

Synthesis and Structural Characterization of Magnesium Amide Complexes Containing $-\text{N}[(\text{R})(\text{SiMe}_3)]$ Ligands

Yongjun Tang,[†] Lev N. Zakharov,[‡] Arnold L. Rheingold,[‡] and Richard A. Kemp^{*,†,§}

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131,
Department of Chemistry and Biochemistry, University of California, San Diego,
La Jolla, California 92093-0358, and Advanced Materials Laboratory,
Sandia National Laboratories, Albuquerque, New Mexico 87106

Received October 13, 2004

Reaction of anhydrous magnesium bromide with 2 equiv of $\text{Me}_3\text{Si}(\text{R})\text{NLi}$ ($\text{R} = i\text{-Pr}$, benzyl, mesityl, and $\text{SiMe}_2t\text{-Bu}$) in diethyl ether at ambient temperature followed by treatment with donor solvents such as THF, hexamethylphosphoramide (HMPA), pyridine (py), or 4-(dimethylamino)pyridine (DMAP) affords $[(\text{Me}_3\text{Si}(\text{R})\text{N})_2\text{Mg}(\text{L})_n]$ [$\text{R} = i\text{-Pr}$, $\text{L} = \text{DMAP}$, $n = 2$, **1**; $\text{R} = \text{benzyl}$, $\text{L} = \text{DMAP}$, $n = 2$, **2**; $\text{R} = \text{benzyl}$, $\text{L} = \text{HMPA}$, $n = 2$, **3**; $\text{R} = \text{mesityl}$, $\text{L} = \text{THF}$, $n = 2$, **4**; $\text{R} = \text{mesityl}$, $\text{L} = \text{py}$, $n = 2$, **5**; $\text{R} = \text{SiMe}_2t\text{-Bu}$, $\text{L} = \text{py}$, $n = 1$, **9**]. If R is cyclohexyl (Cy), the reaction in diethyl ether initially yields the solvent-free dimer $\text{Mg}_2[\text{N}(\text{Cy})(\text{SiMe}_3)]_4$, **6**, which reacts with excess DMAP to yield $\text{Mg}[\text{N}(\text{Cy})(\text{SiMe}_3)]_2(\text{DMAP})_2$, **7**. If R is either the sterically crowded ligand $\text{SiPh}_2t\text{-Bu}$ or adamantyl (Ad), the reaction produces solvent-free $\text{Mg}[\text{N}(\text{SiPh}_2t\text{-Bu})(\text{SiMe}_3)]_2$, **8**, and $\text{Mg}[\text{N}(\text{Ad})(\text{SiMe}_3)]_2(\text{Et}_2\text{O})$, **10**, respectively. All of these complexes were characterized by spectral and analytical data. The structures of complexes **1**, **2**, and **4–10** were confirmed by single-crystal X-ray diffraction analyses.

Introduction

Organomagnesiums and their derivatives are widely applied in organic syntheses; an important subset is commonly known as Grignard reagents. These synthetic applications can provide excellent regio- or stereoselective reactions.^{1,2} For example, a Hauser base such as $i\text{-Pr}_2\text{NMgCl}$ greatly improves the *anti* selectivity in aldol reactions in high yields under thermodynamic conditions versus the general preference for the *syn* product if corresponding lithium derivatives are used.³ Due to their thermal stabilities, magnesium derivatives are often more useful than the corresponding lithium species in synthetically organic chemistry.^{4–7} Furthermore, magnesium amide chemistry is becoming an increasingly active area of study, with potential uses as varied as magnesium source compounds in film depositions by metal organic chemical vapor deposition^{8,9} to precursors used for the fixation of carbon dioxide.^{10–13} However,

structural reports for magnesium amide compounds in the solid state were relatively limited until recently,^{14–24} and the synthetic scheme used is usually the reaction of a secondary amine with a Grignard reagent or magnesium dialkyl.^{25–31} Recent relevant synthetic and structural work includes the structural characterization

* To whom correspondence should be addressed. E-mail: rakemp@unm.edu. Phone: (505) 277-0510. Fax: (505) 277-2609.

[†] University of New Mexico.

[‡] University of California.

[§] Sandia National Laboratories.

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of $\text{Mg}[\text{N}(\text{SiMe}_2\text{Ph})_2]_2$,²⁵ the synthesis (using MgI_2) and structural characterization of $\text{Mg}[\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]_2(\text{THF})_2$,³² and the structural characterization of $\text{Mg}[\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]_2(\text{Et}_2\text{O})$.³³ In this paper, we conveniently synthesize magnesium amide compounds by the reaction of lithium amides of type $\text{LiN}(\text{R})(\text{SiMe}_3)$ with anhydrous MgBr_2 . The introduction of donor solvents such as tetrahydrofuran (THF), hexamethylphosphoramide (HMPA), pyridine (py), and 4-(dimethylamino)pyridine (DMAP) drives the reactions to the mononuclear magnesium species by forming three- or four-coordinated magnesium centers. The coordination to the Mg center is likely due to the electron saturation requirements of the metal center. Here our efforts are directed toward the syntheses and characterization of the magnesium amides when the amides have one trimethylsilyl group present. The interactions of these Mg amides with carbon dioxide to form magnesium carbamates are under study and will be the subject of a report in the near future.

