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Synthesis, Characterization, and Crystal Structures of $\{Me_2Al(\mu\text{-}i\text{-}Pr_2N)_2Mg[(R)NC(Me)N(R)]\}$ (R = *i*-Pr, *t*-Bu): Insertion of a Carbodiimide (RNCNR) into a Mg−C Bond

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Summary: A series of amidino-bridged mixed-metal aluminum−magnesium complexes, $\{[R_2Al(\mu\text{-}R'_2N)_2Mg[(R'')NC(R)N(R'')]\}$ *(R = Me, R′ = i-Pr, R″ = i-Pr,* ***1a****; R = Me, R′ = i-Pr, R″ = t-Bu,* ***1b****; R = Me, R′ = i-Pr, R″ = p-tolyl,* ***1c****; R = Me, R′ = Et, R″ = i-Pr,* ***2a****; R = Me, R′ = Et, R″ = t-Bu,* ***2b****; R = Et, R′ = i-Pr, R″ = i-Pr,* ***3a****; R = Et, R′ = i-Pr, R″ = t-Bu), were prepared by insertion reactions of the aluminum−magnesium complexes* $[R_2Al(\mu\text{-}R'_2N)_2Mg(\mu\text{-}R)]_n$ *(R = Me, Et; R′ = Et, i-Pr) (n = 2, 4) with various substituted carbodiimides and characterized by mass spectra, IR spectra, elemental analysis, and* ^1H *and* ^{13}C *NMR data. The structures of two of the compounds* ***1a****,****b*** *have been determined by single-crystal X-ray diffraction analysis. The structural data show that the bonding of the two nitrogens of the carbodiimide to the magnesium atom is (σ, σ) symmetric and indicate a weak interaction between Mg and C(15).*

Introduction

Over the past several decades, there are several reports on the synthesis of organo−aluminum−magnesium complexes.[1−8] Recently we reported on the interesting chemical properties of the aluminum−magnesium complexes including carbon dioxide fixation.[9−11] Reactions of carbon dioxide with $\{Me_2Al(\mu\text{-}NR_2)_2MgR'\}$ (R = Et, *i*-Pr; R′ = CH_3, C_6H_5, $C_6H_4\text{-}p\text{-}CH_3$) occurred with insertion at metal−carbon and metal−nitrogen bonds. The high reactivity of the four-coordinated magnesium atom in these aluminum−magnesium-bridged complexes is believed to be due to its stronger electrophilicities. In this work, carbodiimides (RNCNR), the molecules isoelectronic with CO_2, are used to react with Mg−C in aluminum−magnesium complexes. Similar insertion reaction of carbodiimides with transition metal complexes (e.g. Zr, Nb, Mo, Ru, Ta, W, etc.) have been reported.[12,13] Here we present the synthesis and characterization of a series of amidino-bridged mixed-metal aluminum−magnesium complexes: $\{[R_2Al(\mu\text{-}R'_2N)_2Mg[(R'')NC(R)N(R'')]\}$ (R = Me, R′ = *i*-Pr, R″ = *i*-Pr, **1a**; R = Me, R′ = *i*-Pr, R″ = *t*-Bu, **1b**; R = Me, R′ = *i*-Pr, R″ = *p*-tolyl, **1c**; R = Me, R′ = Et, R″ = *i*-Pr, **2a**; R = Me, R′ = Et, R″ = *t*-Bu, **2b**; R = Et, R′ = *i*-Pr, R″ = *i*-Pr, **3a**; R = Et, R′ = *i*-Pr, R″ = *t*-Bu). The structures of two of the complexes **1a**,**b** were determined by X-ray diffraction analysis. The carbodiimide acts as a bidentate ligand forming two Mg−N σ bonds. Pyrolysis of these compounds was also examined.

Experimental Section

Apparatus and Materials. All manipulations were carried out in a N_2-flushed glovebag, drybox, or vacuum system. Solvents were distilled and degassed prior to use. All ^1H and ^{13}C NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts are referenced relative to either TMS (^1H), benzene-d_6 (^1H, δ 7.16; $^{13}C\{^1H\}$, δ 128.00), or toluene-d_8 (^1H, δ 7.09 (m), 7.00 (br), 6.98 (m), 2.09 (quint); $^{13}C\{^1H\}$, δ 137.5 (s), 128.9 (t), 128.0 (t), 125.2 (t) 20.4 (sep)). Mass spectral data were obtained on a VG-7025 GC/MS/MS spectrometer. IR spectra were recorded at Nujol mulls between KBr disks on a FT-IR spectrometer. Elemental analyses (C, H, N) were performed at the Analytische Laboratorien, Lindlar, Germany. Deviations from the calculated values in the elemental analyses were attributed to the extremely air-sensitive and hygroscopic nature of these compounds. The starting material, $\{R_2Al(\mu\text{-}NR'_2)_2Mg(\mu\text{-}R)\}_n$, was prepared by following the method previously described by us.[7]

