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Synthesis and Structures of Monomeric Magnesium, Calcium, Strontium, and Barium Amides Involving the *N*,*N*-(2,4,6-Trimethylphenyl)(trimethylsilyl)amido Ligand

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An extended family of aryl-substituted alkaline earth metal silylamides M{N(2,4,6-$Me_3C_6H_2$)($SiMe_3$)}donor$_n$ was prepared using alkane elimination (Mg), salt elimination (Ca, Sr, Ba), and direct metalation (Sr, Ba). Three different donors, THF, TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine), and PMDTA (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) were employed to study their influence on the coordination chemistry of the target compounds, producing monomeric species with the composition M{N(2,4,6-$Me_3C_6H_2$)($SiMe_3$)}$_2$(THF)$_2$ (M = Mg, Ca, Sr, Ba), M{N(2,4,6-$Me_3C_6H_2$)($SiMe_3$)}$_2$TMEDA (M = Ca, Ba), and M{N(2,4,6-$Me_3C_6H_2$)($SiMe_3$)}$_2$PMDTA (M = Sr, Ba). For the heavier metal analogues, varying degrees of agostic interactions are completing the coordination sphere of the metals. Compounds were characterized using IR and NMR spectroscopy in addition to X-ray crystallography.

Introduction

The potential of heavy alkaline earth metal derivatives in synthetic,[1] polymer,[2] and solid-state applications[3] has intensified the search for suitable reagents and source materials. The large ionic radius of the heavier 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, hence preventing reduced solubility and volatility. The heavy alkaline earth metals are also highly reactive, and sterically demanding ligands have been used successfully to kinetically stabilize the metal centers and control reactivity. In this context, the sterically demanding $\{N(SiMe_3)_2\}^-$ ligand has been used extensively to yield stable soluble compounds with low metal coordination numbers,[4] including three-coordinate donor-free dimers in addition to donor-containing monomers.[4,5] In addition to making it possible to isolate compounds with low metal nuclearity and coordination numbers, amides based on the $\{N(SiMe_3)_2\}^-$ ligand exhibit excellent solubility in nonpolar solvents making the bis{bis(trimethylsilyl)}amides useful starting materials for the synthesis of a variety of alkaline earth metal derivatives.[6] This use is limited by their tendency toward N−Si bond cleavage induced either thermally or in the presence of acids with formation of a primary amine and

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silylated substrate.[7] In the presence of excess acid, a second protonation under the formation of NH_3 and a second equivalent of the silylated substrate may be observed. This undesired side reaction may be partially suppressed, but not completely circumvented, by the slow and dilute addition of the acid. Accordingly, the development of soluble alkaline earth metal amides with a reduced tendency toward N−Si bond cleavage to accommodate moderately acidic substrates in the transamination reaction is highly desired.

Bis{bis(trimethylsilyl)}amides have also been discussed as solid-state precursor materials.[8] However, the thermally induced N−Si bond cleavage increases the likelihood of silicon incorporation in the resulting solid-state material. Because these impurities are detrimental for the use of the materials in electronics applications, alternative source materials are needed. However, the preparation of non-silylated heavy alkaline earth metal amides has proven to be very difficult, and oxygen-free examples are limited to pyrazolates[6d,9] and intramolecular coordinating pyrrolates.[10] However, their high thermal sensitivity and reactivity prevent their use as alternative source materials because decomposition, upon heating, rather than intact transport into the gas phase is observed.

The replacement of one silyl group in the bis{bis(trimethylsilyl)}amides by an aromatic substituent produces materials with a significantly reduced tendency toward N−Si bond cleavage, as previously shown in this laboratory with the preparation of the alkaline earth metal amides $M\{N(2,6\text{-}^iPr_2C_6H_3)(SiMe_3)\}_2D_n$ (M = Mg, Ca, Sr, Ba; D = donor).[11] Their monomeric nature and good solubility in a wide array of solvents makes them attractive precursors in both synthetic and solid-state chemistry.

To further investigate the effect of the aryl substituent in the aryl silylamides, we here report on a family of mesityl-substituted (Mes = $2,4,6\text{-}Me_3C_6H_2$) trimethylsilylamides. The reduction of the steric demand for the aryl moiety from $2,6\text{-}^iPr_2C_6H_3$ (Diip) to $2,4,6\text{-}Me_3C_6H_2$ not only provides important information on the coordination chemistry of the alkaline earth metals but also makes potentially more volatile precursors and highly reactive reagents available for the transamination reactions.

The effect of various donors on the coordination chemistry of the target compounds was studied by introducing a variety of donors, including THF, the bidentate TMEDA (*N,N,N′,N′*-tetramethylethylenediamine), and the tridentate PMDTA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) to produce a series of monomeric alkaline earth metal amides, $Mg\{N(Mes)(SiMe_3)\}_2(THF)_2$ (**1**), $Ca\{N(Mes)(SiMe_3)\}_2(THF)_2$ (**2**), $Sr\{N(Mes)(SiMe_3)\}_2(THF)_2$ (**3**), $Ca\{N(Mes)(SiMe_3)\}_2(THF)_2$ (**4**), $Ca\{N(Mes)(SiMe_3)\}_2TMEDA$ (**5**), $Ba\{N(Mes)(SiMe_3)\}_2TMEDA$ (**6**), $Sr\{N(Mes)(SiMe_3)\}_2PMDTA$ (**7**), and $Ba\{N(Mes)(SiMe_3)\}_2PMDTA$ (**8**).

Experimental Details

General Procedures. All of the reactions were carried out under strict inert gas conditions using either a Braun Labmaster 100 drybox or modified Schlenk techniques. The solvents, including hexanes, toluene, and tetrahydrofuran (THF), were distilled from a Na/K alloy and degassed twice just prior to use. PMDTA and TMEDA were dried over CaH_2 and distilled under vacuum. H_2NMes, $ClSiMe_3$, dibutylmagnesium (statistical mix of *n* and *sec* butyl, 1 M solution in heptanes), and the alkaline earth metal iodides were obtained commercially. $HN(Mes)(SiMe_3)$ was synthesized using literature methods.[12] A 30% suspension of KH in mineral oil was washed with hexanes several times to remove the oil, and then the KH was dried in vacuo. Ammonia was dried over Na(s) and condensed into the cooled (−78 °C, dry ice/acetone) reaction mixture. IR spectra were collected as Nujol mulls between KBr plates on a Perkin-Elmer PE 1600-FI-IR spectrometer. ^1H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 spectrometer at 25 °C. Spectra were recorded in C_6D_6 and referenced to residual solvent peaks. Variable-temperature ^1H NMR spectra were collected on the same instrument using $CD_3C_6D_5$. Melting points are uncorrected. Reliable elemental analyses could not be obtained, even when glovebox handling was attempted, because of the high moisture and oxygen sensitivity of the compounds. This is a well-known problem in alkaline earth metal chemistry.[13]

$Mg\{N(Mes)(SiMe_3)\}_2(THF)_2$, 1 (alkane elimination). Undiluted Bu_2Mg (1 mL, 1 mmol) was added slowly via syringe to a solution of 0.415 g of $HN(Mes)(SiMe_3)$ (2 mmol) in 40 mL of hexanes. The initially clear colorless solution was stirred for at least 3 h to produce a slightly cloudy solution. The addition of 10 mL of THF to the solution under continued stirring yielded a colorless clear solution. The solution was then reduced in volume under vacuum until crystallites began to form. The crystallites were redissolved by gentle warming of the flask. After the solution was stored at −23 °C for 24 h, colorless crystals suitable for X-ray diffraction studies were obtained.

