Synthesis, Structure, and Properties of Magnesium Complexes Containing Mixed Cyclopentadienyl and Amido Ligand Sets

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Received May 24, 2002

$[CpMgMe(Et_2O)]_2$ was prepared by dissolving Cp_2Mg and dimethylmagnesium together in diethyl ether. It reacted readily with diphenylamine, 3-amino-2,4-dimethylpentane, 2,6-diisopropylaniline, *N*-isopropylbenzylamine, and diisopropylamine in diethyl ether to afford the dimeric amido complexes $[CpMg(NPh_2)]_2$ (83%), $[CpMg(NHCH(CH(CH_3)_2)_2)]_2$ (75%), $[CpMg(NH^iPr_2C_6H_3)]_2$ (61%), $[CpMg(N(^iPr)(CH_2Ph))]_2$ (62%), and $[CpMg(N^iPr_2)]_2$ (81%) as colorless crystalline solids. Treatment of $[CpMgMe(Et_2O)]_2$ with *N*,*N*,*N*′-trimethylethylenediamine in diethyl ether yielded dimeric $[CpMg(MeNCH_2CH_2NMe_2)]_2$ (76%). The reaction of $[CpMgMe(Et_2O)]_2$ with 2,5-bis(dimethylaminomethyl)pyrrole in diethyl ether led to the formation of the monomeric magnesium pyrrolato complex $[CpMg(Et_2O)(\eta^2\text{-}Me_2NCH_2(C_4H_2N)CH_2NMe_2)]$ (70%). The X-ray crystal structures of $[CpMg(NPh_2)]_2$, $[CpMg(NHCH(CH(CH_3)_2)_2)]_2$, $[CpMg(NH^iPr_2C_6H_3)]_2$, $[CpMg(N(^iPr)(CH_2Ph))]_2$, and $[CpMg(Et_2O)(\eta^2\text{-}Me_2NCH_2(C_4H_2N)CH_2NMe_2)]$ were determined. In the solid state structures, $[CpMg(NPh_2)]_2$, $[CpMg(NHCH(CH(CH_3)_2)_2)]_2$, $[CpMg(NH^iPr_2C_6H_3)]_2$, and $[CpMg(N(^iPr)(CH_2Ph))]_2$ contain one η^5-cyclopentadienyl ligand per magnesium and almost perfectly square Mg_2N_2 cores. The complex $[CpMg(Et_2O)(\eta^2\text{-}Me_2NCH_2(C_4H_2N)CH_2NMe_2)]$ contains one η^5-cyclopentadienyl ligand, one diethyl ether ligand, and one η^2-2,5-bis(dimethylaminomethyl)pyrrolato ligand.

Introduction

Magnesium-doped group 13 nitride semiconductors are widely used in the fabrication of blue and green light-emitting diodes and blue and green laser diodes and in microelectronic devices.[1] These materials are prepared by chemical vapor deposition (CVD) employing a group 13 alkyl, ammonia, and volatile magnesium source compound.[1,2] Over the past twenty years, magnesocene (Cp_2Mg) has been the most widely used dopant precursor in CVD processes.[2] Despite the importance of magnesium-doped group 13 nitride materials, virtually nothing is known about the chemical steps by which Cp_2Mg is converted to optically active defects within the group 13 nitride host materials. We have recently reported that treatment of Cp_2Mg with primary alkylamines results in the formation of adducts of the formula $Cp_2Mg(NH_2R)$.[3] $Cp_2Mg(NH_2R)$ showed no tendency to eliminate cyclopentadiene upon thermolysis at temperatures of up to 200 °C. It is reasonable to expect that magnesium complexes containing amido ligands lie along the film forming reaction coordinate with Cp_2Mg and ammonia and that such species are derived from the elimination of cyclopentadiene through proton transfer from nitrogen to carbon within the coordination sphere of $Cp_2Mg(NH_3)_x$. To gain insight into the formation, structure, and properties of potential models for intermediate species, we set out to prepare cyclopentadienylmagnesium amides of the formula $[CpMg(NRR'_2)]_x$. To date, there are no crystallographically characterized magnesium complexes containing mixed cyclopentadienyl and amido ligand sets. Power has reported the synthesis and spectral characterization of $CpMg(NH^iPr_2C_6H_3)(THF)$, which was made by treatment of Cp_2Mg with 2,6-diisopropylaniline in tetrahydrofuran.[4] Herein, we describe the synthesis, structure, and properties of a series of cyclopentadienylmagnesium complexes that contain primary and secondary amido substituents. These complexes were prepared either by the direct reaction of anilines with Cp_2Mg or by treatment of $[CpMgMe(Et_2O)]_2$ with primary or secondary amines. X-ray crystal structures demonstrate mono-

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10.1021/om020412b CCC: $22.00
Publication on Web 10/02/2002

meric and dimeric structures, depending upon the bulk of the nitrogen atom carbon substituents, the presence of a pendant Lewis base, or solvent coordination. These complexes serve as structural models for species that might be important in film growth and also provide the first detailed insight into magnesium complexes containing mixed cyclopentadienyl and amido ligand sets.

Results

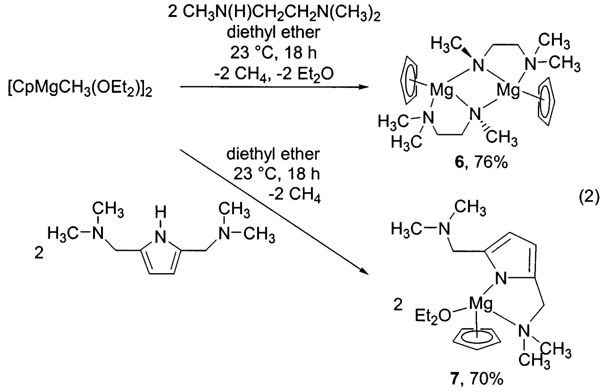
Synthetic Chemistry. Treatment of Cp_2Mg with diphenylamine at ambient temperature in toluene or diethyl ether afforded the dimeric amido complex $[CpMg(NPh_2)]_2$ (**1**) as colorless crystals. However, this reaction was extremely slow and only proceeded to about 30% completion after 72 h at ambient temperature. Furthermore, alkylamines only formed adducts with Cp_2Mg, consistent with our recent report.[3] To obtain a general route to mixed cyclopentadienyl amido complexes, we sought a more reactive starting material. The complex $[CpMgMe(Et_2O)]_2$ is easily prepared from redistribution of Cp_2Mg and dimethylmagnesium in diethyl ether[5] and should be more reactive than Cp_2Mg toward protonation reactions. $[CpMgMe(Et_2O)]_2$ reacted readily with diphenylamine, 3-amino-2,4-dimethylpentane, 2,6-diisopropylaniline, *N*-isopropylbenzylamine, and diisopropylamine in diethyl ether to afford the dimeric amido complexes $[CpMg(NPh_2)]_2$ (**1**, 83%), $[CpMg(NHCH(CH(CH_3)_2)_2)]_2$ (**2**, 75%), $[CpMg(NH^iPr_2C_6H_3)]_2$ (**3**, 61%), $[CpMg(N(^iPr)(CH_2Ph))]_2$ (**4**, 62%), and $[CpMg(N^iPr_2)]_2$ (**5**, 81%) as colorless crystalline solids (eq 1). The structural assignments were based on the spectral and analytical data. In addition, the X-ray crystal structures of compounds **1**−**4** were determined and are described below. In the solid state structures, **1**−**4** are dimeric and contain one η^5-cyclopentadienyl ligand per magnesium atom and almost perfectly square Mg_2N_2 cores. The solid state structures of **2**−**4** feature exclusive *anti*-disposition of the larger substituents on the nitrogen atoms.

