Synthesis, Structure, and Properties of Magnesocene Amine Adducts. Structural Distortions Arising from $N-H\cdots C_5H_5^-$ Hydrogen Bonding and Molecular Orbital Calculations Thereof

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Received June 11, 2003

Magnesocene amine adducts were prepared and characterized. Addition of primary (3-amino-2,4-dimethylpentane, isopropylamine, *tert*-butylamine, benzylamine, cyclohexylamine) and secondary (diethylamine, dibenzylamine, dicyclohexylamine, and *N*-isopropylbenzylamine) amines to magnesocene at ambient temperature in toluene afforded the stable amine adducts $Cp_2Mg(NH_2CH(CH(CH_3)_2)_2)$ (91%), $Cp_2Mg(NH_2iPr)$ (80%), $Cp_2Mg(NH_2tBu)$ (67%), $Cp_2Mg(NH_2CH_2Ph)$ (80%), $Cp_2Mg(NH_2(C_6H_{11}))$ (93%), $Cp_2Mg(NHEt_2)$ (84%), $Cp_2Mg(NH(CH_2Ph)_2)$ (86%), $Cp_2Mg(NH(C_6H_{11})_2)$ (84%), and $Cp_2Mg(NH(iPr)(CH_2Ph))$ (91%). Most adducts can be sublimed at under 100 °C/0.05 Torr in good yields (72−95%) without decomposition (<1% residue). However, $Cp_2Mg(NH_2CH_2Ph)$ decomposes to Cp_2Mg (70% of theory) and $Cp_2Mg(NH_2CH_2Ph)_2$ (75% of theory) under reduced pressure, even at room temperature, and is thus unsuitable for sublimation. The solid-state structures of $Cp_2Mg(NH_2(C_6H_{11}))$, $Cp_2Mg(NH(iPr)(CH_2Ph))$, and $Cp_2Mg(NH_2CH_2Ph)_2$ were determined by X-ray diffraction methods. In the solid-state structures, $Cp_2Mg(NH_2(C_6H_{11}))$ and $Cp_2Mg(NH_2CH_2Ph)_2$ contain one η^5- and one η^2-coordinated cyclopentadienyl ring, while $Cp_2Mg(NH(iPr)(CH_2Ph))$ contains two η^5-cyclopentadienyl rings. Infrared spectroscopy suggests that the adducts are stabilized by $N-H\cdots C_5H_5^-$ hydrogen bonding. Molecular orbital calculations on the model complex $Cp_2Mg(NH_2CH_3)$ support the idea of $N-H\cdots C_5H_5^-$ hydrogen bonding and provide insight into the energetics and exchange processes associated with the hydrogen bond. The $N-H\cdots C_5H_5^-$ hydrogen bond strength is estimated to be 4.2 ± 1.4 kcal/mol, and molecular orbital calculations suggest that the amine hydrogen atoms undergo site exchange by a low-energy intramolecular rotational process that interconverts the η^2- and η^5-cyclopentadienyl ligands.

Introduction

Bis(cyclopentadienyl)magnesium[1] (Cp_2Mg) possesses a sandwich structure similar to that of ferrocene. Cp_2Mg is widely used as a cyclopentadienyl group transfer reagent in the preparation of metal cyclopentadienyl complexes[2] and has also been used as a polymerization catalyst.[3] In the last 20 years, it has been widely employed as a dopant source compound for the growth of p-type semiconductor films by chemical vapor deposition (CVD) techniques.[4] Despite its wide use in CVD processes, Cp_2Mg has many problems, including a high melting point (176 °C),[1] low vapor pressure, and low reactivity toward main-group-element hydrides, as well as strong adsorption to steel reactor surfaces.[5,6] We have a long-term interest in the development of improved magnesium CVD precursors for doping group 13 nitride films.[7] Insight into the mechanism by which Cp_2Mg reacts with ammonia to create intermediates that lead

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10.1021/om030452v CCC: $25.00

to magnesium incorporation into nitride films might suggest new, improved structures for dopant precursors. Given the importance of magnesium-doped group 13 nitride materials,[8] it is surprising that little investigation has been carried out on the reactions leading to magnesium doping with Cp_2Mg. Even though it has long been known that Cp_2Mg and Lewis bases form adducts,[9,10] most adducts have been identified only in solution by NMR spectroscopy and have not been isolated. The adduct $Mg(\eta^5\text{-}Cp)(\eta^2\text{-}Cp)(NH_2tBu)(THF)$, which was prepared from Cp_2Mg and *tert*-butylamine in tetrahydrofuran under reflux conditions, was the only structurally characterized Cp_2Mg adduct until recently.[11] In the past year, the crystal structures of $Cp_2Mg(NH_2CH(CH(CH_3)_2)_2)$[12] and $Cp_2Mg(THF)_2$[13] have appeared. The X-ray crystal structures of several carbene[14,15] and tetrahydrofuran[16] adducts of ring-substituted magnesocenes have been reported.

Within the above context, we report the synthesis, structure, properties, and molecular orbital calculations of Cp_2Mg adducts of primary and secondary alkylamines. These adducts contain one or two amine ligands and variable cyclopentadienyl coordination modes, depending on the nature of the hydrocarbon groups attached to nitrogen. Infrared spectroscopy and molecular orbital calculations suggest that the adducts are stabilized by $N-H\cdots C_5H_5^-$ hydrogen bonding. Most of the adducts can be sublimed without decomposition, although the volatilities appear to be lower than that of Cp_2Mg. These findings are relevant to the activation of Cp_2Mg by ammonia under CVD film growth conditions. A portion of this work was communicated.[12]

Results

Synthesis and Properties of Cp_2Mg Amine Adducts. Treatment of Cp_2Mg with 1 equiv of the primary amines 3-amino-2,4-dimethylpentane, isopropylamine, *tert*-butylamine, benzylamine, and cyclohexylamine or secondary amines diethylamine, dibenzylamine, dicyclohexylamine, and *N*-isopropylbenzylamine afforded $Cp_2Mg(NH_2CH(CH(CH_3)_2)_2)$ (**1**, 91%), $Cp_2Mg(NH_2iPr)$ (**2**, 80%), $Cp_2Mg(NH_2tBu)$ (**3**, 67%), $Cp_2Mg(NH_2CH_2Ph)$ (**4**, 80%), $Cp_2Mg(NH_2(C_6H_{11}))$ (**5**, 93%), $Cp_2Mg(NHEt_2)$ (**6**, 84%), $Cp_2Mg(NH(CH_2Ph)_2)$ (**7**, 86%), $Cp_2Mg(NH(C_6H_{11})_2)$ (**8**, 84%), and $Cp_2Mg(NH(iPr)(CH_2Ph))$ (**9**, 91%), respectively, as colorless or off-white crystalline solids (eq 1). The structural assignments for **1**−**9** were based on spectral and analytical data and on X-ray crystal structure determinations for **1**, **5**, and **9**. In the solid state, **1** and **5** each contain η^5-cyclopentadienyl, η^2-cyclopentadienyl, and amine ligands, as described below (**5**) and in our communication (**1**).[12] Complex **9** contains two η^5-cyclopentadienyl ligands and one *N*-isopropylbenzylamine ligand. Adducts **1**−**9** are stable at ambient temperature and pressure under an inert atmosphere. The ^1H NMR spectra of **1**−**9** contain cyclopentadienyl singlets that range from δ 6.03 to 6.19, which are close to the cyclopentadienyl resonance for Cp_2Mg (δ 5.97). The $^{13}C\{^1H\}$ NMR spectra of **1**−**9** exhibit cyclopentadienyl carbon resonances between 106.71 and 107.74 ppm. For comparison, the carbon atoms of Cp_2Mg resonate at 107.76 ppm. The infrared spectra of **1**−**9** contain nitrogen−hydrogen stretches from 3313 to 3164 cm^{-1} and carbon−hydrogen ($C_5H_5^-$) bends from 773 to 747 cm^{-1}. The low values for the nitrogen−hydrogen stretches are due to $N-H\cdots C_5H_5^-$ hydrogen bonding, as detailed below.

$$\mathrm{Cp_2Mg} + \mathrm{NHRR'} \xrightarrow{\substack{\text{toluene}\\ \text{23 °C, 18 h}}} \mathrm{Cp_2Mg(NHRR')} \qquad (1)$$