Synthesis of the Complexes. In a generalized procedure, an ether solution (50 mL) of $\{R_2Al(\mu\text{-}NR'_2)_2Mg(\mu\text{-}R)\}_n$ was added dropwise to a stirred ether solution of carbodiimide (1:*n* molar ratio) at room temperature under a nitrogen atmosphere. The reaction took place immediately. Pure compounds of **1a**−**3b** were obtained either by recrystallization or by distillation of the crude products.

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Table 1. ^{1}H NMR Spectral Data (δ (ppm))

compd (solvent)	AlR_2	NR'_2	($R''N$)C(R)(NR'')	(R''N)C(R)(NR'')
1a (d^8-toluene)	−0.28 (s), Me	1.29 (d), Me of ^{i}Pr;[a] 3.65 (sep), CH of ^{i}Pr[a]	1.07 (d), Me of ^{i}Pr;[b] 3.44 (sep), CH of ^{i}Pr[b]	1.63 (s), Me
1b (d^6-benzene)	−0.29 (s), Me	1.35 (d), Me of ^{i}Pr;[c] 3.72 (sep), CH of ^{i}Pr[c]	1.24 (s), Me of ^{t}Bu	1.97 (s), Me
1c (d^6-benzene)	−0.30 (s), Me	1.22, 1.30 (d), Me of ^{i}Pr;[d] 3.51 (sep), CH of ^{i}Pr[d]	6.82, 6.86, 7.02, 7.06 (s), aryl H of tolyl; 2.16 (s), Me of tolyl	1.69 (s), Me
2a (d^8-toluene)	−0.43 (s), Me	1.04, 1.06 (t), Me of Et;[e] 2.94, 2.96 (q), CH$_2$ of Et[e]	1.00 (d), Me of ^{i}Pr;[f] 3.31 (sep), CH of ^{i}Pr[f]	1.58 (s), Me
2b (d^8-toluene)	−0.45 (s), Me	1.02 (t), Me of Et;[g] 2.94, 2.96 (q), CH$_2$ of Et[g]	1.17 (d), Me of ^{t}Bu	1.91 (s), Me
3a (d^6-benzene)	0.46 (q), CH$_2$ of Et;[h] 1.56 (t), CH$_3$ of Et[h]	1.31, 1.35 (d), Me of ^{i}Pr;[i] 3.64 (sep), CH of ^{i}Pr[i]	1.11 (d), Me of ^{i}Pr;[j] 3.48 (sep), CH of ^{i}Pr[j]	0.91 (t), CH$_3$ of Et;[k] 2.11 (q), CH$_2$ of Et[k]
3b (d^6-benzene)	0.44 (q), CH$_2$ of Et;[l] 1.55 (t), CH$_3$ of Et[l]	1.37, 1.41 (d), Me of ^{i}Pr;[m] 3.70 (sep), CH of ^{i}Pr[m]	1.27 (s), Me of ^{t}Bu	1.22 (t), CH$_3$ of Et;[n] 2.41 (q), CH$_2$ of Et[n]

[a] $^3J_{H-H} = 6.9$ Hz. [b] $^3J_{H-H} = 6.3$ Hz. [c] $^3J_{H-H} = 6.7$ Hz. [d] $^3J_{H-H} = 6.7$ Hz. [e] $^3J_{H-H} = 6.6$ Hz. [f] $^3J_{H-H} = 6.6$ Hz. [g] $^3J_{H-H} = 6.6$ Hz. [h] $^3J_{H-H} = 7.8$ Hz. [i] $^3J_{H-H} = 6.9$ Hz. [j] $^3J_{H-H} = 6.3$ Hz. [k] $^3J_{H-H} = 7.8$ Hz. [l] $^3J_{H-H} = 7.8$ Hz. [m] $^3J_{H-H} = 6.9$ Hz. [n] $^3J_{H-H} = 7.8$ Hz.