$$[CpMgCH_3(OEt_2)]_2 + 2\ NHRR' \xrightarrow[-2\ CH_4,\ -2\ Et_2O]{\text{diethyl ether, } 23\ °C,\ 18\ h} [CpMg(NRR')]_2 \quad (1)$$

1, R = R' = Ph, 83%
2, R = H, R' $=CH(CH(CH_3)_2)_2$, 75%
3, R = H, R' $=2,6-(CH(CH_3)_2)_2C_6H_3$, 61%
4, R $= CH(CH_3)_2$, R' $=CH_2Ph$, 62%
5, R = R' $= CH(CH_3)_2$, 81%

Compounds **1**−**5** are stable at ambient temperature under inert atmosphere. The primary amido complexes **2** and **3** do not eliminate cyclopentadiene, even upon refluxing in toluene for 18 h. In addition, **1**−**5** do not react further with excess amine upon refluxing in toluene for 18 h. The ^1H NMR spectra of **1**−**5** contain cyclopentadienyl singlets ranging from δ 5.94 to 6.28, which are close to that of Cp_2Mg (δ 5.97). The ^{13}C NMR spectra contain cyclopentadienyl singlets ranging from 106.14 to 106.53 ppm, which are again similar to that of Cp_2Mg (107.74 ppm). The variable-temperature NMR spectra of **1**−**7** are described below.

The reactivity of $[CpMgMe(Et_2O)]_2$ toward several chelating amines was examined to determine if monomeric complexes could be obtained by saturating the coordination sphere of the magnesium ion with additional neutral donor atoms. Thus, treatment of $[CpMgMe(Et_2O)]_2$ with trimethylethylenediamine and 2,5-bis(dimethylaminomethyl)pyrrole in diethyl ether at ambient temperature afforded $[CpMg(MeNCH_2CH_2NMe_2)]_2$ (**6**, 76%) and $[CpMg(Et_2O)(Me_2NCH_2(C_4H_2N)CH_2NMe_2)]$ (**7**, 70%), respectively, as colorless (**6**) or yellow (**7**) solids after workup and crystallization from dichloromethane/hexane (eq 2). The formulations **6** and **7** were assigned on the basis of the spectral and analytical data and by X-ray crystal structure determinations. The molecular structure of **7** is described below. A low-precision X-ray crystal structure determination was carried out on **6**. While the data were not of sufficient quality to present herein, the dimeric structure and ligand arrangement were unambiguously established. The NMR spectra of **6** and **7** are described below.



Volatility Study. To assess their initial viability as CVD precursors, compounds **1**−**7** were evaluated for their volatility. At 0.05 Torr, **2** and **3** sublimed at 160 and 210 °C, respectively, to afford unchanged **2** (58%) and **3** (46%) as colorless crystals. The ^1H and $^{13}C\{^1H\}$ NMR spectra of sublimed **2** and **3** were identical to materials before sublimation, demonstrating that no reaction occurred during the sublimation process. By contrast, sublimation of **4** afforded the magnesocene adduct $Cp_2Mg(NH(^iPr)(CH_2Ph))$ (**8**, 46%, eq 3). Complex **8** can be alternatively prepared by treatment of Cp_2Mg with *N*-isopropylbenzylamine.[3] Complexes **1** and **5**−**7** do not sublime below 200 °C at 0.05 Torr and instead decompose at the heated end of the sublimation apparatus.

$$\underset{\mathbf{4}}{[CpMg(N(iPr)(CH_2Ph))]_2} \xrightarrow[0.05\ torr]{\text{sublimation, } 170\ °C} \underset{\mathbf{8},\ 46\%}{Cp_2Mg(NH(iPr)(CH_2Ph))} + \text{products} \quad (3)$$

Crystal Structures. To establish the solid state geometries, the X-ray crystal structures of **1**−**4** and **7** were determined. Crystallographic data are summarized in Table 1. Selected bond distances and angles are given in Tables 2−6. Perspective views of **1**−**4** and **7** are presented in Figures 1−5.

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Table 1. Crystal Data and Data Collection Parameters for 1−4 and 7

	1	**2**	**3**	**4**	**7**
empirical formula	$C_{34}H_{30}Mg_2N_2$	$C_{24}H_{42}\,Mg_2N_2$	$C_{34}H_{46}Mg_2N_2$	$C_{30}H_{38}Mg_2N_2$	$C_{19}H_{33}MgN_3O$
fw	515.22	407.22	531.34	475.24	343.79
space group	*P*2(1)/*c*	*Pbca*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	8.8142(11)	13.1435(16)	10.5688(12)	10.2789(11)	9.1153(5)
b (Å)	17.121(3)	10.0446(11)	15.5244(16)	14.9156(18)	11.5764(6)
c (Å)	19.086(3)	19.220(2)	10.7148(12)	17.664(2)	20.2425(11)
β (deg)	91.401(3)		109.693(2)	93.830(2)	100.912(2)
V (Å^3)	2879.3(7)	2537.4(5)	1655.2(3)	2702.2(6)	2097.4(2)
Z	4	4	2	4	4
temp (K)	295(2)	295(2)	295(2)	295(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
calcd (g cm^{-3})	1.189	1.066	1.066	1.168	1.089
μ (mm^{-1})	0.108	0.106	0.095	0.109	0.094
$R(F)^a$ (%)	3.59	3.95	3.68	4.38	4.93
$R_w(F^2)^a$ (%)	5.29	9.13	9.06	9.77	11.83

[a] $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$; $R_w(F^2) = \sum\{w(F_o{}^2 - F_c{}^2)^2]/\sum[(wF_o{}^2)^2]^{1/2}$ for $I > 2\sigma(I)$. Quantity minimized = $R_w(F^2)$ for all data.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

Mg(1)−C(25)	2.327(3)	Mg(1)−C(26)	2.350(3)
Mg(1)−C(27)	2.331(3)	Mg(1)−C(28)	2.313(3)
Mg(1)−C(29)	2.326(3)	Mg(2)−C(30)	2.350(3)
Mg(2)−C(31)	2.311(3)	Mg(2)−C(32)	2.300(3)
Mg(2)−C(33)	2.319(4)	Mg(2)−C(34)	2.327(4)
Mg(1)−N(1)	2.1153(17)	Mg(1)−N(2)	2.1050(16)
Mg(2)−N(1)	2.0934(16)	Mg(2)−N(2)	2.1092(17)
N(1)−C(1)	1.434(2)	N(1)−C(7)	1.425(2)
N(2)−C(13)	1.437(2)	N(2)−C(19)	1.424(2)
Mg(1)−Cp1	2.017(2)	Mg(2)−Cp2	2.019(2)
Mg(1)−Mg(2)	2.9859(9)		

