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Monomeric and Dimeric Amidinate Complexes of Magnesium

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Treatment of anhydrous magnesium bromide with 2 equiv of (1,3-di-*tert*-butylacetamidinato)lithium, (1,3-di-*tert*-butylbenzamidinato)lithium, (1,3-diisopropylacetamidinato)lithium, or (1-*tert*-butyl-3-ethylacetamidinato)-lithium (prepared in situ from the corresponding carbodiimide and alkyllithium) in diethyl ether at ambient temperature afforded bis(*N*,*N*′-di-*tert*-butylacetamidinato)magnesium (81%), bis(*N*,*N*′-di-*tert*-butylbenzamidinato)-magnesium (82%), bis[bis(*N*,*N*′-diisopropylacetamidinato)magnesium] (70%), or bis[bis(1-*tert*-butyl-3-ethylacetamidinato)magnesium] (93%), respectively, as colorless crystalline solids. These complexes were characterized by spectral and analytical data and by single-crystal X-ray crystallography for bis(*N*,*N*′-di-*tert*-butylbenzamidinato)-magnesium, bis[bis(*N*,*N*′-diisopropylacetamidinato)magnesium], and bis[bis(1-*tert*-butyl-3-ethylacetamidinato)-magnesium]. In the solid-state structure, bis[bis(1-*tert*-butyl-3-ethylacetamidinato)magnesium] was found to contain $\mu,\eta^2:\eta^1$-amidinato ligands. Bis[bis(*N*,*N*′-diisopropylacetamidinato)magnesium] exists in a monomer−dimer equilibrium in toluene-d_8 between −20 and +60 °C. A van't Hoff analysis of this equilibrium afforded $\Delta H° = -14.7 \pm 0.2$ kcal/mol, $\Delta S° = -44.9 \pm 0.2$ cal/(mol·K), and $\Delta G°(298\ \text{K}) = -1.32 \pm 0.2$ kcal/mol. The potential application of the new compounds in the chemical vapor deposition of magnesium-doped group 13 compound semiconductor films is discussed.

Introduction

Magnesium-doped semiconductors have existing and anticipated applications in the fabrication of blue and green light-emitting diodes, blue and green laser diodes, and in microelectronic devices.[1−6] Magnesium has been found to be the most useful p-type dopant, since it has a very low diffusion constant in common semiconductor matrixes, provides a desirable acceptor energy level, and its compounds exhibit low toxicity. Bis(cyclopentadienyl)magnesium (Cp_2Mg)[6−11] and substituted derivatives[12−15] are almost universally used as magnesium source compounds in film depositions by metal organic chemical vapor deposition, chemical beam epitaxy, and related techniques using molecular precursors. However, Cp_2Mg is a solid with a high melting point (176 °C) and low vapor pressure (sublimes at 160 °C, 0.1 mmHg). The problems associated with Cp_2Mg in doping semiconductor films have been well documented.[6] Moreover, carbon−hydrogen defects are incorporated into GaN films under chemical vapor deposition (CVD) growth conditions with moderate to heavy doping using Cp_2Mg, suggesting that the cyclopentadienyl ligands are the carbon source.[16]

To address the development of new magnesium source compounds, we have been exploring the synthesis and properties of volatile magnesium complexes that contain all-nitrogen coordination spheres.[17,18] Our efforts thus far have yielded dimeric pyrazolato[17] and monomeric silylamide complexes.[18] However, the pyrazolato complexes have only moderate vapor pressures due to the dimeric structures and the silylamide complexes are not useful precursors due to the potential incorporation of silicon in the films. Beyond our compounds, only a handful of neutral magnesium compounds with all-nitrogen coordination spheres and hydrocarbon groups attached to nitrogen have been reported.[19−24] Other previously described magnesium compounds possessing only magnesium−nitrogen bonds contain porphyrin ligands,[25,26] are ionic,[27−31] or contain undesired elements.[32−38]

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(1) Mohamad, S. N.; Salvador, A. A.; Morkoc, H. *Proc. IEEE* **1995**, *83*, 1306.
(2) Morkoc, H.; Mohamad, S. N. *Science* **1995**, *267*, 51.
(3) Gunshor, R. L.; Nurmikko, A. V. *MRS Bull.* **1995**, *20*, 15.
(4) Cao, X. A.; Pearton, S. J.; Ren, F. *Crit. Rev. Solid State Mater. Sci.* **2000**, *25*, 279.
(5) Pankove, J. I.; Moustakas, T. D. *Semicond. Semimet*. (*Gallium Nitride I*) **1998**, *50*, 1.
(6) Ambacher, O. *J. Phys. D: Appl. Phys*. **1998**, *31*, 2653.
(7) Chi, G. C.; Kuo, C. H.; Sheu, J. K.; Pan, C. J. *Mater. Sci. Eng. B* **2000**, *B75*, 210.
(8) Lee, C.-R.; Leem, J.-Y.; Noh, S.-K.; Park, S.-E.; Lee, J.-I.; Kim, C.-S.; Son, S.-J.; Leem, K.-Y. *J. Cryst. Growth* **1998**, *193*, 300.
(9) Neugebauer, J.; Van de Walle, C. G. *J. Appl. Phys*. **1999**, *85*, 3003.
(10) Kozen, A.; Nojima, S.; Tenmyo, J.; Asahi, H. *J. Appl. Phys*. **1986**, *59*, 1156.
(11) Tamamura, K.; Ohhata, T.; Kawai, H.; Kojima, C. *Jpn. J. Appl. Phys*. **1986**, *59*, 3549.
(12) Nakamura, S.; Mukai, T.; Senoh, M.; Iwasa, N. *Jpn. J. Appl. Phys*. **1993**, *31*, L139.
(13) Nakamura, S.; Iwasa, N.; Senoh, M.; Mukai, T. *Jpn. J. Appl. Phys*. **1992**, *31*, 1258.
(14) Nakamura, S.; Senoh, M.; Mukai, T. *J. Appl. Phys*. **1991**, *30*, L1708.
(15) De Mierry, P.; Beaumont, B.; Feltin, E.; Schenk, H. P. D.; Gibart, P.; Jomard, F.; Rushworth, S.; Smith, L.; Odedra, R. *MRS Internet J. Nitride Semicond. Res.* **2000**, *5*, 1.
(16) Yi, G.-C.; Wessels, B. W. *Appl. Phys. Lett*. **1997**, *70*, 357.
(17) Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 2517.
(18) Sebestl, J. L.; Nadasdi, T. T.; Heeg, M. J.; Winter, C. H. *Inorg. Chem*. **1998**, *37*, 1289.
(19) Bailey, P. J.; Dick, C. M. E.; Fabre, S.; Parsons, S. *J. Chem. Soc., Dalton Trans*. **2000**, 1655.
(20) Clegg, W.; Craig, F. J.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E.; O'Neil, P. A.; Reed, D. *Inorg. Chem*. **1997**, *36*, 6238.
(21) Gardiner, M. G.; Hanson, G. R.; Henderson, M. J.; Lee, F. C.; Raston, C. L. *Inorg. Chem*. **1994**, *33*, 2456.
(22) Clegg, W.; Henderson, K. W.; Mulvey, R. E.; O'Neill, P. A. *J. Chem. Soc., Chem. Commun.* **1994**, 769.
(23) Henderson, K. W.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *Polyhedron* **1993**, *12*, 2535.
(24) Dozzi, G.; Del Piero, G.; Cesari, M.; Cucinella, S. *J. Organomet. Chem.* **1980**, *190*, 229.