We now report the syntheses, structures, and reactivities of several solvent-dependent monomers and solvent-free monomers or dimers of magnesium amide compounds. Magnesium amides with various coordination numbers have been prepared and characterized by multinuclear NMR, chemical analyses, and single-crystal X-ray diffraction analyses. With this report we significantly increase the number of well-characterized magnesium silylamides found in the literature.

Experimental Section

General Consideration. All manipulations were carried out in a glovebox or by using standard Schlenk techniques.³⁴ Anhydrous solvents and organic ligands were purchased from Aldrich or Fisher Scientific Company and stored in the drybox over 4 Å molecular sieves. The ligands THF, py, DMAP, and HMPA were used without further purification. Anhydrous MgBr_2 and *n*-BuLi (2.5 M in hexane) were purchased from Aldrich. Silylated amine ligands $(\text{Me}_3\text{Si})(\text{R})\text{NH}$ ($\text{R} = i\text{-Pr}$, cyclohexyl, mesityl, benzyl, $\text{SiMe}_2t\text{-Bu}$, $\text{SiPh}_2t\text{-Bu}$, and adamantyl) were synthesized by literature procedures.^{35,36} ^1H and ^{13}C spectra were obtained on a Bruker AMX 250 spectrometer using C_6D_6 as both solvent and internal reference due to residual peaks. Elemental analyses for carbon, hydrogen, and nitrogen content were performed at Desert Analytics, Tucson, AZ. Although WO_3 was added as an oxidant to the samples to aid in combustion, we consistently had a lower analyzed carbon content than calculated value. We feel this is due to a residual carbide species left upon analysis. The analyzed hydrogen and nitrogen values did not follow this trend of consistently lower values. The preparation and NMR assignments of **1** are given here. The preparations of **2–10** generally follow this procedure and are given in detail in the Supporting Information, along with the corresponding ^1H and ^{13}C NMR spectra with assignments.

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$\text{Mg}[\text{N}(i\text{-Pr})(\text{SiMe}_3)]_2(\text{DMAP})_2$, **1.** In a glovebox a solution of *n*-BuLi (15.2 mL, 38.1 mmol) was added slowly to (*i*-Pr)- $(\text{Me}_3\text{Si})\text{NH}$ (5.00 g, 38.1 mmol) in hexane (50 mL) at 25 °C. The reaction mixture was stirred for 3 h after the addition was completed. The solution was taken to dryness under vacuum, leaving the product as a white solid. The solid was dried under vacuum for 6 h and was then dissolved in 50 mL of anhydrous diethyl ether. To the solution was gradually added anhydrous magnesium bromide (3.51 g, 19.04 mmol) in small portions via a solid addition funnel. The mixture was stirred overnight and then the solvent removed. The residue was held under vacuum for 6 h and was then extracted with a 60 mL portion of hexane, and the extract was filtered through a glass frit covered with Celite filter aid. Hexane was removed under reduced pressure, and the residue, a viscous light yellow liquid, was dissolved in 40 mL of diethyl ether and treated with DMAP (4.65 g, 38.1 mmol). After stirring for 1 h, the solvent was removed under vacuum to yield a white solid (7.26 g, 72%). Recrystallization from toluene/hexane at -20 °C afforded **1** as colorless crystals. ^1H NMR (C_6D_6): δ 0.49 (s, 18H, $-\text{SiMe}_3$), 1.64 (d, 12H, $^3J_{\text{H-H}} = 6.26$ Hz, $\text{Me}_2\text{CH}-$), 2.04 (s, 12H, $\text{Me}_2\text{N}-$), 3.98 (m, 2H, $\text{Me}_2\text{CH}-$), 5.93 (d, 4H, $^3J_{\text{H-H}} = 5.53$ Hz, *m*-py), and 8.64 (d, 4H, $^3J_{\text{H-H}} = 5.53$ Hz, *o*-py). ^{13}C NMR (C_6D_6): δ 4.69 ($-\text{SiMe}_3$), 31.56 ($\text{Me}_2\text{CH}-$), 38.08 ($\text{Me}_2\text{CH}-$), 48.54 ($\text{Me}_2\text{N}-$), 106.39 (*o*-py), 149.97 (*m*-py), 154.82 (*p*-py).

X-ray Crystallography. Crystallographic data and details of X-ray studies for **1**, **2**, and **4–10** are given in Tables 1 and 2. Diffraction data were collected at 100 K on a Bruker Smart Apex CCD diffractometer using $\lambda(\text{Mo K}\alpha) = 0.71073$ Å. Space groups were determined based on systematic absences (**4**, **8**, **10**), intensity statistics (**5**, **6**), and systematic absences and intensity statistics (**1**, **2**, **7**, **9**). SADABS absorption corrections were applied to all data. The structures were solved using the direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2 . In all structures non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were located on the F -maps and refined with isotropic thermal parameters. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package.³⁷

Results and Discussion

Syntheses and Spectroscopic Characterizations.

