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Factors that Influence π- versus η^2-Coordination of β-Diketiminato Ligands in Magnesium Complexes

Hani M. El-Kaderi, Aibing Xia, Mary Jane Heeg, and Charles H. Winter*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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Treatment of *N*-*tert*-butyl-4-(*tert*-butylimino)-2-penten-2-amine with $[CpMgMe(Et_2O)]_2$ in diethyl ether afforded $CpMg(HC(C(Me)N(tBu))_2)$ (90%). A crystal structure determination of this complex revealed a sandwich structure with a π-coordinated β-diketiminato ligand. $CpMg(HC(C(Me)N(tBu))_2)$ did not form isolable adducts with diethyl ether or tetrahydrofuran, but treatment with 4-*tert*-butylpyridine led to the formation of $CpMg(HC(C(Me)N(tBu))_2)$(4-tBupy) (88%). A crystal structure determination showed that $CpMg(HC(C(Me)N(tBu))_2)$(4-tBupy) possesses a η^2-β-diketiminato ligand with some distortion toward π-bonding, but not as much as was found in $CpMg(HC(C(Me)N(tBu))_2)$. Similar treatment of *N*-isopropyl-4-(isopropylimino)-2-penten-2-amine with $[CpMgMe(Et_2O)]_2$ and 4-*tert*-butylpyridine in diethyl ether afforded $CpMg(HC(C(Me)N(iPr))_2)$(tBupy) (73%). The crystal structure of this complex was very similar to that of $CpMg(HC(C(Me)N(tBu))_2)$(4-tBupy). In the absence of 4-*tert*-butylpyridine, $CpMg(HC(C(Me)N(iPr))_2)(OEt_2)$ was isolated, but this complex decomposed slowly to mixtures of Cp_2Mg and $Mg(HC(C(Me)N(iPr))_2)_2$ upon loss of the labile diethyl ether ligand. Treatment of dibutylmagnesium with 2 equiv of *N*-*tert*-butyl-4-(*tert*-butylimino)-2-penten-2-amine or *N*-isopropyl-4-(isopropylimino)-2-penten-2-amine in hexane afforded $Mg(HC(C(Me)N(tBu))_2)_2$ (68%) or $Mg(HC(C(Me)N(iPr))_2)_2$ (78%). Crystal structure determinations of $Mg(HC(C(Me)N(tBu))_2)_2$ and $Mg(HC(C(Me)N(iPr))_2)_2$ revealed η^2-β-diketiminato ligands and approximate tetrahedral geometry about the magnesium ions. The thermal stability and volatility of the complexes were determined through preparative sublimation experiments.

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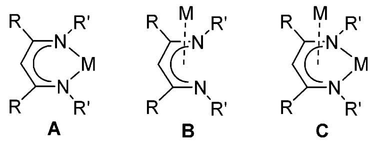
Introduction

Although complexes containing β-diketiminato ligands were first reported in 1968, they were only sporadically used in organometallic and inorganic chemistry before 1990.[1] Since 1990, β-diketiminato ligands $[HC(C(R)N(R'))_2]^-$ have been widely investigated in transition, lanthanide, and main group metal chemistry.[2] β-Diketiminato ligands are isoelectronic with β-diketonato ligands and commonly act as bidentate four-electron donors through formation of two metal−nitrogen σ-bonds (Chart 1, **A**). Other coordination modes have been documented and have been recently reviewed.[2] One particularly intriguing coordination mode involves bonding of a single metal center to the π-cloud of the β-diketiminato ligand (Chart 1, **B**). This latter coordination mode has been structurally authenticated in a small number of main group,[3] transition,[4,5] and lanthanide metal complexes.[6] Another type of π-coordinated β-diketiminato complex consists of a metal ion bonded to the π-face of a MN_2C_3 fragment (Chart 1, **C**), and several examples of this coordination mode have been structurally characterized.[7] Aside from these interesting structural features, β-diketiminato ligands have been employed as important spectator ligands in catalytic processes, often as cyclopentadienyl or β-diketonato ligand replacements.[2] For example, several groups have developed highly active β-diketiminato complexes for the catalytic polymerization of a variety of monomers.[8] The versatility of β-diketiminato ligands is due to the fact that they can be modified at the nitrogen atoms and the carbon

Chart 1



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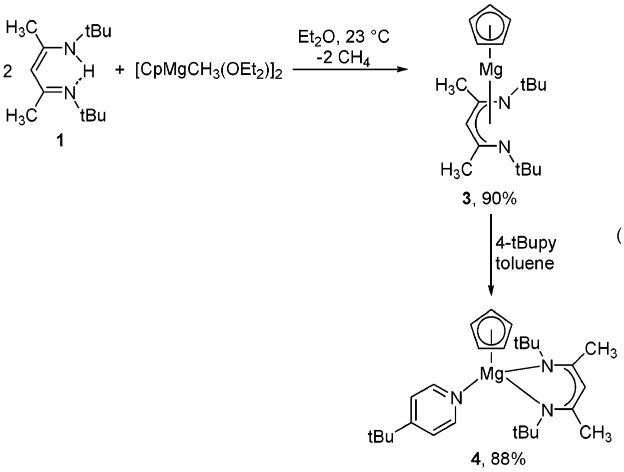
atoms of the ligand core to suit different steric and electronic demands of organometallic complexes.

We are interested in the development of new volatile magnesium complexes that can be used as dopant precursors in the growth of magnesium-doped semiconductor films and which have improved precursor properties relative to bis(cyclopentadienyl)magnesium (Cp_2Mg).[9] In the last twenty years, magnesium has been found to be the most useful p-type dopant in semiconductor films, since it has a very low diffusion constant in common semiconductor matrixes and provides a desirable acceptor energy level and its compounds exhibit low toxicity.[10] Cp_2Mg has been the most widely used magnesium source precursor for the growth of p-type semiconductor films by CVD techniques.[11] In light of recent advances in the chemistry of complexes containing β-diketiminato ligands,[2] we set out to explore magnesium complexes that might lead to volatile source compounds for CVD film growth. Structurally characterized magnesium complexes with β-diketiminato ligands that have been reported to date exhibit the η^2-coordination mode and have employed bulky aryl[12] or silyl substituents[13] on the nitrogen atoms. A magnesium complex of a cyclic bis(β-diketiminato) ligand was also structurally characterized.[14] The complex Mg(HC(C(Me)N(Me))$_2$)$_2$, which contains methyl groups on the nitrogen atoms, was described but not structurally characterized.[15]

Herein we describe the synthesis, structure, and volatility of a series of magnesium complexes with β-diketiminato ligands that contain either *tert*-butyl or isopropyl groups on the nitrogen atoms. An interesting structural progression from π- to η^2-coordination of the β-diketiminato ligands is documented and is dependent upon the steric bulk of the nitrogen atom substituents as well as the nature of the other ligands attached to the magnesium ion. One of the new complexes, CpMg(HC(C(Me)N(tBu))$_2$), adopts a metallocene-like structure and is a rare example of a heteroatom-containing magnesocene analogue. Finally, the volatility and thermal behavior of the new complexes are described.