Mg(1)−N(1)−Mg(2)	90.38(6)	Mg(1)−N(2)−Mg(2)	90.23(6)
N(1)−Mg(1)−N(2)	89.31(6)	N(1)−Mg(2)−N(2)	89.79(6)
N1(1)−Mg(1)−Cp1	134.5(2)	N(2)−Mg(1)−Cp1	135.9(2)
N(1)−Mg(2)−Cp2	133.2(2)	N(2)−Mg(2)−Cp2	136.8(2)

[a] Cp indicates the centroid of the cyclopentadienyl ligands.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2[a]

Mg(1)−C(8)	2.378(2)	Mg(1)−C(9)	2.374(2)
Mg(1)−C(10)	2.382(2)	Mg(1)−C(11)	2.393(2)
Mg(1)−C(12)	2.381(2)	Mg(1)−N(1)	2.0841(16)
Mg(1)−N(1)′	2.0578(15)	Mg(1)−Mg(1)′	2.9312(11)
N(1)−C(1)	1.484(2)	Mg(1)−Cp	2.0706(11)

N(1)−Mg(1)−N(1)′	89.91(6)	Mg(1)−N(1)−Mg(1)′	90.09(6)
Mg(1)−N(1)−C(1)	118.33(12)	Mg(1)′−N(1)−C(1)	128.72(11)

[a] Cp indicates the centroid of the cyclopentadienyl ligands.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3[a]

Mg(1)−C(1)	2.357(2)	Mg(1)−C(2)	2.3337(19)
Mg(1)−C(3)	2.339(2)	Mg(1)−C(4)	2.3708(19)
Mg(1)−C(5)	2.3845(19)	Mg(1)−N(1)	2.0791(13)
Mg(1)−N(1)′	2.0772(12)	Mg(1)−Mg(1)′	2.9884(9)
N(1)−C(6)	1.4276(17)	Mg(1)−Cp	2.0425(9)

Mg(1)−N(1)−Mg(2)	91.95(5)	N(1)−Mg(1)−N(1)′	88.05(5)
Mg(1)−N(1)−C(6)	122.88(9)	Mg(1)′−N(1)−C(6)	126.56(9)

[a] Cp indicates the centroid of the cyclopentadienyl ligands.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4[a]

Mg(1)−C(21)	2.361(4)	Mg(1)−C(22)	2.363(4)
Mg(1)−C(23)	2.386(3)	Mg(1)−C(24)	2.390(3)
Mg(1)−C(25)	2.359(3)	Mg(2)−C(26)	2.414(3)
Mg(2)−C(27)	2.385(3)	Mg(2)−C(28)	2.354(3)
Mg(2)−C(29)	2.385(3)	Mg(2)−C(30)	2.409(3)
Mg(1)−N(1)	2.0940(18)	Mg(1)−N(2)	2.1068(17)
Mg(2)−N(1)	2.1091(18)	Mg(2)−N(2)	2.0885(17)
N(1)−C(1)	1.490(3)	N(1)−C(4)	1.493(3)
N(2)−C(11)	1.487(3)	N(2)−C(14)	1.487(3)
Mg(1)−Cp1	2.086(3)	Mg(2)−Cp2	2.083(3)

Mg(1)−N(1)−Mg(2)	89.42(7)	Mg(1)−N(2)−Mg(2)	89.63(7)
N(1)−Mg(1)−N(2)	90.42(7)	N(1)−Mg(2)−N(2)	90.50(7)
Mg(1)−N(1)−C(1)	116.40(13)	Mg(1)−N(1)−C(4)	110.82(14)
Mg(1)−N(2)−C(11)	108.11(13)	Mg(1)−N(2)−C(14)	117.47(14)
Mg(2)−N(1)−C(1)	107.27(13)	Mg(2)−N(1)−C(4)	117.74(15)
Mg(2)−N(2)−C(11)	117.11(13)	Mg(2)−N(2)−C(14)	110.12(13)
N(1)−Mg(1)−Cp1	132.0(1)	N(2)−Mg(1)−Cp1	135.9(1)
N(1)−Mg(2)−Cp2	135.5(1)	N(2)−Mg(2)−Cp2	132.5(1)

[a] Cp indicates the centroid of the cyclopentadienyl ligands.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 7[a]

Mg(1)−C(15)	2.428(3)	Mg(1)−C(16)	2.427(3)
Mg(1)−C(17)	2.426(3)	Mg(1)−C(18)	2.425(3)
Mg(1)−C(19)	2.419(3)	Mg(1)−N(1)	2.2247(18)
Mg(1)−N(2)	2.0432(16)	Mg(1)−O(1)	2.0940(18)
Mg(1)−Cp	2.139(3)		

N(1)−Mg(1)−N(2)	82.73(7)	N(1)−Mg(1)−O(1)	91.82(6)
N(2)−Mg(1)−O(1)	100.07(6)	N(1)−Mg(1)−Cp	122.8(2)
N(2)−Mg(1)−Cp	129.4(2)	O(1)−Mg(1)−Cp	119.5(2)

[a] Cp indicates the centroid of the cyclopentadienyl ligands.

Complex **1** crystallizes as a dimer, with the cyclopentadienylmagnesium fragments being held together by μ_2-diphenylamido ligands. The Mg_2N_2 ring is nearly perfectly planar, and the plane containing the ipso carbon atoms of the phenyl rings approximately bisects the Mg_2N_2 plane. The cyclopentadienyl ligands are bonded to the magnesium centers in an η^5-fashion, with magnesium−carbon bond lengths that range from 2.30 to 2.35 Å. The magnesium−cyclopentadienyl centroid distances are 2.017(2) and 2.019(2) Å. The magnesium−nitrogen bond lengths range between 2.09 and 2.12 Å. The sum of angles in the Mg_2N_2 core is 359.71°.

Complex **2** crystallizes as a dimer, with the cyclopentadienylmagnesium fragments being held together by μ_2-2,4-dimethyl-3-amidopentane ligands. The Mg_2N_2 ring is planar by symmetry. The organic groups bonded to the nitrogen atoms adopt an *anti*-configuration across the Mg_2N_2 core. The cyclopentadienyl ligands are bonded to the magnesium centers in an η^5-fashion, with magnesium−carbon bond lengths that range from 2.37 to 2.39 Å. The magnesium−cyclopentadienyl centroid distance is 2.0706(11) Å. These values are slightly longer than the related bond lengths in **1** and indicate slightly more crowded coordination spheres about the magnesium atoms in **2**. The magnesium−nitrogen bond lengths are 2.0578(15) and 2.0841(16) Å. These values are slightly shorter than those of **1** and reflect the better

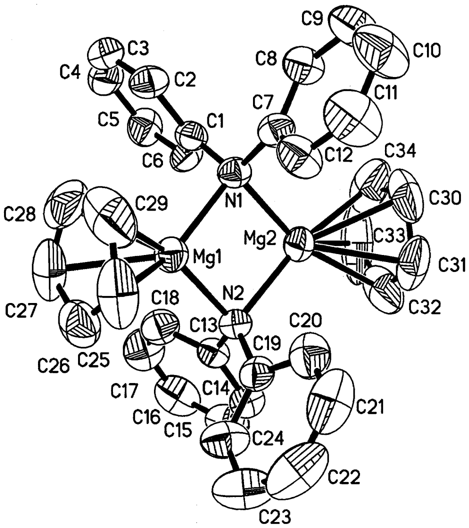


Figure 1. Perspective view of **1** with probability ellipsoids at the 50% level.