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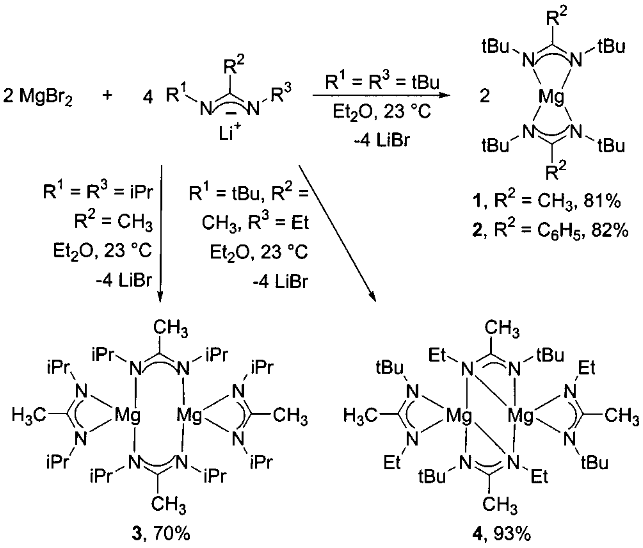
Amidinate ligands are extremely promising for use in CVD source compounds, since all-nitrogen coordination spheres are obtained, the molecular weights of these ligands are relatively low, and the properties of the resultant complexes can be tuned by substitution at the carbon and nitrogen atoms of the ligand core. Despite the desirable attributes and recent widespread use of these ligands in transition,[39−44] lanthanide,[45−49] and main group[50−59] metal chemistry, it is surprising that very few magnesium amidinate complexes have been reported so far.[60−65] With these considerations in mind, we report the synthesis, structure, and reactivity of several monomeric and dimeric amidinate complexes of magnesium. These complexes do not form tetrahydrofuran adducts, possess only magnesium−nitrogen bonds in the coordination sphere, and contain only magnesium, carbon, nitrogen, and hydrogen. Two of the compounds, bis(*N*,*N*′-di-*tert*-butylacetamidinato)magnesium and bis[bis(*N*,*N*′-diisopropylacetamidinato)magnesium], sublime at 70 °C/0.05 Torr and are excellent candidates for CVD precursors. Furthermore, the effect of the nitrogen atom substituents on the structures of the resulting magnesium complexes is discussed. Finally, a monomer−dimer equilibrium of bis[bis(*N*,*N*′-diisopropylacetamidinato)magnesium] is reported.

Scheme 1. Synthesis of **1**−**4**



Results

Synthesis of New Complexes. Treatment of anhydrous magnesium bromide with 2 equiv of (1,3-di-*tert*-butylacetamidinato)lithium, (1,3-di-*tert*-butylbenzamidinato)lithium, (1,3-diisopropylacetamidinato)lithium, or (1-*tert*-butyl-3-ethylacetamidinato)lithium (prepared in situ from the corresponding carbodiimide and alkyllithium) in diethyl ether at ambient temperature afforded bis(*N*,*N*′-di-*tert*-butylacetamidinato)magnesium (**1**, 81%), bis(*N*,*N*′-di-*tert*-butylbenzamidinato)magnesium (**2**, 82%), bis[bis(*N*,*N*′-diisopropylacetamidinato)magnesium] (**3**, 70%), or bis[bis(1-*tert*-butyl-3-ethylacetamidinato)magnesium] (**4**, 93%), respectively, as colorless crystalline solids (Scheme 1). The structural assignments for **1**−**4** were based upon spectral and analytical data and by X-ray crystal structure determinations for **2**−**4** as described below. A crystal structure determination of **1** was not possible due to poor crystal quality, but the related benzamidinate complex **2** was shown to be a monomer in the solid state. The NMR spectra of **1** and **2** in toluene-d_8 showed no evidence for dimeric or oligomeric structures between −80 and +60 °C. Accordingly, the *tert*-butyl groups in **1** and **2** are bulky enough to block dimerization and confer monomeric structures in both solution and the solid state. Complex **3** was found to be dimeric by an X-ray crystal structure determination.