Results

Synthetic Chemistry. The diketimines *N*-*tert*-butyl-4-(*tert*-butylimino)-2-penten-2-amine (**1**) and *N*-isopropyl-4-(isopropylimino)-2-penten-2-amine (**2**) were prepared as white solids following literature procedures.[16] Neither **1** nor **2** reacted with Cp_2Mg in toluene at ambient temperature after 72 h. Accordingly, the stronger nucleophile [CpMgMe(Et_2O)]$_2$ was used instead of Cp_2Mg. [CpMgMe(Et_2O)]$_2$, which was prepared from redistribution of Cp_2Mg and dimethylmagnesium in diethyl ether according to a literature procedure,[17] reacted readily with **1** in diethyl ether at ambient temperature to afford CpMg(HC(C(Me)N(tBu))$_2$) (**3**, 90%) upon removal of diethyl ether under reduced pressure (eq 1). The structural assignment for **3** was



(1)

based on spectral and analytical data, as well as an X-ray structure determination. In the solid state, **3**

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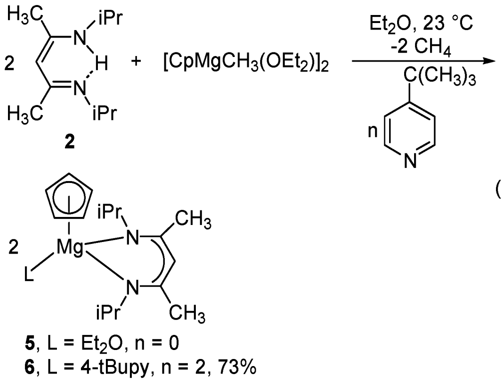
contains one η^5-cyclopentadienyl ligand and one π-bound β-diketiminato ligand. Complex **3** showed no evidence for diethyl ether coordination in the crude reaction mixture. Similarly, **3** could be dissolved in tetrahydrofuran and recrystallized to afford the unchanged complex. However, treatment of **3** with the more compact and basic ligand 4-*tert*-butylpyridine led to the formation of the adduct $CpMg(HC(C(Me)N(tBu))_2)(4\text{-}tBupy)$ (**4**, 88%). A low-precision X-ray crystal structure determination of **4** established the presence of one η^5-cyclopentadienyl ligand, one η^2-β-diketiminato ligand, and one 4-*tert*-butylpyridine ligand.

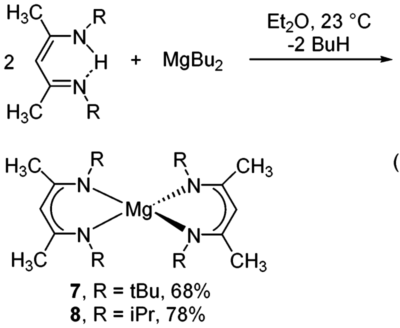
Analogous treatment of $[CpMgMe(Et_2O)]_2$ with **2** in diethyl ether gave a different outcome (eq 2). The crude product $CpMg(HC(C(Me)N(iPr))_2)(OEt_2)$ (**5**) contained a coordinated diethyl ether ligand, as assessed by ^1H NMR spectroscopy. However, slow loss of diethyl ether ligand prevented the isolation of **5** as a pure product. Instead, the treatment of **2** with $[CpMgMe(Et_2O)]_2$ was conducted in the presence of 4-*tert*-butylpyridine, which led to the isolation of $CpMg(HC(C(Me)N(iPr))_2)(4\text{-}tBupy)$ (**6**, 73%) as colorless crystals. Unlike **5**, **6** was stable with regard to loss of 4-*tert*-butylpyridine at ambient temperature and could be handled without decomposition under an inert atmosphere. The structural assignments were based on spectral (**5**, **6**) and analytical data (**6**) as well as X-ray crystallography (**6**). In the solid state structure, **6** contains one η^5-cyclopentadienyl ligand, one η^2-β-diketiminato ligand, and one 4-*tert*-butylpyridine ligand.



(2)

The ^1H NMR spectra of **3**, **4**, and **6** contain C_5H_5 singlets at δ 6.41, 6.43, and 6.64, respectively, which are downfield compared to Cp_2Mg (δ 5.97). The $^{13}C\{^1H\}$ NMR spectra of **3**, **4**, and **6** contain C_5H_5 singlets at 105.87, 105.84, and 104.90 ppm, respectively, which are close to that of Cp_2Mg (107.74 ppm). The hydrogen atoms on the β-CH fragment of the β-diketiminato ligands in **3**, **4**, and **6** resonated at δ 4.20, 4.21, and 4.54. The corresponding carbon resonances for the β-CH fragment of the β-diketiminato ligands in **3**, **4**, and **6** appeared at 94.54, 94.67, and 93.87 ppm. The proton and carbon resonances for the cyclopentadienyl ligand and β-CH fragment of the β-diketiminato ligand in **3** revealed only very small chemical shift changes upon cooling from 20 °C to −80 °C. Thus, there are no NMR spectral characteristics in **3**, **4**, and **6** that allow differentiation between the η^5- and η^2-β-diketiminato bonding modes.