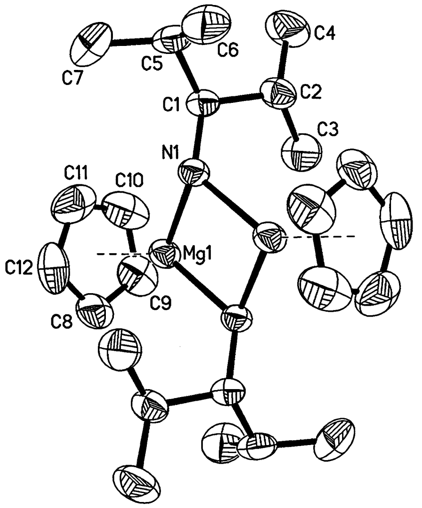


Figure 2. Perspective view of **2** with probability ellipsoids at the 50% level.

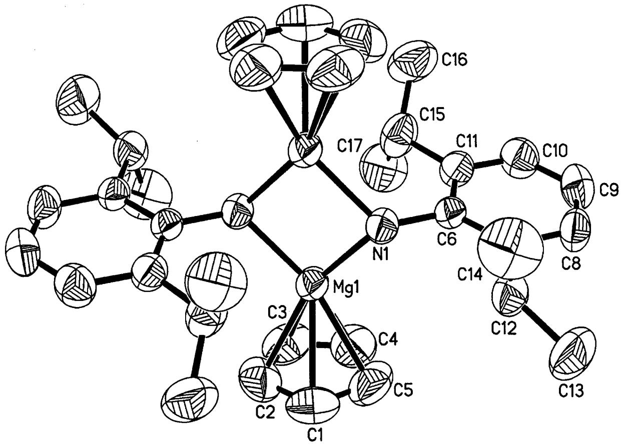


Figure 3. Perspective view of **3** with probability ellipsoids at the 50% level.

donor capability of an alkylamido ligand compared to the diphenylamido ligand. The sum of angles in the Mg_2N_2 core is 360.00°.

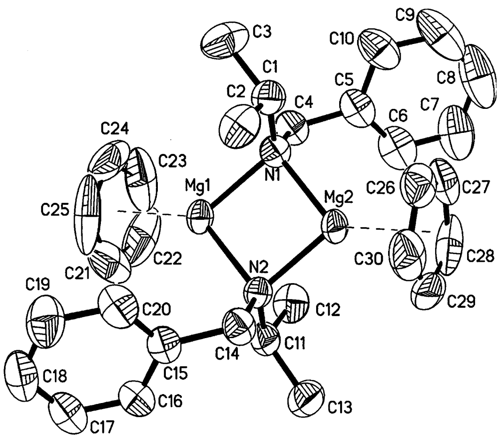


Figure 4. Perspective view of **4** with probability ellipsoids at the 50% level.

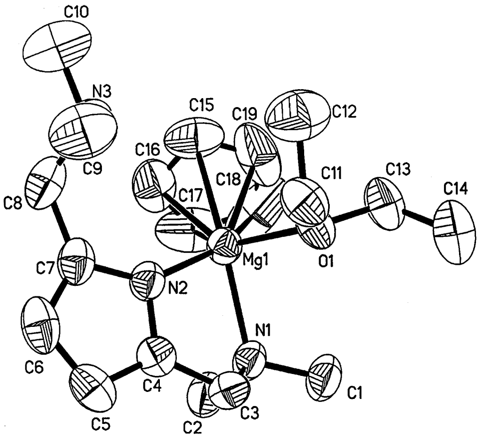


Figure 5. Perspective view of **7** with probability ellipsoids at the 50% level.

Complex **3** crystallizes as a dimer, with the cyclopentadienylmagnesium fragments being held together by μ_2-2,6-diisopropylphenylamido ligands. The 2,6-diisopropylphenylamido ligands adopt an *anti*-configuration within the dimer. The Mg_2N_2 ring is planar by symmetry. The cyclopentadienyl ligands are bonded to the magnesium centers in an η^5-fashion, with magnesium–carbon bond lengths that range from 2.33 to 2.38 Å. The magnesium–cyclopentadienyl centroid distance is 2.0425(9) Å. The magnesium–nitrogen bond lengths are 2.0772(12) and 2.0791(13) Å. These values are slightly shorter than those of **1** and are similar to the values observed in **2**. The sum of angles in the Mg_2N_2 core is 360.00°.

Complex **4** crystallizes as a dimer, with the cyclopentadienylmagnesium fragments being held together by μ_2-*N*-isopropylbenzylamido ligands. The benzyl groups bonded to the nitrogen atoms adopt an *anti*-configuration within the dimer. The Mg_2N_2 ring is planar. The cyclopentadienyl ligands are bonded to the magnesium atoms in an η^5-fashion, with magnesium–carbon bond lengths that range from 2.36 to 2.39 Å. The magnesium–cyclopentadienyl centroid distances are 2.086(3) and 2.083(3) Å. The magnesium–nitrogen bond lengths range between 2.09 and 2.11 Å. These values are slightly longer than those observed in **2** and **3** and are similar to the values observed in **1**. The sum of angles in the Mg_2N_2 core is 359.97°.

Compound **7** exists as a monomeric complex that has a cyclopentadienyl ligand, a diethyl ether ligand, and an η^2-2,5-bis(dimethylaminomethyl)pyrrolato ligand in

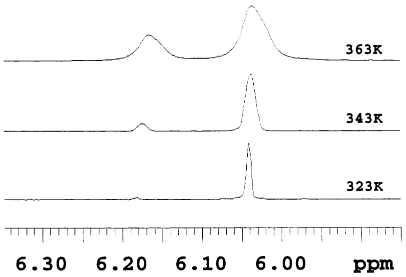


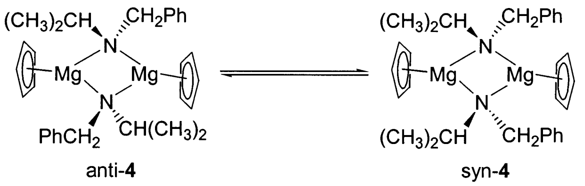
Figure 6. ^{1}H NMR spectra of **4** in toluene-d_8 taken at the indicated temperatures.

Table 7. Equilibrium Constants for 4 at Various Temperatures

T (K)	K_{eq}
313	0.046
323	0.068
333	0.116
343	0.184
353	0.304
363	0.452

which only one dimethylamino moiety coordinates to magnesium. The cyclopentadienyl ligand is bonded to the magnesium ions in an η^5-fashion, with magnesium−carbon bond lengths that range between 2.42 and 2.43 Å. The magnesium−cyclopentadienyl centroid distance is 2.139(3) Å. These values are longer than those observed in **1**−**4** and reflect the increased coordination number of the magnesium center in **7**. The magnesium−nitrogen bond lengths are 2.043(2) (to N(2)) and 2.225(2) Å (to N(1)). The magnesium−oxygen bond length is 2.0940(14) Å.