Yield: 81% yield (0.26 g, 0.82 mmol). mp: 168−174 °C. ^1H NMR (C_6D_6): δ 0.42 (s, 18H, $SiMe_3$), 1.00 (s, 8H, THF), 2.26 (s, 6H, *p*-CH_3Ar), 2.41 (s, 12H, *o*-CH_3Ar), 3.21 (s, 8H, THF), 6.90 (s, 4H, Ar−H). ^{13}C NMR (C_6D_6): δ 4.5 ($SiMe_3$), 20.9 (*p*-CH_3Ar), 21.7 (*o*-CH_3Ar), 24.6 (THF), 69.8 (THF), 125.0 (*p*-CH_3Ar), 129.1 (*m*-CH_3Ar), 135.0 (*o*-CH_3Ar), 153.6 (N−C). IR(cm^{-1}): ν 2916 s, 2723 m, 1459 s, 1377 s, 1298 m, 1210 w, 1153 w, 919 w, 823 w.

General Synthetic Procedure. Salt Elimination, $M\{N(Mes)(SiMe_3)\}_2donor_x$ (donor = THF, $x = 2$, M = Ca (2); donor = TMEDA, $x = 1$, M = Ca (5), Ba (6); donor = PMDTA, $x = 1$, M = Sr (7), Ba (8)). In a typical experiment, 0.08 g (2 mmol) of KH was dissolved in 20 mL of THF and stirred. In a separate Schlenk tube, 0.415 g (2 mmol) of $HN(Mes)(SiMe_3)$ was dissolved

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in 20 mL of THF, and then the mixture was slowly added to the KH suspension at 0 °C. The initially cloudy solution became clear over the course of an hour during which the evolution of hydrogen gas was observed. Alkaline earth metal iodide (1 mmol; Ca, Sr, Ba) was dissolved in 20 mL of THF, to which the potassium amide solution was slowly added via cannula at room temperature. The reaction proceeded immediately as evidenced by the formation of a white residue, presumably KI. After the mixture was stirred for 1 h, all of the volatiles were removed in a vacuum. The residue was then taken up in 40 mL of hexane. The resulting cloudy solution settled within 30 min at room temperature to produce a clear supernatant and a white solid at the bottom of the flask. The supernatant was filtered through a Celite padded filter frit yielding a clear pale yellow solution. For the TMEDA and PMDTA complexes, the donors were then added. The volumes of the individual solutions were then reduced until the formation of small crystallites was observed. The crystallites were redissolved by gentle warming of the solutions. The mother liquors were stored at −23 °C until the formation of X-ray quality crystals was observed.

Ca{N(Mes)(SiMe$_3$)}$_2$(THF)$_2$, 2. CaI_2 (0.294 g, 1 mmol) was used. Colorless platelike crystals formed overnight. Yield: 75% (0.25 g, 0.75 mmol). mp: 136−140 °C. ^{1}H NMR (C_6D_6): δ 0.41(s, 18H, SiMe$_3$), 1.10 (s, 8H, THF), 2.25 (s, 6H, *p*-CH$_3$Ar), 2.39 (s, 12H, *o*-CH$_3$Ar), 3.10 (s, 8H, THF), 6.91 (s, 4H, Ar−H). ^{13}C NMR (C_6D_6): δ 4.1 (SiMe$_3$), 20.9 (*p*-CH$_3$Ar), 21.2 (*o*-CH$_3$Ar), 25.0 (THF), 69.07 (THF), 125.0 (*p*-CH$_3$Ar), 129.2 (*m*-CH$_3$Ar), 133.1 (*o*-CH$_3$Ar), 153.7 (N−C). IR(cm^{-1}): ν 2912 s, 2725 s, 1723 w, 1659 w, 1260 w, 1017 w, 963 w.

M{N(Mes)(SiMe$_3$)}$_2$TMEDA, (M = Ca (5), Ba (6)). CaI_2 (0.294 g, 1 mmol, **5**) or BaI_2 (0.391 g, 1 mmol, **6**) and TMEDA (0.19 mL, 1 mmol) were used. After the addition of TMEDA, the solutions were shaken to mix. They immediately turned cloudy, and tiny crystallites began to form on the walls of the flasks. The crystallites redissolved, upon gentle warming, and the clear dark yellow solutions were placed in the −23 °C freezer. After a few days, rod-shaped crystals suitable for crystallographic studies were observed.

Ca{N(Mes)(SiMe$_3$)}$_2$TMEDA, 5. Yield: 70% (0.21 g, 0.70 mmol.). mp: 130 °C (dec). ^{1}H NMR (C_6D_6): δ 0.38 (s, 18H, SiMe$_3$), 1.43 (s, 4H, −CH$_2$, TMEDA), 1.52 (s, 12H, −CH$_3$,TMEDA), 2.27 (s, 6H, *p*-CH$_3$Ar), 2.45 (s, 12H, *o*-CH$_3$Ar), 6.93 (s, 4H, Ar−H). ^{13}C NMR (C_6D_6): δ 4.5 (SiMe$_3$), 20.9 (*p*-CH$_3$Ar), 22.1 (*o*-CH$_3$Ar), 46.0 (CH$_3$, TMEDA), 56.7 (−CH$_2$, TMEDA), 125.9 (*p*-CH$_3$Ar), 129.7 (*m*-CH$_3$Ar), 132.8 (*o*-CH$_3$Ar), 153.6 (N−C). IR(cm^{-1}): ν 2912 s, 2725 s, 1710 s, 1723 w, 1659 w, 1260 w, 1017 w, 963 w, 722 w.

Ba{N(Mes)(SiMe$_3$)}$_2$TMEDA, 6. Yield: 80% (0.32 g, 0.80 mmol.). mp: 165 °C . ^{1}H NMR (C_6D_6): δ 0.44 (s, 18H, SiMe$_3$), 1.43 (s, 4H, −CH$_2$, TMEDA), 1.46 (s, 12H, −CH$_3$,TMEDA), 2.21 (s, 6H, *p*-CH$_3$Ar), 2.35 (s, 12H, *o*-CH$_3$Ar), 6.90 (s, 4H, Ar−H). ^{13}C NMR (C_6D_6): δ 4.9 (SiMe$_3$), 20.8 (*p*-CH$_3$Ar), 22.2 (*o*-CH$_3$Ar), 44.5 (CH$_3$, TMEDA), 56.4 (−CH$_2$, TMEDA), 124.7 (*p*-CH$_3$Ar), 130.3 (*m*-CH$_3$Ar), 132.3 (*o*-CH$_3$Ar), 152.8 (N−C). IR(cm^{-1}): ν 2912 s, 2725 s, 1723 w, 1659 w, 1260 w, 1017 w, 963 w.