The complex {Me$_2$Al(μ-*i*-Pr$_2$N)$_2$Mg[(*i*-Pr)NC(Me)N(*i*-Pr)]} (**1a**) (colorless solid) was purified by recrystallization from toluene: mp, 143−144 °C; yield, 72%. IR (Nujol mull): 2950 (s), 2916 (s), 2863 (s), 2733 (m), 1654 (m), 1462 (s), 1379 (s), 1269 (br), 1181 (m), 1128 (m), 1025 (m), 977 (m), 921 (s), 809 (m), 692 cm^{-1} (br). Anal. Calcd: C, 62.5; H, 11.9; N, 13.3. Found: C, 62.6; H, 11.7; N, 13.1. The 10 most intense peaks of the mass spectral data (30 eV) are *m*/*z* (relative intensity, ion formula tentatively assigned) 407 (42, [M − Me]$^+$), 322 (100, [M − (*i*-Pr)$_2$N]$^+$), 307 (33, [M − (*i*-Pr)$_2$N − MeH]$^+$), 265 (16, [MeAlMg(*i*-Pr$_2$N)$_2$ − H]$^+$), 250 (44, [AlMg(*i*-Pr$_2$N)$_2$ − H]$^+$), 165 (12, [MeAlMg(*i*-Pr$_2$N) − H]$^+$), 142 (19, [MeC(*i*-PrN)$_2$H]$^+$), 86 (21, [HAl(*i*-Pr)NH]$^+$), 58 (28, [(*i*-Pr)NH]$^+$), and 44 (72, [(*i*-Pr)H]$^+$), with a molecular ion peak at 422 (2, [M]$^+$). The ^{1}H NMR data for all the complexes are listed in Table 1.

The complex {Me$_2$Al(μ-*i*-Pr$_2$N)$_2$Mg[(*t*-Bu)NC(Me)N(*t*-Bu)]} (**1b**) (colorless solid) was purified by recrystallization from toluene: mp, 121−122 °C; yield 81%. IR (Nujol mull): 2955 (s), 2926 (s), 2871 (s), 2753 (m), 1655 (m), 1466 (s), 1377 (s), 1254 (br), 1094 (m), 1027 (m), 969 (m), 917 (s), 805 (m), 666 cm^{-1} (br). Anal. Calcd: C, 63.9; H, 12.3; N, 12.4. Found: C, 62.1; H, 11.1; N, 11.3. The 10 most intense peaks of the mass spectral data of compound **1b** (30 eV) are *m*/*z* (relative intensity, ion formula tentatively assigned) 435 (13, [M − Me]$^+$), 350 (49, [M − (*i*-Pr)$_2$N]$^+$), 334 (13, [M − (*i*-Pr)$_2$N−MeH]$^+$), 292 (12, [MeC((*t*-Bu)N)$_2$Mg(*i*-Pr)$_2$N+H]$^+$), 278 (19, [MeC(*t*-BuN)$_2$Mg(*i*-Pr)$_2$N − MeH]$^+$), 170 (25, [MeC(*t*-BuN)$_2$H]$^+$), 142 (41, [HAlMe(*i*-Pr)$_2$N]$^+$), 99 (44, [(*i*-Pr)$_2$N − H]$^+$), 86 (63, [HAl(*i*-Pr)NH]$^+$), and 58 (100, [(*i*-Pr)NH]$^+$), with a molecular ion peak at 450 (2, [M]$^+$).

The complex {Me$_2$Al(μ-*i*-Pr$_2$N)$_2$Mg[(*p*-tolyl)NC(Me)N(*p*-tolyl)]} (**1c**) (colorless solid) was purified by recrystallization from toluene: mp, 164−165 °C; yield, 78%. IR (Nujol mull): 2963 (s), 2917 (s), 2859 (s), 2732 (m), 1670 (m), 1650 (m), 1613 (m), 1516 (s), 1472 (s), 1429 (s), 1381 (br), 1300 (w), 1225 (m), 1182 (w), 1114 (m), 1020 (w), 981 (m), 923 (w), 969 (m), 868 (m), 808 (w), 727 (m), 687 cm^{-1} (br). Anal. Calcd: C, 69.4; H, 9.9; N, 10.8. Found: C, 69.6; H, 9.7; N, 10.7. The 10 most intense peaks of the mass spectral data of compound **1c** (70 eV) are *m*/*z* (relative intensity, ion formula tentatively assigned) 249 (8, [Al(*i*-Pr$_2$N)$_2$Mg − 2H]$^+$), 235 (32, [Al(*i*-Pr$_2$N)$_2$Mg − Me]$^+$), 123 (32, [Mg(*i*-Pr)$_2$N − H]$^+$), 109 (43, [Mg(*i*-Pr)$_2$N − Me]$^+$), 91 (17, [C$_7$H$_8$]$^+$), 84 (100, [(*i*-Pr)$_2$N − MeH]$^+$), 72 (68, [(*i*-Pr)$_2$N − 2Me + 2H]$^+$), 69 (57, [(*i*-Pr)$_2$N − 2Me − H]$^+$), 57 (72, [(*i*-Pr)N]$^+$), and 43 (52, [HAlMe]$^+$), with a molecular ion peak at 518 (1, [M]$^+$).