1, R = H, R' = $CH(CH(CH_3)_2)_2$, 91%
2, R = H, R' = $CH(CH_3)_2$, 80%
3, R = H, R' = $C(CH_3)_3$, 67%
4, R = H, R' = $CH_2C_6H_5$, 80%
5, R = H, R' = C_6H_{11}, 93%
6, R = R' = CH_2CH_3, 84%
7, R = R' = $CH_2C_6H_5$, 86%
8, R = R' = C_6H_{11}, 84%
9, R = $CH(CH_3)_2$, R' = $CH_2C_6H_5$, 91%

Volatility and Thermal Stability. To evaluate the effect of amine coordination to Cp_2Mg, the volatility and thermal stability of **1**−**9** were examined. Complexes **1**−**3** and **5**−**9** sublimed under preparative conditions (ca. 0.5 g, 1 h sublimation time) between 60 and 90 °C/0.05 Torr to afford the unchanged complexes in 72−95% sublimed yields. In all cases, there was <1% residue left upon sublimation. While the sublimation temperature range was small for **1**−**3** and **5**−**9**, differences in sublimation temperatures and rates between some of the complexes were noticeable. For example, achieving complete sublimation for **1** within 1.0 h required a temperature of 60 °C, whereas **7** required a temperature of 90 °C for complete sublimation within the same time period. To allow comparison of volatility and sublimation rates with Cp_2Mg, the sublimation of **1** (0.4 g, 1.5 mmol) was carried out at various temperatures for 1.0 h side by side with Cp_2Mg (0.4 g, 2.6 mmol). The following yields were obtained for Cp_2Mg/**1**: 45 °C, 65%/69%; 50 °C, 69%/

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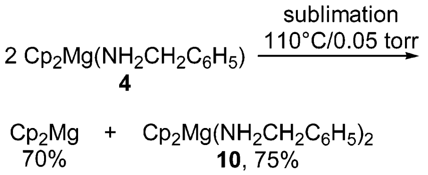
73%; 60 °C, 95%/95%. It is clear that the recovered yields of sublimed material were similar at all temperatures for Cp_2Mg and **1**. Since 2.6 mmol of Cp_2Mg was sublimed versus 1.5 mmol of **1**, Cp_2Mg sublimes at a slightly more rapid rate than **1**. Thus, Cp_2Mg is more volatile than **1**, consistent with its lower molecular weight. It is possible that **1** and the other amine adducts sublime by dissociation of the amine ligands on the surface of the solid, followed by vapor transport, and then adduct re-formation upon reaching the cool section of the sublimation tube.

Unlike **1**−**3** and **5**−**9**, **4** decomposes upon heating. A preparative sublimation of **4** that was carried out in a horizontal tube furnace at 110 °C/0.05 Torr afforded Cp_2Mg (70% of theory) and the new complex $Cp_2Mg(NH_2CH_2Ph)_2$ (**10,** 75% of theory; eq 2). The more volatile



$$\underset{\mathbf{4}}{2\ Cp_2Mg(NH_2CH_2C_6H_5)} \xrightarrow[110°C/0.05\ torr]{sublimation} \underset{70\%}{Cp_2Mg} + \underset{\mathbf{10},\ 75\%}{Cp_2Mg(NH_2CH_2C_6H_5)_2} \quad (2)$$

Cp_2Mg sublimed first and was separated from less volatile **10** because it traveled further into the cold region of the sublimation tube. Complex **10** was also prepared independently in 90% yield from Cp_2Mg and 2 equiv of benzylamine, as described in the Experimental Section. The structural assignment for **10** was based upon spectral and analytical data and by an X-ray crystal structure analysis. The molecular structure of each molecule in **10** contains η^5-cyclopentadienyl, η^2-cyclopentadienyl, and two benzylamine ligands, as described below.

Low temperature ^1H NMR spectra were recorded for **1** and **10**, both of which contain η^5- and η^2-cyclopentadienyl ligands in the solid state. At ambient temperature in toluene-d_8, the cyclopentadienyl resonance for **1** appeared as a sharp singlet at δ 6.15. At −80 °C, this resonance shifted slightly to δ 6.29, but it remained a sharp singlet. There were no major shifts or changes with the other resonances upon cooling from room temperature to −80 °C. It was necessary to use dichloromethane-d_2 for the low-temperature NMR spectra of **10**, due to its limited solubility in toluene. At ambient temperature, the cyclopentadienyl resonance for **10** appeared as a sharp singlet at δ 6.06. Upon cooling to −60 °C, this resonance shifted slightly to δ 5.98, but it remained a sharp singlet. There were no major shifts or changes with the other resonances upon cooling from room temperature to −60 °C. Upon cooling to −80 °C, **10** precipitated. The low-temperature ^1H NMR spectra indicate that exchange between the η^5- and η^2-cyclopentadienyl ligands in **1** and **10** is fast on the NMR time scale, even at or below −60 °C. To estimate the upper limit for the free energy of activation ($\Delta G^{\ddagger}$) for the ligand exchange process, a calculation was made using standard dynamic NMR equations and reasonable assumptions regarding the exchange process.[17] Assuming uncoupled AB exchange between the amine hydrogen atoms of **1**, an upper limit of 183 K for the temperature of coalescence, and a peak separation of 150 Hz, an upper limit for $\Delta G^{\ddagger}$ of about 8.5 kcal/mol is obtained. Thus, the process leading to exchange of the η^2- and η^5-cyclopentadienyl ligands in **1** is very low energy, consistent with the calculations described below.

Table 1. Crystal Data and Data Collection Parameters for 5, 9, and 10

	5	9	10
empirical formula	$C_{16}H_{23}MgN$	$C_{20}H_{25}MgN$	$C_{24}H_{28}MgN_2$
fw	253.66	303.72	368.79
space group	$P2_1/c$	$P\bar{1}$	$C2/c$
a (Å)	10.624(1)	7.768(1)	25.648(9)
b (Å)	19.906(2)	7.892(1)	11.527(4)
c (Å)	14.392(2)	15.083(3)	16.783(5)
α (deg)		79.116(3)	
β (deg)	90.972(2)	89.416(3)	119.418(6)
γ (deg)		80.735(3)	
V (Å^3)	3043.2(5)	896.0(3)	4322(2)
Z	8	2	8
temp (K)	295(2)	295(2)	295(2)
λ (Å)	0.710 73	0.710 73	0.710 73
calcd density (g cm^{-3})	1.107	1.126	1.134
μ (mm^{-1})	0.101	0.096	0.092
$R(F)^a$ (%)	4.92	3.77	5.29
$R_w(F)^b$ (%)	12.10	9.29	14.59

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

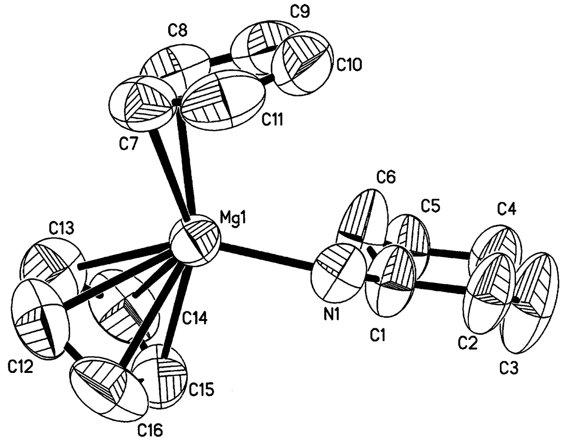


Figure 1. Perspective view of bis(cyclopentadienyl)(cyclohexylamine)magnesium (**5**) with probability ellipsoids at the 50% level.

In a test of thermal stability, a toluene solution of **1** was sealed in a Carius tube and heated at 200 °C for 24 h. ^1H NMR spectroscopic analysis after solvent removal showed only unchanged **1**, and there was no evidence for elimination of cyclopentadiene. To determine the ligand lability in solution, equimolar amounts of **1** and **9** were mixed in benzene-d_6 and then the ^1H NMR spectrum was recorded. The cyclopentadienyl proton resonance appeared at δ 6.11 ppm, which corresponds to the average of the constituent complexes **1** (δ 6.03) and **9** (δ 6.19). The single cyclopentadienyl resonance suggests a fast exchange equilibrium in solution.