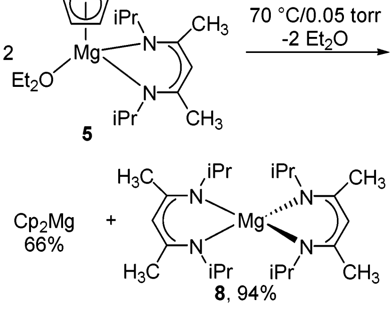
Equation 3 outlines the synthesis of homoleptic β-diketiminato complexes. Treatment of **1** or **2** with commercial dibutylmagnesium in diethyl ether at ambient temperature led to butane evolution and formation of $Mg(HC(C(Me)N(tBu))_2)_2$ (**7**, 68%) and $Mg(HC(C(Me)N(iPr))_2)_2$ (**8**, 78%) as colorless crystalline solids after workup. The structural assignments were based on spectral and analytical data, as well as X-ray crystal structure determinations. In the solid state structures, **7** and **8** each contain two η^2-β-diketiminato ligands. The ^1H NMR spectra of **7** and **8** show singlets for the β-CH fragment of the β-diketiminato ligand at δ 4.48 and 4.40, while the $^{13}C\{^1H\}$ NMR spectra reveal resonances for the associated carbon atom at 96.01 and 95.54 ppm, respectively. These values are similar to those exhibited by **3**, **4**, and **6**.



(3)

Volatility Study. To assess their initial viability as CVD precursors, **3**, **5**, **7**, and **8** were evaluated for their volatility and thermal stability. Complex **3** sublimed without decomposition at 74 °C/0.05 Torr, and sublimed **3** was recovered in 80% yield in a preparative sublimation. There was <1% residue in the preparative sublimation. Cp_2Mg sublimes at 60 °C/0.05 Torr[9a] at a rate similar to that of **3**, indicating that **3** is slightly less volatile than Cp_2Mg. Complexes **7** and **8** sublimed without decomposition at 104 °C/0.05 Torr and 160 °C/0.05 Torr, respectively.

Unlike the others, **5** did not sublime, but instead decomposed upon heating or even upon extended vacuum-drying at ambient temperature. Initial experiments were aimed at preparing the analogue of **3** containing deprotonated **2**, through thermolysis to remove the diethyl ether ligand in **5**. Under no thermolysis conditions was it possible to detect the analogue of **3**. Instead, **5** decomposed to afford mixtures of Cp_2Mg and **8** (eq 4). In a preparative experiment, sublimation of **5** at 70 °C/0.05 Torr afforded Cp_2Mg (66% of theory) and **8** (94% of theory). Cp_2Mg was isolated at the cold end of the sublimation tube, while **8** did not



(4)

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Table 1. Crystal Data and Data Collection Parameters for 3, 6, 7, and 8

	3	6	7	8
empirical formula	$C_{18}H_{30}MgN_2$	$C_{25}H_{39}MgN_3$	$C_{26}H_{50}MgN_4$	$C_{22}H_{42}MgN_4$
fw	298.75	405.90	443.01	386.91
space group	$P2(1)/n$	$Pnma$	$P2(1)/n$	$P2(1)/n$
a (Å)	8.216(2)	12.987(1)	10.015(1)	10.931(3)
b (Å)	24.889(6)	14.543(1)	17.667(1)	18.117(5)
c (Å)	10.073(2)	13.562(1)	15.917(2)	12.223(3)
β (deg)	111.590(6)		90.381(2)	92.494(7)
V (Å^3)	1915.2(7)	2561.3(4)	2816.2(4)	2418.4(11)
Z	4	4	4	4
temp (K)	295(2)	295(2)	295(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
calcd (g cm^{-3})	1.036	1.053	1.045	1.063
μ (mm^{-1})	0.090	0.084	0.081	0.086
$R(F)^a$ (%)	6.00	5.23	5.79	4.91
$R_w(F)^b$ (%)	14.69	12.32	14.26	12.25

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

Mg−N(1)	2.021(2)	Mg−N(2)	2.006(2)
Mg−C(1)	2.729(3)	Mg−C(2)	2.826(3)
Mg−C(3)	2.689(3)	Mg−C(14)	2.360(4)
Mg−C(15)	2.363(3)	Mg−C(16)	2.386(4)
Mg−C(17)	2.382(4)	Mg−C(18)	2.79(4)
N(1)−C(1)	1.318(3)	N(2)−C(3)	1.324(3)
N(1)−C(4)	1.487(3)	N(2)−C(10)	1.487(3)
C(1)−C(2)	1.416(4)	C(2)−C(3)	1.398(4)
Mg−C$_5$	2.081(2)		
N(1)−Mg−N(2)	92.34(8)	Mg(1)−N(1)−C(1)	107.8(2)
Mg−N(2)−C(3)	105.9(2)	N(1)−C(1)−C(2)	121.0(2)
N(2)−C(3)−C(2)	121.7(2)	C(1)−C(2)−C(3)	129.5(3)
N(1)−Mg−C$_5$	131.3(1)	N(2)−Mg−C$_5$	133.8(1)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6

Mg−N(1)	2.186(4)	Mg−N(2)	2.070(3)
Mg−C(15)	2.593(6)	Mg−C(16)	2.540(4)
Mg−C(17)	2.443(4)	N−C(9)	1.319(4)
C(9)−C(10)	1.408(4)	Mg−C$_5$	2.219(6)
N(1)−Mg−N(2)	100.1(1)	N(2)−Mg−N(2′)	94.0(2)
Mg−N(1)−C(1)	128.5(3)	Mg−N(1)−C(5)	116.6(3)
Mg−N(2)−C(9)	113.7(2)	N(2)−C(9)−C(10)	124.0(3)
C(9)−C(10)−C(9′)	131.4(4)		

sublime at this temperature. Apparently, the isopropyl groups in **5** are not sufficiently bulky to block intermolecular interactions that lead to ligand redistribution.