The complex {Me$_2$Al(μ-Et$_2$N)$_2$Mg[(*i*-Pr)NC(Me)N(*i*-Pr)]} (**2a**) (colorless liquid) was purified by distillation at 60 °C, 10^{-3} Torr (yield, 52%). IR (Nujol mull): 2964 (s), 2926 (s), 2869 (s), 2727 (m), 1657 (m), 1471 (s), 1410 (m), 1380 (s), 1280 (m), 1207 (m), 1104 (br), 1032 (br), 974 (m), 918 (m), 802 (m), 730 (m), 671 cm^{-1} (br). The 10 most intense peaks of the mass spectral data of compound **2a** (30 eV) are *m*/*z* (relative intensity, ion formula tentatively assigned) 58 (100, [(*i*-Pr)NH]$^+$), 69 (67, [(*i*-Pr)NC]$^+$), 142 (34, [MeC(*i*-PrN)$_2$ + H]$^+$), 43 (33, [(*i*-Pr)]$^+$), 85 (22, [HAlNEt$_2$ − Me]$^+$), 99 (22, [AlNEt$_2$]$^+$), 111 (18, [C((*i*-Pr)N)$_2$ − Me]$^+$), 127 (15, [C(N(*i*-Pr))$_2$ + H]$^+$), 351 (10, [M − Me]$^+$), and 294 (7, [M − NEt$_2$]$^+$), with a molecular ion peak at 366 (5, [M]$^+$).

The complex {Me$_2$Al(μ-Et$_2$N)$_2$Mg[(*t*-Bu)NC(Me)N(*t*-Bu)]} (**2b**) (colorless liquid) was purified by distillation at 72 °C, 10^{-3} Torr (yield, 61%). IR (Nujol mull): 2969 (s), 2921 (s), 2876 (s), 2725 (m), 1657 (m), 1463 (s), 1410 (s), 1380 (s), 1265 (m), 1200 (m), 1175 (m), 1105 (br), 1035 (br), 959 (m), 922 (m), 810 (m), 729 (m), 670 cm^{-1} (br). Anal. Calcd: C, 60.8; H, 12.0; N, 14.2. Found: C, 60.1; H, 11.5; N, 12.8. The 10 most intense peaks of the mass spectral data of compound **2b** (70 eV) are *m*/*z* (relative intensity, ion formula tentantively assigned) 379 (7, [M − Me]$^+$), 365 (5, [M − Et]$^+$), 322 (6, [M − (Et$_2$N)]$^+$), 211 (15, [Me$_2$Al(Et$_2$N)$_2$Mg − Me + H]$^+$), 170 (27, [MeC(*t*-BuN)$_2$ + H]$^+$), 155 (22, [C(*t*-BuN)$_2$H]$^+$), 99 (62, [Al(Et$_2$N)]$^+$), 98 (100, [Al(Et$_2$N) − H]$^+$), 58 (67, [HAlMe$_2$]$^+$), and 42 (51, [AlMe]$^+$), with a molecular ion peak at 394 (3, [M]$^+$).

The complex {Et$_2$Al(μ-*i*-Pr$_2$N)$_2$Mg[(*i*-Pr)NC(Et)N(*i*-Pr)]} (**3a**) (colorless liquid) was purified by distillation at 77 °C, 10^{-3} Torr (yield, 75%). IR (Nujol mull): 2964 (s), 2926 (s), 2869 (s), 2727 (m), 1657 (m), 1471 (s), 1410 (m), 1380 (s), 1280 (m), 1207 (m), 1104 (br), 1032 (br), 974 (m), 918 (m), 802 (m), 730 (m), 671 cm^{-1} (br). The 10 most intense peaks of the mass spectral data of compound **3a** (30 eV) are *m*/*z* (relative intensity, ion formula tentatively assigned) 351 (10, [M − Me]$^+$), 294 (7, [M − Et$_2$N]$^+$), 142 (34, [MeC((*i*-Pr)N)$_2$ + H]$^+$), 127 (15, [C((*i*-Pr)N)$_2$ + H]$^+$), 111 (18, [C((*i*-Pr)N)$_2$ − Me]$^+$), 99 (22, [Al(Et$_2$N)]$^+$), 85 (22, [HAl(Et$_2$N) − Me]$^+$), 69 (67, [(*i*-Pr)NC]$^+$), 58 (100, [(*i*-Pr)NH]$^+$), and 43 (33, [(*i*-Pr)]$^+$), with a molecular ion peak at 366 (5, [M]$^+$).