M{N(Mes)(SiMe$_3$)}$_2$PMDTA, (M = Sr, 7; Ba, 8). SrI_2 (0.341 g, 1 mmol, **7**) or BaI_2 (0.391 g, 1 mmol, **8**) and PMDTA (0.263 mL, 1.25 mmol) were used. After a few days, slightly tan rod-shaped crystals were observed.

Sr{N(Mes)(SiMe$_3$)}$_2$PMDTA, 7. Yield: 85% (0.35 g, 0.85 mmol.). mp: 125 °C. ^{1}H NMR (C_6D_6, 298 K): δ 0.42 (s, 18H, SiMe$_3$), 1.49 (s, 3H, −CH$_3$, PMDTA), 1.71 (s, 8H, −CH$_2$, PMDTA), 1.74 (s, 12H, −CH$_3$, PMDTA), 2.32 (s,6H, *p*-CH$_3$Ar), 2.47 (s, 12H, *o*-CH$_3$Ar), 6.97 (s, 4H, Ar−H). ^{13}C NMR (C_6D_6): δ 4.8 (SiMe$_3$), 21.0 (*p*-CH$_3$Ar), 22.5 (*o*-CH$_3$Ar), 45.8 (−CH$_3$, PMDTA), 56.7 (−CH$_2$, PMDTA), 57.7 (−CH$_3$, PMDTA), 125.0 (*p*-CH$_3$Ar), 129.5 (*m*-CH$_3$Ar), 133.1 (*o*-CH$_3$Ar), 155.5 (N−C). IR(cm^{-1}): ν 2912 s, 2725 s, 1723 w, 1659 w, 1260 w, 1017 w, 963 w.

Variable-Temperature ^{1}H NMR Study of 7 in $CD_3C_6D_5$. A diagram is available in the Supporting Information. ^{1}H NMR (353 K): δ 0.51 (s, 18H, SiMe$_3$), 2.05 (s, 23H, −CH$_3$, PMDTA; 8H, −CH$_2$, PMDTA; 12H, −CH$_3$, PMDTA), 2.43(s, 6H, *p*-CH$_3$Ar), 2.62 (s, 12H, *o*-CH$_3$Ar), 7.07 (s, 4H, Ar−H). ^{1}H NMR (298 K): δ 0.58 (s, 18H, SiMe$_3$), 1.40 (s, 4H, −CH$_2$, PMDTA), 1.71 (s, 4H, −CH$_2$, PMDTA), 1.96 (s, 15H, −CH$_3$, PMDTA), 2.52(s, 6H, *p*-CH$_3$Ar), 2.63 (s, 12H, *o*-CH$_3$Ar), 7.10 (s, 4H, Ar−H). ^{1}H NMR (273 K): 0.59 (s, 18H, SiMe$_3$), 1.31, 1.39 (d, 4H, −CH$_2$, PMDTA), 1.64, 1.65 (d, 4H, −CH$_2$, PMDTA), 1.91 (s, 15H, −CH$_3$, PMDTA), 2.50 (s, 6H, *p*-CH$_3$Ar), 2.59, 2.70 (d, 12H, *o*-CH$_3$Ar), 7.13 (s, 4H, Ar−H). ^{1}H NMR (248 K): δ 0.60 (s, 12H, SiMe$_3$), 0.64 (s, 6H, SiMe$_3$), 1.17, 1.22, 1.27, 1.31 (q, 4H, −CH$_2$, PMDTA), 1.62, 1.63 (d, 4H, −CH$_2$, PMDTA), 1.86 (15H, −CH$_3$, PMDTA), 2.59 (s, 6H, *p*-CH$_3$Ar), 2.67 (s, 6H, *o*-CH$_3$Ar), 2.73 (s, 6H, *o*-CH$_3$Ar), 7.14, 7.15 (d, 4H, Ar−H).

Ba{N(Mes)(SiMe$_3$)}$_2$PMDTA, 8. Yield: 80% (0.37 g, 0.80 mmol.) mp: 140 °C. ^{1}H NMR (C_6D_6): δ 0.44 (s, 18H, SiMe$_3$), 1.28 (s, 3H, −CH$_3$, PMDTA), 1.68 (s, 8H, −CH$_2$, PMDTA), 1.71 (s, 12H, −CH$_3$, PMDTA), 2.29 (s, 6H, *p*-CH$_3$Ar), 2.44 (s, 12H, *o*-CH$_3$Ar), 6.98 (s, 4H, Ar−H). ^{13}C NMR (C_6D_6): δ 5.0 (SiMe$_3$), 20.9 (*p*-CH$_3$Ar), 22.0 (*o*-CH$_3$Ar), 44.6 (−CH$_3$, PMDTA), 56.6 (−CH$_2$, PMDTA), 57.1 (−CH$_3$, PMDTA), 124.5 (*p*-CH$_3$Ar), 129.8 (*m*-CH$_3$Ar), 132.9 (*o*-CH$_3$Ar), 155.0 (N−C). IR(cm^{-1}): ν 2912 s, 2725 s, 1723 w, 1659 w, 1260 w, 1017 w, 963w.

General Method. Direct Metalation, M{N(Mes)(SiMe$_3$)}$_2$(THF)$_2$ (M = Sr (3), M = Ba (4)). In a typical experiment, 20 mL of THF was added to 1 mmol of Sr or Ba metal. In a separate flask, 0.415 g (2 mmol) of HN(Mes)(SiMe$_3$) was dissolved in 20 mL of THF. This amine solution was added to the metal. The resulting mixture was then cooled to −78 °C (acetone/CO$_2$(s)) followed by the condensation of anhydrous ammonia, upon which the mixture turned dark blue. The solution was stirred overnight at −78 °C and then gradually allowed to warm to room temperature, upon which the ammonia slowly evaporated and all of the the metal reacted. All of the volatiles were removed in a vacuum, and 40 mL of hexane was added to the residue. The resulting pale yellow solutions were filtered and stored at −23 °C. Crystallization of the product did not occur, even after storage at −23 °C, but solid reaction products were obtained upon removal of the mother liquor in a vacuum.

Sr{N(Mes)(SiMe$_3$)}$_2$(THF)$_2$, 3. After the residue was washed with hexane, the composition and purity of the compound were confirmed by ^{1}H NMR spectroscopy. Yield: 40% (0.26 g, 0.40 mmol). mp: 210 °C (dec). ^{1}H NMR (C_6D_6): δ 0.09 (s, 18H, SiMe$_3$), 1.40 (s, 8H, THF), 1.85 (s, 6H, *p*-CH$_3$Ar), 1.91 (s, 12H, *o*-CH$_3$Ar), 3.56 (s, 8H, THF), 6.73 (s, 4H, Ar−H).