Crystal Structures of 5, 9, and 10. To establish the solid-state geometries, the X-ray crystal structures of **5**, **9**, and **10** were determined. Crystallographic data are summarized in Table 1, perspective views are presented in Figures 1−3, and selected bond lengths and angles are listed in Tables 2−4. The X-ray crystal structure of **1** was reported previously.[12]

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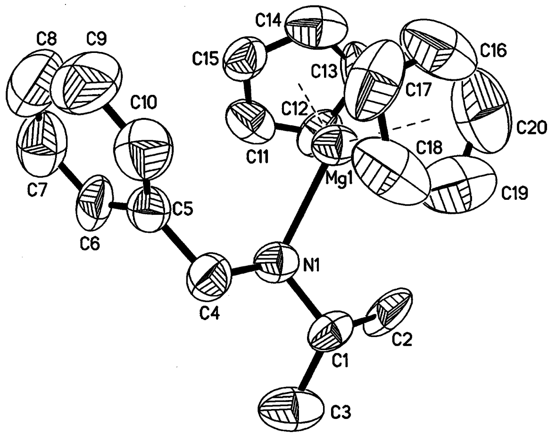

Figure 2. Perspective view of bis(cyclopentadienyl)(*N*-isopropylbenzylamine)magnesium (**9**) with probability ellipsoids at the 50% level.

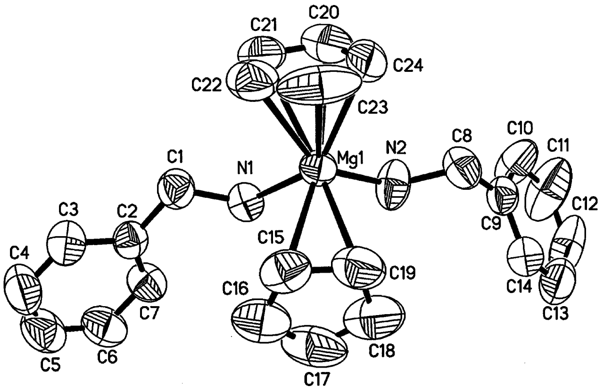

Figure 3. Perspective view of bis(cyclopentadienyl)bis(benzylamine)magnesium (**10**) with probability ellipsoids at the 50% level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Mg(1)–N(1)	2.098(3)	Mg(1)–C(13)	2.430(4)
Mg(1)–C(7)	2.276(3)	Mg(1)–C(14)	2.371(4)
Mg(1)–C(8)	2.422(3)	Mg(1)–C(15)	2.376(4)
Mg(1)–C(11)	2.724(4)	Mg(1)–C(16)	2.410(3)
Mg(1)–C(12)	2.441(4)		
Mg(1)–N(1)–C(1)		124.5(2)	

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9

Mg(1)–N(1)	2.210(4)	Mg(1)–C(16)	2.618(10)
Mg(1)–C(11)	2.565(7)	Mg(1)–C(17)	2.471(8)
Mg(1)–C(12)	2.535(6)	Mg(1)–C(18)	2.386(5)
Mg(1)–C(13)	2.392(5)	Mg(1)–C(19)	2.430(9)
Mg(1)–C(14)	2.382(6)	Mg(1)–C(20)	2.582(14)
Mg(1)–C(15)	2.497(7)		
Mg(1)–N(1)–C(1)	115.5(3)	Mg(1)–N(1)–C(4)	113.9(3)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 10

Mg(1)–N(1)	2.146(3)	Mg(1)–C(23)	2.443(4)
Mg(1)–N(2)	2.156(2)	Mg(1)–C(24)	2.444(3)
Mg(1)–C(20)	2.471(3)	Mg(1)–C(15)	2.540(3)
Mg(1)–C(21)	2.483(3)	Mg(1)–C(19)	2.459(4)
Mg(1)–C(22)	2.457(3)		
Mg(1)–N(1)–C(1)	117.8(2)	Mg(1)–N(2)–C(8)	123.4(2)

Complex **5** contains η^5-cyclopentadienyl, η^2-cyclopentadienyl, and cyclohexylamine ligands. There are two independent molecules within the unit cell; Table 2 gives selected bond lengths and angles only for the molecule containing Mg(1). The magnesium–carbon bond lengths to the η^5-cyclopentadienyl ligands average 2.43(3) Å. The other cyclopentadienyl ligand on each independent magnesium atom is η^2-coordinated. The magnesium–carbon bond lengths for the η^2-cyclopentadienyl ligands range between 2.27 and 2.44 Å (Mg(1)–C(7) = 2.276(3) Å, Mg(1)–C(8) = 2.422(3) Å; Mg(2)–C(28) = 2.316(3) Å, Mg(2)–C(29) = 2.436(3) Å), while the remaining carbon atoms of the η^2-cyclopentadienyl group are located further from the magnesium ion. The η^2-cyclopentadienyl ligand attached to Mg(1) has long contacts to the uncoordinated carbon atoms (Mg(1)–C(9) = 2.932(3) Å, Mg(1)–C(10) = 3.091(3) Å, Mg(1)–C(11) = 2.724(3) Å). The related values for Mg(2) are less definitive (Mg(2)–C(30) = 2.747(3) Å, Mg(2)–C(31) = 2.809(3) Å, Mg(2)–C(32) = 2.525(3) Å) but are not outside the realm of the η^2 assignment. The magnesium–nitrogen bond lengths are 2.098(3) and 2.110(3) Å. There are two hydrogen atoms on each nitrogen atom of the two independent molecules that can participate in hydrogen bonding. These four hydrogen atoms all show contacts to the η^2-cyclopentadienyl ligands. The centroid defined by atoms C(9), C(10), and C(11) has an intramolecular contact to H(1)N(1) (2.73 Å) to one side and an intermolecular contact to H(2)N(2) (2.69 Å) to the opposite side. In the second independent molecule, a centroid defined by atoms C(30) and C(31) has an intramolecular contact to H(1)N(2) (2.79 Å) to one side and an intermolecular contact to H(2)N(1) (2.64 Å) to the opposite side of the η^2-cyclopentadienyl ligand. Thus, like **1**,[12] **5** is stabilized in the solid state by both intramolecular and intermolecular hydrogen bonding.

Unlike **1** and **5**, **9** contains two approximately eclipsed η^5-cyclopentadienyl ligands. However, the bonding of the cyclopentadienyl ligands to the magnesium ion is highly distorted. The cyclopentadienyl ligands have magnesium–carbon bond lengths that range from 2.382(6) to 2.618(10) Å. Within each cyclopentadienyl ligand, there are two longer (2.535–2.618 Å), one intermediate length (2.471(8), 2.497(7) Å), and two shorter (2.386–2.430 Å) magnesium–carbon bonds. In the cyclopentadienyl ligand containing C(11)–C(15), the longer magnesium–carbon bonds (to C(11), C(12), and C(15)) are found with the carbon atoms that are pointed toward the *N*-isopropylbenzylamine ligand. In the cyclopentadienyl ligand containing C(16)–C(20), the longer magnesium–carbon bonds (to C(16), C(17), and C(20)) are found with the carbon atoms that are situated farthest from the *N*-isopropylbenzylamine ligand. The nitrogen-bound carbon atoms are pointed toward the cyclopentadienyl ligand containing C(16)–C(20). The unusual magnesium–carbon bond length arrangement in the cyclopentadienyl ligand containing C(16)–C(20) may arise through slippage of the cyclopentadienyl ligand away from the amine carbon substituents to alleviate steric interactions. The magnesium–cyclopentadienyl centroid distances are 2.1695(21) Å (C(11)–C(15)) and 2.1966(38) Å (C(16)–C(20)). These values are longer than those found in **1**[12] and **5**, due to the increased steric congestion associated with accommodation of a secondary amine ligand. The magnesium–nitrogen bond length is 2.210(4) Å, which is 0.10–0.11 Å longer than the related values in **1**[12] and **5**. Since steric congestion in **9** is not relieved by formation of a η^2-cyclopentadienyl ligand, the magnesium−nitrogen bond length increases. The angle between the planes of the cyclopentadienyl ligands is 44.67(29)°. This angle is not directly comparable to the related values in **1** and **5**, due to the presence of η^2-cyclopentadienyl ligands in the latter compounds. The cyclopentadienyl ligand containing C(11)−C(15) is planar to within 0.0014 Å, while the cyclopentadienyl ligand containing C(16)−C(20) is planar to only 0.025 Å. The nitrogen-bound hydrogen atom shows no close contacts to the centroids of any of the cyclopentadienyl ligands, suggesting that hydrogen bonding is either absent or extremely weak. It is possible that the observed distortions in the magnesium−carbon bonding are due to steric effects of accommodating the amine ligand.