A summary of our synthetic results is presented in Scheme 1. In diethyl ether, MgBr_2 reacts with 2 equiv of lithium silylamides to give $\text{Mg}[\text{N}(\text{R})(\text{SiMe}_3)]_2(\text{Et}_2\text{O})_2$ ($\text{R} = i\text{-Pr}$, benzyl, mesityl), $\text{Mg}[\text{N}(\text{R})(\text{SiMe}_3)]_2(\text{Et}_2\text{O})$ ($\text{R} = \text{adamantyl}$), or $\text{Mg}[\text{N}(\text{R})(\text{SiMe}_3)]_2$ ($\text{R} = \text{SiPh}_2t\text{-Bu}$). The ether adducts of the magnesium amides, which could be isolated as viscous, light yellow liquids, could not be solidified even if held for 24 h under vacuum. However, they could be crystallized as solvent-coordinated white solids after treatment with stronger donor solvents such as THF, pyridine, DMAP, or HMPA. The resulting compounds are all extremely air and moisture sensitive, whether in the solid state or in solution. $\text{Mg}[\text{N}(i\text{-Pr})(\text{SiMe}_3)]_2(\text{Et}_2\text{O})_2$ is a volatile viscous liquid that can be sublimed at 72 °C at 10^{-2} Torr, albeit with some decomposition, but $\text{Mg}[\text{N}(\text{benzyl})(\text{SiMe}_3)]_2(\text{Et}_2\text{O})_2$ and $\text{Mg}[\text{N}(\text{mesityl})(\text{SiMe}_3)]_2(\text{Et}_2\text{O})_2$ show no volatility and decompose around 80 °C in a vacuum. Obviously, the ether adducts cannot be purified by distillation. However, the weakly coordinating ether molecules in these

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Table 1. Crystallographic Data for Complexes 1, 2, 4, 5, and 7 Containing Two Solvent Molecules Coordinated to Mg^a

	1	2	4	5	7
empirical formula	C ₂₆ H ₅₂ MgN ₆ Si ₂	C ₃₄ H ₅₂ MgN ₆ Si ₂	C ₃₂ H ₅₆ MgN ₂ O ₂ Si ₂	C ₃₄ H ₅₀ MgN ₄ Si ₂	C ₃₂ H ₆₀ MgN ₆ Si ₂
fw	529.23	625.31	581.28	595.27	609.35
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	C2/c	C2/c	P2 ₁ /n	P1	C2/c
a, Å	31.064(2)	24.2471(16)	13.4473(8)	12.0451(7)	10.4814(19)
b, Å	11.9434(9)	8.6536(6)	16.0187(9)	15.9172(9)	18.532(3)
c, Å	17.9159(13)	20.1913(14)	16.3754(9)	18.6838(10)	18.641(3)
α, deg	90	90	90	91.729(1)	90
β, deg	99.475(1)	122.682(1)	101.875(1)	101.358(1)	94.469(3)
γ, deg	90	90	90	90.445(1)	90
V, Å ³	6556.3(8)	3565.9(4)	3451.9(3)	3510.0(3)	3609.8(11)
Z, Z'	8, 1	4, 0.5	4, 1	4, 2	4, 0.5
calc density, g/cm ³	1.072	1.165	1.118	1.126	1.121
μ, mm ⁻¹	0.151	0.149	0.150	0.147	0.145
absorp corr (T _{min} /T _{max})	SADABS (0.895)	SADABS (0.888)	SADABS (0.891)	SADABS (0.903)	SADABS (0.776)
no. of reflns collected	20 359	10 995	21 381	22 299	8554
no. of unique reflns (R _{int})	7477(0.0375)	4063(0.0283)	7815(0.0285)	15436(0.0182)	3928(0.0306)
no. of obsd reflns	5523	3281	6585	12753	3144
R1 (I > 2σ(I))	0.0467	0.0446	0.0470	0.0439	0.0429
wR2 (I > 2σ(I))	0.1150	0.1151	0.1165	0.1101	0.1101
GOF ²	1.009	1.028	1.158	1.027	1.060

^a For all crystal structure determinations Mo Kα radiation (λ = 0.71073 Å) was used.

Table 2. Crystallographic Data for Complexes 6, 8, 9, and 10 Containing at Most One Solvent Molecule Coordinated to Mg^a

	6	8	9	10
empirical formula	C ₃₆ H ₈₀ Mg ₂ N ₄ Si ₄	C ₃₈ H ₅₆ MgN ₂ Si ₄	C ₂₃ H ₅₃ MgN ₃ Si ₄	C ₃₀ H ₅₈ MgN ₂ OSi ₂
fw	730.02	677.52	508.35	543.27
T, K	100(2)	100(2)	100(2)	100(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	P1	P2 ₁ /n	C2/c	P2 ₁ /n
a, Å	9.7033(9)	12.8708(7)	12.5908(6)	11.4854(9)
b, Å	10.2273(10)	17.1592(10)	22.8478(11)	16.9421(13)
c, Å	11.7211(11)	18.2267(10)	11.3638(5)	16.8527(13)
α, deg	87.909(2)	90	90	90
β, deg	77.606(2)	100.0690(10)	106.5780(10)	102.533(2)
γ, deg	75.957(2)	90	90	90
V, Å ³	1101.97(18)	3963.4(4)	3133.2(3)	3201.2(4)
Z, Z'	1, 0.5	4, 1	4, 0.5	4, 1
calc density, g/cm ³	1.100	1.135	1.078	1.127
μ, mm ⁻¹	0.192	0.193	0.225	0.155
absorp corr (T _{min} /T _{max})	SADABS (0.891)	SADABS (0.857)	SADABS (0.891)	SADABS (0.821)
no. of reflns collected	6948	24732	9741	19 761
no. of unique reflns (R _{int})	4844(0.0206)	9032(0.0295)	3558(0.0177)	7242(0.0294)
no. of obsd reflns	4328	7316	3279	5946
GOF	1.039	1.040	1.074	1.030
R1 (I > 2σ(I))	0.0584	0.0421	0.0293	0.0419
wR2 (I > 2σ(I))	0.1572	0.1063	0.0792	0.1005
GOF	1.039	1.040	1.074	1.030

^a For all crystal structure determinations Mo Kα radiation (λ = 0.71073 Å) was used.