Ba{N(Mes)(SiMe$_3$)}$_2$(THF)$_2$, 4. After the residue was washed with hexane, the composition and purity of the compound were confirmed by ^{1}H NMR spectroscopy. Yield: 45% (0.31 g, 0.45 mmol). mp: 164 °C (dec). ^{1}H NMR (C_6D_6): δ 0.09 (s, 18H, SiMe$_3$), 1.40 (s, 8H, THF), 2.14 (s, 6H, *p*-CH$_3$Ar), 2.18 (s, 12H, *o*-CH$_3$Ar), 3.56 (s, 8H, THF), 6.83 (s, 4H, Ar−H).

Single-Crystal X-ray Diffraction Studies. X-ray quality crystals for compounds **1**, **2**, and **5**−**8** 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 (Infineum). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[14] The intensity data sets for all compounds were collected using the Bruker SMART system, complete with a 3-circle goniometer and an APEX-CCD detector. Data for compounds **1**, **2**, and **5**−**8** were collected at 95, 96, 93, 94, 90, and 84 K, respectively, using a custom built low-temperature device from Professor H. Hope (UC Davis). Further data collection, structure solution, and refinement details have been reported previously.[15] Disorder was detected in compounds **5** and **7**; the affected positions were refined using split positions with 50/50 occupancies. Affected groups included the TMEDA donor in compound **5**, and one CH_3 group on a $SiMe_3$ moiety. In addition, the PMDTA donor was affected in compound **7**.

A CSD search was carried out using CONQUEST with restrained contact distances between a 2 Å metal and the $H(CH_2X)$ moiety of 2−3.5 Å to compare the agostic interactions observed in compounds **2**, and **5**−**8**. Because of the difficulty of locating and calculating hydrogen bond distances in the usual search mode, we carried out an advanced search using normalized hydrogen atom positions.[16]

Results and Discussion

Synthetic Chemistry. Three different synthetic methods were employed to prepare the target compounds: alkane elimination to synthesize the magnesium derivative **1** (eq 1), direct metalation to produce compounds **3** and **4** (eq 2), and salt elimination to prepare compounds **1**, **2**, and **5**−**8** (eqs 3 and 4).

Alkane elimination has been used extensively to prepare a host of magnesium derivatives.[11,17] This route is attractive because of the commercial availability of Bu_2Mg, its good solubility in various solvents, the simple reaction conditions, and the easy workup.

$$Bu_2Mg + 2HN(Mes)(SiMe_3) \xrightarrow[THF]{hexane} Mg\{N(Mes)(SiMe_3)\}_2(THF)_2 + 2BuH \quad (1)$$

The metalation of Bu_2Mg with sterically demanding silylamides is solvent dependent with a smooth reaction in hexane but only incomplete elimination in a donor solvent such as THF. The solvent dependency might be explained by the prevention of the metal−ligand coordination necessary to ensure a smooth reaction caused by the weak basicity of the silylamines and the preferred coordination of the stronger base THF. Because the initial step is thought to be the amine coordination to the metal, the relative base strengths of the ligand and solvent play a major role. Competition between ligation and solvation also affects the second elimination step. Here, a bulky silylamide has already congested the metal center, further reducing the probability for the coordination of the second amine to the metal center. In this context, the isolation of the heteroleptic butylmagnesium amides, $^nBuMg\{N(2,6\text{-}^iPr_2C_6H_3)(SiMe_3)\}(THF)_2$,[11] and $[^sBuMg\{HN(2,4,6\text{-}^tBu_3C_6H_2\}]_2$,[18] even in the presence of two equivalents of amine can be understood. Consequently, homoleptic silylamides are preferentially obtained in hydrocarbon solvents. THF adducts of the bis(silyl)amides may be obtained by the addition of THF to the homoleptic amides.

While alkane elimination is a powerful and simple method for the preparation of magnesium derivatives, the lack of suitable calcium, strontium, and barium organometallics has severely limited the extension of this route toward the heavier alkaline earth metals. Accordingly, the heavier alkaline earth metal amides **3** and **4** were prepared by direct metalation, and compounds **5**−**8** were synthesized through salt elimination. The magnesium derivative **1** was also prepared to demonstrate the general application of salt elimination.

Direct metalation (eq 2), involving the treatment of alkaline earth metals dissolved in ammonia with 2 equiv of amine is utilized extensively to prepare barium bis{bis(trimethylsilyl)}amide.[19] While ammonia solvation is an effective method to activate the heavy alkaline earth metals, highly reactive metals can also be obtained by other methods such as the reduction of metal iodides with potassium,[20] lithium naphthalenide,[1] or the distillation of the metals, as routinely performed by Westerhausen et al.[4] However, the ammonia method is very easy requiring neither additional purification steps, such as the removal of KI or naphthalene, nor any special setup. Moreover, ammonia evaporates readily upon warming the reaction mixture, which allows a facile workup. Additional advantages include easily accessible, inexpensive starting materials, and the potential for scale-up.

Because the reactivity of the alkaline earth metals increases as the group descends, this method performs best for the barium analogues, whereas only modest yields are observed for the strontium derivatives. The method is not applicable for the lighter congeners.

$$M(s) + 2HN(Mes)(SiMe_3) \xrightarrow{THF/NH_3(l)} M\{N(Mes)(SiMe_3)\}_2(THF)_2 + H_2 \quad (2)$$

In the present work, direct metalation did not proceed smoothly, and significant amounts of unreacted ligand remained, even after extended reaction times. These results agree with previous experiments focused on the preparation of the related $M\{N(Diip)(SiMe_3)\}_2donor_n$ amides, where only modest yields were observed.[11] Because it is the synthetic route of choice to prepare $Ba\{N(SiMe_3)_2\}_2(THF)_2$ in our laboratory, it is surprising that the replacement of a silyl group by an aromatic substituent renders the direct metalation route more problematic. A possible explanation for the sluggish reactions may be the increased steric demand of the ligand system. That said, direct metalation does produce

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pure compounds in modest yields (40−45%) after the initial products are washed with hexanes to remove the unreacted amine. This additional purification step might be worthwhile, when the simple inexpensive starting materials and quick easy workup are considered.

Salt elimination (eqs 3 and 4) was mentioned initially for the preparation of $Ba\{N(SiMe_3)_2\}_2(THF)_2$ by reacting $BaCl_2$ with 2 equiv of $NaN(SiMe_3)_2$ in low yields.[21] Instead, the use of the alkaline earth metal iodides with potassium amides, as used to prepare compounds **1**, **2**, and **5**−**8**, produces the target compounds with much improved yields and shorter reaction times. The combination of alkaline earth metal iodides and potassium amide has several advantages: the alkaline earth metal iodides are soluble in THF, allowing homogeneous reaction conditions, and KI typically precipitates cleanly from THF, preventing the formation of adducts and driving the equilibrium toward the products.

$$\mathrm{HN(Mes)(SiMe_3)} + \mathrm{KH} \xrightarrow[\substack{45\ \mathrm{min} \\ 0\ ^\circ\mathrm{C}}]{\mathrm{THF}} \mathrm{KN(Mes)(SiMe_3)} + \mathrm{H_2} \quad (3)$$

$$2\mathrm{KN(Mes)(SiMe_3)} + \mathrm{MI_2} \xrightarrow[\mathrm{(M = Ca,\ Sr,\ Ba)}]{\mathrm{THF/hexane}} \mathrm{M\{N(Mes)(SiMe_3)\}_2(THF)_2} + 2\mathrm{KI} \quad (4)$$

Donors were introduced to prepare compounds **5**−**9** by treating the amide-THF-based stock solutions with approximately equimolar amounts of TMEDA and PMDTA. In all cases, THF was cleanly replaced by the bidentate and tridentate donors, as expected because of the chelate effect. Donor exchange reactions have been used previously to prepare a selection of magnesium bis{bis(trimethylsilyl)}-amides, replacing THF by a selection of more basic nitrogen donors.[8]

Spectroscopic Studies. Compounds **1**, **2**, and **5**−**8** were characterized using ^1H, ^{13}C NMR, and IR spectroscopy, while the stoichiometry of compounds **3** and **4** was confirmed by ^1H NMR spectroscopy. Pertinent data are listed in the Experimental Details. Correct integration in the ^1H NMR spectrum for all compounds confirmed the purity of the bulk samples and the stoichiometry indicated by the crystallographic analysis.