Crystal Structures

To establish the solid state geometries, the X-ray crystal structures of **3** and **6**−**8** were determined. Crystallographic data are summarized in Table 1. Selected bond distances and angles are given in Tables 2−5. Table 6 summarizes the bonding parameters of the β-diketiminato ligands. Perspective views of **3** and **6**−**8** are presented in Figures 1−4. In addition, the crystal structure of **4** was determined. The quality of the structural data was not as high as those of **6**, and the structural parameters were very similar to that of **6**. Accordingly, the structure of **4** is not discussed herein.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 7

Mg−N(1)	2.089(3)	Mg−N(2)	2.085(3)
Mg−N(3)	2.085(3)	Mg−N(4)	2.082(3)
N(1)−C(5)	1.328(4)	N(2)−C(8)	1.321(4)
N(3)−C(18)	1.323(4)	N(4)−C(21)	1.326(4)
C(5)−C(7)	1.411(4)	C(7)−C(8)	1.416(4)
C(18)−C(20)	1.408(4)	C(20)−C(21)	1.407(4)
N(1)−Mg−N(2)	100.2(1)	N(3)−Mg−N(4)	100.1(1)
N(1)−Mg−N(3)	116.2(1)	N(1)−Mg−N(4)	112.9(1)
N(2)−Mg−N(3)	113.6(1)	N(2)−Mg−N(4)	114.6(1)
Mg−N(1)−C(5)	117.3(2)	Mg−N(2)−C(8)	117.2(2)
Mg−N(3)−C(18)	117.4(2)	Mg−N(4)−C(21)	116.8(2)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 8

Mg−N(1)	2.054(2)	Mg−N(2)	2.061(2)
Mg−N(3)	2.065(2)	Mg−N(4)	2.052(2)
N(1)−C(4)	1.327(3)	N(2)−C(7)	1.332(3)
N(3)−C(15)	1.319(3)	N(4)−C(18)	1.318(4)
C(4)−C(6)	1.388(4)	C(6)−C(7)	1.413(4)
C(15)−C(17)	1.412(4)	C(17)−C(18)	1.399(4)
N(1)−Mg−N(2)	98.0(1)	N(3)−Mg−N(4)	97.7(1)
N(1)−Mg−N(3)	114.6(1)	N(1)−Mg−N(4)	117.8(1)
N(2)−Mg−N(3)	111.9(1)	N(2)−Mg−N(4)	117.8(1)
Mg−N(1)−C(4)	118.6(1)	Mg−N(2)−C(7)	118.7(2)
Mg−N(3)−C(15)	119.8(2)	Mg−N(4)−C(18)	119.5(2)

Table 6. Summary of Metrical Data for the β-Diketiminato Ligands in 3, 6, 7, and 8

complex	a−b angle (deg)^a	b−c angle (deg)^a	Mg···C$_\alpha$ (Å)	Mg···C$_\beta$ (Å)
3	55.5(1)	19.6(1)	2.729(5) 2.689(5)	2.826(5)
6	38.0(1)	9.7(1)	2.866(5)	3.081(5)
7	12.5(1)	1.5(1)	2.931(5) 2.942(5)	3.177(5)
	4.1(1)	0.9(1)	2.952(5) 2.935(2)	3.198(5)
8	0.6(1)	0.8(1)	2.945(5) 2.934(5)	3.159(5)
	0.6(1)	0.9(1)	2.938(5) 2.929(5)	3.159(5)

[a] a = plane defined by MgN$_2$, b = plane defined by N$_2$(C$_\alpha$)$_2$, c = plane defined by (C$_\alpha$)$_2$C$_\beta$.

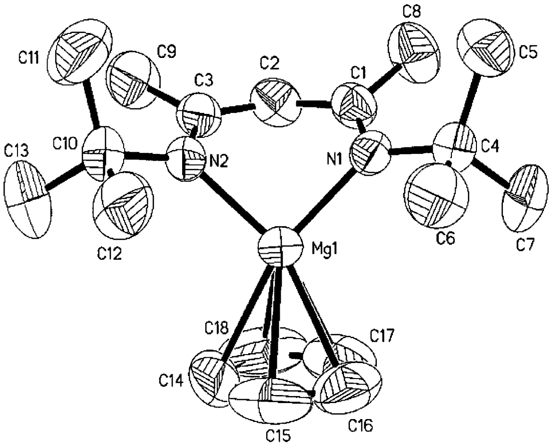

Figure 1. Perspective view of **3** with thermal ellipsoids at the 50% probability level.

Compound **3** crystallizes as a monomer, with one η^5-cyclopentadienyl ligand and one π-coordinated β-diketiminato ligand bonded to the magnesium center. The magnesium−carbon bond lengths associated with the cyclopentadienyl ligand range from 2.360(4) to 2.386(4) Å. The magnesium−cyclopentadienyl centroid distance is 2.081(2) Å. The magnesium−nitrogen bond lengths are 2.006(4) and 2.021(3) Å. The dihedral angle between the planes of the β-diketiminato ligand C$_3$N$_2$ core and the cyclopentadienyl ligand is 18.1°. The

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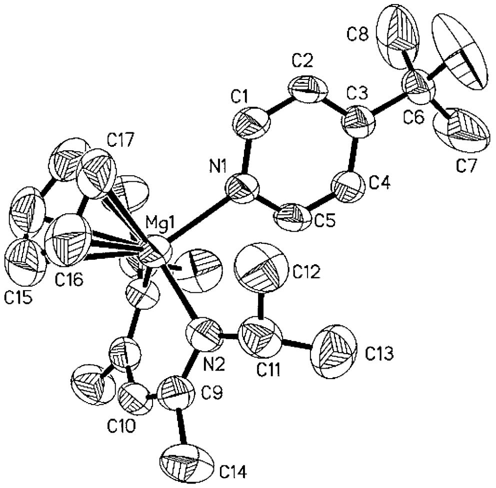

Figure 2. Perspective view of **6** with thermal ellipsoids at the 50% probability level.

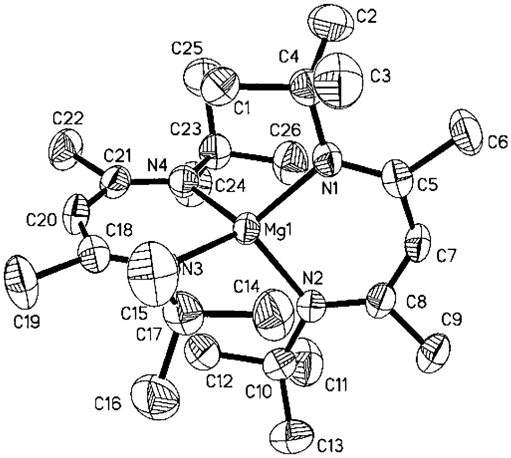

Figure 3. Perspective view of **7** with thermal ellipsoids at the 50% probability level.