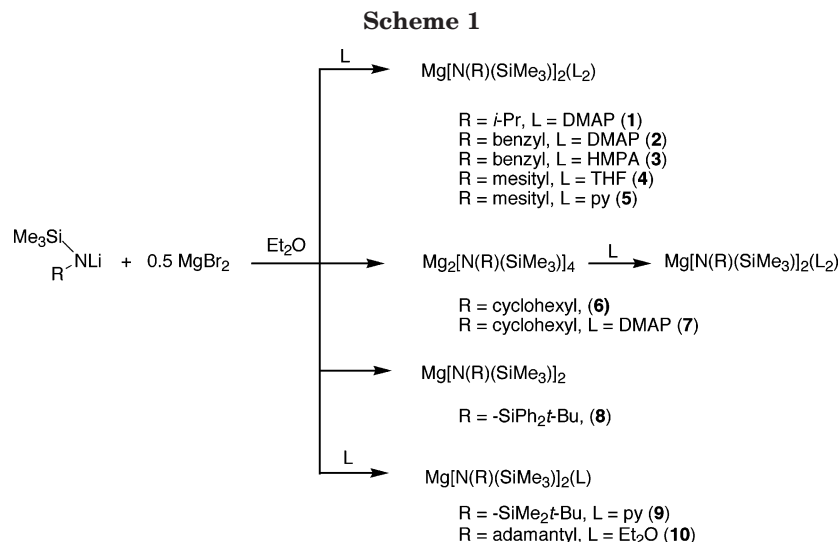
amide compounds can be replaced by stronger donor solvents such as THF, pyridine, DMAP, or HMPA. These compounds with the stronger donors form white solids and can be purified by recrystallization from toluene or hexane at -20 °C to produce pure colorless crystals.

We find that the Et₂O ligands in Mg[N(*i*-Pr)(SiMe₃)₂](Et₂O)₂ are displaced by DMAP, a stronger donor than ether, to yield Mg[N(*i*-Pr)(SiMe₃)₂](DMAP)₂, **1**, as colorless needles-shaped crystals after workup. The same principle is also utilized in other preparations: Mg[N(benzyl)(SiMe₃)₂](Et₂O)₂ can be reacted with either DMAP or HMPA to form colorless rectangular-shaped crystals of Mg[N(benzyl)(SiMe₃)₂](DMAP)₂, **2**, and Mg[N(benzyl)(SiMe₃)₂](HMPA)₂, **3**. Using the mesityl derivative it can be shown that THF or pyridine can replace ether in Mg[N(mesityl)(SiMe₃)₂](Et₂O)₂ to yield

colorless crystals of Mg[N(mesityl)(SiMe₃)₂](THF)₂, **4**, and Mg[N(mesityl)(SiMe₃)₂](py)₂, **5**, respectively.

There is no evidence to suggest the existence of any dimeric structures in solution at room temperature in the ¹H and ¹³C NMR spectra of **1–5**. However, the NMR data are not conclusive regarding the nuclearity of these species. The monomeric nature in the structures of **1**, **2**, **4**, and **5** is further confirmed by the solid-state X-ray single-crystal structures (vide infra). The individual assignments for the ¹H and ¹³C NMR spectra of **1–5** are relatively straightforward and are given in the Supporting Information.

Interestingly, when [(Cy)(TMS)N]Li is used as the lithium amide, the reaction of MgBr₂ with 2 equiv of this lithium amide in anhydrous ether forms a solvent-free, dimeric compound Mg₂[N(Cy)(SiMe₃)₄], **6**, which can be recrystallized from hexane at -20 °C to give



colorless needle-shaped crystals. The surprising fact that no ether was present was noted by the lack of resonances attributable to ether in the ^1H or ^{13}C NMR spectra. The lack of solvent resonances was the first indication that the structure of **6** may be dimeric; the ^1H and ^{13}C NMR spectra also indicated this structure due to the larger number of resonances present in each spectrum than one would expect for a simple, monomeric structure. The $\text{Me}_3\text{Si}-$ groups in the ^1H NMR spectrum consist of two singlets of equal intensities at δ 0.28 and 0.37 ppm, the $-\text{CH}_2-$ resonances consist of complex multiplets at δ 0.88–2.25 ppm, and the $-\text{CH}-$ resonances further downfield consist of multiplets at δ 2.80–3.00 ppm. We find these peaks consistent with the existence of a dimeric structure in solution for **6** (Figure 1). The dimeric structure would give rise to two different $-\text{SiMe}_3$ groups, one on a terminal amide and one on an amide that bridges two Mg atoms. The ^{13}C NMR spectrum allows an even clearer picture to emerge, as the carbon resonances of the cyclohexyl groups do not overlap as do the resonances in the ^1H NMR spectrum. In the ^{13}C NMR spectrum, there are two resonances for each carbon atom in the $-\text{N}[(\text{Cy})(\text{SiMe}_3)_2]$ groups. Again, the ^{13}C spectrum is consistent with bridging and terminal ligands both being present in **6**, indicating the structure shown in Figure 1 is likely the one in solution. Interestingly, a crystal structure of **6** indicates that this confirmation is adopted in the solid state (vide infra).