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(25) For example, see: McKee, V.; Ong, C. C.; Rodley, G. A. *Inorg. Chem.* **1984**, *23*, 4242.
(26) For example, see: Mani, N. S.; Beall, L. S.; Miller, T.; Anderson, O. P.; Hope, H.; Parkin, S. R.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2095.
(27) Bottomley, G. A.; Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Geue, R. J.; Hagen, K. S.; Harrowfield, J. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; See, A. J.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1994**, *47*, 143.
(28) Paul, P. P.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 5, 3316.
(29) Willey, G. R.; Palin, J.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1994**, 1799.
(30) Drew, M. G. B.; Claire, P. P. K.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1988**, 215.
(31) Waters, A. F.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 147.
(32) Rees, W. S., Jr.; Luten, H. A.; Just, O. *Chem. Commun.* **2000**, 735.
(33) Caro, C. F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 1433.
(34) Fleischer, R.; Stalke, D. *J. Organomet. Chem.* **1998**, *550*, 173.
(35) Fleischer, R.; Stalke, D. *Inorg. Chem.* **1997**, *36*, 2413.
(36) Olmstead, M. M.; Grigsby, W. J.; Chacon, D. R.; Hascall, T.; Power, P. P. *Inorg. Chim. Acta* **1996**, *251*, 273.
(37) Clegg, W.; Henderson, K. W.; Mulvey, R. E.; O'Neil, P. A. *J. Chem. Soc., Chem. Commun.* **1993**, 969.
(38) Sohrin, Y.; Kokusen, H.; Kihara, S.; Matsui, M.; Kushi, Y.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 4128.
(39) Guiducci, A. E.; Cowley, A. R.; Skinner, M. E. G.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2001**, 1392.
(40) Vendemiati, B.; Prini, G.; Meetsma, A.; Hessen, B.; Teuben, J. H.; Traverso, O. *Eur. J. Inorg. Chem.* **2001**, 707.
(41) Hideo, K.; Yamaguchi, Y.; Nagashima, H. *J. Am. Chem. Soc.* **2001**, *123*, 500.
(42) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909.
(43) Decker, J. M.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4417.
(44) Cotton, F. A.; Murillo, C. A.; Isabel, P. *Inorg. Chem.* **1999**, *38*, 2182.
(45) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *133*, 219
(46) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782.
(47) Doyle, D.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **2000**, 4093.
(48) Schmidt, J. A. R.; Arnold, J. *Chem. Commun.* **1999**, 2149.
(49) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197.
(50) Meier, R. J.; Koglin, E. *J. Phys. Chem. A* **2001**, *105*, 3867.
(51) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Dalton Trans.* **2000**, 1663.
(52) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924.
(53) Blais, P.; Chivers, T.; Downard, A.; Parvez, M. *Can. J. Chem.* **2000**, *78*, 10.
(54) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274.
(55) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1999**, *18*, 4700.
(56) Dagorne, S.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1999**, *18*, 4619.
(57) Barker, J.; Aris, D. R.; Blacker, N. C.; Errington, W.; Phillips, P. R.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1999**, *586*, 138.
(58) Chivers, T.; Downard, A.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 4347.
(59) Schoeller, W. W.; Sundermann, A.; Reiher, M. *Inorg. Chem.* **1999**, *38*, 29.
(60) Kincaid, K.; Gerlach, C. P.; Giesbrecht, G. R.; Hagdorn, J. R.; Whitener, G. D.; Shafir, A.; Arnold, J. *Organometallics* **1999**, *18*, 5360.
(61) Walther, D.; Gebhardt, P.; Fischer, R.; Kreher, U.; Görls, H. *Inorg. Chim. Acta* **1998**, *281*, 181.
(62) Srinivas, B.; Chang, C. C.; Chen, C. H.; Chiang, M. Y.; Chen, I.-T.; Wang, Y.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1997**, 957.
(63) Li, M.-D.; Chang, C. C.; Wang, Y.; Lee, G.-H. *Organometalics* **1996**, *15*, 2571.
(64) Westerhausen, M.; Hausen, H.-D. *Z. Anorg. Allg. Chem.* **1992**, *615*, 27.
(65) Cotton, F. A.; Haefner, S. C.; Matonic, J. H.; Wang, X.; Murillo, C. A. *Polyhedron* **1997**, *16*, 541.

In toluene-d_8 solution, **3** exists in a monomer−dimer equilibrium between −20 and +60 °C, as assessed by NMR spectroscopy. At or below −20 °C, only resonances due to the dimeric structure were observed in the ^{1}H NMR spectrum. At or above 60 °C, only resonances due to the monomeric structure were observed in the ^{1}H NMR spectrum. Between −20 and +60 °C, mixtures of monomeric and dimeric structures were observed. A van't Hoff analysis of this equilibrium process is outlined below. These results suggest that the isopropyl substituents are not sufficient to provide a monomeric formulation, and dimerization occurs in the solid state and at low temperature in solution to afford **3**. The structure of **4** in the solid state is a dimer, but the bridging amidinate ligand is bonded in a μ,η^2:η^1-fashion as opposed to the μ,η^1:η^1-acetamidinate ligands present in **3**. The unusual bonding interaction in **4** appears to be due to the reduced steric demand of the nitrogen atom bearing the ethyl group, which allows an increase in coordination number at magnesium. While **4** is obtained as a single isomer in the solid state, NMR spectra at or below ambient temperature revealed a complex pattern of resonances. If a dimeric structure for **4** is maintained in solution and it is assumed that the planes of the bridging and terminal amidinate ligands will be approximately perpendicular to each other, then there are four possible diastereomers that are related by syn and anti relationships of the *tert*-butyl groups within the dimeric unit. At 80 °C in toluene-d_8, bridging and terminal amidinate ligand site exchange was fast on the NMR time scale.

Attempts were made to prepare tetrahydrofuran adducts of **1**−**4**. Complexes **1**−**4** were dissolved in tetrahydrofuran and were allowed to stir for 18 h at ambient temperature. After isolation and vacuum-drying, ^{1}H NMR spectroscopy did not reveal any coordination of tetrahydrofuran, and only **1**−**4** were recovered. Interestingly, the tetrahydrofuran complexes Mg(RNC(R′)NR)$_2$(THF)$_2$ (R = ^{i}Pr, R′ = Ph, Et, ^{i}Pr; R = ^{t}Bu, R′ = Et) have been prepared by treatment of MgR′$_2$ with the carbodiimides in tetrahydrofuran, followed by crystallization from concentrated tetrahydrofuran solutions.[62] The fact that tetrahydrofuran adducts were not isolated from **1**−**4** suggests that tetrahydrofuran ligand coordination to the Mg(RNC(R′)NR)$_2$ unit is very weak and that the neutral donor ligands are easily lost upon isolation and vacuum-drying.

Volatility Evaluation. As part of our long-term goal of preparing new source compounds for chemical vapor deposition, we examined the volatility and thermal stability of **1**−**4**. Complex **1** sublimed at 70 °C/0.05 Torr without visible residue to afford unchanged **1**. In a preparative sublimation (ca. 0.5 g), sublimed **1** was isolated with 83% recovery and there was <2% residue left upon sublimation. For comparison, bis(cyclopentadienyl)magnesium sublimes at 160 °C/0.05 Torr in the same apparatus. Complex **2** decomposed upon sublimation at 120 °C/0.05 Torr to afford unchanged **2** (26% recovery) and a unidentified residue. The higher sublimation temperature of **2**, compared to **1**, is consistent with the higher lattice energy present in **2** due to arene π-stacking interactions associated with the phenyl substituents. Complex **3** sublimed at 70 °C/0.1 Torr to afford unchanged **3**. On a scale of 0.200 g, sublimed **3** was recovered in 80% yield and there was <2% residue left after completion of the sublimation. The fact that dimeric **3** sublimes at the same temperature as monomeric **1** suggests that **3** departs from the solid as a monomer and then recombines in the cool portion of the apparatus to reform the dimeric complex. Since the melting point of **3** (110 °C) is higher than the sublimation temperature (70 °C), a monomer−dimer equilibrium must be accessible on the surface of crystalline **3**. Complex **4** sublimed at 108 °C/0.05 Torr to afford unchanged **4** (70% recovery on a 0.150 g scale) and 3% residue in the sublimation flask.

