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Monomeric Three- and Four-Coordinate Magnesium Amides

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Treatment of bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium with 2 equiv of 2,3,5-collidine, 2-picoline, 4-picoline, or 3,5-lutidine in benzene at room temperature for 18 h afforded bis(bis(trimethylsilyl)amido)bis-(2,3,5-collidine)magnesium (80%), bis(bis(trimethylsilyl)amido)bis(2-picoline)magnesium (70%), bis(bis(trimethylsilyl)amido)bis(4-picoline)magnesium (48%), or bis(bis(trimethylsilyl)amido)bis(3,5-lutidine)magnesium (58%), respectively. Sublimation of bis(bis(trimethylsilyl)amido)bis(2,3,5-collidine)magnesium (90 °C, 0.1 mmHg) and bis(bis(trimethylsilyl)amido)bis(2-picoline)magnesium (115 °C, 0.1 mmHg) afforded colorless crystals of bis(bis(trimethylsilyl)amido)(2,3,5-collidine)magnesium (53%) and bis(bis(trimethylsilyl)amido)(2-picoline)-magnesium (46%), respectively. Treatment of bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium with 1 equiv of 2,6-lutidine in benzene at room temperature for 18 h afforded bis(bis(trimethylsilyl)amido)(2,6-lutidine)-magnesium (56%). The X-ray crystal structures of bis(bis(trimethylsilyl)amido)bis(2,3,5-collidine)magnesium, bis(bis(trimethylsilyl)amido)bis(4-picoline)magnesium, bis(bis(trimethylsilyl)amido)(2-picoline)magnesium, and bis(bis(trimethylsilyl)amido)(2,6-lutidine)magnesium were determined. Bis(bis(trimethylsilyl)amido)bis(2,3,5-collidine)magnesium crystallizes in the monoclinic space group $C2/c$ with $a = 11.8410(7)$ Å, $b = 20.5413(13)$ Å, $c = 15.5746(10)$ Å, $\beta = 93.072(2)°$, $V = 3782.8(4)$ Å^3, and $Z = 4$. Bis(bis(trimethylsilyl)amido)bis(4-picoline)-magnesium crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.4914(6)$ Å, $b = 11.8504(6)$ Å, $c = 15.4546(9)$ Å, $\alpha = 99.3180(10)°$, $\beta = 98.4180(10)°$, $\gamma = 111.5320(10)°$, $V = 1718.8(2)$ Å^3, and $Z = 2$. Bis(bis(trimethylsilyl)-amido)(2-picoline)magnesium crystallizes in the orthorhombic space group $Pbca$ with $a = 18.4536(14)$ Å, $b = 15.2326(9)$ Å, $c = 20.614(2)$ Å, $V = 5794.6(7)$ Å^3, and $Z = 8$. Bis(bis(trimethylsilyl)amido)(2,6-lutidine)-magnesium crystallizes in the orthorombic space group $Pbca$ with $a = 18.6221(13)$ Å, $b = 15.3236(9)$ Å, $c = 20.9085(14)$ Å, $V = 5966.4(7)$ Å^3, and $Z = 8$. Application of the these complexes as source compounds in chemical vapor deposition processes is discussed.

Introduction

Magnesium-doped group 13 nitrides are among the leading-candidate materials for the fabrication of stable, high-luminosity blue and green photonic devices.[1] Desirable attributes of magnesium include a low diffusion constant in common semiconductor matrixes, desirable acceptor energy level, and low toxicity of its compounds.[2] Bis(cyclopentadienyl)magnesium (Cp_2Mg)[3] and substituted derivatives[4] are almost universally used as the magnesium source in film depositions by metal organic chemical vapor deposition (MOCVD), chemical beam epitaxy (CBE), and related techniques using molecular precursors. However, Cp_2Mg is a solid with a high melting point and low vapor pressure. Moreover, cyclopentadienyl ligands are well-known to bond strongly to metals; their cleavages from metals are high-energy processes.[5] The low vapor pressure and low reactivity of Cp_2Mg engender the so-called "memory effect", where Cp_2Mg adsorbs to the walls of the reactor during doped film growth and then slowly desorbs after the dopant precursor flow is ceased.[6] The "memory effect" leads to broad doping profiles and represents a severe impediment to device performance where abrupt doping profiles are required. Given the well-documented problems associated with Cp_2Mg, it is surprising that there has been very little work reported on alternative source compounds. The source $Mg(Al(CH_3)_4)_2$ has been used to dope $Ga_xAl_{1-x}As$ films[7] and affords high doping levels and almost flat doping profiles (virtually no "memory

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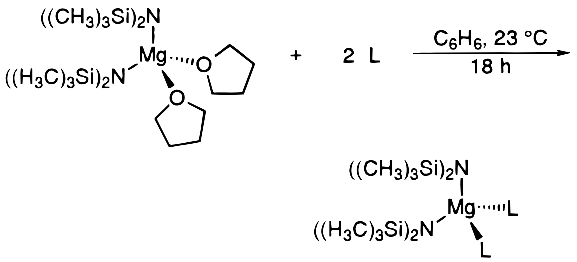
effect"). While $Mg(Al(CH_3)_4)_2$ is probably unsuitable for general use due to the aluminum content and its facile reversion to the constituent alkyls, it demonstrates that more volatile source compounds can dramatically affect film characteristics. With these considerations in mind, we report the synthesis, structure, and reactivity of several three- and four-coordinate magnesium amides. These compounds are substantially more volatile than Cp_2Mg and represent potentially superior source compounds. Furthermore, we report the crystal structures of the first neutral, monomeric three-coordinate magnesium compounds.