Complex **10** exists in the solid state with η^5-cyclopentadienyl, η^2-cyclopentadienyl, and benzylamine ligands. Both benzyl groups are splayed away from the center of the Cp_2Mg core to minimize steric interactions. The magnesium−carbon bonds associated with the η^5-cyclopentadienyl ligand range between 2.443 and 2.483 Å, and the magnesium−cyclopentadienyl centroid distance is 2.1706(17) Å. The latter value is similar to those found in **9** but longer than those for **1**[12] and **5**. The magnesium−carbon bond lengths for the η^2-cyclopentadienyl ligand are 2.459(4) and 2.540(3) Å. The other magnesium−carbon distances in the η^2-cyclopentadienyl ligand range between 3.137 and 3.518 Å and are not consistent with bonding interactions. The magnesium−nitrogen bond lengths are 2.156(2) and 2.146(3) Å. These bond lengths are longer than the related values in **1**[12] (2.112(3) Å) and **5** (2.098(3) Å) but are shorter than the value in **9** (2.210(4) Å). Formation of the η^2-cyclopentadienyl ligand in **10** clearly allows closer approach of the nitrogen atoms to the magnesium atom than is possible in **9**. The nitrogen−magnesium−nitrogen angle is 90.75(11)°. The magnesium−nitrogen−carbon angles associated with the benzylamine ligands are 117.84(17) and 123.4(2)°. These values are larger than the idealized tetrahedral case (109.5°) but probably reflect relief of steric interactions. The angle between the planes of the cyclopentadienyl ligands is 72.69(12)°. This angle is larger than the related values in **1** and **5**, presumably due to increased steric congestion in **10**. The cyclopentadienyl ligand containing C(15)−C(19) is planar to within 0.0061 Å, while the cyclopentadienyl ligand containing C(20)−C(24) is planar to within 0.0073 Å. The protons on N(1) have notable contacts to the cyclopentadienyl ligands. The atoms C(16), C(17), and C(18) comprise the carbon atoms of the η^2-cyclopentadienyl ligand that are not bonded to the magnesium ion and define a centroid that is 2.63 Å from the intramolecular proton H(01) on N(1). Also, the η^5-cyclopentadienyl ligand has a centroid with a linear intermolecular contact of 2.58 Å to H(02) (Mg(1)−centroid−H(02) = 168(3)°). The protons on N(2) do not show similar intermolecular contacts.

The structural parameters of **1**,[12] **5**, **9**, and **10** can be compared with those of Mg(η^5-Cp)(η^2-Cp)(NH_2tBu)(THF)[11] and Mg(η^5-Cp)(η^1-Cp)$(THF)_2$,[13] which are the only structurally characterized Cp_2Mg adducts besides **1** that have been reported to date. Mg(η^5-Cp)(η^2-Cp)(NH_2tBu)(THF), like **10** and similar to **1** and **5**, exists with η^5-cyclopentadienyl, η^2-cyclopentadienyl, *tert*-butylamine, and tetrahydrofuran ligands. The average magnesium−carbon bond length associated with the η^5-cyclopentadienyl ligand, 2.46(1) Å, is similar to the related value in **10** but is slightly longer than the values in **1** and **5**. The η^2-cyclopentadienyl ligand is characterized by magnesium−carbon bond lengths of 2.370(3) and 2.688(3) Å, and it was pointed out by the authors that this ligand might be equally well described as η^1.[11] In contrast, the η^2-cyclopentadienyl ligands in **1**, **5**, and **10** are clearly η^2 and not η^1. The magnesium−nitrogen bond length was 2.140(2) Å, which is similar to the values for **10** and is between the values for **1**, **5**, and **9**. Mg(η^5-Cp)(η^1-Cp)$(THF)_2$, like **1** and **5**, contains η^5-cyclopentadienyl, η^1-cyclopentadienyl, and tetrahydrofuran ligands.[13] The η^5-cyclopentadienyl ligand has magnesium−carbon bond lengths that range from 2.417 to 2.479 Å and a magnesium−cyclopentadienyl centroid distance of 2.137(1) Å. These values are similar to those of **10** but longer than those of **1** and **5**, due to the lower coordination number in the latter complexes. The other cyclopentadienyl ligand is bonded to magnesium in an η^1 fashion, with a magnesium−carbon distance of 2.282(2) Å. The other magnesium−carbon distances were >2.70 Å. The short magnesium−carbon distance in Mg(η^5-Cp)(η^1-Cp)$(THF)_2$ is similar to those in **1**[12] and **5** but considerably shorter than those observed in **10**. Apparently, accommodation of the η^2-cyclopentadienyl ligand in **10** is achieved at the expense of shorter magnesium−carbon interactions.

Molecular Orbital Calculations on $Cp_2Mg(NH_2CH(CH_3)_2)$ (2) and $Cp_2Mg(NH_2CH_3)$ (11). To help characterize the N−H···$C_5H_5^-$ hydrogen bonding, molecular orbital calculations were carried out on **2** and a simplified analogue, $Cp_2Mg(NH_2CH_3)$ (**11**), where the isopropyl substituent on the nitrogen atom of **2** was replaced by a methyl group. Calculations were performed with the B3LYP hybrid density functional[18−20] and the 6-311++G(d,p) basis set[21] using the GAUSSIAN suite of programs.[22] The optimized geometries calculated for **2** and **11** are in good agreement with the X-ray crystallographic data for structures **1** and **5**. The calculated and observed distances between the magnesium center and carbon atoms of the η^5-cyclopentadienyl ligand agree to within ±0.03 Å, indicating that calculations reproduce the metal−cyclopentadienyl interactions satisfactorily. The calculated magnesium−nitrogen distances are ca. 0.06 Å longer than those observed in **1** and **5**. Both the X-ray and calculated structures clearly show an interaction between the nitrogen-bound hydrogen atoms and the uncoordinated carbon atoms of the η^2-cyclopentadienyl ligands. The positions of the hydrogen atoms are difficult to determine reliably from the X-ray structure. However, the calculated and experimental distances between the nitrogen atom and the nearest carbon atom on the η^2-cyclopentadienyl ligand are in good agreement and are considerably shorter than expected for a simple van der Waals contact between nitrogen-bound hydrogen atom and the cyclopentadienyl

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(22) Frisch, M. J.; et al. Gaussian 01, Development Version (Revision B.03+); Gaussian, Inc., Pittsburgh, PA, 2002.

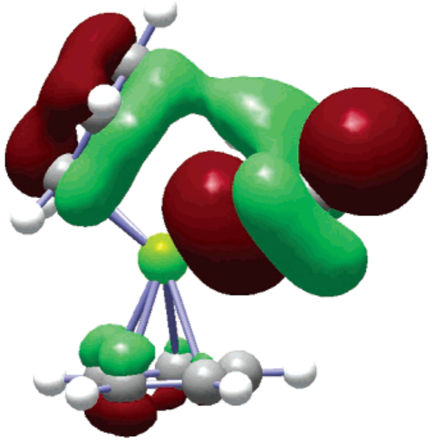

Figure 4. Molecular orbital of **11** that involves the hydrogen bonding. One nitrogen-bound hydrogen atom forms a bonding interaction with the π-system of the uncoordinated carbon atoms of the η^2-cyclopentadienyl ligand. The other nitrogen-bound hydrogen atom is not involved in a hydrogen bond.

ligand. The calculated N−H···C distances, 2.30 and 2.28 Å, are in fact very similar to the hydrogen bond lengths in ammonia dimer (2.2−2.3 Å[23]), indicating that there is a significant hydrogen bond between the amine and η^2-cyclopentadienyl ligands. The experimentally determined N−H···C distances in **5** and **10** range between 2.63 and 2.73 Å.