Table 1. Crystal Data and Data Collection Parameters for **2**−**4**

	2	**3**	**4**
empirical formula	$C_{30}H_{46}MgN_4$	$C_{32}H_{68}Mg_2N_8$	$C_{32}H_{68}Mg_2N_8$
fw	487.02	613.56	613.56
space group	$C2/c$	$C2/c$	$P2_1/c$
a (Å)	25.110(4)	23.447(3)	10.135(2)
b (Å)	8.7234(12)	9.7360(12)	17.162(4)
c (Å)	18.430(3)	18.431(2)	22.503(5)
β (deg)	129.155(2)	111.095(2)	91.799(5)
V (Å^3)	3130.4(8)	3925.6(8)	3912.3(15)
Z	4	4	4
T (K)	295(2)	295(2)	295(2)
λ (Å)	0.710 73	0.710 73	0.710 73
calcd (g cm^{-3})	1.033	1.038	1.042
μ (mm^{-1})	0.079	0.091	0.092
$R(F)^a$ (%)	5.35	4.22	3.95
$R_w(F)^b$ (%)	13.13	10.01	7.21

[a] $R(F) = \sum||Fo| - |F_c||/\sum |F_o|$. [b] $R_w(F)^2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

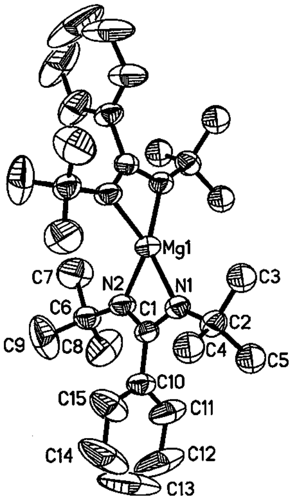

Figure 1. Perspective view of bis(N,N-di-*tert*-butylbenzamidinato)magnesium (**2**) with thermal ellipsoids at the 50% probability level.

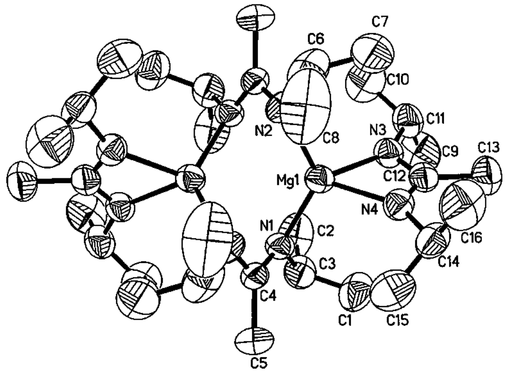

Figure 2. Perspective view of bis[bis(N,N-diisopropylacetamidinato)magnesium] (**3**) with thermal ellipsoids at the 50% probability level.

Crystal Structures of 2−**4.** To establish the solid-state geometries, the X-ray crystal structures of **2**−**4** were determined. Crystallographic data for **2**−**4** are summarized in Table 1. Perspective views of **2**−**4** are presented in Figures 1−3, along with selected bond lengths and angles in Tables 2−4.

Complex **2** exists as a four-coordinate monomer in which the amidinate ligands are coordinated in a chelating η^2-fashion (Figure 1). Such coordination affords distorted tetrahedral

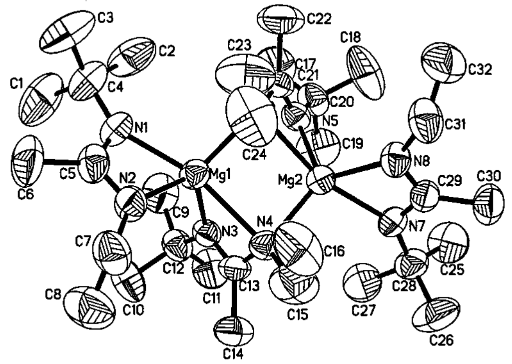

Figure 3. Perspective view of bis[bis(1-*tert*-butyl-3-ethylacetamidinato)magnesium] (**4**) with thermal ellipsoids at the 50% probability level.

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

Mg−N(1)	2.0406(17)	Mg−N(2)	2.0426(18)
N(1)−Mg-N(2)	65.77(7)	N(1)−Mg−N(2′)	133.31(7)
N(1)−Mg−N(1′)	144.79(11)	N(2)−Mg−N(2′)	125.81(11)

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

Mg(1)−N(1)	2.1073(16)	Mg(1)−N(4)	2.0948(17)
Mg(1)−N(2)	2.1018(17)	Mg(1)−**Mg(1′)**	3.0861(12)
Mg(1)−N(3)	2.0859(16)		
N(1)−Mg(1)−N(2)	128.12(7)	N(2)−Mg(1)−N(3)	107.92(7)
N(1)−Mg(1)−N(3)	114.77(7)	N(2)−Mg(1)−N(4)	115.06(7)
N(1)−Mg(1)−N(4)	109.10(7)	N(3)−Mg(1)−N(4)	64.71(7)

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

Mg(1)−N(1)	2.124(2)	Mg(2)−N(4)	2.113(2)
Mg(1)−N(2)	2.070(2)	Mg(2)−N(5)	2.087(2)
Mg(1)−N(3)	2.0962(19)	Mg(2)−N(6)	2.368(2)
Mg(1)−N(4)	2.380(2)	Mg(2)−N(7)	2.132(2)
Mg(1)−N(6)	2.126(2)	Mg(2)−N(8)	2.062(2)
Mg(1)−Mg(2)	3.0594(12)		
N(1)−Mg(1)−N(2)	63.77(9)	N(4)−Mg(2)−N(5)	123.56(8)
N(1)−Mg(1)−N(3)	117.88(9)	N(4)−Mg(2)−N(6)	89.76(8)
N(1)−Mg(1)−N(4)	164.29(9)	N(4)−Mg(2)−N(7)	104.68(8)
N(1)−Mg(1)−N(6)	104.33(8)	N(4)−Mg(2)−N(8)	120.65(8)
N(2)−Mg(1)−N(3)	110.03(8)	N(5)−Mg(2)−N(6)	59.69(7)
N(2)−Mg(1)−N(4)	101.82(9)	N(5)−Mg(2)−N(7)	115.98(8)
N(2)−Mg(1)−N(6)	126.13(9)	N(5)−Mg(2)−N(8)	111.88(8)
N(3)−Mg(1)−N(4)	59.24(7)	N(6)−Mg(2)−N(7)	163.36(8)
N(3)−Mg(1)−N(6)	120.43(8)	N(6)−Mg(2)−N(8)	101.62(8)
N(4)−Mg(1)−N(6)	89.13(8)	N(7)−Mg(2)−N(8)	64.05(8)

geometry about the magnesium atom. The magnesium−nitrogen bond lengths are 2.0406(17) (Mg−N(1)) and 2.0426(18) Å (Mg−N(2)). The geometry about magnesium is characterized by N(1)−Mg−N(2′), N(1)−Mg−N(1′), and N(2)−Mg-N(2′) angles of 133.31(7), 144.79(11), and 125.81(11)°, respectively. The nitrogen−magnesium−nitrogen angle within the amidinate ligand is 65.77(7)°. Within the MgN$_2$C metallacycle, the carbon atom (C(1)) projects 0.128 Å above the plane defined by Mg, N(1), and N(2).