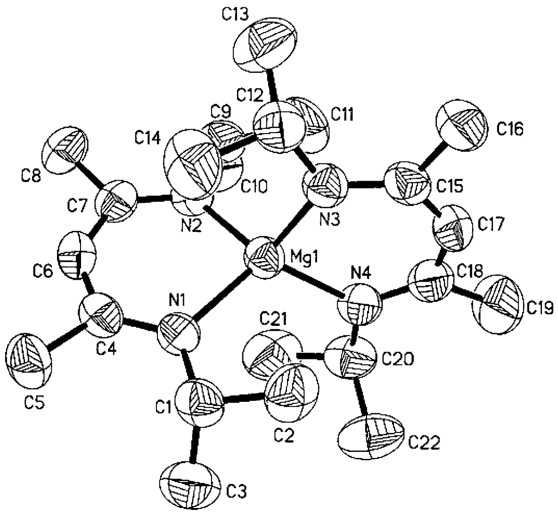

Figure 4. Perspective view of **8** with thermal ellipsoids at the 50% probability level.

nitrogen–carbon bond lengths of the β-diketiminato core are 1.318(3) and 1.324(3) Å, reflecting delocalized nitrogen–carbon bonding. Further analysis of the bonding between the magnesium ion and the β-diketiminato ligand is described below.

Compound **6** crystallizes as a monomer, with one η^5-cyclopentadienyl ligand, one η^2-β-diketiminato ligand, and one 4-*tert*-butylpyridine ligand bonded to the magnesium center. The two halves of the molecule are related by a mirror plane. The magnesium–carbon bond lengths associated with the cyclopentadienyl ligand are 2.443(4) (to C(17)), 2.540(4) (to C(16)), and 2.593(6) Å (to C(15)). The shortest magnesium–carbon bond is to C(17), which is closest to the 4-*tert*-butylpyridine ligand. The longest magnesium–carbon bond length is to C(15), which is furthest from the neutral ligand. Thus, coordination of the 4-*tert*-butylpyridine ligand causes the cyclopentadienyl ligand to slide away, apparently for steric reasons. The magnesium–cyclopentadienyl centroid distance is 2.219(4) Å, which is longer than the related value in **3** due to the increased coordination number in **6** and the distortions in the cyclopentadienyl ligand bonding noted above. The magnesium–nitrogen bond length is 2.070(3) Å, which is longer than those observed in **3**. The dihedral angle of the planes of the β-diketiminato and cyclopentadienyl ligands is 8.7°. Further analysis of the β-diketiminato ligand bonding is given below. The nitrogen–carbon bond length of the β-diketiminato core is 1.319(4) Å, reflecting delocalized nitrogen–carbon bonding. The magnesium–nitrogen bond length for the 4-*tert*-butylpyridine ligand is 2.186(4) Å.

Complex **7** crystallizes as a monomer, with two η^2-β-diketiminato ligands bonded to the tetrahedral magnesium center. Unlike **3** and **6**, the magnesium atom resides nearly in the C_3N_2 plane. The magnesium–nitrogen bond lengths range from 2.082(3) to 2.089(3) Å. These values are longer than those of **3**, due to accommodation of the bulky *tert*-butyl groups attached to the nitrogen atoms. The nitrogen–carbon bond lengths of the β-diketiminato cores range from 1.321(4) to 1.328(4) Å, reflecting delocalized nitrogen–carbon bonding. The dihedral angle of the two β-diketiminato ligands is 87.3(1)°. Further analysis of the β-diketiminato ligand bonding is given below.

Compound **8** crystallizes as a monomer, with two η^2-β-diketiminato ligands bonded to the tetrahedral magnesium center. The magnesium–nitrogen bond lengths range from 2.052(2) to 2.065(2) Å, which are smaller than the related values in **7** due to the decreased bulk of the isopropyl groups on the nitrogen atoms. The nitrogen–carbon bond lengths of the β-diketiminato cores range from 1.318(4) to 1.332(3) Å, reflecting delocalized nitrogen–carbon bonding. The dihedral angle of the two β-diketiminato ligands is 88.7(1)°. Further analysis of the β-diketiminato ligand bonding is given below.

Table 6 summarizes key metrical parameters associated with the β-diketiminato ligands in **3**, **6**, **7**, and **8**. To assess the bonding, the angles between the planes incorporating the atoms MgN_2 (a), $N_2(C_\alpha)_2$ (b), and $(C_\alpha)_2C_\beta$ (c) were calculated. The a/b angle assesses the movement of the magnesium atom over the π-face of the β-diketiminato ligand, while the b/c angle measures the distortion of C_β toward the magnesium atom due to possible bonding interactions. The largest angular distortions were found in **3**. The a/b angle was 55.5(1)°, while the b/c angle was 19.6(1)°. Thus, the magnesium atom lies over part of the π-cloud of the β-diketiminato

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ligand, and C_β is bent substantially out of the $N_2(C_\alpha)_2$ plane toward the magnesium ion. The corresponding values in **6** are a/b = 38.0(1)° and b/c = 9.7(1)°, which are substantially smaller than those observed in **3**. The values observed in **7** (a/b = 4.1(1)°, 12.5(1)°; b/c = 1.5(1)°, 0.9(1)°) and **8** (a/b = 0.6(1)°, 0.6(1)°; b/c = 0.8(1)°, 0.9(1)°) are consistent with planar or nearly planar MgN_2C_3 rings and serve as a reference for β-diketiminato ligands where there is essentially no bonding between the magnesium ion and the out-of-plane π-orbitals of the β-diketiminato ligands. The Mg−C_α and Mg−C_β distances also serve as a measure of the amount of π-bonding between the magnesium ion and the β-diketiminato ligands. In **7** and **8**, the Mg−C_α distances are between 2.93 and 2.95 Å and the Mg−C_β distances are between 3.16 and 3.20 Å. In **3**, these values are 2.689(3) and 2.729(3) Å for Mg−C_α and 2.826(3) Å for Mg−C_β. The values in **3** are much shorter than the analogous nonbonding values in **7** and **8** and suggest some π-bonding interactions in **3**. In **6**, the Mg−C_α distance is 2.866(5) Å and the Mg−C_β distance is 3.081(5) Å. We have recently reported a detailed study of amine adducts of Cp_2Mg, including the structural characterization of a range of complexes containing η^2-cyclopentadienyl ligands and highly distorted η^5-cyclopentadienyl ligands.[9a] In the complex (η^5-Cp)(η^2-Cp)Mg($NH_2C_6H_{11}$), the magnesium−carbon "bonding" distances associated with the η^2-cyclopentadienyl ligand were between 2.28 and 2.42 Å. The next nearest magnesium−carbon distance was 2.72 Å, which we suggested constitutes a weak interaction at best. Accordingly, the Mg−C_α distances in **3** are at the edge of bonding interactions, and such interactions are probably very weak. The Mg−C_β distance in **3** is clearly too long for anything but a weak bonding interaction and probably represents instead a distortion induced by electrostatic interactions between the positively charged magnesium ion and C_β with a partial negative charge on it. The Mg−C_α and Mg−C_β distances in **6** are also too long to be consistent with bonding interactions and instead probably result from electrostatic interactions between the positively charged magnesium ion and the negatively polarized carbon atoms of the β-diketiminato ligands.