Results

Synthetic Chemistry. Treatment of bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium[8] with 2 equiv of 2,3,5-collidine, 2-picoline, 4-picoline, or 3,5-lutidine in benzene at room temperature for 18 h afforded bis(bis(trimethylsilyl)amido)bis(2,3,5-collidine)magnesium (**1**, 80%), bis(bis(trimethylsilyl)amido)bis(2-picoline)magnesium (**2**, 70%), bis(bis(trimethylsilyl)amido)bis(4-picoline)magnesium (**3**, 48%), or bis(bis(trimethylsilyl)amido)bis(3,5-lutidine)magnesium (**4**, 58%), respectively, as outlined in eq 1. The structures of **1**−**4** were assigned on the basis of spectral and analytical data and by X-ray crystal structure determinations of **1**, **3**, and **4** (vide infra). The yields of **1** and **2** are higher than those of **3** and **4** because the isolation procedures for **1** and **2** were carefully optimized in the initial stages of the investigation.

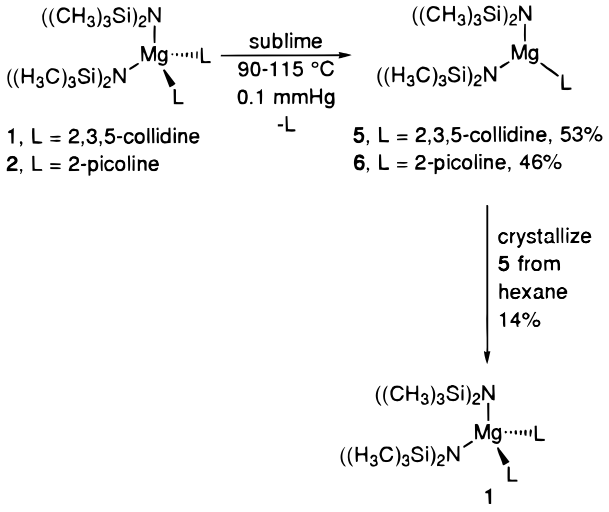


(1)

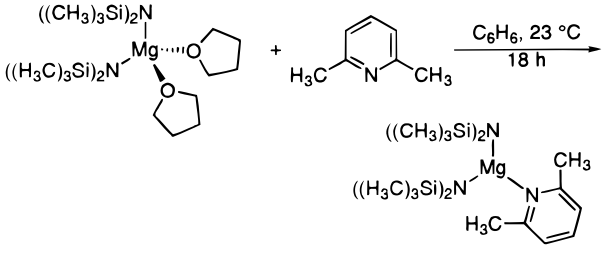
1, L = 2,3,5-collidine, 80%
2, L = 2-picoline, 70%
3, L = 4-picoline, 48%
4, L = 3,5-lutidine, 58%

Sublimation of **1** (90 °C, 0.1 mmHg) and **2** (115 °C, 0.1 mmHg) afforded colorless crystals of bis(bis(trimethylsilyl)amido)(2,3,5-collidine)magnesium (**5**, 53%) and bis(bis(trimethylsilyl)amido)(2-picoline)magnesium (**6**, 46%), respectively (Scheme 1). The low yields of **5** and **6** were a result of their "greasy" nature, which led to significant handling losses upon scraping from the sublimation apparatus. Preparation on a larger scale should lead to higher yields. The presence of only one substituted pyridine ligand in **5** and **6** was evident from their ^1H and $^{13}C\{^1H\}$ NMR spectra and microanalysis data. The monomeric nature of **5** and **6** in the solid state was established by an X-ray crystal structure determination of **6**. The reactivity of **5** was probed. Treatment of **5** with 2,3,5-collidine (1 equiv) in hexane afforded **1** (46% crystallized yield), demonstrating that **5** is unsaturated with respect to ligand addition. Attempted crystallization of **5** from hexane afforded colorless crystals of **1** (14%), which indicates the highly labile nature of **5**. Thus a redistribution equilibrium is accessible in hexane and is driven by crystallization of **1**. Complexes **5** and **6** can be resublimed at 90 °C (0.1 mmHg) and 115 °C (0.1 mmHg), respectively, without any evidence of thermal decomposition. By contrast, bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium[8] and the bis(bis(trimethylsilyl)amido)magnesium dimer[9] sublime at about 140 °C under the same conditions. Thus, the three-coordinate complexes **5** and **6** are substantially more volatile than even closely related structures.