Compound **3** exists as a four-coordinate, dimeric complex in which each magnesium atom is bonded to the nitrogen atoms of one amidinate ligand in a terminal, chelating η^2-fashion and to the nitrogen atoms of two amidinate ligands with μ_2-interactions (Figure 2). The η^2-interaction is characterized by magnesium−nitrogen bond lengths of 2.0859(16) (Mg(1)−N(3)) and 2.0948(17) Å (Mg(1)−N(4)). The μ_2-amidinato interactions have magnesium−nitrogen bond lengths of 2.1073(16) (Mg(1)−N(1)) and 2.1018(17) Å (Mg(1)−N(2)). These bond lengths are 0.04−0.06 Å longer than the magnesium−nitrogen bond lengths in **2**. The nonbonded Mg⋯Mg distance is 3.0861(12) Å. The geometry about each magnesium center is distorted tetrahedral, with nitrogen−magnesium−nitrogen angles that range from 64.71(7) to 128.12(7)°. The nitrogen−magnesium−nitrogen angles of the chelating amidinate ligands are the most acute.

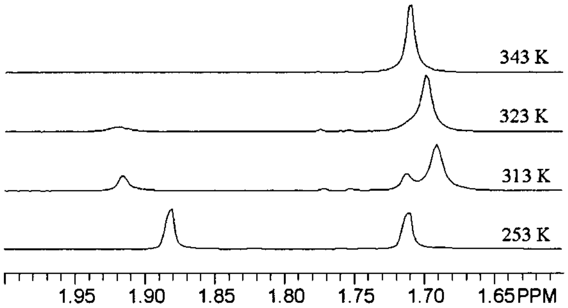

Figure 4. ^{1}H NMR spectra of **3** in toluene-d_8 taken at the indicated temperatures.

Table 5. Equilbrium Constants for **3** at Various Temperatures

T (K)	K_{eq} (L/mol)	T (K)	K_{eq} (L/mol)
265.8	198.7	323.8	1.26
291.2	16.72	329.0	0.921
308.2	4.47	339.1	0.475
318.5	2.08		

Compound **4** exists as a dimeric complex in which each magnesium atom is bonded to the nitrogen atoms of one amidinate ligand in a terminal η^2-fashion and to the nitrogen atoms of two bridging amidinate ligands with μ_2-interactions (Figure 3). Unlike **3**, the bridging amidinate ligands in **4** form an extra magnesium−nitrogen bond to afford a $\mu,\eta^2:\eta^1$-bridging ligand, which is a novel coordination mode for amidinate ligands. The unusual fifth magnesium−nitrogen bonds of the bridging amidinate ligands are longer (2.380(2) and 2.368(2) Å) than the other magnesium−nitrogen bonds (2.124(2) (Mg(1)−N(1), 2.070(2) (Mg(1)−N(2), 2.0962(19) (Mg(1)−N(3)), and 2.126(2) Å (Mg(1)−N(6)). The geometry about each magnesium atom can be viewed as distorted square pyramidal with Mg(1)−N(6) and Mg(2)−N(4) being the axial bonds of each square pyramid. The distorted square pyramidal distortion is characterized by N(1)−Mg(1)−N(6), N(2)−Mg(1)−N(6), N(3)−Mg(1)−N(6), and N(4)−Mg(1)−N(6) angles of 104.33(8), 126.13(9), 120.43(8), and 89.13(8)°, respectively. Again, the most acute angles are associated with the nitrogen−magnesium−nitrogen angles of the chelating amidinate ligands (59.24(7)° (N(3)−Mg(1)-N(4)) and 63.77(9)° (N(1)−Mg(1)-N(2))).

van't Hoff Analysis. Variable-temperature ^{1}H NMR spectra of **3** were recorded between −80 and +80 °C in toluene-d_8. Figure 4 shows the amidinate methyl group resonance region in the ^{1}H NMR spectra that were obtained at various temperatures and emphasizes the observed dimeric structure at −20 °C, the mixture of resonances for monomeric and dimeric structures between −20 and +60 °C, and the monomeric structure at 70 °C. Equilibrium constants (K_{eq}) for the monomer−dimer equilibrium were determined from the concentrations of monomeric and dimeric species calculated from the ^{1}H NMR spectra at various temperatures and are given in Table 5. Analysis of these data for dimerization of two monomeric units using standard procedures for van't Hoff analyses[66] afforded $\Delta H^\circ = -14.7 \pm 0.2$ kcal/mol, $\Delta S^\circ = -44.9 \pm 0.2$ cal/(mol·K), and $\Delta G^\circ(298\ \mathrm{K}) = -1.32 \pm 0.2$ kcal/mol. Hence, the favorable enthalpy for conversion of the 2 equiv of the monomer

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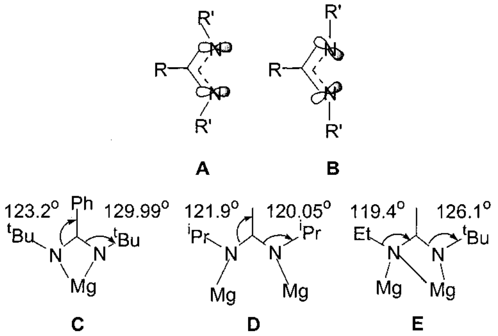
(66) For example, see: Levine, I. N. *Physical Chemistry*, 3rd ed.; McGraw-Hill: New York, 1988; pp 177−180.

Chart 1. Angular Data for Amidinate Ligands



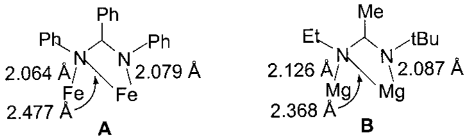
to the dimer is offset by the $T\Delta S°$ term when the temperature is sufficiently high.