The complex {Et$_2$Al(μ-*i*-Pr$_2$N)$_2$Mg[(*t*-Bu)NC(Et)N(*t*-Bu)]} (**3b**) (colorless liquid) was purified by distillation at 87 °C, 10^{-3} Torr (yield 51%). IR (Nujol mull): 2969 (s), 2921 (s), 2876 (s), 2725 (m), 1657 (m), 1463 (s), 1410 (s), 1380 (s), 1265 (m), 1200 (m), 1175 (m), 1105 (br), 1035 (br), 959 (m), 922 (m), 810 (m), 729 (m), 670 cm^{-1} (br). The 10 most intense peaks of the mass spectral data of compound **3b** (70 eV) are *m*/*z* (relative intensity, ion formula tentatively assigned) 379 (7, [M − Me]$^+$), 365 (5, [M − Et]$^+$), 322 (6, [M − (Et$_2$N)]$^+$), 211 (15, [Me$_2$Al(Et$_2$N)$_2$Mg − Me + H]$^+$), 170 (27, [MeC((*t*-Bu)N)$_2$ + H]$^+$), 155 (22, [C(*t*-BuN)$_2$H]$^+$), 99 (62, [Al(Et$_2$N)]$^+$), 84 (100, [AlEt$_2$ − H]$^+$), 56 (42, [(*t*-Bu) − H]$^+$), and 42 (51, [AlMe]$^+$), with a molecular ion peak at 394 (3, [M]$^+$).

Structure Determination. Suitable single crystals of compounds **1a**,**b** for X-ray measurements were sealed in glass capillaries. Preliminary examination and intensity data collection were carried out with an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensity data were collected by using the θ−2θ scan mode for $2\theta \le 45°$ and corrected for absorption and decay. Both structures were solved by MUL-

Table 2. Crystallographic Data Refinement Details for Compounds 1a,b

	compd	
	1a	**1b**
formula	$C_{22}H_{51}N_4AlMg$	$C_{24}H_{55}N_4AlMg$
fw	422.96	451.01
a, Å	10.648(4)	9.912(5)
b, Å	22.149(6)	19.648(4)
c, Å	12.038(3)	15.296(4)
β, deg	92.83(3)	92.19(3)
V, Å^3	2836(2)	2977(2)
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
2θ range, deg	14.00−23.10	17.10−24.68
cryst size, mm	0.50 × 0.50 × 0.50	0.30 × 0.50 × 0.50
Z	4	4
D_{calc}, g·cm^{-3}	0.991	1.006
μ, cm^{-1}	1.025	1.009
λ, Å	0.710 70	0.710 70
no. of rflns measd	3721	3881
no. of unique rflns	3687	3881
no. of rflns $I_0 > 2.0\sigma(I_0)$	1488	1808
transm factors (min, max)	0.975, 1.000	0.803, 1.000
R_F	0.079	0.060
R_W	0.079	0.058
GoF	1.38	1.40
max Δ/σ	0.0037	0.0097
radiation	Mo Kα	Mo Kα

TAN and refined by full-matrix least-squares analyses on F with $w = 1.0/[\sigma^2(F_o) + 0.0001F_o^2]$. One isopropyl group of compound **1a** is disordered. Site occupancy of 50% was assigned for each of the disordered carbon atoms (C8 and C8′) and subsequently refined anisotropically. Scattering factors for the neutral atoms and anomalous scattering coefficients for non-hydrogen atoms were taken from the literature.[15] All calculations were carried out with a Micro Vax 3600 computer using the NRC VAX program package.[16] A summary of data collected on the crystal structures is given in Table 2. Selected bond distances and angles are listed in Table 3.