Van't Hoff Analysis for 4. Variable-temperature ^{1}H NMR spectra of **4** were recorded between 40 and 100 °C in toluene-d_8. Figure 6 shows the cyclopentadienyl resonance region in the ^{1}H NMR spectra that were obtained at various temperatures. At or below ambient temperature, a single cyclopentadienyl resonance was observed that appears to correspond to the dimeric *anti*-**4** that is observed in the solid state. Between 40 and 100 °C, two sharp cyclopentadienyl singlets were observed, and their relative intensities changed with temperature. This observation is consistent with an equilibrium between *anti*-**4** and *syn*-**4** (eq 4). Equilibrium constants (K_{eq}) for the *syn*−*anti* equilibrium were determined from the concentrations of the two cyclopentadienyl resonances calculated from the ^{1}H NMR spectra at various temperatures and are given in Table 7. Analysis of these data for conversion of the *anti*-**4** to *syn*-**4** using standard procedures for van't Hoff analyses[6] afforded $\Delta H° = 10.4 \pm 0.2$ kcal/mol, $\Delta S° = 26.9 \pm 0.2$ cal/mol·K, and $\Delta G°(298\ K) = 1.9 \pm 0.2$ kcal/mol. Hence, the unfavorable enthalpy for conversion of *anti*-**4** to *syn*-**4** is offset by the $T\Delta S°$ term when the temperature is sufficiently high.



(4)

Variable-Temperature NMR Spectra of 1−3 and 5−7.

The NMR spectra of **1**−**3**, **5**, and **6** revealed several different types of behavior. Complexes **1**, **2**, and **5** each exhibit a single sharp cyclopentadienyl proton resonance at δ 5.84, 6.28, and 6.21, respectively, at ambient temperature in benzene-d_6. Even at 130 °C in toluene-d_8, **2** still showed a sharp singlet at δ 6.28 for the cyclopentadienyl protons, suggesting that a *syn*−*anti* equilibrium similar to that of **4** is inaccessible even at higher temperatures. At ambient temperature in toluene-d_8, analytically pure **3** exhibited three cyclopentadienyl proton resonances at δ 6.19, 6.15, and 6.06 in a 46:46:8 ratio. The ratio of the three cyclopentadienyl resonances did not change between 0 and −80 °C, perhaps due to slow rates of exchange at these temperatures. Upon warming from ambient temperature to 70 °C, the resonance at δ 6.19 gradually reduced in relative intensity and disappeared at 70 °C. The ^{1}H NMR spectrum at 70 °C showed cyclopentadienyl resonances at δ 6.10 and 6.04 in a ratio of 86:14. The behavior may correspond to a mixture of *anti*-**3**, *syn*-**3**, and the monomeric species CpMg(NH(2,6-^{i}Pr$_2$C$_6$H$_3$)). The large steric profile of the 2,6-diisopropylphenylamido ligand may destabilize *anti*-**3** and *syn*-**3** sufficiently so that monomeric CpMg(NH(2,6-^{i}Pr$_2$C$_6$H$_3$)) can exist in solution. At ambient temperature in benzene-d_6, the ^{1}H NMR spectrum of **6** revealed a singlet at δ 6.19 for the cyclopentadienyl protons, three singlets for the nitrogen-bound methyl groups (δ 2.16, 1.69, 1.67), and four distinct resonances for the diastereotopic protons of the ethylene bridge in the nitrogen ligand. These data are consistent with retention of a dimeric structure in solution, where the rate of dissociation of the neutral dimethylamino moieties is slow on the NMR time scale.

The ^{1}H NMR spectrum of **7** at ambient temperature revealed broad singlets at δ 6.29 for the cyclopentadienyl protons, as well as broad singlets at δ 6.00, 3.32, and 1.99 for the 2,5-bis(dimethylaminomethyl)pyrrolato ligand. Also observed were sharp resonances for free diethyl ether. The fact that the resonances for the cyclopentadienyl and pyrrolato ligands were broad suggested an exchange process that is more complex than intramolecular exchange between the coordinated and uncoordinated dimethylamino moieties. Upon cooling to −40 °C, the ^{1}H NMR spectrum became more complex. A sharp singlet appeared at δ 5.96, which exactly matches the chemical shift for Cp$_2$Mg at this temperature. Resonances consistent with the core structure of **7** were observed at δ 6.37 (C_5H_5), 6.36, and 6.07 (pyrrolato aromatic CH), 3.06 and 3.02 (pyrrolato methylene groups), and 1.85 and 1.72 (pyrrolato methyl groups), although sharp resonances for free diethyl ether were still observed at this temperature. Additional resonances for a species containing only pyrrolato ligands were observed at δ 6.41, 6.34, and 6.32 (pyrrolato aromatic CH), 3.13 (pyrrolato methylene groups), and 2.01 and 1.97 (pyrrolato methyl groups). Upon cooling to −80 °C, the cyclopentadienyl resonances due to **7** (δ 6.42) and Cp$_2$Mg (δ 6.04) were still observed, but the rest of the spectrum was extremely complex. Below −60 °C, the diethyl ether resonance became very broad, suggesting a dynamic process involving coordination to magnesium. While the solution behavior of **7** is complicated, the ^{1}H NMR spectra suggest an equilibrium

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[6] For example, see: Levine, I. N. *Physical Chemistry, Third Edition*; McGraw-Hill: New York, 1988; pp 177−180.

between **7**, Cp_2Mg, and one or more bis(pyrrolato)-magnesium complexes.

Discussion

This work presents the first detailed description of the synthesis and structure of magnesium cyclopentadienyl amido complexes. As noted in the Introduction, Power prepared $CpMg(NH^iPr_2C_6H_3)(THF)$ by treatment of Cp_2Mg with 2,6-diisopropylaniline in tetrahydrofuran; however, the X-ray crystal structure of this compound was not determined.[4] Consistent with the very slow reaction between Cp_2Mg and diphenylamine to afford **1** that is documented herein, Power obtained only a 14% yield of $CpMg(NH^iPr_2C_6H_3)(THF)$. We have recently reported that alkylamines form adducts with Cp_2Mg and that there is no evidence for cyclopentadiene elimination from these adducts.[3] The very slow rates of cyclopentadiene elimination upon treatment of Cp_2Mg with amines and anilines is certainly due to the much lower pK_a of cyclopentadiene ($pK_a = 18$) compared to those of amines ($pK_a \approx 40$) and anilines ($pK_a \approx 30$).[7] By comparison, $[CpMgMe(Et_2O)]_2$ is more reactive toward protonation by primary and secondary amines because of the extreme basicity of CH_3^- (pK_a of $CH_4 \approx 56$).[7]