Compared to the free ligand, the deprotonated amide signals are shifted significantly, allowing a clear distinction between the neutral and anionic ligands. The chemical shift for the $SiMe_3$ group on the neutral ligand at 0.09 shifts to 0.38−0.44 ppm for the anionic ligand. Similar trends are observed for the *p*-methyl groups with a shift from 2.17 to 2.21−2.29 ppm, the *o*-methyl groups with a shift from 2.23 to 2.35−2.47 ppm, and the *m*-hydrogen atoms on the aromatic ligand with a shift from 6.81 to 6.90−6.98 ppm. These values are similar to those for the divalent amides $E\{N(Mes)(SiMe_3)\}_2$ (E = Ge,[22] Sn[23]) and the boron amides $(X)RBN(Mes)(SiMe_3)$ (X = Cl, R = ^{t}Bu)[24] and $C_6H_5FN(H)C(CH_3)_3N((Mes)(SiMe_3))$.[25]

The crystallographic characterization of compounds **2** and **5**−**8** (see below) indicated varying degrees of agostic interactions, as listed in Table 1. Compound **7** was examined by variable-temperature (VT) ^1H NMR spectroscopy to determine if these interactions are maintained in solution. A graphical representation of this experiment can be found in the Supporting Information, while individual values are listed in the Experimental Details. The crystallographic analysis of **7** (Figure 3) showed four agostic interactions involving each of the two trimethylsilyl groups in addition to two contacts to one *o*-methyl group ranging in length from 2.90 to 3.19 Å (H11A, 2.90 Å; H7B, 2.95 Å; H11B 3.12 Å; and H22C, 3.19 Å). VT ^1H NMR spectra were recorded in the temperature range of 248 to 353 K using $C_6D_5CD_3$ as the solvent. The spectrum at 353 K exhibits only one signal for the *o*-methyl groups of the ligand. This signal begins to broaden at 298 K and splits into two broad but distinct peaks of equal intensity (6H each, 2.59 and 2.70 ppm) at 273 K. Further cooling to 248 K results in sharper signals, but no further splitting is observed. As expected, the *p*-methyl signal does not split and remains a singlet at 2.51 ppm with correct integration (6H). Each trimethylsilyl group is involved in one agostic interaction, and the singlet at 0.51 ppm broadens, upon cooling to 298 K, and splits at 248 K into two peaks with a ratio of 12H/6H with signals at 0.60 and 0.64 ppm. Further cooling to 223 K results in sharper signals, but no further splitting is observed. The PMDTA resonances at 353 K are combined into one broad signal at 2.05 ppm. The peaks begin to split into three distinct signals, upon cooling of the sample to 298 K. Further cooling to 248 K results in the signals becoming better defined with the signals for all methyl groups at 1.95 ppm (15H, CH_3), the methylene signals neighboring the central nitrogen atom at 1.76 ppm (4H, CH_2), and the methylene signals near the outer nitrogen donors at 1.37 ppm (4H, CH_2). The split of the average PMDTA signal into three distinct peaks is independent from the fluctuational behavior of **7** and is observed upon the cooling of a pure sample of PMDTA.[26] Hence, VT ^1H NMR data are consistent with the agostic interaction seen in the solid-state structure of **7**.

Further analysis of the splitting pattern of the *o*-methyl and the trimethylsilyl groups, which split into distinct signals at 273 and 248 K, respectively, by linear extrapolation of $\Delta\nu$ (chemical shift difference in Hz between the split signals at T_c)[27a,b,c] and the insertion of the values into the Gutowsky−

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Table 1. Averaged Bond Lengths and Bond Angles of $\mathrm{M\{N(Mes)(SiMe_3)\}_2(THF)_2}$ (M = Alkaline Earth Metal) and Related Compounds