Addition of a coordinating solvent such as DMAP breaks apart the dimeric structure of **6** and yields a tetracoordinated monomer, $\text{Mg}[\text{N}(\text{Cy})(\text{SiMe}_3)_2](\text{DMAP})_2$, **7**, similar in nature to **1–5**. The ^1H and ^{13}C spectra were consistent with a straightforward assignment of a monomeric structure. The carbon resonances of the cyclohexyl and $-\text{SiMe}_3$ moieties no longer appear as

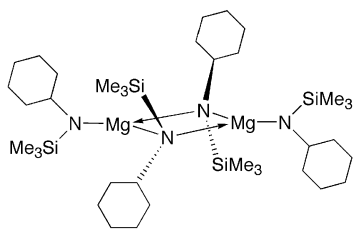


Figure 1. Proposed structure of **6** in solution.

bridging/terminal peaks in the ^{13}C NMR spectrum, but rather one each, indicating that only one type of ligand (terminal) is present.

Interestingly, when MgBr_2 was treated with 2 equiv of the bulky amide $\text{Li}[\text{N}(\text{SiPh}_2t\text{-Bu})(\text{SiMe}_3)]$ in diethyl ether, a solvent-free complex **8** appeared to form. However, in this case, NMR data did not indicate the presence of a dimeric structure as we had seen in **6**. Along with phenyl resonances the ^1H NMR spectrum contains two sharp peaks at δ 0.23 and 1.06 ppm for the $-\text{SiMe}_3$ group and the $t\text{-Bu}$ group, respectively. The ^{13}C NMR resonances for these two peaks are at δ 6.56 and 29.06 ppm. Thus, our initial view indicated by NMR was that this bulky ligand system afforded a rare example of a solvent-free Mg bis(amide). Indeed, the solid-state structure of **8** was further confirmed by single-crystal X-ray diffraction analysis to be this postulated structure.

Using another related, but slightly less bulky, ligand with MgBr_2 produced different results. Addition of 2 equiv of $\text{Li}[\text{N}(\text{SiMe}_2t\text{-Bu})(\text{SiMe}_3)]$ to MgBr_2 in ether followed by excess pyridine produced $\text{Mg}[\text{N}(\text{SiMe}_2t\text{-Bu})(\text{SiMe}_3)_2](\text{py})$, **9**. Analysis of the ^1H and ^{13}C NMR data indicated a different solvent stoichiometry from those seen above. In the cases of **1–5** and **7** we had seen two coordinating solvent molecules and a roughly tetrahedral geometry for Mg. In this case, ^1H NMR integration data indicated there was only one py present, thus implying a trigonal geometry around Mg for **9** rather than tetrahedral. The other ^1H and ^{13}C resonances present were relatively straightforward to assign. When we used 2 equiv of another bulky ligand, $\text{Li}[\text{N}(\text{Ad})(\text{SiMe}_3)]$, with MgBr_2 in ether we obtained $\text{Mg}[\text{N}(\text{Ad})(\text{SiMe}_3)_2](\text{Et}_2\text{O})$, **10**. Again, ^1H and ^{13}C NMR analysis indicated the reaction yielded a product with only one solvent molecule coordinated to Mg rather than the expected two solvent molecules. We can speculate that as the R groups on the $-\text{N}(\text{R})(\text{TMS})$ ligands increase in steric bulk, it becomes more and more difficult to obtain a tetrahedral geometry by addition of two solvent molecules, and either the trigonal or solvent-free geometries become favored.

X-ray Crystallographic Studies. The X-ray crystal structure determinations of $\text{Mg}[\text{N}(i\text{-Pr})(\text{SiMe}_3)_2](\text{DMAP})_2$, **1** (Figure 2), $\text{Mg}[\text{N}(\text{benzyl})(\text{SiMe}_3)_2](\text{DMAP})_2$, **2**, Mg-

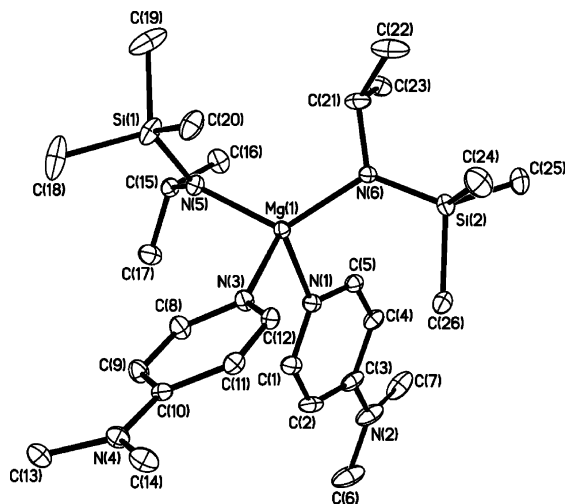


Figure 2. Thermal ellipsoid plot of $\text{Mg}[\text{N}(i\text{-Pr})(\text{SiMe}_3)_2(\text{DMAP})_2]$, **1** (30% probability). The H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): $\text{Mg}(1)\text{--N}(6)$ 2.0040(1), $\text{Mg}(1)\text{--N}(5)$ 2.0314(1), $\text{Mg}(1)\text{--N}(1)$ 2.1560(15), $\text{Mg}(1)\text{--N}(3)$ 2.1537(5), $\text{N}(5)\text{--Si}(1)$ 1.6867(15), $\text{N}(6)\text{--Si}(2)$ 1.6818(15); $\text{N}(5)\text{--Mg}(1)\text{--N}(6)$ 121.44(6), $\text{N}(1)\text{--Mg}(1)\text{--N}(3)$ 104.57(6).