Scheme 1. Preparation and Reactivity of **5** and **6**



Treatment of bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium with 2,6-lutidine (1 equiv) in benzene at room temperature for 18 h afforded bis(bis(trimethylsilyl)amido)(2,6-lutidine)magnesium (**7**, 56%; eq 2). The structure of **7** was based upon spectral and analytical data and an X-ray crystal structure determination (vide infra). It is interesting to note that the formation of **7** entails displacement of 2 equiv of tetrahydrofuran by 1 equiv of 2,6-lutidine.



(2)

7, 56%

To gain insight into the solution structures of the three-coorinate complexes, a solution molecular weight study was performed on **5** in cyclohexane. Data collected on 0.0302 and 0.0439 *m* solutions of **5** afforded molecular weights of 442 and 447, respectively. These data are consistent with a monomeric formulation ($M_r = 466$) in cyclohexane solution.

Crystal Structures of 1, 3, 6, and 7. The X-ray crystal structures of **1**, **3**, **6**, and **7** were determined in order to establish their molecular geometries. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2−5, and perspective views are presented in Figures 1−4. Further data are available in the Supporting Information. The crystal structure of **4** was also determined and is deposited in the Supporting Information.

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Table 1. Experimental Crystallographic Data for **1**, **3**, **6**, and **7**

	1	**3**	**6**	**7**
empirical formula	$C_{28}H_{58}MgN_4Si_4$	$C_{24}H_{50}MgN_4Si_4$	$C_{18}H_{43}MgN_3Si_4$	$C_{19}H_{45}MgN_3Si_4$
fw	587.45	531.35	438.22	452.25
space group	*C*2/*c*	$P\bar{1}$	*Pbca*	*Pbca*
a (Å)	11.8410(7)	10.4914(6)	18.4536(14)	18.6221(13)
b (Å)	20.5413(13)	11.8504(6)	15.2326(9)	15.3236(9)
c (Å)	15.5746(10)	15.4546(9)	20.614(2)	20.9085(15)
α (deg)		99.3180(10)		
β (deg)	93.072(2)	98.4180(10)		
γ (deg)		111.5320(10)		
V ($Å^3$)	3782.8(4)	1718.8(2)	5794.6(7)	5966.4(7)
Z	4	2	8	8
T (K)	295(2)	295(2)	295(2)	295(2)
$\lambda_{Mo\ K\alpha}$ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g/cm^{-3})	1.032	1.027	1.005	1.007
μ (mm^{-1})	0.195	0.208	0.234	0.229
R(*F*) (%)	4.32	4.46	8.42	8.39
$R_w(F)$ (%)	10.53	11.57	17.84	15.31

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Mg−N(1)	2.0467(14)	Mg−N(2)	2.259(2)
N(1)−Mg−N(1)′	120.95(10)	N(1)−Mg−N(1)	119.87(6)
N(1)−Mg−N(2)′	102.20(5)	N(2)−Mg−N(2)′	87.93(8)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Mg−N(1)	2.028(2)	Mg−N(3)	2.205(2)
Mg−N(2)	2.032(2)	Mg−N(4)	2.209(2)
N(1)−Mg−N(2)	125.52(8)	N(2)−Mg−N(3)	117.24(7)
N(1)−Mg−N(3)	101.73(7)	N(3)−Mg−N(4)	86.80(7)
N(1)−Mg−N(4)	119.00(8)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **6**

Mg−N(1)	1.969(3)	Mg−N(3)	2.098(4)
Mg−N(2)	1.959(4)		
N(1)−Mg−N(2)	137.3(2)	N(2)−Mg−N(3)	111.9(2)
N(1)−Mg−N(3)	110.3(2)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **7**

Mg−N(1)	1.974(3)	Mg−N(3)	2.158(3)
Mg−N(2)	1.976(3)		
N(1)−Mg−N(2)	133.73(14)	N(2)−Mg−N(3)	111.97(13)
N(1)−Mg−N(3)	114.29(13)		

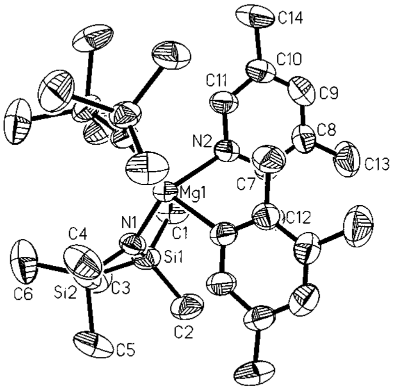

Figure 1. Perspective view of **1** with thermal ellipsoids at the 30% probability level.