Analysis of the molecular orbitals and the electron density provides some insight into the nature of the hydrogen bonding. Mulliken population analysis indicates that electrostatics stabilizes the N−H···$C_5H_5^-$ interaction. The free carbon atoms of the η^2-cyclopentadienyl ligand have charges of −0.10 to −0.22 and the hydrogen atoms on the nitrogen atoms have charges of 0.24 and 0.27, with the higher charge on the atoms involved in the hydrogen bonding. The charge on the magnesium ion is 0.96, while the charge on the nitrogen atom is −0.44. Inspection of the molecular orbitals reveals a bonding interaction between the π-orbitals of the uncoordinated carbon atoms on the η^2-cyclopentadienyl ligand and the nitrogen−hydrogen bond, as shown in Figure 4. This interaction is consistent with a hydrogen bond. The other nitrogen-bound hydrogen atom is not involved in a hydrogen bond.

One approach for assessing the strength of the N−H···$C_5H_5^-$ hydrogen bond is to rotate the amine to break the interaction. Figure 5 shows a series of structures along this path. The amine is rotated about the nitrogen−carbon bond, and the remaining coordinates are allowed to relax. The energy climbs as the nitrogen−hydrogen bond is moved away from the η^2-cyclopentadienyl ligand (A → B). Next, the η^5-cyclopentadienyl ligand rotates by about 40°. The energy continues to rise as the nitrogen−hydrogen bond is forced to rotate further (B → C). Finally, there is a sudden drop in energy as the η^5-cyclopentadienyl ring adopts η^2 bonding to interact with the second nitrogen−hydrogen bond and the other cyclopentadienyl ligand becomes coordinated in an η^5 fashion (C → D). Such a sudden drop in energy is typical of a coordinate driving approach.[24] The maximum in the energy represents an upper bound to the barrier to amine rotation. This energy, 2.8 kcal/mol, is also an estimate of the N−H···$C_5H_5^-$ hydrogen bond strength, since the bond is broken at the maximum but the cyclopentadienyl ligands have not rearranged to form a bond with the second nitrogen−hydrogen bond. When the process is repeated in the reverse direction, a similar energy profile is obtained (but this time without as much cyclopentadienyl ring rotation). The energy at the crossing of the two curves provides a lower bound for rotation,[25] which yields 2.3 ± 0.5 kcal/mol as an estimate of the rotation barrier.

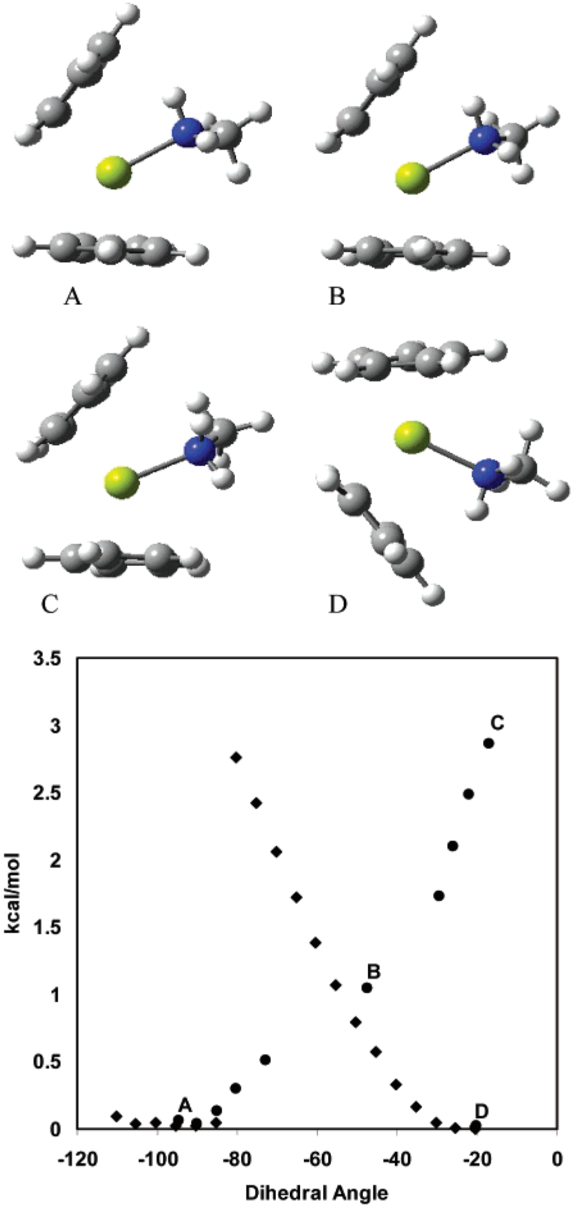

Figure 5. Geometries and energies of amine rotation in **11**.

An alternative approach for calculating the N−H···$C_5H_5^-$ hydrogen-bond strength is to flip the η^2-cyclopentadienyl ligand so as to break the interaction (Chart 1). The energy for this isomerization, 5.6 kcal/mol, is an upper bound for the N−H···$C_5H_5^-$ hydrogen

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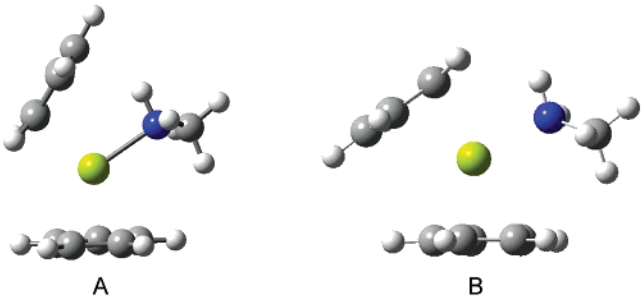
Chart 1. Theoretically Predicted Structures of 12 with the Minimized Structure (A) and with the η^2-Cyclopentadienyl Ligand Reversed (B)



bond strength, since the stabilizing interactions of the η^2-cyclopentadienyl ligand with the rest of the molecule are also reduced in this process. Together, the two approaches yield an estimate of 4.2 ± 1.4 kcal/mol for the $N-H\cdots C_5H_5^-$ hydrogen bond strength.

Discussion

The central discovery described herein is the surprisingly stable complexes that are formed between Cp_2Mg and primary and secondary amines. These compounds greatly expand the number of known magnesocene adducts. Structurally characterized adducts to date include Mg(η^5-Cp)(η^2-Cp)(NH_2tBu)(THF),[11] our previous report of **1**,[12] and the recently described complex Mg(η^5-Cp)(η^1-Cp)$(THF)_2$.[13] Mg(η^5-Cp)(η^2-Cp)(NH_2tBu)(THF) exists with η^5- and η^2-cyclopentadienyl ligands, but hydrogen bonding was not described in the report.[11] Reanalysis of the structure data from the Cambridge Crystallographic Database indicates that one of the amine hydrogen atoms forms an intramolecular close contact of 2.274 Å with the centroid of the three uncoordinated carbon atoms of the η^2-cyclopentadienyl ligand. The other nitrogen-bound hydrogen atom has no intermolecular contacts within 3.7 Å. Lehmkuhl has reported the isolation and spectral characterization of $Cp_2Mg(L)$ (L = 1,4-dioxane, DME, TMEDA) and Cp_2MgL_x (L_x = $(THF)_{2.42}$, $(pyridine)_2$),[10] although crystal structures were not reported for these complexes. Several adducts of ring-substituted magnesocenes have been crystallographically characterized. The solid-state structure of $Mg(C_5(CH_3)_5)_2$(1,3,4,5-tetramethylimidazol-2-ylidene) features an η^5-pentamethylcyclopentadienyl ligand with an average magnesium−carbon bond length of 2.477(20) Å[14] and an approximately η^3-pentamethylcyclopentadienyl ligand with magnesium−carbon bond lengths of 2.309, 2.466, and 2.606 Å. In addition, the carbene carbon atom is bonded to the magnesium ion. The related carbene adduct $Mg(C_5(CH_3)_4H)_2$(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) possesses a very similar structure, with η^5- and η^3-pentamethylcyclopentadienyl ligands.[15] These adducts are stable and isolable due to the very strong donor characteristics of the carbene ligand. Finally, a series of *ansa*-magnesocenes with tetrahydrofuran ligands has been structurally characterized.[16] Because the cyclopentadienyl donors are tied together by short linker groups and impose a bent cyclopentadienyl−magnesium−cyclopentadienyl fragment, the magnesium centers are more accessible sterically to the tetrahydrofuran ligands, resulting in stable complexes. Lewis base adducts of the heavier group 2 metallocenes are well-known and well characterized.[14,15,26] The more widespread occurrence of the heavier group 2 metallocene adducts, relative to magnesocene adducts, is undoubtedly due to relief in steric interactions from the larger interannular separation.