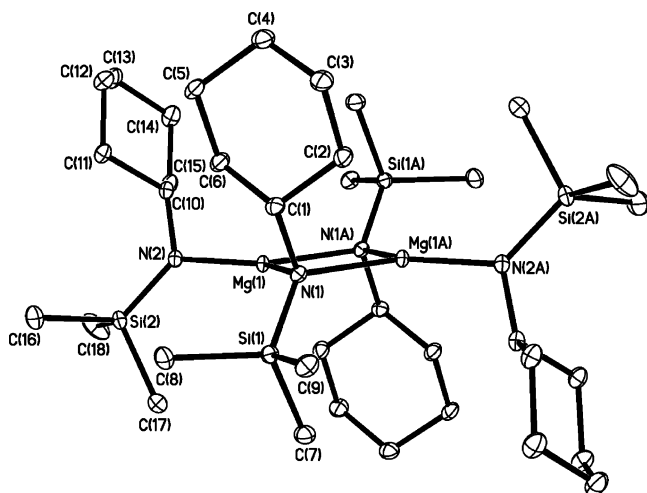


Figure 3. Thermal ellipsoid plot of $\text{Mg}_2[\text{N}(\text{Cy})(\text{SiMe}_3)_4]$, **6** (30% probability). The H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): $\text{Mg}(1)\text{--N}(1)$ 2.1292(19), $\text{Mg}(1)\text{--N}(1\text{A})$ 2.1033(18), $\text{Mg}(1)\text{--N}(2)$ 1.9733(18), $\text{N}(1)\text{--Si}(1)$ 1.7437(18), $\text{N}(2)\text{--Si}(2)$ 1.7007(18); $\text{N}(1)\text{--Mg}(1)\text{--N}(1\text{A})$ 92.20(7), $\text{Mg}(1)\text{--N}(1)\text{--Mg}(1\text{A})$ 87.80(7), $\text{N}(1)\text{--Mg}(1)\text{--N}(2)$ 135.29(7), $\text{N}(2)\text{--Mg}(1)\text{--N}(1\text{A})$ 132.14(7), $\text{Mg}(1)\text{--N}(2)\text{--Si}(2)$ 128.49(10), $\text{Mg}(1)\text{--N}(2)\text{--C}(10)$ 108.06(12), $\text{C}(1)\text{--N}(1)\text{--Si}(1)$ 108.52(13), $\text{C}(10)\text{--N}(2)\text{--Si}(2)$ 123.45(13).

$[\text{N}(\text{mesityl})(\text{SiMe}_3)_2(\text{THF})_2]$, **4**, $\text{Mg}[\text{N}(\text{mesityl})(\text{SiMe}_3)_2(\text{py})_2]$, **5**, $\text{Mg}_2[\text{N}(\text{Cy})(\text{SiMe}_3)_4]$, **6** (Figure 3), $\text{Mg}[\text{N}(\text{Cy})(\text{SiMe}_3)_2(\text{DMAP})_2]$, **7**, $\text{Mg}[\text{N}(\text{SiPh}_2t\text{-Bu})(\text{SiMe}_3)_2]$, **8**, (Figure 4), $\text{Mg}[\text{N}(\text{SiMe}_2t\text{-Bu})(\text{SiMe}_3)_2(\text{py})]$, **9** (Figure 5), and $\text{Mg}[\text{N}(\text{Ad})(\text{SiMe}_3)_2(\text{Et}_2\text{O})]$, **10** have been performed. A summary of the crystal data for **1**, **2**, **4**, **5**, and **7** [overall formula $\text{Mg}[\text{N}(\text{R})(\text{SiMe}_3)_2(\text{L}_2)]$] is given in Table 1, and the summary of the data for **6**, **8**, **9**, and **10** [overall formula $\text{Mg}[\text{N}(\text{R})(\text{SiMe}_3)_2(\text{L}_n)]$ ($n = 0, 1$)] is shown in Table 2. Selected bond distances and angles are listed in the figure captions.

Mg[N(R)(SiMe₃)₂(L₂) Compounds (1, 2, 4, 5, and 7). Compounds with the overall formula of $\text{Mg}[\text{N}(\text{R})\text{--}$

