency of the reaction. Interestingly, homoleptic compounds can only be obtained if nondonating solvents are employed. Use of etheral solvents led to the reproducible isolation of a unique monomeric heteroleptic magnesium amide.

The target compounds are currently being investigated as potential starting materials for the synthesis of a variety of organometallic alkaline earth metal derivatives by transamination. Moreover, synthetic concepts learned in this study will be used toward the synthesis of silicon-free amides, which will be developed as volatile precursor materials for solid-state applications.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**, **2**, and **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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