As noted in the Results, the amine ligands in **1**−**10** showed nitrogen−hydrogen stretches that are consistent with hydrogen bonding. The only possible hydrogen bond acceptors in **1**−**10** are the cyclopentadienyl ligand π-clouds. The structural results for **5** and **10** demonstrate the presence of such intermolecular and intramolecular hydrogen bonds. We searched the Cambridge Crystallographic Database (version 5.24, Nov 2002) and were unable to find any complexes in which a ligand containing coordinated oxygen−hydrogen or nitrogen−hydrogen fragments leads to a slipped cyclopentadienyl ligand, with the exception of **1**[13] and Mg(η^5-Cp)(η^2-Cp)(NH_2tBu)(THF)[11] noted above. This search did find 145 hits for metal cyclopentadienyl complexes containing coordinated nitrogen−hydrogen and oxygen−hydrogen bonds that are within 2.9 Å of the cyclopentadienyl centroids, and it is possible that there is some degree of $E-H\cdots C_5H_5$ electrostatic interaction in these complexes. However, the solid-state structure of **9** did not show any close contacts between the amine hydrogen atom and the cyclopentadienyl ligands, raising the possibility that hydrogen bonding is absent or extremely weak in complexes that do not exhibit η^2 or other slipped cyclopentadienyl ligands. There is an intermolecular hydrogen bond in **10** between a nitrogen-bound hydrogen atom and an η^5-cyclopentadienyl ligand; thus, hydrogen bonds remain possible in η^5-cyclopentadienyl complexes containing coordinated nitrogen−hydrogen and oxygen−hydrogen bonds. Hydrogen bonding between nitrogen−hydrogen bonds and the π-clouds of various neutral aromatic compounds is well precedented.[27,28] Such interactions usually entail a hydrogen−arene centroid distance of 2.75−3.11 Å.[28] Since the cyclopentadienyl ligand is aromatic and considerably more electron rich than a neutral aromatic compound due to the formal negative charge, its π-system should be a much better hydrogen bond acceptor than neutral aromatic π-systems. Consistent with this interpretation, the hydrogen−cyclopentadienyl centroid distances in **1**,[12] **5**, and **10** above range between 2.62 and 2.79 Å. The presence of $N-H\cdots C_5H_5^-$ hydrogen bonding raises the issue of how much this interaction contributes to

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(26) For selected examples, see: (a) Engelhardt, L. M.; Junk, P. C.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 1500. (b) Williams, R. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1990**, *112*, 2454. (c) Gardiner, M. G.; Raston, C. L.; Kennard, C. H. L. *Organometallics* **1991**, *10*, 3680. (d) Burkey, D. J.; Alexander, E. K.; Hanusa, T. P. *Organometallics* **1994**, *13*, 2773. (e) Hays, M. L.; Hanusa, T. P.; Nile, T. A. *J. Organomet. Chem.* **1996**, *514*, 73. (f) Burkey, D. J.; Hanusa, T. P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 2452. (g) Matare, G. J.; Kane, K. M.; Shapiro, P. J.; Vij, A. *J. Chem. Crystallogr.* **1998**, *28*, 731. (h) Hammel, A.; Schwarz, W.; Weidlein, J. *J. Organomet. Chem.* **1989**, *378*, 347. (i) Molander, G. A.; Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J. *Organometallics* **1996**, *15*, 3817.

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the unusual cyclopentadienyl bonding modes: i.e., η^2-cyclopentadienyl ligands in **1**, **5**, and **10**. Our data and those of the previously reported magnesocene–carbene adducts[14,15] offer some insight into this question. The carbene adducts $Mg(C_5(CH_3)_5)_2$(1,3,4,5-tetramethylimidazol-2-ylidene)[14] and $Mg(C_5(CH_3)_4H)_2$(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)[15] contain η^3-cyclopentadienyl ligands. It was suggested that the slipped η^3-cyclopentadienyl ligands in these complexes are due to accommodation of the steric bulk of the carbene ligands, rather than overlap of the filled cyclopentadienyl π-system with the empty out-of-plane p orbital on the carbene carbon atom, since the carbene–cyclopentadienyl carbon–carbon distances are too long to allow such a bonding interaction.[14,15] It is likely that hydrogen bonding increases the thermal stability of **1**–**10**, relative to adducts with ligands that are not capable of hydrogen bonding. For example, $Cp_2Mg(THF)_{2.42}$ reverts completely to Cp_2Mg upon vacuum drying at 20 °C/10^{-3} Torr for 6 h.[10] In contrast, **1**–**3** and **5**–**9** can be sublimed quantitatively without any evidence of reversion to Cp_2Mg. However, as noted above, the amount of stabilization afforded by the hydrogen bonding is <8.5 kcal/mol.

Triethylamine and diisopropylamine formed adducts with Cp_2Mg, as determined by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, but upon workup only Cp_2Mg was isolated. Apparently, these amines are too bulky to form isolable adducts. Lehmkuhl was similarly unable to isolate the triethylamine adduct of Cp_2Mg.[10] Treatment of Cp_2Mg with ammonia in several solvents (tetrahydrofuran, toluene) led to immediate precipitation of a white solid. This solid was insoluble in all unreactive solvents that were tried; we are continuing to pursue characterization of this material. Interestingly, Cp_2Mg forms a conducting solution at −33 °C in liquid ammonia, suggesting that one or two of the cyclopentadienyl ligands dissociates to form ionic complexes with cyclopentadienide anions and magnesium–ammine cations.[29] The insoluble precipitates that we observed may correspond to such ionic compounds. In this vein, Behrens has recently reported that dissolution of Cp_2Mg in dimethyl sulfoxide affords the ionic complex $[Mg(dmso)_6][C_5H_5]_2$, which contains uncoordinated cyclopentadienyl counterions.[13] Lehmkuhl proposed that Cp_2Mg can coordinate up to three tetrahydrofuran ligands, since material analyzed as $Cp_2Mg(THF)_{2.42}$ was isolated upon dissolution of Cp_2Mg in tetrahydrofuran.[10] The outcome of the reaction between **1**–**9** and additional equivalents of the respective amines varied depending on the nature of the amine, and in no case other than **10** was a pure, well characterized compound obtained. Treatment of **1** and **3** with an excess of the respective amines afforded only **1** and **3** after solvent removal and vacuum drying. Apparently, 3-amino-2,4-dimethylpentane and *tert*-butylamine are sufficiently bulky to destabilize the formation of isolable bis(amine) adducts. Treatment of **2** and **5** with an excess of the respective amines in toluene led to immediate precipitation of white solids. NMR analysis indicated that the precipitates had a higher amine content than **2** and **5**, but the integrations did not lead to reasonable cyclopentadienyl to amine ratios. Recrystallization of the precipitates did not improve the integrations, and sublimations gave back **2** and **5**.

The final issue involves relating the results described herein to the activation of Cp_2Mg by ammonia under CVD conditions. While Cp_2Mg is used nearly universally as the dopant precursor for growth of magnesium-doped group 13 nitride films,[4,8] there has been very little information reported about the chemical reactions leading to magnesium incorporation in these materials. Our results imply that ammonia adducts of Cp_2Mg lie along the film-forming reaction coordinate in CVD processes employing ammonia and a group 13 alkyl source compound. It has been established that Cp_2Mg is about twice as efficient as 1,1′-dimethylmagnesocene in incorporating magnesium into GaN films grown using metal organic vapor phase epitaxy.[6d] On the basis of the results described herein and previous adducts of ring-substituted magnesocenes,[14–16] is likely that Cp_2Mg forms a more stable ammonia adduct than 1,1′-dimethylmagnesocene, due to steric repulsion from the methyl groups in the latter compound and the higher expected Lewis acidity of the magnesium center in Cp_2Mg. Formation of a more stable ammonia adduct with Cp_2Mg would give the complex a longer lifetime in the CVD reactor, which would allow more time for the presumably slow elimination of cyclopentadiene to occur. Cyclopentadiene elimination would lead to reactive magnesium amide complexes that can contribute to magnesium incorporation into the growing GaN film. The gas-phase reaction of Cp_2Mg^+ with ammonia has been examined,[30] and it was found that cyclopentadiene radical elimination occurs with concomitant formation of $CpMg(NH_3)_n^+$ ($n = 1$–3). However, this chemistry is only minimally relevant to the present work because of the positive charge in Cp_2Mg^+.