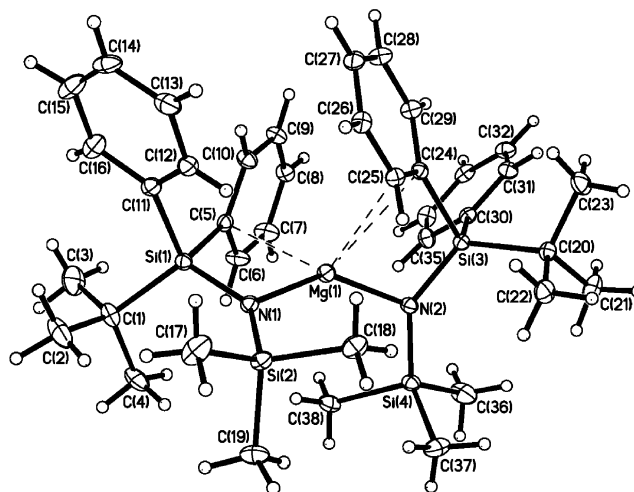


Figure 4. Thermal ellipsoid plot of $\text{Mg}[\text{N}(\text{SiPh}_2t\text{-Bu})(\text{SiMe}_3)_2]$, **8** (30% probability). Selected bond lengths (Å) and bond angles (deg): $\text{Mg}(1)\text{--N}(1)$ 1.9863(14), $\text{Mg}(1)\text{--N}(2)$ 1.9761(15), $\text{N}(1)\text{--Si}(1)$ 1.6932(14), $\text{N}(1)\text{--Si}(2)$ 1.7094(13), $\text{N}(2)\text{--Si}(3)$ 1.6967(14), $\text{N}(2)\text{--Si}(4)$ 1.7156(13), $\text{Mg}(1)\cdots\text{C}(5)$ 2.558(2), $\text{Mg}(1)\cdots\text{C}(24)$ 2.792(2), $\text{Mg}(1)\cdots\text{C}(25)$ 2.646(2), $\text{N}(1)\text{--Mg}(1)\text{--N}(2)$ 140.15(6), $\text{Mg}(1)\text{--N}(1)\text{--Si}(1)$ 103.13(7), $\text{Mg}(1)\text{--N}(1)\text{--Si}(2)$ 120.89(8), $\text{N}(1)\text{--Si}(1)\text{--C}(5)$ 102.12(7), $\text{N}(1)\text{--Si}(1)\text{--C}(1)$ 116.18(8), $\text{N}(1)\text{--Si}(1)\text{--C}(11)$ 112.06(7), $\text{Mg}(1)\text{--N}(2)\text{--Si}(3)$ 108.34(7), $\text{Mg}(1)\text{--N}(2)\text{--Si}(4)$ 118.02(7), $\text{N}(2)\text{--Si}(3)\text{--C}(24)$ 104.13(7), $\text{N}(2)\text{--Si}(3)\text{--C}(20)$ 116.41(7), $\text{N}(2)\text{--Si}(3)\text{--C}(30)$ 112.78(7).

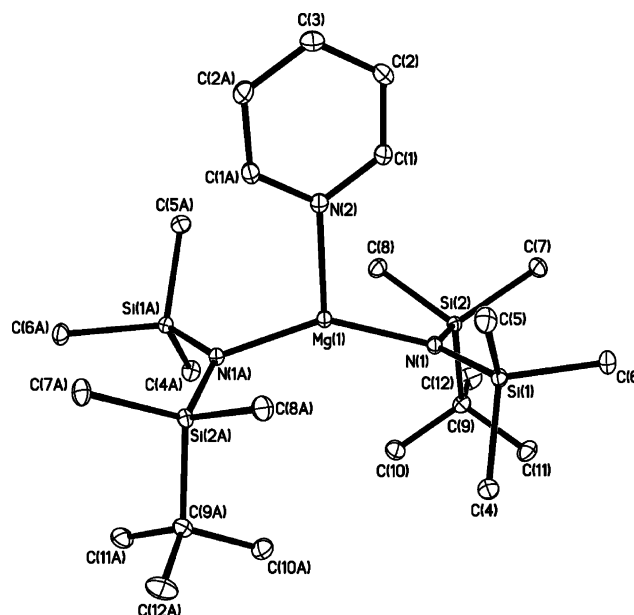


Figure 5. Thermal ellipsoid plot of $\text{Mg}[\text{N}(\text{SiMe}_2t\text{-Bu})(\text{SiMe}_3)_2(\text{py})]$, **9** (30% probability). The H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): $\text{Mg}(1)\text{--N}(1)$ 1.9914(9), $\text{Mg}(1)\text{--N}(2)$ 2.1314(15), $\text{N}(1)\text{--Si}(1)$ 1.7071(10), $\text{N}(1)\text{--Si}(2)$ 1.7049(10), $\text{N}(1)\text{--Mg}(1)\text{--N}(1\text{A})$ 144.41(6), $\text{N}(2)\text{--Mg}(1)\text{--N}(1)$ 107.79(3).

$(\text{SiMe}_3)_2(\text{L}_2)]$ are monomeric, four-coordinate Mg complexes containing two Mg–N bonds to the amides as well as two Mg–(solvent) bonds, and the structure of **1** in Figure 2 exemplifies this group. The geometry of the four-coordinated magnesium atoms can be broadly described as distorted tetrahedral. The molecules of **2** and **7** have C_2 symmetry; the Mg atom is on a 2-fold axis. The $\text{N}(6)\text{--Mg}(1)\text{--N}(5)$ angle of $121.44(6)^\circ$ in **1** is

slightly smaller than that of the corresponding N(1)–Mg(1)–N(1A) angle in **7** of 123.96(8)° and is significantly smaller than the N(1)–Mg(1)–N(1A) angle found in **2** (126.26(8)°). If the correlation of wider N–Mg–N bond angles with more sterically demanding ligands is correct, this would imply that the benzyl group is slightly larger as a substituent on the amide than either *i*-Pr or cyclohexyl groups. Similarly, **4** and **5** both have mesityl groups on the amide, but differ in the solvent coordinated to Mg (**4**, THF; **5**, py). The crystal structure of **5** contains two symmetrically independent molecules. The N(1)–Mg(1)–N(2) angle in **4** (134.35(7)°) is close to the corresponding angle in **5** (132.61(6)° for one of the independent molecules), both of which are significantly larger than the corresponding angles in **1**, **2**, or **7**. Although the coordinated solvent molecules have now been changed to THF or py from DMAP, it can be reasonably assumed that the larger N–Mg–N angles seen in the mesityl derivatives indicate the increase in steric bulk of the –N[(mesityl)(SiMe₃)] ligand. The mesityl groups in both **4** and **5** are located as far away as possible from each other in the solid-state structures. Again, we attribute this feature to the increase in steric bulk of the mesityl group causing the aromatic groups to be widely separated.