Complex **1** crystallized as a distorted tetrahedral monomer with two bis(trimethylsilyl)amido ligands and two 2,3,5-collidine ligands (Figure 1). The distorted tetrahedral geometry was characterized by N(1)−Mg−N(1)′ and N(2)−Mg−N(2)′ angles of 120.95(10) and 87.93(8)°, respectively, which emphasizes the extremely bulky nature of the bis(trimethylsilyl)amido ligands. The magnesium−nitrogen bond length was 2.0467(14) Å for the bis(trimethylsilyl)amido ligand and 2.259(2) Å for the 2,3,5-collidine ligand.

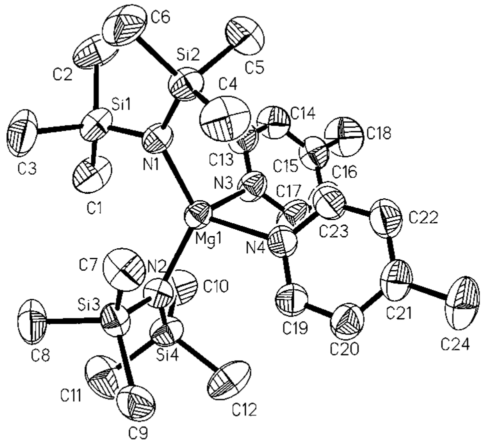

Figure 2. Perspective view of **3** with thermal ellipsoids at the 30% probability level.

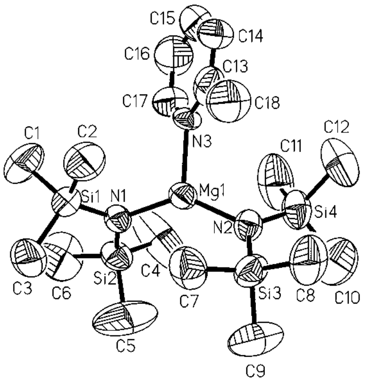

Figure 3. Perspective view of **6** with thermal ellipsoids at the 30% probability level.

Complex **3** crystallized as a distorted tetrahedral monomer with two bis(trimethylsilyl)amido ligands and two 4-picoline ligands (Figure 2). The distorted tetrahedral geometry was demonstrated by N(1)−Mg−N(2) and N(3)−Mg−N(4) angles of 125.52(8) and 86.80(7)°, respectively. These angles illustrate the extremely bulky nature of the bis(trimethylsilyl)amido ligands. The magnesium−nitrogen bond lengths for the bis(trimethylsilyl)amido ligands were 2.028(2) (Mg−N(1)) and 2.032(2) Å (Mg−N(2)), while the values for the 4-picoline ligands were 2.205(2) Å (Mg−N(3)) and 2.209(2) Å (Mg−N(4)). The bond lengths in **3** are slightly shorter than the

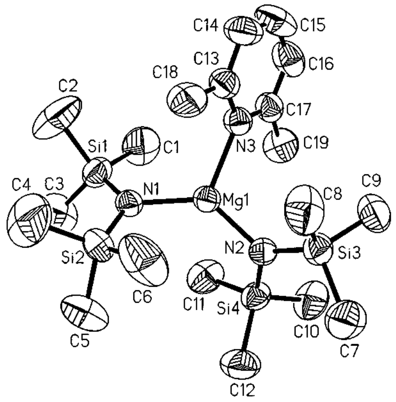

Figure 4. Perspective view of **7** with thermal ellipsoids at the 30% probability level.

analogous values in **1**, probably due to the less sterically encumbering nature of the 4-picoline ligand as compared to the 2,3,5-collidine ligand.

Complex **6** crystallized in trigonal planar geometry with two bis(trimethylsilyl)amido ligands and one 2-picoline ligand (Figure 3). The sum of the angles about magnesium was 359.5°, indicating nearly perfect planarity. The N(1)−Mg−N(2) angle was 137.3(2)°, consistent with the large steric bulk of the bis(trimethylsilyl)amido ligands. The plane of the 2-picoline ligand is approximately perpendicular to the plane of the three nitrogens, apparently to avoid steric interactions with the silyl methyl groups. The magnesium−nitrogen bond lengths for the bis(trimethylsilyl)amido ligands were 1.969(3) Å (Mg−N(1)) and 1.959(4) Å (Mg−N(2)), while the value for the 2-picoline ligand was 2.098(4) Å (Mg−N(3)). These values are considerably shorter than the analogous values for **1** and **3** and reflect the diminished steric interactions and increased electronic unsaturation present in **6**.