Table 7. Summary of Metrical Data for Selected π-Coordinated β-Diketiminato Ligands in Complexes from the Literature

complex[a]	M−N (Å)	M···C_α (Å)	M···C_β (Å)
$Ba_2L_3(N(SiMe_3)_2)^3$	2.635(4)	3.161(5)	3.202(5)
	2.689(4)	3.244(5)	
$ZrCl_3(L)^{4a}$	2.138(5)	2.61(1)	2.54(1)
	2.187(5)	2.60(1)	
$Zr(L)(indenyl)Cl_2{}^{4b}$	2.201(2)	2.748(2)	2.703(2)
	2.192(1)	2.713(2)	
$Ti(L)Cl_3{}^{4c}$	1.995(4)	2.559(5)	2.535(4)
		2.535(5)	
$[CpZr(L)Cl]_2[B(Ar_F)_4]_2{}^{4d}$	2.110(3)	2.651(3)	2.657(3)
	2.141(2)	2.706(3)	
$Nd(L)_2Cl^{6a}$	2.397(6)	2.972	3.051
	2.442(6)	3.021	

[a] L = substituted β-diketiminato ligand; see references for substituents on N and C_α.

Discussion

A central issue is to analyze the bonding of the β-diketiminato ligand in the complexes described herein and to compare the coordination modes to related complexes in the literature. Table 7 lists bond length parameters from selected complexes that possess π-bonded β-diketiminato ligands with out-of-plane distortions similar to that observed in **3**. These data allow some comparison to the β-diketiminato ligand bonding modes described herein. Inspection of the bond length trends in Table 7 reveals that the shortest bond lengths in π-β-diketiminato ligands are to the nitrogen atoms. The bond lengths from the metal atoms to C_α and C_β are about 0.47−0.60 and 0.35−0.56 Å longer than the metal−nitrogen bond lengths. For **3**, the Mg−C_α distance is about 0.70 Å longer than the metal−nitrogen bond lengths, and the Mg−C_β distance is about 0.82 Å longer than the metal−nitrogen bond lengths. As far as similarities go, the general structure of the magnesium-β-diketiminato fragment in **3** is close to previously reported complexes with π-bonded β-diketiminato ligands. Thus, the magnesium atom in **3** resides essentially above the nitrogen atoms of the β-diketiminato ligand and has much longer contacts to C_α and C_β. However, the differences between Mg−C_α and Mg−C_β distances and the metal−nitrogen bond lengths in **3** are much longer than the complexes listed in Table 7. The complexes listed in Table 7 consist of large metal ions (Ba, Zr, Nd) and/or metal ions that are capable of dπ−pπ bonding to the carbon-based π-orbitals of the β-diketiminato ligand (Ti, Zr). By contrast, magnesium is a smaller metal ion that will naturally have longer Mg−C distances than larger metals if the magnesium atom is situated over the nitrogen atoms. In addition, the bonding in **3** should be predominantly ionic, which may not favor strong bonding interactions to the carbon atoms of the β-diketiminato ligand. The preference for π-bonding to the β-diketiminato ligand in **3** appears to arise from steric effects associated with the *tert*-butyl substituents on the nitrogen atoms. These substituents block coordination of diethyl ether and tetrahydrofuran, and only the more compact 4-*tert*-butylpyridine is able to coordinate to form **4**. Furthermore, η^2-coordination of the β-diketiminato ligands would lead to crowding between the cyclopentadienyl ligand and the *tert*-butyl groups, thus favoring the π-coordination mode. In his review,[2a] Lappert suggested that the formation of π-β-diketiminato ligands results from steric crowding around the metal centers. Our results with **3** are consistent with this model. The η^2-β-diketiminato ligands and lack of π-bonding in **7** and **8** arise from accommodation of the *tert*-butyl and isopropyl substituents about the magnesium centers.

Structurally characterized magnesium complexes with β-diketiminato ligands that have been reported to date have possessed the η^2-coordination mode, with essentially planar MgN_2C_3 rings.[12−15] This coordination mode is apparently driven by better accommodation of the bulky nitrogen atom substituents (aryl or trimethylsilyl) in the η^2-mode, compared to the π-mode. We carried out an analysis similar to that in Table 6 on all magnesium complexes containing β-diketiminato ligands that were reported in the latest release of the Cambridge Crystallographic Database (version 5.25, November 2003). The full data are presented in the Supporting Information. The structural distortions that are present in these complexes are far less than those observed in **3** and equal to or less than those observed in **6**−**8**. These

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data support our contention that **3** contains a new bonding mode for the β-diketiminato ligand. It is very likely that the previously described[15] complex Mg(HC(C(Me)N(Me))$_2$)$_2$ adopts a structure very similar to that of **7** and **8**. Metallocene-like structures in bis(β-diketiminato)magnesium complexes may not be accessible energetically with simple alkyl groups on the nitrogen atoms. Complex **3** is a rare example of a heteroatom-containing sandwich complex of magnesium. Herbereich reported a series of bis(boratabenzene)magnesium complexes that adopt sandwich structures.[18] These were the only examples of heteroatom-containing magnesocene analogues that were found in a search of the Cambridge Crystallographic Database (version 5.25, November 2003). The phospholide complex [Mg(C_4Et_4P)(THF)(μ-Cl)]$_2$ contains an η^5-phospholide ligand.[19]