The X-ray crystal structures of **1**−**4** and **6** are dimeric with Mg_2N_2 cores. Only a handful of bis(dialkylamido)-magnesium complexes have been structurally characterized, and these complexes are all dimeric in the solid state with Mg_2N_2 cores.[8,9] The crystal structures of $Mg_2(N(CH_2Ph)_2)_4$, $Mg_2(N(CH_2Ph)_2)_4(THF)_2$, and $Mg_2(N(CH_2Ph)_2)_4(HMPA)_2$ possess bridging magnesium−nitrogen bond lengths of 2.08−2.14 Å, with the shorter bond lengths being observed for three-coordinate magnesium centers, and the longer bond lengths being observed for the four-coordinate centers with coordinated neutral Lewis bases.[8] The complex $Mg_2(N(C_6H_{11})_2)_4$ has bridging magnesium−nitrogen bond lengths of 2.10−2.11 Å.[4] These bridging magnesium−nitrogen bond lengths are similar to those observed herein in **1**−**4** (2.08−2.11 Å). The crystal structure of bis[(2-dimethylamido-1-methylamido)ethane]magnesium features a dimeric Mg_2N_2 core with magnesium−nitrogen bond lengths of 2.12 and 2.15 Å, which are longer than the related values observed in **1**−**4**.[9] There has been very little coordination chemistry reported for the 2,5-bis-(dimethylaminomethyl)pyrrolato ligand.[10,11] It is a tridentate donor ligand in several aluminum complexes[10] and is bidentate in a molybdenum complex.[11] Upon the basis of the crystal structure of **7**, coordination of a tridentate 2,5-bis(dimethylaminomethyl)pyrrolato ligand to the $CpMg^+$ fragment would lead to a strained ligand environment. To avoid this strain, a molecule of diethyl ether coordinates to the magnesium center in **7**. The magnesium−oxygen bond length of 2.094(1) Å in **7** is longer than those in $Cp_2Mg(^tBuNH_2)(THF)$ (2.067(2) Å),[4] $[(THF)MgNPh]_6$ (2.04 Å),[12] and $[((Et_2O)Mg)_6(NPh)_4Br_4]$ (2.026(14) Å)[13] but shorter than the 2.165(15) Å observed in $Mg(THF)_4(Br)_2$.[14]

Several other classes of cyclopentadienylmagnesium complexes containing mixed ligand sets have been reported.[5,15−19] These include $[CpMg(alkyl)]_x$,[5,15,16] $[CpMg(OR)]_x$,[17] and complexes containing CpMgX fragments (X = halogen).[18,19] Like **1**−**6** described herein, complexes of the formula $[CpMg(alkyl)]_x$ appear to have considerable stability with respect to redistribution to form Cp_2Mg and $Mg(alkyl)_2$. The complex $[CpMg(CH_3)(OEt_2)]_2$ is stable toward redistribution at ambient temperature in solution, but decomposition to Cp_2Mg and $Mg(CH_3)_2$ occurs upon sublimation.[5,16] The complex $CpMg(CH_2C(CH_3)_3)$ was prepared by fusion of Cp_2Mg with $Mg(CH_2C(CH_3)_3)_2$ and exists as a monomeric species in the gas phase, as determined by electron diffraction methods.[15] Complexes of the formula $[CpMg(OR)(py)_2]$ appear to be monomeric and stable toward redistribution in pyridine solution, but equilibria between $[CpMg(OR)]_x$, Cp_2Mg, and $[Mg(OR)_2]_x$ are present in solution in the absence of a strongly coordinating solvent.[17] The complexes $[(C_5R_5)MgCl(OEt_2)]_2$ and $[((Me_2NCH_2CH_2)C_5R_4)MgX]_2$ (R = H or Me; X = Cl, Br) can be isolated as pure materials and are stable with respect to redistribution in solution.[18] The lack of stability of **7** toward redistribution in solution probably reflects the poor donor capability of the diethyl ether ligand and the apparent inability of the 2,5-bis(dimethylaminomethyl)-pyrrolato ligand to become a tridentate donor to the magnesium center. Accordingly, redistribution in solution lowers the energy of the system by leading to species with better donor ligands.

The van't Hoff analysis of the equilibrium between *anti*-**4** and *syn*-**4** provides some insight into the stability of the dimeric structures of **1**−**6**. In particular, the large positive entropy value suggests a transition state in which *anti*-**4** dissociates to 2 equiv of the monomeric species "$CpMg(NH(^iPr)(CH_2Ph))$", which can then recombine to afford either *anti*-**4** or *syn*-**4**. The relatively small enthalpy value suggests that the bond energies holding the Mg_2N_2 core together are low. There are few equilibrium measurements in the literature to which

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the data for **4** can be compared. Henderson and Mulvey have described a monomer−dimer equilibrium that occurs for $[Mg(NCH_2Ph)_2]_2$ in toluene solution, although a van't Hoff analysis was not performed.[8] We have recently described the van't Hoff analysis for a monomer−dimer equilibrium that occurs for bis[bis(*N*,*N′*-diisopropylacetamidinato)magnesium].[20] Equilibrium parameters for the equilibrium between a dimer and two monomers were $\Delta H° = 14.7 \pm 0.2$ kcal/mol, $\Delta S° = 44.9 \pm 0.2$ cal/mol·K, and $\Delta G°(298\ K) = 1.32 \pm 0.2$ kcal/mol. These values are very similar to those of **4**, consistent with our proposal that *anti*−*syn* exchange in **4** occurs by dissociation to monomers.

The results described herein can be related to the CVD growth of magnesium-doped GaN films using Cp_2Mg, trimethylgallium, and ammonia as precursors.[1,2] Since the pK_a of ammonia (40)[7] is similar to many of the alkylamines that were studied herein, the protonolysis of the cyclopentadienyl ligands in Cp_2Mg by ammonia should have a very slow rate in a CVD process compared to the more rapid protonolyses of the gallium−carbon bonds by ammonia. Once protonolysis of the first cyclopentadienyl ligand occurs, the product $[CpMg(NH_2)]_x$ should react even more slowly with ammonia, by analogy with **1**−**7**. Hence, Cp_2Mg is likely to be a relatively inefficient precursor for the incorporation of magnesium into compound semiconductors during a CVD process. However, since the growth of magnesium-doped GaN is carried out at very high temperatures (ca. 1050 °C),[1,2] it is possible that the slow rates of cyclopentadienyl ligand protonolysis by ammonia may actually assist in magnesium incorporation into the growing film. In other words, the relatively slow gas phase reactions between Cp_2Mg and ammonia do not deplete the magnesium growth nutrients before they reach the film growth ambient. Finally, it has been reported that carbon−hydrogen defects are incorporated into GaN films under CVD growth conditions with moderate to heavy doping using Cp_2Mg, suggesting that the cyclopentadienyl ligands are the carbon source.[21] It is possible that the carbon content arises from incorporation of $[CpMg(NH_2)]_x$ (or other ammonia-derived species containing CpMg fragments) onto the surface of the growing film. Continued film growth would result in a carbon-containing defect. Carbon-free magnesium growth species may result from either redistribution of $[CpMg(NH_2)]_x$ to Cp_2Mg and $[Mg(NH_2)_2]_x$ or by protonolysis of $[CpMg(NH_2)]_x$ with ammonia to afford cyclopentadiene and $[Mg(NH_2)_2]_x$.