compound[b]	CN	M−N (Å) (av)	M−D (Å) (av)	N−Si (Å) (av)	N−C (Å) (av)	N−M−N (deg)	D−M−D (deg)	M···H (Å) agostic interactions	ref
$\mathrm{Mg(NR_2)_2}$	2	1.966(6)[d]	NA	1.707(1)	NA	162.8(3)	NA	NA	17c
$\mathrm{\{Mg(NR'_2)_2\}_2}$	3	2.145(9)[c]	NA	1.77(1)	NA	95.8(4)[i]	NA	NA	5d
		1.98(1)[d]		1.712(8)		84.2(2)[j]			
$\mathrm{Mg(NR'_2)_2(THF)_2}$	4	2.021(5)[d]	2.094(5)	1.706(5)	NA	127.9(2)	89.8(2)	NA[h]	29
$\mathrm{Mg(NR''')_2(THF)_2}$, **1**	4	2.023(1)[d]	2.055(1)	1.711(1)	1.430(2)	134.35(6)	103.25(5)	NA	*a*
$\mathrm{\{Ca(NR'_2)_2\}_2}$	3+4	2.48(2)[c]	NA	1.733(7)	NA	89.2(4)[i]	NA	2.339−2.829[g]	5a
	3+5	2.28(1)[d]		1.697(8)		90.7(4)[j]			
$\mathrm{Ca(NR'_2)_2(THF)_2}$	4+3	2.301(6)[d]	2.377(6)	1.686(1)	NA	121.25(1)	81.43(1)	2.792−2.866[f,g]	30
$\mathrm{Ca(NR'_2)_2(py)_2}$	4+4	2.321(1)[d]	2.539(1)	1.692(1)	NA	119.63(2)	87.08(1)	2.805−2.826	18
$\mathrm{Ca(NR'_2)_2TMEDA}$	4+4	2.328(1)[d]	2.598(1)	1.697(1)	NA	122.14(4)	71.03(4)	2.892−2.987	18
$\mathrm{Ca(NR'')_2(THF)_2}$	4	2.326(8)[d]	2.356(8)	1.703(8)	1.412(1)	128.16(1)	87.94(1)	NA	11
$\mathrm{Ca(NR''')_2(THF)_2}$, **2**	4+1	2.304(6)[d]	2.343(4)	1.692(6)	1.410(8)	137.55(1)	96.34(8)	H21A 2.89	*
$\mathrm{Ca(NR''')_2TMEDA}$, **5**	4+2	2.311(2)[d]	2.529(2)	1.695(2)	1.406(3)	126.43(9)	72.15(6)[e]	H9B 2.77	*
$\mathrm{\{Sr(NR'_2)_2\}_2}$	3+7	2.638(4)[c]	NA	1.701(4)	NA	83.90(8)[i]	NA	2.454−3.183[g]	5b
		2.435(2)[d]		1.697(4)		96.0(8)[j]			
$\mathrm{Sr(NR'_2)_2(THF)_2}$	4+6	2.458(1)[d]	2.534(1)	1.674(2)	NA	120.6(2)	84.7(2)	2.861−3.144[f,g]	30
$\mathrm{Sr(NR'')_2(THF)_2}$	4+2	2.480(6)[d]	2.511(4)	1.692(6)	1.402(8)	123.61(2)	82.99(2)	2.933−3.178[f]	11
$\mathrm{Sr(NR''')_2PMDTA}$, **7**	5+4	2.501(4)[d]	2.857(6)	1.690(4)	1.410(6)	113.57(7)	110.63(6)	H7B 2.95 H11A 2.90 H11B 3.12 H22C 3.19	*a*
$\mathrm{\{Ba\ (NR'_2)_2\}_2}$	3+8	2.822(7)[c]	NA	1.703(7)	NA	81.9(1)[i]	NA	2.320−3.226[g]	5c
	3+7	2.576(3)[d]		1.688(7)		98.1(1)[j]			
$\mathrm{Ba\ (NR')_2THF_2}$	4+8	2.592(1)[d]	2.731(1)	1.682(1)	NA	116.77(2)	91.4(2)	3.056−3.197[g]	5c
$\mathrm{Ba(NR'')_2THF_2}$	4+2	2.635(4)[d]	2.693(3)	1.688(4)	1.394(6)	123.55(2)	78.56(2)	H42 2.987[f] H5 3.188[f]	11
$\mathrm{Ba(NR''')_2TMEDA}$, **6**	4+2	2.628(2)[d]	2.858(2)	1.678(2)	1.384(3)	123.98(8)	62.62(8)	H7C 2.78	*a*
$\mathrm{Ba(NR''')_2PMDTA}$, **8**	5+5	2.67(1)[d]	2.95(2)	1.69(1)	1.40(2)	118.33(2)	112.44(2)	H7C 3.00 H21B 2.84 H31B 3.23 H31C 3.10 H32A 3.11	*a*

[a] This work. [b] D = Donor; R = $\mathrm{SiPh_2Me}$; R′ = $\mathrm{SiMe_3}$; R″ = $\mathrm{(2,6\text{-}^{\mathit{i}}Pr_2C_6H_3)SiMe_3}$; R‴ = $\mathrm{(2,4,6\text{-}Me_3C_6H_2)SiMe_3}$; N = $\mathrm{N_{ligand}}$. [c] Bridging. [d] Terminal. [e] Average. [f] CSD(CONQUEST) search with restrained contact distances between a 2A metal to $\mathrm{H(CH_2X)}$ moiety of 2−3.5 Å. [g] On the basis of the .res file from CCDC, hydrogens were added in order to see the environment of the metal center. [h] No .res file available from CCDC. [i] $\mathrm{N_{bridging}{-}M{-}N_{bridging}}$. [j] $\mathrm{M{-}N_{bridging}{-}M}$.

Holm[27d,e] and Eyring[27f] equations allowed the calculation of the hindered rotation of the affected groups as caused by the agostic interactions. The values were found to be ΔG^* = 14.60 and 13.64 kcal mol^{-1} for the *o*-methyl and the trimethylsilyl groups, respectively. These values are in the same range as the restricted rotation caused by a weak CH···Li agostic interaction in $\mathrm{(^{\mathit{t}}Bu_2MeSi)_3SiLi}$ which was calculated to be 11.1(0.3) kcal mol^{-1}.[28]

Structural Aspects. Compounds **1**, **2**, and **5**−**8** were characterized using single-crystal X-ray crystallography. Table 1 summarizes the geometrical parameters of the compounds in addition to those from some closely related species, while Table 2 summarizes pertinent details in regard to the crystal data, data collection, and structure refinement. Illustrations of compounds **1**, **6**, **7**, and **8** are shown in Figures 1−4, while compound **2** is represented in the synopsis illustration. Compounds **1** and **2** are isostructural, as are **5** and **6**, and will therefore be described together.

$\mathbf{M\{N(2,4,6\text{-}Me_3C_6H_2)(SiMe_3)\}_2(THF)_2}$ (M = Mg (1, Figure 1), Ca (2)). Each asymmetric unit contains one molecule without crystallographically imposed symmetry. Compound **1** displays a four-coordinate metal center with severely distorted tetrahedral geometry. Compound **2** exhibits a five-coordinate (4 + 1) metal center involving two THF and amide contacts in addition to one agostic interaction (2.89 Å) from H21A connected to one of the trimethylsilyl groups. Average M−N and M−O bond lengths are 2.023(2) and 2.055(2) Å for **1** and 2.304(6) and 2.343(4) Å for **2**, respectively. The N−M−N angle is 134.35(6)° for **1** and 137.55(1)° for **2**, while the O−M−O angles are 95.91(5)° and 96.34(8)° for **1** and **2**, respectively, illustrating the bulk of the amido ligand. The coordination environment in **2** may be described as severely distorted trigonal bipyramidal with O1 and H21A atoms in axial positions (O1−Ca−H21A 159.78°). The sterically demanding amide ligands and the second THF molecule are located in the equatorial plane with a N(ligand)−Ca−N(ligand) angle of 137.55(1)°. Accordingly, the ligand−metal−donor angles are narrow, 100.62(9)° and 108.16(9)°. The angles between the equatorial plane and the axial ligands involving the axial THF donor are above 90°. They are below 90° on the side of the hydrogen atom.

$\mathbf{M\{N(2,4,6\text{-}Me_3C_6H_2)(SiMe_3)\}_2TMEDA}$ (M = Ca (5), Ba (6, Figure 2)). Both molecules possess a center of symmetry; therefore, only one-half of the molecules are present in each asymmetric unit. In both compounds two amido ligands and one TMEDA donor are connected to the metal center. The coordination environment at each metal center is completed by two agostic interactions, 2.77 (H9B) for **5** and 2.78 (H7C) for **6**, resulting in a coordination number of 4 + 2. The M−N(ligand) bond lengths are 2.311-

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Table 2. Crystallographic Data for Compounds **1**, **2**, and **5**−**8**[a]