Our final comments relate to the thermal stability and volatility of the complexes described herein and their potential use as film growth precursors. Complexes **3**, **7**, and **8** are volatile, do not decompose in preparative sublimations, and thus could be used as film growth precursors. Complex **3** sublimes at nearly the same temperature as Cp_2Mg and thus has a volatility approaching that of the most widely used magnesium film growth precursor. We have recently reported several studies describing the reaction of Cp_2Mg with primary and secondary alkylamines as a model for CVD film growth that involves treatment of Cp_2Mg with ammonia.[9a,e,f] Treatment of Cp_2Mg with a variety of alkylamines afforded adducts with reduced hapticity (or distorted bonding) of one cyclopentadienyl ligand, and in no case was elimination of a cyclopentadienyl ligand by protonolysis observed.[9a,f] While our model experiments were carried out at much lower temperatures (~23 °C) than CVD film growth experiments (~1050 °C for GaN:Mg[10]), our work does suggest that removal of the first cyclopentadienyl ligand from Cp_2Mg through protonolysis by ammonia is not particularly facile. Since elimination of the first cyclopentadienyl ligand in Cp_2Mg must be an important step for magnesium incorporation in film growth, replacement of a cyclopentadienyl ligand by a more reactive ligand could lead to more efficient magnesium incorporation. Thus, treatment of **3** with ammonia could lead to a low-energy transamination process[20] that eliminates **1** and affords highly reactive magnesium complexes containing one cyclopentadienyl ligand. The transamination process in **3** should be favorable, due to facile ammonia coordination to the magnesium ion (as loosely modeled herein by **4**), followed by proton transfer from the ammine nitrogen atom to a β-diketiminato ligand nitrogen atom and subsequent elimination of **1**. By contrast, there is a large difference in basicity between ammonia (pK_a ~33) and the cyclopentadiene (pK_a ~15.5),[21] thus accounting for our observed lack of cyclopentadiene elimination upon treatment of Cp_2Mg with alkylamines. Last, β-diketiminato complexes have not been used as film growth precursors. However, a recent paper has described the synthesis, structure, thermal stability, and volatility of a series of zirconium complexes that might serve as precursors for zirconium nitride film growth.[22]

Experimental Section

General Considerations. All reactions were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Hexanes were distilled from phosphorus pentoxide. Dichloromethane was distilled from calcium hydride. Cp_2Mg,[23] *N*-*tert*-butyl-4-(*tert*-butylimino)-2-penten-2-amine (**1**),[16] and *N*-isopropyl-4-(isopropylimino)-2-penten-2-amine (**2**)[16] were prepared according to literature procedures.

^1H NMR spectra were obtained at 300 MHz, while $^{13}C\{^1H\}$ NMR spectra were obtained at 100 MHz. Spectra were recorded in benzene-d_6 unless specified otherwise. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of [CpMg(HC(C(Me)N(tBu))$_2$)] (3). A 100 mL Schlenk flask was charged with Cp_2Mg (0.147 g, 0.950 mmol), $MgMe_2$ (0.052 g, 0.95 mmol), and diethyl ether (30 mL). The solution was stirred at ambient temperature for 1 h, and then **1** (0.400 g, 1.90 mmol) was added. The mixture was stirred for an additional 18 h. Removal of the volatile components under reduced pressure afforded **3** as a pale yellow solid (0.510 g, 90%): mp 88−90 °C; IR (Nujol, cm^{-1}) 1639 (w), 1537 (s), 1270 (s), 1211 (s), 1191 (s), 1027 (w), 1011 (m), 982 (w), 842 (w), 767 (s); ^1H NMR (benzene-d_6, δ) 6.41 (s, 5H, C_5H_5), 4.20 (s, 1H, β-C*H*), 1.82 (s, 6H, CCH_3), 1.19 (s, 18H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 165.84 (α-*C*), 105.86 (C_5H_5), 94.54 (β-*C*), 53.45 ($C(CH_3)_3$), 32.41 ($C(CH_3)_3$), 24.35 ($C(CH_3)$). Anal. Calcd for $C_{18}H_{30}MgN_2$: C, 72.37; H, 10.12; N, 9.38. Found: C, 71.91; H, 10.18; N, 9.27.

Preparation of [CpMg(HC(C(Me)N(tBu))$_2$)(4-(CH_3)$_3$C-C_6H_5N)] (4). A 50 mL Schlenk flask was charged with **3** (0.250 g, 0.837 mmol) and hexane (30 mL). The resultant solution was treated with 4-*tert*-butylpyridine (0.113 g, 0.837 mmol) and was stirred at ambient temperature for 2 h. Removal of volatile components afforded **4** as a white crystalline solid (0.318 g, 88%): mp 107−109 °C; IR (Nujol, cm^{-1}) 1597 (m), 1537 (s), 1402 (s), 1305 (w), 1262 (s), 1190 (s), 1070 (w), 1029 (w), 1011 (s), 984 (w), 963 (w), 843 (w), 818 (w), 767 (s), 723 (s); ^1H NMR (benzene-d_6, δ) 8.56 (m, 2H, py C*H*), 6.82 (m, 2H, py C*H*), 6.43 (s, 5H, C_5H_5), 4.21 (s, 1H, β-C*H*), 1.84 (s, 6H, CH_3), 1.18 (s, 18H, $C(CH_3)_3$), 0.98 (s, 9H, $(CH_3)_3CC_5H_5N$); $^{13}C\{^1H\}$ NMR (benzene-d_6, ppm) 165.84 (α-*C*), 159.21 (γ-*C* of py), 150.28 (α-*C* of py), 120.62 (β-*C* of py), 105.84 (C_5H_5), 94.67 (β-*C*), 53.54 ($C(CH_3)_3$), 33.06 ($C(CH_3)_3$ of py), 32.47 ($C(CH_3)_3$), 30.29 ($C(CH_3)_3$ of py), 24.57 (CCH_3). Anal. Calcd for $C_{27}H_{43}MgN_3$: C, 74.73; H, 9.99; N, 9.68. Found: C, 73.46; H, 9.78; N, 9.58.