Experimental Section

General Considerations. All reactions were performed under argon using either glovebox or Schlenk line techniques. Toluene, tetrahydrofuran, diethyl ether, and hexane were distilled from sodium. Dichloromethane was distilled from phosphorus pentoxide. Diisopropylamine and *N*-isopropylbenzylamine were purchased from Aldrich Chemical Co. and were distilled from calcium hydride prior to use. Diphenylamine and *N*,*N*,*N′*-trimethylethylenediamine were purchased from Aldrich Chemical Co. and were used as received. 2,6-Diisopropylaniline and 3-amino-2,4-dimethylpentane were purchased from Fisher Scientific Inc. and were used as received. Cp_2Mg[22] and 2,5-bis(dimethylamino)pyrrole[23] were prepared according to literature procedures.

^1H NMR spectra were obtained at 300 MHz, while $^{13}C\{^1H\}$ NMR spectra were obtained at 75 MHz in the indicated solvents. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Despite several attempts with spectroscopically pure materials and the use of V_2O_5 as a combustion enhancer, carbon analyses within ±0.4% of the calculated values could not be obtained for **1**, **4**, and **6**. Previous workers have suggested that low carbon microanalyses arise from the formation of refractory magnesium carbides during the combustion process.[24] Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of $[(Cp)Mg(NPh_2)]_2$ (1). A 100 mL Schlenk flask was charged with Cp_2Mg (0.309 g, 2.00 mmol), dimethylmagnesium (0.108 g, 2.00 mmol), and diethyl ether (30 mL). This solution was stirred at ambient temperature for 1 h, and then diphenylamine (0.724 g, 4.00 mmol) was added. The mixture was stirred for an additional 18 h. Removal of the volatile components, followed by crystallization of the crude solid from dichloromethane/hexane, afforded **1** as colorless crystals (0.853 g, 83%): mp 215−219 °C; IR (Nujol, cm^{-1}) 1591 (s), 1580 (s), 1244 (s), 1178 (s), 1078 (m), 1026 (m), 1004 (s), 783 (s), 753 (s), 688 (s); ^1H NMR (benzene-d_6, δ) 7.07 (m, 8H, $C_6\mathit{H}_2H_2'H'$), 6.84 (m, 4H, $C_6H_2H_2'\mathit{H}'$), 6.73 (m, 8H, $C_6H_2\mathit{H}_2'H'$), 5.94 (s, 10H, $C_5\mathit{H}_5$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 150.70 (s, C_{ipso} of Ph ring), 129.97 (s, C_{meta} of Ph ring), 123.13 (s, C_{ortho} of Ph ring), 122.48 (s, C_{para} of Ph ring), 106.37 (s, C_5H_5). Anal. Calcd for $C_{34}H_{30}Mg_2N_2$: C, 79.26; H, 5.87; N, 5.44. Found: C, 77.95; H, 5.90; N, 5.23.

Preparation of $[CpMg(NHCH(CH(CH_3)_2)_2)]_2$ (2). In a procedure similar to the preparation of **1**, Cp_2Mg (0.464 g, 3.00 mmol), dimethylmagnesium (0.163 g, 3.00 mmol), and 3-amino-2,4-dimethylpentane (0.82 mL, 6.0 mmol) were reacted to afford colorless crystals of **2** (0.918 g, 75%): mp 185−187 °C; IR (Nujol, cm^{-1}) 3262 (m), 1605 (m), 1004 (s), 990 (s), 968 (s), 942 (s), 761 (s), 610 (s); ^1H NMR (benzene-d_6, δ) 6.28 (s, 10H, $C_5\mathit{H}_5$), 2.15 (br t, 2H, $NHC\mathit{H}(CH(CH_3)_2)_2$), 1.59 (septet, J = 6.6 Hz, 4H, $NHCH(C\mathit{H}(CH_3)_2)_2$), 0.73 (d, J = 6.6 Hz, 12H, $NHCH(CH(C\mathit{H}_3)(CH_3)'))$, 0.63 (d, J = 6.6 Hz, 12H, $NHCH(CH(CH_3)(C\mathit{H}_3)'))$, −1.56 (s, 2H, $N\mathit{H}CH(CH(CH_3)_2)_2$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 106.14 (s, C_5H_5), 64.51 ($NH\mathit{C}H(CH(CH_3)_2)_2$), 31.76 ($NHCH(\mathit{C}H(CH_3)_2)_2$), 20.66 ($NHCH(CH(\mathit{C}H_3)_2)_2$). Anal. Calcd for $C_{24}H_{42}Mg_2N_2$: C, 70.79; H, 10.40; N, 6.88. Found: C, 70.69; H, 10.35; N, 6.87.

Preparation of $[CpMg(NH(2,6\text{-}^iPr_2C_6H_3))]_2$ (3). In a procedure similar to the preparation of **1**, Cp_2Mg (0.309 g, 2.00 mmol), dimethylmagnesium (0.108 g, 2.00 mmol), and 2,6-diisopropylaniline (0.709 g, 4.00 mmol) were reacted to afford colorless crystals of **3** (0.650 g, 61%): mp 215−217 °C; IR (Nujol, cm^{-1}) 3284 (m), 1623 (m), 1594 (m), 1329 (s), 1237 (s), 1215 (s), 1185 (s), 1008 (s), 823 (s), 776 (s), 747 (s), 680 (s); the ^1H NMR spectrum indicates an equilibrium mixture in a 46:46:8 ratio according to the cyclopentadienyl resonances at δ 6.10, 6.06, and 6.01. Tentative assignments: (1) 7.10−6.90 (m, $C_6\mathit{H}_5$), 6.10 (s, $C_5\mathit{H}_5$), 2.74 (septet, J = 6.9 Hz, $C\mathit{H}(CH_3)_2$), 1.77 (s, $N\mathit{H}$), 1.28 (d, J = 6.9 Hz, $CH(C\mathit{H}_3)_2$); (2) 7.10−6.90 (m, $C_6\mathit{H}_5$), 6.06 (s, $C_5\mathit{H}_5$), 2.88 (septet, J = 6.9 Hz, $C\mathit{H}(CH_3)_2$), 2.03 (s, $N\mathit{H}$), 1.35 (d, J = 6.9 Hz, $CH(C\mathit{H}_3)_2$); (3) 7.10−6.90 (m, $C_6\mathit{H}_5$), 6.01 (s, $C_5\mathit{H}_5$), 2.77 (septet, J = 6.9 Hz, $C\mathit{H}(CH_3)_2$), 2.05 (s, $N\mathit{H}$), 1.23 (d, J = 6.9 Hz, $CH(C\mathit{H}_3)_2$); the $^{13}C\{^1H\}$ NMR spectrum was too complex to allow assignment of resonances.

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Anal. Calcd for $C_{34}H_{46}Mg_2N_2$: C, 76.85; H, 8.73; N, 5.27. Found: C, 76.63; H, 8.73; N, 5.24.