Complex **7** crystallized in trigonal planar geometry with two bis(trimethylsilyl)amido ligands and one 2,6-lutidine ligand (Figure 4). The sum of the angles about magnesium was 359.99°, indicating nearly perfect planarity. The large N(1)−Mg−N(2) angle (133.73(14)°) is indicative of the steric bulk of the two bis(trimethylsilyl)amido ligands. The plane of the 2,6-lutidine ligand is approximately perpendicular to the plane of the three nitrogens, apparently to avoid steric interactions between the lutidine and silyl methyl groups. The magnesium−nitrogen bond lengths for the bis(trimethylsilyl)amido ligands were 1.974(3) Å (Mg−N(1)) and 1.976(3) Å (Mg−N(2)), while the value for the 2-picoline ligand was 2.158(3) Å (Mg−N(3)). The fact that **7** crystallizes from hexane at −20 °C as the three-coordinate species, while **2** is obtained rather than **6** under similar conditions, illustrates the increased steric profile of the 2,6-lutidine ligand compared to the other pyridine-based ligands used in this study.

Complexes **6** and **7** are the first neutral, three-coordinate, monomeric magnesium compounds that have been structurally characterized. Three-coordinate magnesium centers have been structurally characterized in polynuclear complexes[10] and in several ionic complexes.[11] The extremely bulky nature of the bis(trimethylsilyl)amido ligand is probably the dominant contribution to the kinetic stability of **6** and **7**.

Discussion

The complexes described herein, especially **5**, represent extremely promising source compounds for doping semiconductor films. Compounds **1**−**7** are substantially more volatile than Cp_2Mg (sublimes at 160 °C in the same apparatus used to sublime **1**−**7**). Furthermore, **5** has a melting point of 94 °C and can be easily maintained in the liquid state for steady transport. While **1**−**7** contain silicon (a potential n-type dopant for group 13−15 semiconductors), the large excesses of ammonia that are typically used in the deposition of magnesium-doped semiconductor films[3] should remove the (trimethylsilyl)amide ligands as volatile and unreactive compounds that are swept out of the growth ambient. The identification of three-coordinate magnesium amides as stable, volatile structures should allow the synthesis of analogues that do not contain silicon or other potential dopants. We are continuing to pursue the synthesis of improved magnesium source compounds, as well the evaluation of these compounds for doping GaAs and GaN films.[12] These studies will be reported in due course.

Experimental Section

General Considerations. All manipulations were performed under argon using either drybox or Schlenk line techniques. Hexane was distilled over sodium. Benzene-d_6 was dried over 4-Å molecular sieves. 2,3,5-Collidine, 2-picoline, 4-picoline, 3,5-lutidine, and 2,6-lutidine were purchased commercially (Aldrich Chemical Co. or Acros Organics) and distilled from calcium hydride onto 4-Å molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were obtained at 300 and 75 MHz, respectively, in benzene-d_6. Infrared spectra were recorded using Nujol mulls. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points are uncorrected.

Bis(bis(trimethylsilyl)amido)bis(2,3,5-collidine)magnesium (1). A 100-mL Schlenk flask was charged with bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium (0.344 g, 0.703 mmol), a magnetic stir bar, and benzene (40 mL). 2,3,5-Collidine (0.196 g, 1.62 mmol) was then added to this solution. The mixture was stirred for 18 h at room temperature. The volatile components were removed at reduced pressure to afford a yellow-orange solid. This solid was extracted into hexane (10 mL) and the resultant solution was filtered through a 2-cm pad of Celite. The filtrate was cooled to −20 °C for 18 h to afford colorless blocks of **1** (0.330 g, 80%): mp 72−73 °C; IR (Nujol, cm^{-1}) 1249 (s), 1211 (m), 1148 (m), 1021 (s), 973 (s), 887 (s), 841 (s), 782 (s), 748 (s), 738 (s), 726 (s), 661 (s), 610 (s), 537 (s); ^{1}H NMR (C_6D_6, δ) 8.39 (s, 2,3,5-collidine C***H***), 6.63 (s, 2,3,5-collidine C***H***), 2.43 (s, 2,3,5-collidine C***H***$_3$), 1.81 (s, 2,3,5-collidine C***H***$_3$), 1.69 (s, 2,3,5-collidine C***H***$_3$), 0.33 (s, Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C_6D_6, ppm) 154.32 (s, 2,3,5-collidine ***C***CH$_3$), 147.00 (s, 2,3,5-collidine ***C***H), 139.41 (s, 2,3,5-collidine ***C***H), 132.00 (s, 2,3,5-collidine ***C***CH$_3$), 131.26 (s, 2,3,5-collidine ***C***CH$_3$), 22.04 (s, 2,3,5-collidine ***C***CH$_3$), 18.62 (s, 2,3,5-collidine C***C***H$_3$), 17.45 (s, 2,3,5-collidine C***C***H$_3$), 5.87 (s, Si(***C***H$_3$)$_3$).

Anal. Calcd for $C_{28}H_{58}MgN_4Si_4$: C, 57.25; H, 9.95; N, 9.54. Found: C, 56.25; H, 10.00; N, 9.61.