Discussion

Magnesium complexes containing two monoanionic, bidentate nitrogen donor ligands are relatively rare.[19,21,32−35,67,68] The volatility and thermal stability of many of these complexes have not been reported. Rees has reported that $Mg(N(SiMe_3)CH_2CH_2CH_2NMe_2)_2$ sublimes at 80 °C/10^{-2} Torr and does not decompose during the sublimation.[32] However, this compound contains silicon and may not be useful as a CVD precursor for group 13 nitride films due to undesired silicon incorporation in the films. Raston has described the synthesis of bis(1,4-di-*tert*-butyl-1,4-diazabutadiene)magnesium and noted that it sublimes at 100 °C/0.03 Torr.[21] This compound combines volatility with minimal element content (Mg, N, C, H). While this compound is potentially useful as a source compound for in CVD, it is formally a magnesium(0) complex and may not deliver magnesium(II) to the growing film. Complexes **1** and **3** described herein sublime at 70 °C/0.05 Torr, which can be compared with the much higher sublimation temperature of the widely used source compound Cp_2Mg (160 °C/0.05 Torr) and the nitrogen-based complexes of Rees[32] and Raston.[21] The high volatility, minimal element content, and lack of direct magnesium−carbon bonds make **1** and **3** very attractive structures for use in CVD. In fact, **1** and **3** are the most volatile magnesium complexes with all-nitrogen coordination spheres that have been reported to date.

Complexes **1**−**4** document an interesting set of solid-state structural changes that occur upon variation of the nitrogen atom substituents. *tert*-Butyl groups are clearly required to obtain monomeric structures, although the similar sublimation temperatures of **1** and **3** suggest that the latter has an accessible dimer−monomer equilibrium on the surface of the solid. Incorporation of a smaller ethyl group on nitrogen leads to **4**, which contains $\mu,\eta^2:\eta^1$-bridging amidinate ligands. Jordan[69] has proposed that, in an idealized amidinate structure with 120° bond angles at the carbon and nitrogen centers, the nitrogen sp^2 donor orbitals project in parallel directions and a bridging bonding mode should be favored (Chart 1, **A**). Increasing the R−C−N and C−N−R′ angles will cause the nitrogen lone pair orbitals to project more toward the center of the amidinate ligand "mouth" and should favor a chelating bonding mode (Chart 1, **B**). The structural results obtained with **1**−**4** are consistent with Jordan's model. In **3**, the $C_{bridge}{-}N{-}CH(CH_3)_2$ angle is 120.05° and $N{-}C_{bridge}{-}CH_3$ is 121.9° (Chart 1, **D**), leading to a predicted bridging mode, as observed experimentally. In **2**, the $C_{bridge}{-}N{-}C(CH_3)_3$ angle is 129.99° (Chart 1, **C**), which is much larger than the related value in **3** due to the increased steric demand associated with the *tert*-butyl substituent. Accordingly, the chelating coordination mode is observed. The unusual coordination mode in **4** can be attributed to the significant steric demand of the *tert*-butyl group and much smaller steric effects of the ethyl group. The $C_{bridge}{-}N{-}C(CH_3)_3$ angle of **4** is 126.1° while the $CH_3CH_2{-}N{-}C_{bridge}$ angle is 119.4° (Chart 1, **E**).

Chart 2. Bond Length Data in $\mu,\eta^2:\eta^1$-Amidinate Complexes



The magnesium−nitrogen bond lengths of **1**−**4** are similar to the related values previously reported for $\{Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[({}^iPr)NC(Me)N({}^iPr)]\}$ (2.062(8), 2.079(8) Å),[63] $\{Me_2Al(\mu\text{-}{}^iPr_2N)_2Mg[(tBu)NC(Me)N(tBu)]\}$ (2.064(5), 2.063(5) Å),[63] $\{Mg[({}^iPrN)_2CNiPr_2]_2(THF)\}$ (2.066(7), 2.183(6) Å),[62] and $[Mg({}^iPrNCPhNiPr)_2(THF)_2]$ (2.168(6), 2.161(6) Å).[62] The most striking structural feature in **1**−**4** is the unusual bridging $\mu,\eta^2:\eta^1$-admidinate ligand that is observed in **4**. A search of the Cambridge Crystallographic Database revealed that a bridging $\mu,\eta^2:\eta^1$-benzamidinate ligand was previously documented in $Fe_2(PhNC(Ph)NPh)_4$.[70] Chart 2 summarizes the metrical parameters associated with the bridging benzamidinate ligand in $Fe_2(PhNC(Ph)NPh)_4$ (**A**) and the bridging acetamidinate ligand in **4** (**B**). Since the sizes of the magnesium ion and high spin iron(II) ion are similar,[71] the bond lengths can be compared directly. In the bridging benzamidinate ligand of $Fe_2(PhNC(Ph)NPh)_4$ (Chart 2, **A**) there are two short iron−nitrogen bond lengths (2.064, 2.079 Å) and one long iron−nitrogen bond length (2.477 Å). The difference between the short and long bond lengths is 0.406 Å. In **4** (Chart 2, **B**), the short magnesium−nitrogen bond lengths are 2.087 and 2.126 Å, and the long magnesium−nitrogen bond length is 2.368 Å. The difference between the short and long bond lengths is 0.262 Å. The bonding of the bridging ligand in **4** is clearly stronger than in $Fe_2(PhNC(Ph)NPh)_4$. Jordan has also reported several cationic aluminum and gallium complexes that contain $\mu,\eta^2:\eta^1$-amidinate ligands in the solid-state structures.[54] The complex $Li_2(tolNCHNtol)_2(OEt_2)_2$ contains $\mu,\eta^2:\eta^1$-formamidinate ligands.[65] A similar $\mu,\eta^2:\eta^1$-coordination mode has been documented for the bridging ditolyltriazenido ligand in $[Rh_2(\mu\text{-}CO)(bipy)(Ph_2PCH_2CH_2PPh_2)(tolNNNtol)_2]^{2+}$.[72] In addition, a $\mu,\eta^2:\eta^2$-benzamidinate ligand was described in $K_2((Me_3Si)NC(Ph)N(PhC{=}C(tBu)_2)_2$.[73]

The results of the van't Hoff analysis for **3** offer insight into the energetics of chelating versus bridging acetamidinate ligands in magnesium complexes. The enthalpy of dimerization of −14.7 kcal/mol to afford **3** from two monomeric equivalents indicates that the formation of the two bridging amidinate

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(67) Engelhardt, L. M.; Junk, P. C.; Paralinghug, W. C.; Sue, W. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 930.

(68) Freitag, S.; Kolodziejski, W.; Pauer, F.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1993**, 3479.

(69) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1997**, *16*, 5183.

(70) Cotton, F. A.; Daniels, L. M.; Matonic, A.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 277.

(71) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 1997; pp 111, 1074.

(72) Connelly, N. G.; Hopkins, P. M.; Orpen, A. G.; Rosair, G. M.; Viguri, F. *J. Chem. Soc., Dalton Trans.* **1992**, 2097.