In all the reported compounds the average Mg–N(amide) distances are in a narrow range ((2.0087(15) Å (**1**), 2.0130(13) Å (**2**), 2.0232(17) Å (**4**), 2.0293(14) Å (**5**), and 2.0305(14) Å (**7**)) and can be compared to that found in Mg[N(SiMe₃)₂](THF)₂, 2.0210(5) Å.²⁴ As expected, the Mg–N(amide) bond lengths are significantly shorter, by approximately 0.15 Å, than the donor–acceptor Mg–N(solvent) bonds formed by the coordinated py or DMAP molecules.

Solvent-Free Mg[N(R)(SiMe₃)₂]₂ Compounds (6** and **8**).** X-ray crystallography reveals the centrosymmetric dimeric structure of **6**, containing three-coordinate magnesium centers with one terminal and two bridging amide ligands (Figure 3). The structure of **6** is notable for the lack of any solvent molecules coordinated to Mg. In the central Mg₂(μ₂-N)₂ cycle the two Mg(1)–N(bridging) distances (2.1033(18) and 2.1292(19) Å) are close and significantly longer than the Mg(1)–N(terminal) distance of 1.9733(18) Å. The N(1A)–Mg(1)–N(1) and Mg(1)–N(1)–Mg(1A) angles (92.20(7)° and 87.80(7)°, respectively) are close to 90°, resulting in a slightly distorted rectangular cycle. Moreover, the N(1A)–Mg(1)–N(1)–N(2) fragment is planar with the N(2)–Mg(1)–N(1A), N(2)–Mg(1)–N(1), and N(1A)–Mg(1)–N(1) angles of 132.14(7)°, 135.29(7)°, and 92.20(7)°, respectively. Due to symmetry considerations this indicates that the N(1A)–Mg(1A)–N(1)–N(2A) fragment is planar as well. The molecular structure of **6** is similar to that found in Mg₂[N(CH₂Ph)]₄.²⁷

The structure of **8** in the solid state is monomeric with the magnesium atom bonded only to two bulky terminal –[N(SiPh₂*t*-Bu)(TMS)] ligands (Figure 4). The lack of

solvent molecules coordinated to Mg makes **8** an unusual example of a solvent-free Mg bis(amide). The geometry at the magnesium center is found to be distorted from linearity in part due to weak interactions between the Mg and the aromatic rings on the bulky amide ligands. The short Mg···C contact (Mg(1)···C(5) 2.558(2) Å, Mg(1)···C(24) 2.792(2) Å, and Mg(1)···C(25) 2.646(2) Å) and the decreasing angles Mg(1)–N(1)–Si(1), N(1)–Si(1)–C(5) (103.13(7)° and 102.12(7)°, respectively) and Mg(1)–N(2)–Si(3), N(2)–Si(3)–C(24) (108.34(7)° and 104.13(7)°, respectively) with respect to other similar angles confirm the existence of such an interaction. This structure is very rare for a magnesium bis(amide) of formula Mg(NR₂)₂ (R = alkyl, aryl, or related group) in the solid state. The sterically bulky ligands can stabilize the magnesium center and help satisfy the metal's requirement for electron density. The angles between the two amide nitrogen and the magnesium atoms N(2)–Mg(1)–N(1) (140.15(6)°) is significantly smaller than the corresponding angle (162.8(3)°) found in Mg[N(SiMePh₂)₂]₂,²⁵ but much larger than those in compounds **1**, **2**, **4**, **5**, and **7**. The distances of Si(1)–N(1) (1.6932(14) Å) and Si(2)–N(1) (1.7094(13) Å) to the two different Si substituents are close, and the distances for Mg(1)–N(2) (1.9761(15) Å) and Mg(1)–N(1) (1.9863(14) Å) are close as well.

Mg[N(R)(SiMe₃)₂]₂(L) Compounds (9** and **10**).** Structural characterization indicates that in the solid state compounds **9** and **10** are monomeric. In both cases, the Mg atom is coordinated to two terminal amide ligands and one solvent molecule in a trigonal fashion (Figure 5). Molecule **9** has C₂ symmetry; the Mg(1), N(2), and C(3) atoms are on a crystallographic 2-fold axis. The adamantyl groups in **10** do reside as far apart as possible, roughly interchangeable by a C₂ rotation. The N(1A)–Mg(1)–N(1) angle (144.41(6)°) in **9** is noticeably larger than the corresponding angle in **10**, N(1)–Mg(1)–N(2) (138.77(6)°). The structures of **9** and **10** reveal rare examples of monomeric, three-coordinate geometries in magnesium diamide molecules.³³

Acknowledgment. We thank the National Science Foundation, Grant No. CHE-0213165, for financial support. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94-AL85000.

Supporting Information Available: Crystallographic data in CIF format for **1**, **2**, and **4–10**. Thermal ellipsoid plots for **2**, **4**, **5**, **7**, and **10** are also shown. Experimental syntheses of all compounds are given in depth, and the NMR assignments are also presented and the assignments detailed. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

OM049203C