Bis(bis(trimethylsilyl)amido)bis(2-picoline)magnesium (2). In a fashion similar to the preparation of **1**, bis(bis(trimethylsilyl)amido)-

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(12) Cederberg, J. G.; Sebestl, J.; Winter, C. H.; Kuech, T. F. Work in progress.

bis(tetrahydrofuran)magnesium (0.497 g, 1.016 mmol) and 2-picoline (0.226 g, 2.43 mmol) were reacted in benzene (40 mL) to afford **2** as a pale orange solid (0.378 g, 70%). Complex **2** was extremely soluble in hexane and would not crystallize, even after extended cooling of concentrated solutions at −20 °C: mp 103−105 °C; IR (Nujol, cm^{-1}) 1277 (m), 1242 (s), 1160 (m), 1109 (m), 1061 (m), 1007 (s), 894 (s), 875 (s), 824 (s), 791 (s), 763 (s), 750 (s), 728 (m), 667 (s), 648 (m), 635 (m), 611 (s); ^{1}H NMR (C$_6$D$_6$, δ) 8.58 (broad d, 3- or 6-***H*** of 2-picoline), 6.71 (t, $J = 7.8$ Hz, 4- or 5-***H*** of 2-picoline), 6.37 (broad t, $J = 6.5$ Hz, 4- or 5-***H*** of 2-picoline), 6.28 (broad d, 3- or 6-***H*** of 2-picoline), 2.47 (s, C***H***$_3$ of 2-picoline), 0.30 (s, Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm) 158.41 (s, 2-***C*** of 2-picoline), 148.88 (s, ***C***H of 2-picoline), 139.52 (s, ***C***H of 2-picoline), 125.50 (s, ***C***H of 2-picoline), 121.94 (s, ***C***H of 2-picoline), 24.10 (s, C***C***H$_3$ of 2-picoline), 5.86 (s, Si(***C***H$_3$)$_3$).

Anal. Calcd for $C_{24}H_{50}MgN_4Si_4$: C, 54.25; H, 9.49; N, 10.54. Found: C, 45.58; H, 9.63; N, 8.79.

Bis(bis(trimethylsilyl)amido)bis(4-picoline)magnesium (3). In analogy with the preparation of **1**, bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium (0.491 g, 1.01 mmol) and 4-picoline (0.187 g, 2.01 mmol) were reacted in benzene (60 mL) for 18 h at room temperature. The volatile components were removed under reduced pressure to yield a yellow solid (0.520 g, 97%). The solid product was extracted into hexane (30 mL), and the resultant solution was filtered through a 2-cm pad of Celite. The filtrate was cooled to −20 °C for 24 h to afford colorless blocks of **3** (0.250 g, 48%): mp 125−126 °C; IR (Nujol, cm^{-1}) 1244 (s), 1213 (m), 1071 (m), 1020 (s), 991 (s), 891 (s), 831 (s), 778 (m), 747 (s), 662 (s), 610 (m), 539 (m); ^{1}H NMR (C$_6$D$_6$, δ) 8.46 (d of d, $J = 2.6$ Hz, 2- and 6-***H*** of 4-picoline), 6.39 (d, $J = 3.0$ Hz, 3- and 5-***H*** of 4-picoline), 1.61 (s, C***H***$_3$ of 4-picoline), 0.48 (s, Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm) 151.01 (s, 4-***C*** of 4-picoline), 150.10 (s, ***C***H of 4-picoline), 125.31 (s, ***C***H of 4-picoline), 20.58 (s, C***C***H$_3$ of 4-picoline), 6.87 (s, Si(***C***H$_3$)$_3$).

Anal. Calcd for $C_{24}H_{50}MgN_4Si_4$: C, 54.25; H, 9.49; N, 10.54. Found: C, 52.11; H, 9.46; N, 10.24.

Bis(bis(trimethylsilyl)amido)bis(3,5-lutidine)magnesium (4). In analogy with the preparation of **1**, bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium (0.690 g, 1.41 mmol) and 3,5-lutidine (0.303 g, 2.83 mmol) were reacted in benzene (60 mL) for 18 h at room temperature. Removal of the volatile components at reduced pressure afforded a bright yellow solid (0.780 g, 99%). The solid product was extratcted into hexane (50 mL), and the resultant solution was filtered through a 2-cm pad of Celite. The filtrate was cooled to −20 °C for 48 h to afford colorless blocks of **4** (0.450 g, 58%): mp 123−124 °C; IR (Nujol, cm^{-1}) 1244 (s), 1180 (m), 1153 (m), 1037 (m), 989 (s), 951 (m), 892 (s), 876 (s), 829 (s), 781 (m), 766 (m), 750 (s), 710 (s), 661 (s), 635 (m), 611 (m); ^{1}H NMR (C$_6$D$_6$, δ) 8.49 (broad s, 2- and 6-***H*** of 3,5-lutidine), 6.62 (broad s, 4-***H*** of 3,5-lutidine), 1.79 (s, C***H***$_3$ of 3,5-lutidine), 0.49 (s, Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm) 148.18 (s, 2- and 6-***C*** of 3,5-lutidine), 139.93 (s, ***C*** of 3,5-lutidine), 133.81 (s, ***C*** of 3,5-lutidine), 17.71 (s, C***C***H$_3$ of 3,5-lutidine), 6.86 (s, Si(***C***H$_3$)$_3$).