Preparation of $[CpMg(N(^iPr)(CH_2C_6H_5))]_2$ (4). In a procedure similar to the preparation of **1**, Cp_2Mg (0.309 g, 2.00 mmol), dimethylmagnesium (0.108 g, 2.00 mmol), and *N*-isopropylbenzylamine (0.597 g, 4.00 mmol) were reacted to yield colorless crystals of **4** (0.586 g, 62%): mp 169−171 °C; IR (Nujol, cm^{-1}) 1624 (w), 1594 (w), 1112 (m), 1004 (s), 886 (m), 776 (s), 746 (s), 747 (s), 694 (s), 629 (s); ^1H NMR (benzene-d_6, δ) 7.26 (m, 4H, $C_6H_2H_2'H'$), 7.10 (m, 6H, $C_6H_2H_2'H'$), 6.05 (s, 10H, C_5H_5), 3.30 (s, 4H, $CH_2C_6H_5$), 2.32 (sept, $J = 6.6$ Hz, 2H, $CH(CH_3)_2$), 0.72 (d, $J = 6.6$ Hz, 12H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (benzene-d_6, δ): 141.96 (s, C_{ipso} of Ph ring), 130.44 (s, C_{ortho} of Ph ring), 128.89 (s, C_{meta} of Ph ring), 127.80 (s, C_{para} of Ph ring), 106.40 (s, C_5H_5), 52.88 (s, $CH_2C_6H_5$), 47.73 (s, $CH(CH_3)_2$), 24.06 (s, $CH(CH_3)_2$). Anal. Calcd for $C_{30}H_{38}Mg_2N_2$: C, 75.82; H, 8.06; N, 5.89. Found: C, 74.74; H, 8.01; N, 5.70.

Sublimation of **4** leads to the formation of **8** (46%). The spectral and analytical data of **8** are presented in the Supporting Information.

Preparation of $[CpMg(N^iPr_2)]_2$ (5). In a procedure similar to the preparation of **1**, Cp_2Mg (0.155 g, 1.00 mmol), dimethylmagnesium (0.054 g, 1.00 mmol), and diisopropylamine (0.202 g, 2.00 mmol) were reacted to afford colorless crystals of **5** (0.305 g, 80%): mp 240 °C (dec); IR (Nujol, cm^{-1}) 1613 (w), 1344 (m), 1085 (s), 1003 (s), 979 (s), 940 (s), 776 (s), 752 (s); ^1H NMR (benzene-d_6, δ) 6.21 (s, 10H, C_5H_5), 2.67 (septet, $J = 5.1$ Hz, 4H, $CH(CH_3)_2$), 0.89 (d, $J = 5.1$ Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 106.53 (s, C_5H_5), 46.51 (s, $CH(CH_3)_2$), 25.36 (s, $CH(CH_3)_2$). Anal. Calcd for $C_{22}H_{38}Mg_2N_2$: C, 69.63; H, 10.02; N, 7.38. Found: C, 69.30; H, 9.98; N, 7.30.

Preparation of $[CpMg(N(CH_3)CH_2CH_2N(CH_3)_2)]_2$ (6). In a procedure similar to the preparation of **1**, Cp_2Mg (0.155 g, 1.00 mmol), dimethylmagnesium (0.054 g, 1.0 mmol), and *N*,*N*,*N′*-trimethylethylenediamine (0.204 g, 2.00 mmol) were reacted to afford **6** as a white solid (0.288 g, 76%): mp 264−266 °C; IR (Nujol, cm^{-1}) 1591 (m), 1344 (s), 1285 (m), 1248 (m), 1141 (m), 1100 (s), 1008 (m), 938 (s), 842 (s), 757 (s), 721 (s); ^1H NMR (benzene-d_6, δ) 6.19 (s, 10H, C_5H_5), 2.82 (d, $J = 12.9$ Hz, 2H, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 2.50 (t, $J = 12.9$ Hz, 2H, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 2.16 (s, 6H, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 1.92 (t, $J = 12.9$ Hz, 2H, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 1.69 (s, 6H, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 1.67 (s, 6H, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 1.52 (d, $J = 12.3$ Hz, 2H, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 104.25 (s, C_5H_5), 61.69 (s, $(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 53.20 ($(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 46.98 ($(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 46.61 ($(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$), 42.32 ($(CH_3)NC(H)(H)'C(H)(H)'N(CH_3)(CH_3)'$). Anal. Calcd for $C_{20}H_{36}Mg_2N_4$: C, 63.03; H, 9.52; N, 14.70. Found: C, 62.03; H, 9.35; N, 14.31.

Preparation of $[CpMg(\eta^2\text{-}NMe_2CH_2(C_4H_2N)CH_2NMe_2)(Et_2O)]$ (7). In a procedure similar to the preparation of **1**, Cp_2Mg (0.309 g, 2.00 mmol), dimethylmagnesium (0.109 g, 2.00 mmol), and 2,5-bis(dimethylaminomethyl)pyrrole (0.725 g, 4.00 mmol) were reacted to yield **7** as a yellow solid (0.963 g, 70%): mp 82−84 °C; IR (Nujol, cm^{-1}) 1601 (m), 1403 (m), 1344 (s), 1261 (m), 1168 (m), 1138 (s), 1008 (s), 978 (s), 840 (m), 765 (s), 736 (s), 720 (m), 672 (w); ^1H NMR (benzene-d_6, δ) 6.40 (br s, 5H, C_5H_5), 6.0 (br s, 2H, $(CH_3)_2NCH_2(C_4H_2N)CH_2N(CH_3)_2$), 3.34 (br s, 4H, $(CH_3)_2NCH_2(C_4H_2N)CH_2N(CH_3)_2$), 3.23 (q, $J = 6.6$ Hz, 4H, $CH_3CH_2OCH_2CH_3$), 1.97 (br s, 12H, $(CH_3)_2NCH_2(C_4H_2N)CH_2N(CH_3)_2$), 0.93 (t, $J = 6.6$ Hz, 6H, $CH_3CH_2OCH_2CH_3$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 135.05 (s, C_{ipso} of C_4H_2N), 106.59 (s, CH of C_4H_2N), 105.31 (s, C_5H_5), 65.33 (s, $CH_3CH_2OCH_2CH_3$), 61.42 (br s, $(CH_3)_2NCH_2(C_4H_2N)CH_2N(CH_3)_2$), 44.92 (br s, $(CH_3)_2NCH_2(C_4H_2N)CH_2N(CH_3)_2$), 14.76 (s, $CH_3CH_2OCH_2CH_3$). Anal. Calcd for $C_{19}H_{33}MgN_3O$: C, 66.38; H, 9.68; N, 12.22. Found: C, 66.22; H, 9.24; N, 12.32.

X-ray Crystallographic Structure Determination for 1−4 and 7. Crystalline samples for X-ray structural determinations were mounted in thin-walled capillaries under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A full sphere of data was collected for each sample at 10 s/frame at 0.3° between frames and was integrated with the manufacturer's SMART and SAINT software, respectively. Absorption corrections were applied with Sheldrick's SADABS, and the structures were solved and refined using the programs of SHELXL-97. Complexes **1**−**4** and **7** crystallize as neutral compounds from CH_2Cl_2/hexane with no associated ions or solvent. Complex **7** crystallizes from CH_2Cl_2/hexane and contains one diethyl ether molecule as a ligand.

Acknowledgment. We are grateful to the Office of Naval Research (grant no. N00014-99-1-0957) for support of this research.

Supporting Information Available: Synthetic procedure and spectral and analytical data for **8**. X-ray crystallographic files for the structure determinations of **1**−**4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020412B