(73) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3113.

ligands lowers the energy of the system. This observation suggests that the chelating η^2-*N*,*N*′-diisopropylacetamidinate ligand is strained and does not have optimum charge contact with the magnesium center in a monomeric structure. A key finding in the present study is that **1** and **2** show no tendency to dimerize in solution or in the solid state, indicating that a *tert*-butyl group on nitrogen eliminates an energy gain upon dimerization due to unfavorable steric interactions within a dimeric structure. Bickelhaupt has described a monomer−dimer equilibrium that occurs with magnesiacyclohexane and is relevant to the equilibrium reported herein for **3**.[74−76] In tetrahydrofuran, the dimer 1,7-dimagnesiacyclododecane is strongly favored over the monomeric magnesiacyclohexane, with $K(301\ \mathrm{K}) = 609$, $\Delta H = -11.5$ kcal/mol, and $\Delta S = -25$ cal/(mol·K). Bickelhaupt suggested that the large negative entropy associated with the dimerization was the reason higher polymers of magnesiacyclohexane were not observed. In **3** and **4**, there was no evidence for oligomeric species higher than the observed dimers. The lack of such oligomers in **3** and **4** is likewise probably due to the very negative entropies of association, as exemplified by the negative entropy of dimerization for **3**. Henderson and Mulvey have described a monomer−dimer equilibrium that occurs for $[\mathrm{Mg(NCH_2Ph)_2}]_2$ in toluene solution, although a van't Hoff analysis was not performed.[20,77]

Experimental Section

General Considerations. All reactions were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Diethyl ether and hexane were distilled from sodium. 1,3-Di-*tert*-butylcarbodiimide, 1,3-diisopropylcarbodiimide, 1-*tert*-butyl-3-ethylcarbodiimide, methyllithium, phenyllithium, and magnesium bromide were purchased from Aldrich Chemical Co.

^{1}H and ^{13}C{^{1}H} NMR were obtained at 300 or 75 MHz in benzene-d_6 or toluene-d_8. 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 Bis(*N*,*N*′-di-*tert*-butylacetamidinato)magnesium (1). A 100-mL Schlenk flask was charged with 1,3-di-*tert*-butylcarbodiimide (1.05 mL, 5.45 mmol) and diethyl ether (40 mL). To this stirred solution at ambient temperature was added a 1.4 M solution of methyllithium in diethyl ether (3.90 mL, 5.46 mmol). The resultant colorless solution was stirred at ambient temperature for 2 h. This solution was then added by a cannula to a separate Schlenk flask containing magnesium bromide (0.500 g, 2.72 mmol) dissolved in diethyl ether (20 mL). The reaction mixture was stirred for 18 h at ambient temperature. The volatile components were then removed under reduced pressure, and the resultant white solid was extracted with hexane (90 mL). The hexane extract was filtered through a 2-cm pad of Celite on a coarse glass frit to afford a colorless solution. Removal of the hexane under reduced pressure afforded **1** as a white solid (0.750 g, 81%). An analytical sample was obtained by sublimation at 70 °C (0.05 mmHg) to afford **1** as colorless crystals: mp 97−99 °C; IR (Nujol, cm^{-1}) 1660 (m), 1410 (vs), 1354 (vs), 1246 (s), 1201 (vs), 1104 (m), 1033 (s), 1004 (m), 892 (w), 825 (s), 798 (m), 742 (w), 724 (w), 657 (w); ^{1}H NMR ($\mathrm{C_6D_6}$, 22 °C, δ) 1.98 (s, 6 H, $\mathrm{C{-}C}H_3$), 1.26 (s, 36 H, $\mathrm{C(C}H_3)_3$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 22 °C, ppm) 173.98 (s, $C\mathrm{{-}CH_3}$), 49.70 (s, $C\mathrm{(CH_3)_3}$), 32.68 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 17.79 (s, $\mathrm{C{-}}C\mathrm{H_3}$). Anal. Calcd for $\mathrm{C_{20}H_{42}MgN_4}$: C, 66.20; H, 11.67; N, 15.44. Found: C, 65.83; H, 11.50; N, 15.43.

Preparation of Bis(*N*,*N*′-di-*tert*-butylbenzamidinato)magnesium (2). In a fashion similar to the preparation of **1**, a solution of (1,3-di-*tert*-butylbenzamidinato)lithium (prepared from 1,3-di-*tert*-butylcarbodiimide (1.05 mL, 5.45 mmol) and a 1.8 M solution of phenyllithium in cyclohexane (3.03 mL, 5.45 mmol)) in diethyl ether (40 mL) was treated with magnesium bromide (0.500 g, 2.72 mmol) in diethyl ether (20 mL) to afford **2** as a white solid (0.800 g, 82%). An analytical sample was grown by crystallization from hexane at −20 °C to afford **2** as colorless crystals: mp 224−226 °C; IR (Nujol, cm^{-1}) 3077 (w), 3052 (w), 1947 (w), 1895 (w), 1813 (w), 1768 (w), 1709 (w), 1645 (m), 1601 (w), 1403 (vs), 1380 (s), 1250 (m), 1201 (s), 1060 (s), 1015 (m), 918 (m), 843 (w), 784 (s), 735 (m), 709 (s), 597 (m); ^{1}H NMR ($\mathrm{C_6D_6}$, 22 °C, δ) 7.22 (m, 4 H, *o*-$\mathrm{C_6}H_2\mathrm{H_{2'}H}$), 7.02 (m, 6 H, m and p$-\mathrm{C_6H_2}H_{2'}H$), 1.17 (s, 36 H, $\mathrm{C(C}H_3)_3$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 22 °C, ppm) 176.57 (s, C−Ph), 139.37 (s, ipso-C of Ph group), 129.77 (s, ortho C−H of Ph group), 127.58 (s, para C−H of Ph group), 126.93 (s, meta C−H of Ph group), 50.66 (s, $C\mathrm{(CH_3)_3}$), 33.64 (s, $\mathrm{C(}C\mathrm{H_3)_3}$). Anal. Calcd for $\mathrm{C_{30}H_{46}MgN_4}$: C, 73.99; H, 9.52; N, 11.50. Found: C, 73.71; H, 9.46; N, 11.52.