Experimental Section

General Considerations. All reactions were performed under argon using either Schlenk line or glovebox techniques. Toluene was distilled from sodium and hexane was distilled from P_2O_5. 3-Amino-2,4-dimethylpentane was purchased from Fisher Scientific, Inc., and was used as received. Isopropylamine, *tert*-butylamine, benzylamine, cyclohexylamine, diethylamine, dibenzylamine, dicyclohexylamine, and *N*-isopropylbenzylamine were purchased from Aldrich Chemical Co. and were used as received. Cp_2Mg was prepared according to a literature procedure.[1]

^1H and $^{13}C\{^1H\}$ NMR were obtained at 300 or 75 MHz in benzene-d_6. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of $Cp_2Mg(NH_2CH(CH(CH_3)_2)_2)$ (1). A 100 mL Schlenk flask, equipped with a magnetic stir bar, was charged with Cp_2Mg (0.309 g, 2.00 mmol) and toluene (10 mL). 3-Amino-2,4-dimethylpentane (0.28 mL, 2.0 mmol) was added to this solution, and then the flask was sealed with a rubber septum. The solution was stirred at ambient temperature for 18 h. The volatile components were removed under reduced pressure to afford **1** as a colorless crystalline solid (0.490 g, 91%): mp 71–74 °C; IR (Nujol, cm^{-1}) 3313 (m), 3223 (m), 3067 (m), 1586 (m), 1257 (w), 1149 (s), 1004 (s), 758 (s), 631 (w); ^1H NMR (benzene-d_6, δ) 6.19 (s, 10H, C_5H_5), 1.90 (apparent

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pentet, $J = 5.4$ Hz, 1H, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$), 1.20 (m, 2H, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$), 0.76 (broad s, 2H, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$), 0.51 (d, $J = 6.6$ Hz, 6H, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$), 0.49 (t, $J = 6.6$ Hz, 6H, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 107.07 (s, C_5H_5), 61.04 (s, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$), 30.16 (s, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$), 19.73 (s, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$), 17.55 (s, $NH_2CH(CH(CH_3)_2)(CH(CH_3)_2)'$). Anal. Calcd for $C_{17}H_{27}MgN$: C, 75.70; H, 10.09; N, 5.19. Found: C, 75.58; H, 9.91; N, 5.08.

Preparation of $Cp_2Mg(NH_2iPr)$ (2). In a fashion similar to the preparation of **1**, treatment of isopropylamine (0.26 mL, 3.00 mmol) with Cp_2Mg (0.465 g, 3.00 mmol) afforded **2** as a colorless crystalline solid (0.559 g, 87%): mp 143−146 °C; IR (Nujol, cm^{-1}) 3277 (w), 3210 (m), 3070 (m), 1569 (m), 1196 (m), 1159 (s), 1071 (m), 1038 (m), 1005 (s), 758 (s), 588 (w); ^1H NMR (benzene-d_6, δ) 6.15 (s, 10H, C_5H_5), 2.20 (septet, $J = 6.6$ Hz, 1H, $CH(CH_3)_3$), 0.43 (d, $J = 6.0$ Hz, 6H, $CH(CH_3)_3$), 0.39 (broad s, 2H, NH_2); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 106.89 (C_5H_5), 42.63 ($CH(CH_3)_3$), 24.15 ($CH(CH_3)_3$). Anal. Calcd for $C_{13}H_{19}MgN$: C, 73.10; H, 8.97; N, 6.56. Found: C, 72.96; H, 9.07; N, 6.62.

Preparation of $Cp_2Mg(NH_2tBu)$ (3). In a fashion similar to the preparation of **1**, treatment of *tert*-butylamine (0.42 mL, 4.0 mmol) with Cp_2Mg (0.618 g, 4.00 mmol) afforded **3** as a colorless crystalline solid (0.610 g, 67%): mp 178−181 °C; IR (Nujol, cm^{-1}) 3238 (m), 3201 (m), 3060 (m), 1564 (m), 1265 (w), 1130 (s), 1008 (s), 762 (s), 601 (w); ^1H NMR (benzene-d_6, δ) 6.18 (s, 10H, C_5H_5), 0.56 (s, 9H, $C(CH_3)_3$), 0.51 (broad s, 2H, NH_2); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 107.63 (C_5H_5), 42.63 ($C(CH_3)_3$), 30.45 (s, $C(CH_3)_3$). Anal. Calcd for $C_{14}H_{21}MgN$: C, 73.87; H, 9.30; N, 6.15. Found: C, 74.16; H, 9.36; N, 5.99.

Preparation of $Cp_2Mg(NH_2CH_2C_6H_5)$ (4). In a fashion similar to the preparation of **1**, treatment of benzylamine (0.110 g, 1.00 mmol) with Cp_2Mg (0.155 g, 1.00 mmol) afforded **4** as colorless thin plates (0.212 g, 80%): mp 140−150 °C; IR (Nujol, cm^{-1}) 3262 (m), 3173 (m), 3100 (m), 3050 (m), 1580 (m), 1303 (w), 1137 (s), 1005 (s), 769 (s), 695 (m), 662 (m); ^1H NMR (benzene-d_6, δ) 7.15−6.68 (m, 5H, C_6H_5), 6.06 (s, 10H, C_5H_5), 2.89 (t, $J = 7.2$ Hz, 2H, CH_2), 0.69 (broad s, 2H, NH_2); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 138.65 (s, ipso-*C* of C_6H_5), 129.10 (s, para-*C*H of C_6H_5), 128.13 (s, meta-*C*H of C_6H_5), 127.53 (s, ortho-*C*H of C_6H_5), 107.43 (C_5H_5), 45.48 (CH_2). Anal. Calcd for $C_{17}H_{19}MgN$: C, 78.04; H, 7.32; N, 5.35. Found: C, 77.81; H, 7.50; N, 5.32.

Preparation of $Cp_2Mg(NH_2(C_6H_{11}))$ (5). In a fashion similar to the preparation of **1**, treatment of cyclohexylamine (0.34 mL, 3.0 mmol) with Cp_2Mg (0.465 g, 3.00 mmol) afforded **5** as an off-white solid (0.710 g, 93%): mp 148−153 °C dec; IR (Nujol, cm^{-1}) 3276 (w), 3209 (m), 3067 (m), 1586 (m), 1261 (w), 1135 (m), 1004 (s), 762 (s), 590 (m); ^1H NMR (benzene-d_6, δ) 6.14 (s, 10H, C_5H_5), 1.94 (m, 1H, $CH(CH_2)_2(CH_2)_2CH_2$), 1.4−0.3 (m, 12H, $CH(CH_2)_2(CH_2)_2CH_2$ and NH_2); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 107.06 (s, C_5H_5), 49.87 (s, $CH(CH_2)_2(CH_2)_2CH_2$), 35.05 (s, $CH(CH_2)_2(CH_2)_2CH_2$), 25.08 (s, $CH(CH_2)_2(CH_2)_2CH_2$), 24.91 (s, $CH(CH_2)_2(CH_2)_2CH_2$). Anal. Calcd for $C_{16}H_{23}MgN$: C, 75.76; H, 9.14; N, 5.52. Found: C, 75.41; H, 9.01; N, 5.20.

Preparation of $Cp_2Mg(NHEt_2)$ (6). In a fashion similar to the preparation of **1**, treatment of diethylamine (0.30 mL, 3.0 mmol) with Cp_2Mg (0.465 g, 3.00 mmol) afforded **6** as an off-white solid (0.218 g, 84%): mp 123−129 °C dec; IR (Nujol, cm^{-1}) 3231 (m), 3067 (m), 1589 (w), 1258 (w), 1146 (m), 1004 (s), 758 (s); ^1H NMR (benzene-d_6, δ) 6.12 (s, 10H, C_5H_5), 1.66 (pentet, $J = 7.5$ Hz, 4H, CH_2CH_3), 1.13 (broad s, 1H, NH_2), 0.50 (t, $J = 7.5$ Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 106.71 (s, C_5H_5), 43.14 (s, CH_2CH_3), 14.08 (s, CH_2CH_3). Anal. Calcd for $C_{14}H_{21}MgN$: C, 73.87; H, 9.30; N, 6.15. Found: C, 73.66; H, 9.01; N, 6.16.