Results and Discussion

Synthesis and Characterization of Amidine-Bridged Complexes. The precursor complexes **1**−**3** were allowed to react with carbodiimide in a 1:n molar ratio giving the amidino-bridged complexes $\{R_2Al(\mu\text{-}NR'_2)_2Mg[(R''N)C(R)(NR'')]\}$ (eq 1). These precursor

$$\{R_2Al(\mu\text{-}(R'_2N)_2)Mg(\mu\text{-}R)\}_n + nR''N{=}C{=}NR'' \rightarrow n\{R_2Al(\mu\text{-}(R'_2N)_2)Mg[(R''N)C(R)(NR'')]\} \quad (1)$$

R = Me, R′ = *i*-Pr, R″ = *i*-Pr (**1a**), R″ = *t*-Bu (**1b**),
R″ = *p*-tolyl (**1c**); R = Me, R′ = Et, R″ = *i*-Pr (**2a**),
R″ = *t*-Bu (**2b**); R = Et, R′ = *i*-Pr, R″ = *i*-Pr (**3a**),
R″ = *t*-Bu (**3b**)

complexes and products are extremely air-sensitive and hygroscopic. The structures of two of the complexes **1a**,**b** were determined by single-crystal X-ray diffraction techniques, and the other amido complexes are consistent with the data obtained from ^{1}H and ^{13}C NMR and mass spectra and elemental analyses.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 1a,b

1a		**1b**	
	Distances		
Al···Mg	2.848(4)	Al···Mg	2.865(3)
Al−N(1)	1.945(8)	Al−N(1)	1.950(6)
Al−N(2)	1.958(8)	Al−N(2)	1.974(5)
Al−C(1)	1.96(1)	Al−C(1)	1.98(1)
Al−C(2)	1.97(1)	Al−C(2)	1.95(1)
Mg−N(1)	2.155(7)	Mg−N(1)	2.174(5)
Mg−N(2)	2.152(8)	Mg−N(2)	2.163(5)
Mg−N(3)	2.062(8)	Mg−N(3)	2.064(5)
Mg−N(4)	2.079(8)	Mg−N(4)	2.063(5)
Mg···C(15)	2.44(1)	Mg···C(15)	2.45(1)
N(1)−C(3)	1.49(1)	N(1)−C(3)	1.49(1)
N(3)−C(15)	1.32(1)	N(3)−C(15)	1.32(1)
N(4)−C(15)	1.32(1)	N(4)−C(15)	1.32(1)
N(3)−C(17)	1.46(1)	N(3)−C(17)	1.46(1)
N(4)−C(20)	1.44(1)	N(4)−C(21)	1.47(1)
C(15)−C(16)	1.54(2)	C(15)−C(16)	1.54(1)
	Angles		
Mg···Al−N(1)	49.1(2)	Mg···Al−N(1)	49.3(2)
Mg···Al−N(2)	49.0(2)	Mg···Al−N(2)	48.9(2)
N(1)−Al−N(2)	96.6(3)	N(1)−Al−N(2)	96.5(2)
Al···Mg−N(1)	43.0(2)	Al···Mg−N(1)	42.9(2)
Al···Mg−N(2)	43.4(2)	Al···Mg−N(2)	43.5(1)
N(1)−Mg−N(2)	85.1(3)	N(1)−Mg−N(2)	85.0(2)
Al−N(1)−Mg	87.9(3)	Al−N(1)−Mg	87.8(2)
Al−N(2)−Mg	87.6(3)	Al−N(2)−Mg	87.6(2)
Al−N(1)−C(3)	115.9(6)	Al−N(1)−C(3)	106.5(4)
Al−N(1)−C(6)	118.6(7)	Al−N(1)−C(6)	111.2(4)
Al···Mg−N(3)	165.1(3)	Al···Mg−N(3)	163.1(2)
Al···Mg−N(4)	131.3(2)	Al···Mg−N(4)	131.3(2)
Al···Mg···C(15)	129.2(2)	Al···Mg···C(15)	164.0(2)
N(3)−Mg−N(4)	65.6(3)	N(3)−Mg−N(4)	65.6(2)
N(3)−Mg···C(15)	32.9(3)	N(3)−Mg···C(15)	32.9(2)
N(4)−Mg···C(15)	32.7(3)	N(4)−Mg···C(15)	32.8(2)
N(1)−Mg−N(3)	131.4(3)	N(1)−Mg−N(3)	130.9(2)
N(1)−Mg−N(4)	126.0(2)	N(1)−Mg−N(4)	126.0(2)
N(1)−Mg···C(15)	136.5(3)	N(1)−Mg···C(15)	138.2(2)
N(2)−Mg−N(3)	134.0(3)	N(2)−Mg−N(3)	132.6(2)
N(2)−Mg−N(4)	122.9(3)	N(2)−Mg−N(4)	122.6(2)
N(2)−Mg···C(15)	136.6(3)	N(2)−Mg···C(15)	135.8(2)
Mg−N(3)−C(15)	89.4(6)	Mg−N(3)−C(15)	89.6(4)
Mg−N(4)−C(15)	88.8(5)	Mg−N(4)−C(15)	89.8(4)
N(3)−C(15)−N(4)	116.2(8)	N(3)−C(15)−N(4)	115.0(5)
N(3)−C(15)−C(16)	121.6(9)	N(3)−C(15)−C(16)	122.3(6)
N(4)−C(15)−C(16)	122.2(9)	N(4)−C(15)−C(16)	122.7(6)
Mg−N(3)−C(17)	148.7(7)	Mg−N(3)−C(17)	144.8(5)
Mg−N(4)−C(20)	149.5(6)	Mg−N(4)−C(21)	144.1(4)
C(15)−N(3)−C(17)	121.8(8)	C(15)−N(3)−C(17)	125.5(6)
C(15)−N(4)−C(20)	121.6(8)	C(15)−N(4)−C(21)	126.1(5)