	1	**2**	**5**	**6**	**7**	**8**
formula	$MgN_2O_2Si_2C_{32}H_{56}$	$CaN_2O_2Si_2C_{32}H_{56}$	$CaN_4Si_2C_{30}H_{56}$	$BaN_4Si_2C_{30}H_{56}$	$SrN_5Si_2C_{33}H_{63}$	$BaN_5Si_2C_{33}H_{63}$
fw	581.28	597.05	569.05	666.31	673.68	723.40
a (Å)	13.453(1)	13.410(2)	13.664(7)	13.718(5)	10.455(4)	10.513(1)
b (Å)	16.017(1)	15.942(2)	14.184(8)	14.144(5)	10.636(4)	9.981(1)
c (Å)	16.389(1)	17.126(1)	17.428(9)	17.779(6)	17.407(7)	36.063(4)
α (deg)	90	90	90	90	77.982(1)	90
β (deg)	101.905(2)	102.473(1)	95.729(1)	100.061(1)	82.906(1)	97.402(2)
γ (deg)	90	90	90	90	87.274 (1)	90
V (Å^3)	3455.4(5)	3574.76(7)	3360.9(3)	3396.6(2)	1878.28(1)	3752.8(6)
Z	4	4	4	4	2	4
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/n$
d_{calc} (mg/m^3)	1.117	1.109	1.125	1.303	1.191	1.280
linear obs coeff (mm^{-1})	0.150	0.270	0.282	1.263	1.527	1.150
T (K)	95(2)	96(2)	93(2)	94(2)	90(2)	84(2)
2θ range (deg)	1.79−28.30	1.76−25.00	2.07−25.00	2.08−28.00	1.20−28.00	1.96−25.00
independent reflns	8319	6225	2969	4094	9014	6616
No. of params	364	352	196	168	415	377
R_1, wR2 (all data)[b]	0.0556, 0.1035	0.0904, 0.1865	0.0525, 0.1275	0.0339, 0.0696	0.0500, 0.1083	0.0957, 0.1353
R_1, wR2 ($>2\sigma$)[b]	0.0388, 0.0938	0.0640,0.1721	0.0442, 0.1207	0.0287, 0.0676	0.0402, 0.1033	0.0714, 0.1276

[a] Mo Kα ($\lambda = 0.71073$ Å). [b] $R_1 = \Sigma/|F_o| - |F_c|/|\Sigma|F_d$ and $wR2 = [\Sigma_w(F_o^2 - F_2^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$.

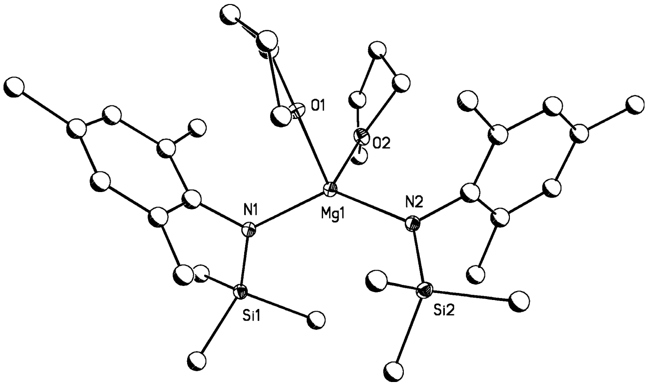

Figure 1. Computer-generated plot of **1** with anisotropic displacement parameters depicting a 30% probability for all non-carbon atoms. The hydrogen atoms have been omitted for clarity.

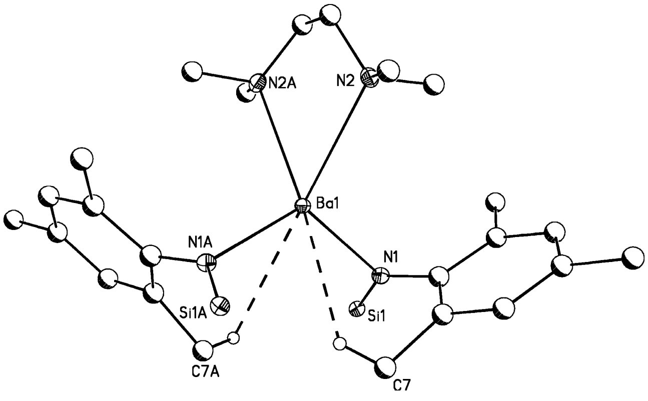

Figure 2. Computer-generated plot of **6** with anisotropic displacement parameters depicting a 30% probability for all non-carbon atoms showing the agostic interactions. The non-agostic hydrogen atoms and the methyls on the silyl group have been omitted for clarity.

(2) Å for **5** and 2.628(2) Å for **6**. As expected, the metal−donor contacts are longer with lengths of 2.529(2) Å for **5** and 2.858(2) Å for **6**. The nitrogen−metal−nitrogen angles within the bidentate donor are narrow as expected with values of 72.15(6) and 62.62(8)° for **5** and **6**, respectively**.** Thus, both compounds exhibit a distorted octahedral geometry with N2 and H9B in the trans positions with an angle of 170.72° (average angles due to disorder) for **5** and N2 and a H7C angle of 170.44° for **6**. The sterically demanding amide ligands, the second nitrogen of the TMEDA donor, and the second agostic hydrogen center are located in the equatorial

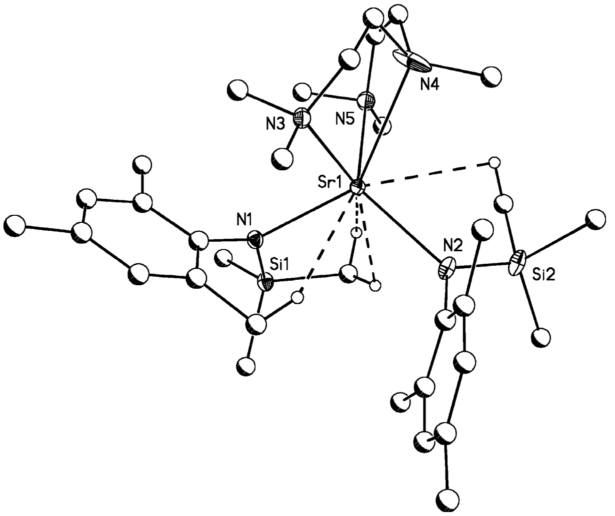

Figure 3. Computer-generated plot of **7** with anisotropic displacement parameters depicting a 30% probability for all non-carbon atoms showing the agostic interactions. The non-agostic hydrogen atoms have been omitted for clarity.

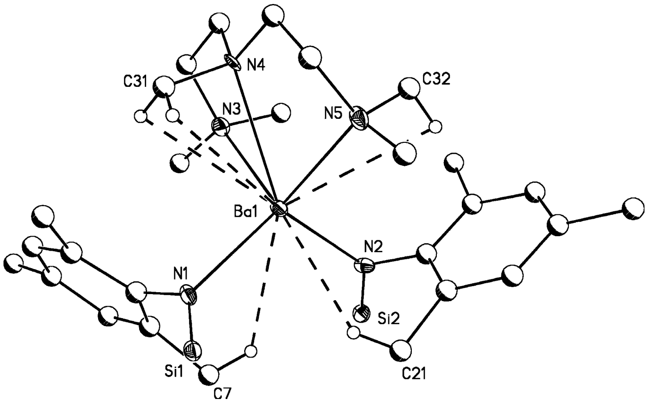

Figure 4. Computer-generated plot of **8** with anisotropic displacement parameters depicting a 30% probability for all non-carbon atoms showing the agostic interactions. The non-agostic hydrogen atoms and methyls from the silyl group have been omitted for clarity.

plane with a N(ligand)−metal−N(ligand) angle of 126.43(9)° for **5**, dissected by agostic interactions with N(ligand)−Ca−H angles of 66.27 and 68.08°. Other angles within the equatorial plane are 106.0(8) (average) and 116.7(8) Å (average) for the donor−metal−ligand angle, again demonstrating the large steric demand of the ligand. The geometry in **6** is rather similar with a ligand−metal−ligand angle of 123.98(8)°, again dissected by agostic interactions with N(ligand)−metal−H angles of 61.23 and 67.50°. Ligand−metal−donor angles within the equatorial plane are 115.07(6) and 112.25(6)°. The distortion of octahedral geometry in both compounds is caused by the narrow donor−metal−donor angles (72.2(1)° (average) for **5** and 62.62(8)° for **6**) spanning the equatorial plane and the axial positions.