Preparation of [CpMg(HC(C(Me)N(iPr))$_2$)(4-(CH_3)$_3$C-C_6H_5N)] (6). In a procedure similar to the preparation of **3**, Cp_2Mg (0.155 g, 1.00 mmol), $MgMe_2$ (0.054 g, 1.00 mmol), and **2** (0.335 g, 2.00 mmol) were allowed to react in diethyl ether (20 mL). The resultant solution was then treated with 4-*tert*-butylpyridine (0.270 g, 2.00 mmol). Removal of the volatile components, followed by crystallization of the crude solid from dichloromethane/hexane, afforded **6** as pale yellow crystals (0.588 g, 73%): mp 173−175 °C (dec); IR (Nujol, cm^{-1}) 1612 (m), 1531 (m), 1512 (m), 1417 (s), 1228 (w), 1122 (m), 975 (w),

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759 (s); ^{1}H NMR (benzene-d_6, δ) 8.64 (m, 2H, py CH), 6.73 (m, 2H, py CH), 6.64 (s, 5H, C_5H_5), 4.54 (s, 1H, β-CH), 3.60 (sept, J = 6.6 Hz, 2H, CH(CH_3)$_2$), 1.96 (s, 6H, C(CH_3)$_3$), 0.96 (d, J = 6.6 Hz, 12H, CH(CH_3)$_2$), 0.86 (s, 9H, (CH_3)$_3$CC_5H_5N); ^{13}C{^{1}H} NMR (dichloromethane-d_2, ppm) 165.77 (α-C), 164.18 (γ-C of py), 149.78 (α-C of py), 121.76 (β-C of py), 104.90 (C_5H_5), 93.87 (β-C), 49.74 (NCH(CH_3)$_2$), 35.39 (C(CH_3)$_3$), 30.40 (NCH(CH$_3$)$_2$), 24.67 (C(CH$_3$)$_3$), 22.87 (α-CCH$_3$). Anal. Calcd for $C_{25}H_{39}MgN_3$: C, 73.98; H, 9.68; N, 10.35. Found: C, 73.84; H, 9.61; N, 10.37.

Preparation of [Mg(HC(C(Me)N(tBu))$_2$)$_2$] (7). Method a. A 100 mL Schlenk flask was charged with **1** (0.35 g, 1.9 mmol) and diethyl ether (30 mL). This solution was cooled to −78 °C and then treated with nBuLi (2.0 M in hexane, 0.96 mL, 1.92 mmol). The resultant mixture was allowed to warm to ambient temperature and was stirred for an additional 3 h. The yellow solution was added by cannula to a solution of $MgBr_2$ (0.176 g. 0.96 mmol) in diethyl ether (20 mL), and the resultant mixture was stirred for 8 h at ambient temperature. Removal of the volatile components, followed by crystallization of the crude solid from hexane, afforded **7** as colorless crystals (0.338 g, 79%): mp 307−309 °C; IR (Nujol, cm^{-1}) 1524 (m), 1410 (m), 1299 (w), 1259 (m), 1185 (s), 1086 (w), 1029 (s), 967 (s), 724 (s); ^{1}H NMR (benzene-d_6, δ) 4.40 (s, 2H, β-CH), 2.05 (s, 12H, C(CH_3)), 1.53 (s, 36H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, ppm) 165.54 (α-C), 96.01 (β-C), 54.89 (C(CH_3)$_3$), 33.56 (C(CH$_3$)$_3$), 26.65 (CCH$_3$). Anal. Calcd for $C_{26}H_{50}MgN_4$: C, 70.49; H, 11.38; N, 12.65. Found: C, 70.68; H, 11.20; N, 12.86.

Method b. Treatment of **2** with 0.5 equiv of dibutylmagnesium in diethyl ether at ambient temperature for 3 h, followed by recrystallization of the crude solid from hexane at −30 °C, afforded **7** (68%).

Preparation of [Mg(HC(C(Me)N(iPr))$_2$)] (8). In a fashion similar to the preparation of **7**, method b, treatment of **2** (0.335 g, 2.00 mmol) with dibutylmagnesium (1.0 M in heptane, 1.00 mL, 1.00 mmol) in diethyl ether (30 mL) afforded a white solid after removal of the volatile components. Sublimation at 160 °C/0.05 Torr afforded **8** as colorless crystals (0.300 g, 78%): mp 118−120 °C; IR (Nujol, cm^{-1}) 1535 (s), 1519 (s), 1379 (s), 1337 (s), 1306 (m), 1259 (s), 1161 (w), 1145 (m), 1142 (m), 1092 (w), 1023 (s), 985 (w), 798 (s); ^{1}H NMR (benzene-d_6, δ) 4.48 (s, 2H, β-CH), 3.65 (sept, J = 6.4 Hz, 4H, CH(CH_3)$_2$), 1.91 (s, 12H, CCH_3), 1.29 (d, J = 6.4 Hz, 24H, CH(CH_3)$_2$); ^{13}C{^{1}H} (benzene-d_6, ppm) 165.76 (α-C), 94.54 (β-C), 50.15 (CH(CH_3)$_2$), 25.57 (CH(CH$_3$)$_2$), 22.87 (CCH$_3$). Anal. Calcd for $C_{22}H_{42}MgN_4$: C, 68.30; H, 10.94; N, 14.48. Found: C, 68.26; H, 10.70; N, 14.37.

Sublimation of 4 to Afford Cp_2Mg and 8. In a procedure similar to the preparation of **3**, Cp_2Mg (0.213 g, 1.37 mmol), dimethylmagnesium (0.0742 g, 1.37 mmol), and **2** (0.500 g, 2.74 mmol) were reacted in diethyl ether (20 mL). Removal of the volatile components, followed by sublimation at 70 °C/0.05 Torr, afforded Cp_2Mg (0.140 g, 66%) at the cold end of the sublimation tube and **8** (0.500 g, 94%) at the hot end of the sublimation tube.

X-ray Crystallographic Structure Determination for 1−4. 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 hemisphere of data was collected for each sample at 10 s/frame and 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 **3** and **7** were crystallized by sublimation and contain no associated ions or solvent. Complex **8** crystallizes from dichloromethane/hexane and has no associated ions or solvent. Complex **6** crystallizes also from dichloromethane/hexane and contains one *tert*-butylpyridine ligand.

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Supporting Information Available: Tables of structural data for **3**, **4**, **6**, **7**, and **8**. X-ray crystallographic files reported in this paper in CIF format for the structure determinations of **3**, **4**, **6**, **7**, and **8** may be obtained free of charge via the Internet at http://pubs.acs.org.

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