Description of the Structures. Compounds **1a**,**b** possess similar structural features except for the substituents of the [(R″)NC(Me)N(R″)] groups. ORTEP views of the complexes **1a**,**b** are shown in Figures 1 and 2, respectively. Selected bond distances and bond angles are listed in Table 3. The molecular structure of **1b** is refined by considering a disorder for C8($^2/_3$) and C8′($^1/_3$). The two molecules, **1a**,**b**, both exist as monomers possessing two coplanar heterocyclic four-membered rings AlN(1)N(2)Mg and MgN(4)C(15)N(3). The average distances of the bridged Mg−N of 2.154(8) Å in **1a** and 2.167 (5) Å in **1b** are normal for a σ bond. Interestingly, the Mg−N distance of the AlN_2Mg moiety is *ca.* 0.08 Å longer than that of the $MgCN_2$ moiety in compounds **1a**,b, which suggests that the chelating ligand (amidino) was more nucleophilic than the bridging ligand (amido). Also, the Mg−C(15) distance of 2.44(1) Å is longer than expected for a σ bond (2.0−2.2 Å) indicating a weak interaction between Mg and C(15). The distances of N(3)−C(15) and N(4)−C(15) are the same (1.32(1) Å) indicating the partial double-bond character. Hence the C(15) has an sp^2 structure, as do N(3) and N(4). The unusual bond length of d(C(6)−C(8))

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[15] Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computering 3: Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon: Oxford, U.K., 1985; p 167.

[16] Barker, J.; Kilner, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2687.

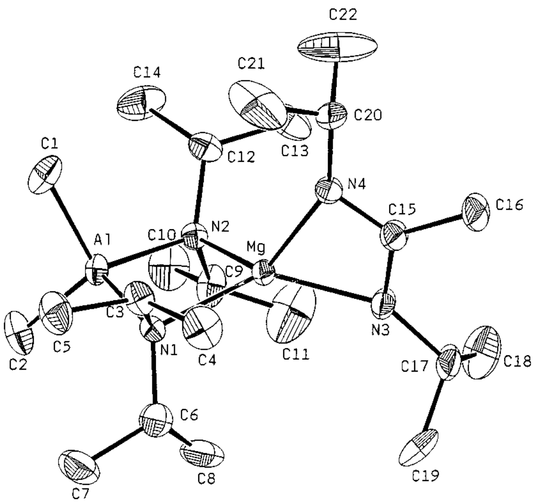


Figure 1. ORTEP view of the complex {$Me_2Al(\mu$-*i*-$Pr_2N)_2$-Mg[(*i*-Pr)NC(Me)N(*i*-Pr)]}, **1a**. Thermal ellipsoids are drawn at 50% probability level.

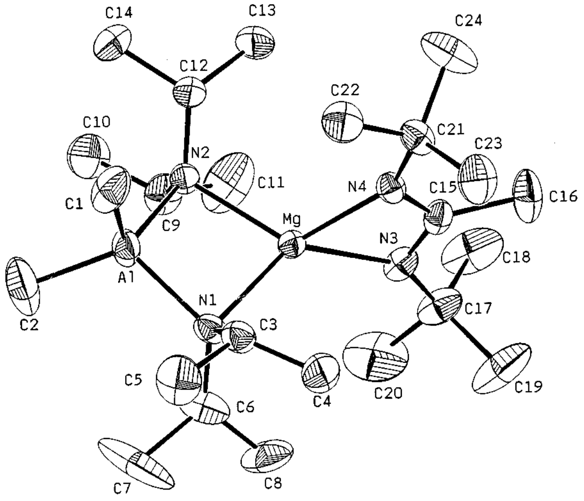
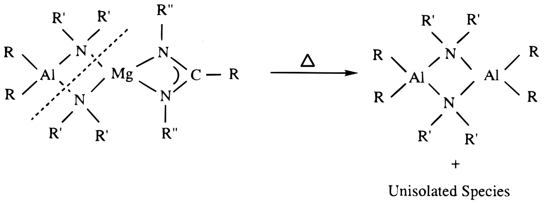


Figure 2. ORTEP view of the complex {$Me_2Al(\mu$-*i*-$Pr_2N)_2$-Mg[(*t*-Bu)NC(Me)N(*t*-Bu)]}, **1b**. Thermal ellipsoids are drawn at 50% probability level.