Anal. Calcd for $C_{26}H_{54}MgN_4Si_4$: C, 55.83; H, 9.73; N, 10.02. Found: C, 53.13; H, 9.61; N, 10.39.

Bis(bis(trimethylsilyl)amido)(2,3,5-collidine)magnesium (5). Sublimation of **1** (1.951 g, 3.321 mmol) at 90 °C (0.1 mmHg) in a 1-in. glass tube using a horizontal tube furnace afforded colorless blocks of **5** (0.816 g, 53%): mp 94 °C; IR (Nujol, cm^{-1}) 1241 (s), 1004 (s), 931 (w), 893 (m), 873 (s), 839 (s), 824 (s), 789 (w), 747 (m), 665 (m), 610 (m); ^{1}H NMR (C$_6$D$_6$, δ) 8.47 (s, 2,3,5-collidine C***H***), 6.53 (s, 2,3,5-collidine C***H***), 2.45 (s, 2,3,5-collidine C***H***$_3$), 1.74 (s, 2,3,5-collidine C***H***$_3$), 1.56 (s, 2,3,5-collidine C***H***$_3$), 0.34 (s, Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm) 154.21 (s, 2,3,5-collidine ***C***CH$_3$), 146.54 (s, 2,3,5-collidine ***C***H), 141.56 (s, 2,3,5-collidine ***C***CH$_3$), 133.74 (s, 2,3,5-collidine ***C***H), 132.49 (s, 2,3,5-collidine ***C***CH$_3$), 21.80 (s, 2,3,5-collidine C***C***H$_3$), 18.46 (s, 2,3,5-collidine C***C***H$_3$), 17.23 (s, 2,3,5-collidine C***C***H$_3$), 5.86 (s, N(Si(***C***H$_3$)$_3$)$_2$).

Anal. Calcd for $C_{20}H_{47}MgN_3Si_4$: C, 51.52; H, 10.16; N, 9.01. Found: C, 48.10; H, 9.85; N, 8.49.

Bis(bis(trimethylsilyl)amido)(2-picoline)magnesium (6). Sublimation of **2** (0.366 g, 0.689 mmol) at 115 °C (0.1 mmHg) in a 1-in. glass tube using a horizontal tube furnace afforded colorless blocks of **6** (0.138 g, 46%): mp 110−111 °C; IR (Nujol, cm^{-1}) 1305 (m), 1277 (m), 1242 (s), 1160 (m), 1061 (m), 999 (s), 894 (s), 875 (s), 826 (s), 793 (s), 763 (s), 750 (s), 728 (m), 667 (s), 648 (m), 635 (m), 611 (m); ^{1}H NMR (C$_6$D$_6$, δ) 8.57 (broad d, 3- or 6-***H*** of 2-picoline), 6.73 (t, $J = 7.8$ Hz, 4- or 5-***H*** of 2-picoline), 6.38 (broad t, $J = 6.3$ Hz, 4- or 5-***H*** of 2-picoline), 6.30 (broad d, 3- or 6-***H*** of 2-picoline), 2.47 (s, C***H***$_3$ of 2-picoline), 0.31 (s, Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm) 158.41 (s, 2-***C*** of 2-picoline), 148.84 (s, ***C***H of 2-picoline), 139.68 (s, ***C***H of 2-picoline), 125.60 (s, ***C***H of 2-picoline), 122.02 (s, ***C***H of 2-picoline), 24.05 (s, C***C***H$_3$ of 2-picoline), 5.84 (s, Si(***C***H$_3$)$_3$).

Anal. Calcd for $C_{18}H_{43}MgN_3Si_4$: C, 49.34; H, 9.89; N, 9.59. Found: C, 47.64; H, 9.74; N, 9.31.

Bis(bis(trimethylsilyl)amido)(2,6-lutidine)magnesium (7). A 100-mL Schlenk flask was charged with bis(bis(trimethylsilyl)amido)bis(tetrahydrofuran)magnesium (0.863 g, 1.77 mmol), a magnetic stir bar, and benzene (60 mL). 2,6-Lutidine (0.189 g, 1.77 mmol) was then added to this solution. The mixture was stirred for 18 h at room temperature. Removal of the volatile components under reduced pressure afforded a bright yellow solid (0.750 g, 94%). The solid product was extratcted into hexane (50 mL), and the resultant solution was filtered through a 2-cm pad of Celite on a coarse glass frit. The filtrate was maintained at −20 °C for 48 h to afford colorless blocks of **7** (0.422 g, 56%): mp 157−159 °C; IR (Nujol, cm^{-1}) 1277 (m), 1242 (s), 1168 (m), 1110 (m), 992 (s), 875 (s), 823 (s), 784 (s), 750 (s), 667 (s), 634 (m), 612 (m), 570 (s); ^{1}H NMR (C$_6$D$_6$, δ) 6.68 (t, $J =$ 7.7 Hz 4-***H*** of 2,6-lutidine), 6.20 (d, $J = 3.9$ Hz 3- and 5-***H*** of 2,6-lutidine), 2.60 (s, C***H***$_3$ of 2,6-lutidine), 0.31 (s, Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm) 158.02 (s, 2- and 6-***C*** of 2,6-lutidine), 140.06 (s, 3- and 5-***C***H of 2,6-lutidine), 123.07 (s, 4-***C***H of 2,6-lutidine), 24.76 (s, C***C***H$_3$ of 2,6-lutidine), 5.79 (s, Si(***C***H$_3$)$_3$).