Preparation of Bis[bis(*N*,*N*′-diisopropylacetamidinato)magnesium] (3). In a fashion similar to the preparation of **1**, (1,3-diisopropylacetamidinato)lithium (prepared from 1,3-diisopropylcarbodiimide (0.85 mL, 5.46 mmol) and a 1.4 M solution of methyllithium in diethyl ether (3.90 mL, 5.45 mmol)) in diethyl ether (40 mL) was treated with magnesium bromide (0.500 g, 2.72 mmol) in diethyl ether (20 mL) to afford **3** as a white solid (0.690 g, 70%). An analytical sample was obtained by crystallization from hexane at −20 °C to afford **3** as colorless crystals: mp 108−110 °C; IR (Nujol, cm^{-1}) 1653 (w), 1619 (m), 1503 (s), 1332 (s), 1309 (s), 1257 (w), 1209 (m), 1171 (s), 1119 (m), 1045 (w), 1015 (m), 936 (w), 877 (w), 806 (m), 623 (m), 582 (m). Anal. Calcd for $\mathrm{C_{32}H_{68}Mg_2N_8}$: C, 62.64; H, 11.17; N, 18.26. Found: C, 62.57; H, 11.12; N, 18.36.

NMR data for the monomer: ^{1}H NMR (toluene-d_8, 80 °C, δ) 3.42 (septet, $J = 6.0$ Hz, 4 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 1.72 (s, 6 H, $\mathrm{C{-}C}H_3$), 1.06 (d, $J = 6.0$ Hz, 24 H, $\mathrm{CH(C}H_3)_2$); ^{13}C{^{1}H} NMR (toluene-d_8, 80 °C, ppm) 170.84 (s, $C\mathrm{{-}CH_3}$) 45.52 (s, $C\mathrm{H(CH_3)_2}$), 26.07 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 10.82 (s, $\mathrm{C{-}}C\mathrm{H_3}$).

NMR data for the dimer: ^{1}H NMR (toluene-d_8, −60 °C, δ) 3.55 (septet, $J = 6.0$ Hz, 4 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.45 (septet, $J = 6.0$ Hz, 4H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 1.86 (s, 6 H, $\mathrm{C{-}C}H_3$), 1.72 (s, 6 H, $\mathrm{C{-}C}H_3$), 1.49 (d, $J = 6.0$ Hz, 12 H, $\mathrm{CH(C}H_3)_2$), 1.30 (d, $J = 6.0$ Hz, 12 H, $\mathrm{CH(C}H_3)_2$), 1.29 (d, $J = 6.0$ Hz, 12 H, $\mathrm{CH(C}H_3)_2$), 1.16 (d, $J = 6.0$ Hz, 12 H, $\mathrm{CH(C}H_3)_2$); ^{13}C{^{1}H} NMR (toluene-d_8, −80 °C, ppm) 176.22 (s, $C\mathrm{{-}CH_3}$), 171.00 (s, $C\mathrm{{-}CH_3}$), 48.70 (s, $C\mathrm{H(CH_3)_2}$), 46.80 (s, $C\mathrm{H(CH_3)_2}$), 27.23 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 26.83 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 25.81 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 24.87 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 14.70 (s, $\mathrm{C{-}}C\mathrm{H_3}$), 12.28 (s, $\mathrm{C{-}}C\mathrm{H_3}$).

Preparation of Bis[bis(1-*tert*-butyl-3-ethylacetamidinato)magnesium] (4). In a fashion similar to the preparation of **1**, treatment of (1-*tert*-butyl-3-ethylacetamidinato)lithium (prepared from 1-*tert*-butyl-3-ethylcarbodiimide (0.85 mL, 5.48 mmol) and a 1.6 M solution of methyllithium in diethyl ether (3.42 mL, 5.48 mmol)) in diethyl ether (40 mL) with magnesium bromide (0.500 g, 2.72 mmol) in diethyl ether (20 mL) afforded **4** as a white solid (0.775 g, 93%). An analytical sample was grown by crystallization from hexane at −20 °C to afford **4** as colorless crystals: dec range 127−133 °C; IR (Nujol, cm^{-1}) 1500 (vs), 1421 (s), 1358 (s), 1328 (s), 1212 (s), 1160 (m), 1123 (m), 1063 (w), 1022 (m), 1011 (m), 981 (w), 877 (w), 821 (m), 776 (w), 761 (w); ^{1}H NMR (toluene-d_8, 80 °C, δ) 3.09 (q, $J = 7.2$ Hz, 8 H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.89 (s, 12 H, $\mathrm{C{-}C}H_3$), 1.31(s, 36 H, $\mathrm{C(C}H_3)_3$), 1.14 (t, $J = 7.2$ Hz, 12 H, $\mathrm{CH_2C}H_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 80 °C, ppm) 174.50 (s, $C\mathrm{{-}CH_3}$) 50.68 (s, $C\mathrm{(CH_3)_3}$), 41.27 (s, $C\mathrm{H_2CH_3}$), 32.95 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 17.99 (s, $\mathrm{C{-}}C\mathrm{H_3}$), 15.66 (s, $\mathrm{CH_2}C\mathrm{H_3}$). Anal. Calcd for $\mathrm{C_{32}H_{68}Mg_2N_8}$: C, 62.64; H, 11.17; N, 18.26. Found: C, 62.39; H, 11.02; N, 17.93.

van't Hoff Analysis for 3. A 5-mm NMR tube was charged with **3** (0.020 g, 0.033 mmol) and toluene-d_8 (0.80 mL) and was sealed with a plastic cap. ^{1}H NMR spectra were recorded between −80 and +80 °C. For analysis of the data, see the text and Supporting Information.

X-ray Crystallographic Structure Determinations for 2−4. Crystalline samples were mounted in sealed thin wall capillaries under nitrogen atmosphere for X-ray data collection. Diffraction data were collected at room temperature on a Bruker P4/CCD diffractometer

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(74) Holtkamp, H. C.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1969**, *19*, 279.

(75) Spek, A. L.; Schat, G.; Holtkamp, H. C.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1977**, *131*, 331.

(76) Freijee, F. J. M.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1982**, *240*, 217.

(77) See also: Henderson, K. W.; Allan, J. F.; Kennedy, A. R. *Chem. Commun.* **1997**, 1149.

equipped with Mo radiation. For each collection, 1650 frames were collected at 10 s/frame with 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 SHELX-97. All molecules crystallized as neutral compounds with no associated ions or solvent. Complex **2** is reported in the space group *C*2/*c* and exhibited significant disorder in the ligand substituents, as evidenced by large thermal parameters. One of the *tert*-butyl groups is best defined as occupying three partial positions in a 2:1:1 ratio. The structure was also solved in space group *Cc*, but the disorder was not diminished. Complex **3** consists of a dimer occupying a crystallographic 2-fold axis. Complex **4** contains one whole dimer in the asymmetric unit. The molecule exhibits noncrystallographic 2-fold symmetry. Partial occupancy atoms for C16 and C24 were employed to describe positional disorder. Further data are contained in the Supporting Information.

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Supporting Information Available: Plot and data for the van't Hoff analysis of **3** and X-ray crystallographic files in CIF format for the structure determinations of **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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