= 1.34(2) Å and *d*(C(20)−C(22)) = 1.39(2) Å probably results from the disorder of the isopropyl of the bridged *i*-Pr_2N moiety in **1a**, and likewise, *d*(C(6)−C(8′)) = 1.35(2) Å in **1b**.

Spectral Data. With the carbodiimide insertion, the N=C=N moiety appears with partial double-bond character N$\overline{\text{- -}}$C$\overline{\text{- -}}$N in the organoaluminum amidinomagnesium complexes. Their ^{13}C NMR spectra display chemical shifts in the range $\delta = 174-182$ ppm assigned to the sp^2-hybridization carbon of [(R″)NC(R)N(R″)] moiety, similar to that of [Pt{(R′)NC(R)N(R′)}$_2$].[18] Infrared spectra show absorptions in the range 1650−1660 cm^{-1} assigned to the stretching frequency of N$\overline{\text{- -}}$C$\overline{\text{- -}}$N of the [(R″)NC(R)N(R″)] moiety.[14] The tentative assignments were used to support the characterization of these amidino complexes as well as their mass spectra, which show the monomeric ion peak. The ^1H NMR spectral data were in good agreement with the X-ray data. For compound **1a**, the ^1H NMR spectrum (toluene-d_8) showed two sets of doublets and septets at $\delta = 1.29$ (24H), 1.07 (12H) and at $\delta = 3.65$ (4H), 3.44 (2H), respectively, which are due to the methyl protons and methine protons of the isopropyl groups. The chemical shifts at $\delta = -0.28$ (s, 6H) and 1.63 (s, 3H) are due to the methyl protons attached to the aluminum atom and the migrated methyl protons, respectively. For compound **1b**, the ^1H NMR spectrum (benzene-d_6) showed a doublet at $\delta = 1.37$ (24H) and a septet at $\delta = 3.73$ (4H) which are due to the methyl protons and methine protons of the isopropyl groups, respectively. The chemical shifts at $\delta = -0.19$ (s, 6H), 1.19 (s, 18H), and 1.97 (s, 3H) are due to the methyl protons attached to the aluminum atom, the methyl protons in *tert*-butyl groups, and the migrated methyl protons, respectively. The ^1H NMR spectra of the other complexes are well in agreement with the carbodiimide insertion products. The ^1H NMR spectral assignments for all the complexes are listed in Table 1.

Pyrolysis of Aluminum−Magnesium Amidine Complexes. The reactions of {$R_2Al(\mu$-$NR'_2)_2Mg(\mu$-$R)$}$_n$ with carbodiimide in a 1:*n* ratio give the amidine-bridged complexes {$R_2Al(\mu$-$NR'_2)_2$Mg[(R″)NC(R)N(R″)]}. When subjected to pyrolysis, a dialuminum amido complex and some unisolated species were obtained. We believe that the dialuminum complexes [$R_2Al(\mu$-$NR'_2)]_2$ were obtained from the thermal decomposition of aluminum−magnesium amidine complexes, and when heated to 80 °C, **1a**,**c** produce [$Me_2Al(\mu$-*i*-$Pr_2N)]_2$. When heated to 110 °C, **2a**,**b** produce [$Me_2Al(\mu$-$EtN_2)]_2$, and when heated to 130 °C, **3a**,**b** produce [$Et_2Al(\mu$-*i*-$Pr_2N)]_2$ and some unisolated species as shown in eq 2. The unisolated species could be a polymer of $MeMg(Et_2N)$ which is insoluble in organic solvents and which would be difficult to isolate and purify.



(2)

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Supporting Information Available: Tables of ^{13}C NMR data, X-ray parameters, anisotropic displacement coefficients for non-hydrogen atoms, complete fractional coordinates and isotropic displacement coefficients, and complete bond distances and angles and an ORTEP diagram (15 pages). Ordering information is given on any current masthead page. A list of structure factors (41 pages) is available from the authors upon request.

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