M{N(2,4,6-$Me_3C_6H_2$)($SiMe_3$)}$_2$PMDTA (M = Sr (7, Figure 3), Ba (8, Figure 4)). In compounds **7** and **8**, one molecule without crystallographically imposed symmetry is present in the asymmetric unit. In each compound, a tridentate PMDTA donor and two amido ligands are bound to the metal center. In addition, there are four agostic interactions for **7** and five agostic interactions for **8**, resulting in the coordination numbers of 5 + 4 and 5 + 5, respectively. The average M−N(ligand) bond lengths are 2.501(4) Å for **7** and 2.67(1) Å for **8**. The metal−donor distances are, as expected, longer with lengths of 2.857(6) Å for **7** and 2.95(2) Å for **8**. The N(ligand)−M−N(ligand) angles are 113.57(7)° for **7** and 118.33(2)° for **8** with the two outer nitrogen centers at the donor exhibiting N(donor)−M−N(donor) angles of 110.63(6)° (**7**) and 112.44(2)° (**8**). Metal−hydrogen distances in **7** are 2.95 (C(7)−H(7B)···Sr(1)), 2.90 (C(11)−H(11A)···Sr(1)), 3.12 (C(11)−H(11B)···Sr(1)), and 3.19 Å (C(22)−H(22C)···Sr(1)), and the agostic interactions in compound **8** are 3.00 (C(7)−H(7C)···Ba(1)), 2.84 (C(21)−H(21B)···Ba(1)), 3.23 (C(31)−H(31B)···Ba(1)), 3.10 C(31)−H(31C)···Ba(1), and 3.11 Å (C(32)−H(32A)···Ba(1)).

The Mg−N and Mg−O bond lengths in **1** compare favorably with four-coordinate Mg{N($SiMe_3$)$_2$}$_2$(THF)$_2$,[29] as shown in Table 1. The metal−ligand and metal−donor bond lengths in the heavier metal analogues, **2**−**8**, lengthen in accord with the increase in the metal radius.

The comparison of the steric bulk within the three groups of amido ligands, {N($SiMe_3$)$_2$}$^-$, {N(Diip)($SiMe_3$)}$^-$, and {N(Mes)($SiMe_3$)}$^-$, clearly shows the {N(Diip)($SiMe_3$)}$^-$ ligand to be the most sterically demanding, as demonstrated by the comparison of the Ca−N(ligand) bond lengths in the four-coordinate Ca{N($SiMe_3$)$_2$}$_2$(THF)$_2$ (2.301(6) Å),[30] Ca{N(Mes)($SiMe_3$)}$_2$(THF)$_2$, **2** (2.304(6) Å), and Ca{N(Diip)($SiMe_3$)}$_2$(THF)$_2$ (2.326(8) Å) compounds.[11] The proximity of the values for {N($SiMe_3$)$_2$}$^-$ and {N(Mes)($SiMe_3$)}$^-$ may be explained by small differences in their steric bulk because the aryl substituent approaches a dimensionality of two, whereas the $SiMe_3$ group displays a three-dimensional geometry.

Counterintuitively, the increase in metal−ligand bond length coincides with a decrease in ligand−metal−ligand angle. If the arguement is strictly based on ligand size, the bulkiest amide, {N(Diip)($SiMe_3$)}$^-$, would be expected to adopt the largest N−M−N angles, whereas the smaller ligands, {N($SiMe_3$)$_2$}$^-$ and {N(Mes)($SiMe_3$)}$^-$, would have narrower angles because of the reduced steric repulsion. Interestingly, the largest N−M−N angle is observed for Ca{N(Mes)($SiMe_3$)}$_2$(THF)$_2$ (**2**, 137.55(1)°), whereas the bulkier Ca{N(Diip)($SiMe_3$)}$_2$(THF)$_2$[11] has significantly smaller angles with values of 128.16(1) and 121.25(1)° for Ca{N($SiMe_3$)$_2$}$_2$(THF)$_2$.[30] The deviations from the expected geometry may be explained by the agostic interaction in compound **2** (H21A−Ca, 2.89 Å), but none are seen for Ca{N($SiMe_3$)$_2$}$_2$(THF)$_2$ [30] and Ca{N(Diip)($SiMe_3$)}$_2$(THF)$_2$.[11] Agostic interactions increase in number for the heavier amides, as detailed in Table 1, suggesting that these interactions play a major role in stabilizing the heavy alkaline earth metal derivatives with low metal coordination numbers. This observation is further substantiated by the extensive agostic interactions observed in the family of donor-free dimeric [M{N($SiMe_3$)$_2$}$_2$]$_2$ (M = Mg,[5d] Ca,[5a] Sr,[5b] Ba[5c]) (see Table 1). Compounds as diverse as the calcium organometallic, Ca{C($SiMe_3$)$_3$}$_2$,[31] the ate complexes, [Li{μ-N($SiMe_3$)$_2$}$_2$Ca{N($SiMe_3$)$_2$}][32] and {(Cp*)$_2$Ca(μ-Me_3Al·THF)}$_2$,[33] and a primary calcium amide, [{HC(C(Me)$_2$N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}Ca{N(H)-2,6-^{i}PrC$_6$H$_3$}(THF)],[34] further support this view.

Conclusion

A new family of alkaline earth metal amides bearing the {N(Mes)($SiMe_3$)}$^-$ ligand was synthesized and characterized. The magnesium compounds can be most easily prepared by alkane elimination in a hydrocarbon solvent, while the preferred method for the heavier analogues is salt elimination. Direct metalation produces the compounds in only modest yields, and additional purification steps to remove excess ligand are needed. However, the use of inexpensive readily accessible reagents counteracts some of the preparative disadvantages.

Structural trends within the group of amides correlate with increasing metal radii. Agostic interactions play a major role in the structural chemistry of the heavy alkaline earth complexes, especially for those where sterically demanding ligands reduce the number of metal−ligand interactions.

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Supporting Information Available: Variable-temperature ^{1}H NMR spectrum of compound **7** in toluene-d_8 at different temperatures (K) along with a plot showing the splitting pattern dependent on temperature. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications 247151−247156. Copies of this data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax (+44)1223-336-033, e-mail deposit@ccdc.cam.ac.uk).

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