Anal. Calcd for $C_{19}H_{45}MgN_3Si_4$: C, 50.46; H, 10.03; N, 9.29. Found: C, 48.11; H, 9.91; N, 9.27. Crystals suitable for X-ray crystallography were grown by sublimation at 100 °C (0.1 mmHg).

Reaction of 5 with 2,3,5-Collidine To Afford 1. A 100-mL Schlenk flask was charged with **5** (0.245 g, 0.525 mmol)), 2,3,5-collidine (0.0749 mL, 0.578 mmol), hexane (30 mL), and a stir bar. The reaction mixture was stirred for 18 h at 23 °C, and the flask was then placed in a −20 °C freezer. After 48 h, crystals of **1** were isolated (0.141 g, 46%). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** isolated in this way were identical to those of material prepared as described above.

Crystallization of 1 from 5 in Hexane. A 100-mL Schlenk flask was charged with **5** (0.320 g, 0.686 mmol) and hexane (10 mL). The flask was placed in a −20 °C freezer. After 1 week, crystals of **1** were isolated (0.056 g, 14%). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** isolated in this way were identical to those of material prepared as described above.

Crystal Structure Determinations of 1, 3, 6, and 7. Single-crystal diffraction data were collected at ambient temperature on a Siemens/Bruker P4-CCD diffractometer with the SMART collection software and SAINT processing. For each structure, a hemisphere of data was collected with 10 s frames at 0.3° between each frame and resolution out to 56° in 2θ. All samples were sealed in thin-walled glass capillaries under an inert atmosphere for use in the diffraction experiment. Absorption corrections were applied with the program SADABS,[13] and the structures were solved and refined on F^2 with the programs of SHELXS and SHELXL-93.[13] Table 1 lists the crystallographic parameters. All of the magnesium crystals reported herein were obtained as large masses grown together in different orientations, and the problem was to cut a fragment with integrity from the solid. Multiple trials with each compound were necessary to obtain a fragment suitable for the diffraction experiment.

A colorless crystalline fragment (0.7 × 0.3 × 0.4 mm^3) of **1** yielded 17 874 total raw reflections; 4005 reflections were obtained after averaging ($R_{\text{int}} = 0.048$). Hydrogen atoms were placed in observed positions and refined isotropically; all other atoms were anisotropically described. The asymmetric unit contains one-half molecule on a

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(13) Sheldrick, G. SHELXS-86 and SHELXL-93, University of Göttingen, Germany, 1986 and 1993, respectively.

crystallographic 2-fold axis. The final *R* values including all data were R1 = 0.081 and wR2 = 0.117.

Crystals of **3** were obtained as irregular colorless crystals. A fragment of dimensions 0.45 × 0.45 × 0.35 mm^3 was chosen for data collection. A total of 16 479 reflections were integrated from the 1390 frames; 6742 reflections were obtained after averaging (R_{int}= 0.022). Hydrogen atoms were placed in observed positions and refined isotropically; all other atoms were anisotropically described. The asymmetric unit contains one molecule. The final *R* values including all data were R1 = 0.072 and wR2 = 0.133.

A colorless irregular crystal of **6** of dimensions 0.36 × 0.28 × 0.26 mm^3 produced 29 445 integrated reflections which averaged into 6477 unique data with R_{int}= 0.13. Hydrogen atoms were placed in calculated positions; all other atoms were anisotropically refined. The asymmteric unit consists of one neutral molecule showing positional disorder in the trimethylsilane groups. The final *R* values including weak data reflect the disorder problem, but the identification of the structure is unambiguous: R1 = 0.25 and wR2 = 0.24.

A colorless crystal of **7** of dimensions 0.40 × 0.28 × 0.26 mm^3 was cut and sealed in a capillary. A total of 30 663 integrated reflections averaged into 6681 unique data with R_{int}= 0.013. Hydrogen atoms were placed in calculated positions, while all others were described anisotropically. One molecule was present in the asymmetric unit. Final *R* values including weak reflections were R1 = 0.23 and wR2 = 0.20.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **3**, **4**, **6**, and **7** are available on the Internet only. Access information is given on any current masthead page.

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