Preparation of $Cp_2Mg(NH(CH_2C_6H_5)_2)$ (7). In a fashion similar to the preparation of **1**, treatment of dibenzylamine (0.197 g, 1.00 mmol) with Cp_2Mg (0.155 g, 1.00 mmol) afforded **7** as an off-white solid (0.302 g, 86%): mp 115−118 °C; IR (Nujol, cm^{-1}) 3196 (m), 3055 (m), 1601 (w), 1259 (m), 1112 (m), 1096 (m), 1008 (s), 747 (s); ^1H NMR (benzene-d_6, δ) 7.06 (m, 10H, C_6H_5), 6.05 (s, 10H, C_5H_5), 3.20 (t, $J = 6.3$ Hz, 4H, CH_2), 1.88 (broad s, 1H, NH); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 138.25 (s, ipso-*C* of C_6H_5), 128.85 (s, ortho-*C*H of C_6H_5), 128.68 (s, meta-*C*H of C_6H_5), 127.92 (s, para-*C*H of C_6H_5), 106.96 (s, C_5H_5), 52.47 (s, CH_2). Anal. Calcd for $C_{24}H_{25}MgN$: C, 81.95; H, 7.16; N, 3.98. Found: C, 81.71; H, 7.16; N, 3.94.

Preparation of $Cp_2Mg(NH(C_6H_{11})_2)$ (8). In a fashion similar to the preparation of **1**, treatment of dicyclohexylamine (0.181 g, 1.00 mmol) with Cp_2Mg (0.155 g, 1.00 mmol) afforded **8** as an off-white solid (0.218 g, 84%): mp 142−145 °C; IR (Nujol, cm^{-1}) 3238 (w), 3164 (w), 3075 (m), 1601 (m), 1261 (m), 1157 (s), 1008 (s), 769 (s), 605 (w); ^1H NMR (benzene-d_6, δ) 6.04 (s, 10H, C_5H_5), 2.45 (broad m, 2H, $CH(CH_2)_2(CH_2)_2CH_2)$), 1.82−0.98 (m, 20H, $CH(CH_2)_2(CH_2)_2CH_2$), 0.53 (broad s, 1H, NH); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 107.74 (s, C_5H_5), 53.27 (s, $CH(CH_2)_2(CH_2)_2CH_2$), 34.65 (s, $CH(CH_2)_2(CH_2)_2CH_2$), 26.57 (s, $CH(CH_2)_2(CH_2)_2CH_2$), 25.48 (s, $CH(CH_2)_2(CH_2)_2CH_2$). Anal. Calcd for $C_{22}H_{33}MgN$: C, 78.69; H, 9.90; N, 4.17. Found: C, 78.78; H, 9.81; N, 4.09.

Preparation of $Cp_2Mg(NH(iPr)(CH_2C_6H_5))$ (9). In a fashion similar to the preparation of **1**, treatment of *N*-isopropylbenzylamine (0.149 g, 1.00 mmol) with Cp_2Mg (0.155 g, 1.00 mmol) afforded **9** as a colorless crystalline solid (0.276 g, 91%): mp 126−128 °C; IR (Nujol, cm^{-1}) 3231 (m), 1586 (m), 1257 (m), 1135 (m), 1008 (s), 795 (s), 773 (s), 736 (s), 721 (s), 691 (s); ^1H NMR (benzene-d_6, δ) 7.12 (m, 10H, C_6H_5), 6.03 (s, 10H, C_5H_5), 3.28 (d, $J = 6.6$ Hz, 2H, $CH_2C_6H_5$), 2.44 (m, 1H, $CH(CH_3)_2$), 0.99 (broad s, 1H, NH), 0.80 (d, $J = 6.0$ Hz, 6H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 138.88 (s, ipso-*C* of C_6H_5), 128.81 (s, ortho-*C*H of C_6H_5), 128.60 (s, meta-*C*H of C_6H_5),127.79 (s, para-*C*H of C_6H_5), 107.38 (s, C_5H_5), 50.98 (s, $CH_2C_6H_5$), 47.91 (s, $CH(CH_3)_2$), 22.32 (s, $CH(CH_3)_2$). Anal. Calcd for $C_{20}H_{25}MgN$: C, 79.09; H, 8.30; N, 4.61. Found: C, 78.88; H, 8.28; N, 4.51.

Preparation of $(Cp)_2Mg(NH_2CH_2C_6H_5)_2$ (10). Sublimation of **4** (0.200 g, 0.763 mmol) in a 2.5 cm glass tube in a horizontal furnace at 80 °C (0.05 Torr) afforded colorless crystals of Cp_2Mg (0.041 g, 70%) at the cold end of the tube. Further sublimation at 110 °C afforded **10** (0.105 g, 75%) at the middle of the tube as colorless crystals: mp 130 °C dec; IR (Nujol, cm^{-1}) 3262 (m), 3100 (m), 3048 (m), 1576 (m), 1303 (w), 1137 (s), 1008 (s), 769 (s), 698 (m), 595 (m); ^1H NMR (dichloromethane-d_2, δ) 7.40−7.18 (m, 10H, C_6H_5), 6.06 (s, 10H, C_5H_5), 3.54 (t, $J = 7.8$ Hz, 4H, $CH_2C_6H_5$), 1.34 (t, $J = 7.8$ Hz, 4H, NH_2); $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, ppm) 140.13 (s, ipso-*C* of C_6H_5), 129.36 (s, ortho-*C*H of C_6H_5), 128.27 (s, para-*C*H of C_6H_5), 127.59 (s, meta-*C*H of C_6H_5), 106.57 (s, C_5H_5), 45.72 (s, $CH_2C_6H_5$). Anal. Calcd for $C_{24}H_{28}MgN_2$: C, 78.16; H, 7.65; N, 7.60. Found: C, 75.37; H, 7.46; N, 7.09. The carbon and nitrogen analyses could not be obtained within ±0.4% of the calculated values, despite two attempts with V_2O_5 added as a combustion enhancer.

Complex **10** was independently prepared from Cp_2Mg (0.155 g, 1.00 mmol) and benzylamine (0.220 g, 2.00 mmol) in 90% yield.

X-ray Crystallographic Structure Determinations of 5, 9, and 10. Crystalline samples were mounted in sealed thin-walled capillaries under a nitrogen atmosphere for X-ray data collection. All crystal structures were collected at room temperature on a Bruker P4/CCD diffractometer equipped with Mo radiation. For each collection, a full sphere of data was collected at 10 s/frame with 0.2 or 0.3° between each frame. The frame data were integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program, and the structure was solved and refined using the programs of SHELXL-97. All reported crystal structures consist of monomeric neutral complexes with no associated solvent or ions. All atoms occupy general positions in the unit cell. The crystals were colorless and striated bundles of needles (**5**), barrels (**9**), or flat rods (**10**). For the most part, hydrogen atoms were placed in observed positions and refined isotropically. Only **9** had some hydrogen atoms placed in calculated positions. Complex **5** showed obvious signs of twinning in the CCD photos, and a dominant lattice was chosen while other spots were ignored. Two independent molecules are present in the asymmetric unit. There is significant disorder in the cyclohexyl groups of one of these independent molecules, which is evidenced by large thermal parameters.

Acknowledgment. We are grateful to the Office of Naval Research (Grant No. N00014-99-1-0957 to C.H.W.) and the National Science Foundation (Grant No. CHE-0131157 to H.B.S.) for support of this research. J.E.K. thanks the Institute for Scientific Computing at Wayne State University for support provided by a NSF-IGERT Fellowship.

Supporting Information Available: Tables giving X-ray crystallographic data for the structure determinations of **5**, **9,** and **10**, views of **5**, **9**, and **10** showing intramolecular and intermolecular hydrogen bonding, and tables of final positional parameters for the calculations; X-ray data for **5**, **9**, and **10** are also available as electronic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030452V