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Chemical Reactivitives of $[Me_2Al(\mu\text{-}N\textit{i}Pr_2)_2MgMe]_4$ and $[Me_2Al(\mu\text{-}N\textit{i}Pr_2)_2MgCl]_2$: Crystal Structures of $[Me_2Al(\mu\text{-}Pz)_2AlMe_2]$, $[Me_2Al(\mu\text{-}Pz)_2Mg(\mu\text{-}Pz)_2AlMe_2]$, and $[Me_2Al(\mu\text{-}N\textit{i}Pr_2)(\mu\text{-}Me)Mg(\mu\text{-}N\textit{i}Pr_2)(\mu\text{-}Me)AlMe_2]$

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$[Me_2Al(\mu\text{-}N\textit{i}Pr_2)_2MgMe]_4$ (**A**) reacted with chloroform to give the starting material $[Me_2Al(\mu\text{-}N\textit{i}Pr_2)_2MgCl]_2$ (**4**) in high yield. Compound **4** underwent metathesis with LiR (R = $t\text{-}C_4H_9$, C_6H_5) to give $[Me_2Al(\mu N\textit{i}Pr_2)_2MgR]_n$ (n = 1, 2). Compound **A** reacted with pyrazole (Pz) in a molar ratio 1:1 to produce $[Me_2Al(\mu\text{-}N\textit{i}Pr_2)_2Mg(Pz)]_2$ (**1**), and in a molar ratio 1:3 to produce degradation products $[Me_2Al(\mu\text{-}Pz)_2AlMe_2]_4$ (**2**) and $[Me_2Al(\mu\text{-}Pz)_2Mg(\mu\text{-}Pz)_2AlMe_2]$ (**3**). Compound **A** reacted with $AlMe_3$ to give $[Me_2Al(\mu\text{-}N\textit{i}Pr_2)_2Mg(\mu\text{-}Me)_2AlMe_2]$ (**8**). Compound **8** isomerized to $[Me_2Al(\mu\text{-}N\textit{i}Pr_2)(\mu\text{-}Me)Mg(\mu\text{-}N\textit{i}Pr_2)(\mu\text{-}Me)AlMe_2]$ (**7**) upon heating. Compound **7** was also obtained from reaction of $AlMe_3$ with $Mg(N\textit{i}Pr_2)_2$ in a molar ratio 3:1. The crystal structures of compounds **2**, **3**, and **8** were determined by xray diffraction analysis.

INTRODUCTION

Although polynuclear complexes of aluminum and magnesium have long been of chemical interest, few papers appeared.[1-5] We discovered the unsymmetric interaction Mg ··· Me-Mg in $\{[Me_2Al(\mu\text{-}N(\textit{i}Pr)_2]_2Mg(\mu\text{-}Me)\}_4$ (**A**),[6] and agostic interaction in $[\{(R_2N)Mg(Me)\}_2\{Mg(NR_2)(NR_2AlMe_3\}_2]$ (R = $SiMe_3$)[7] in research on the chemical properties of aluminum-magnesium compounds. Nucleophilic attack of alcohols, amines, and iodine at magnesium atoms of compound A and $[Me_2Al(\mu\text{-}NEt_2)_2MgMe]_2$ (**B**) is reported.[8] By metathesis compounds with an $\{AlMg\}_2$ framework were formed that on partial degradation yielded {AlMgAl} compounds. Here we report chemical reactions of $\{AlMg\}_2$ with nucleophiles in varied stoichiometry, and also with electrophiles.

EXPERIMENTAL SECTION

General Conditions

All manipulations were undertaken in a glovebag flushed with N_2, a drybox, or a vacuum system. Solvents were distilled and degassed according to standard procedures before use. ^1H, ^{13}C and ^{27}Al NMR spectra were measured (Varian VXR-300 spectrometer). Chemical shifts are referred to TMS (^1H) or benzene-d_6 (^1H, δ 7.15; $^{13}C\{^1H\}$, δ 128.00). ^{27}Al NMR spectral signals were referred to $Al(H_2O)_6^{3+}$. Mass spectral data were obtained on a spectrometer (VG-7025 GC/MS/MS). IR spectra were recorded as Nujol mulls between KBr discs on a FT-IR spectrometer (Bio-Rad FTS-40). Elemental analyses (C, H, N) were performed (Analytische Laboratorien, H. Malissa and G. Reuter GmbH, Germany). Deviation of analytical results of elemental analyses from calculated values is attributed to the extreme sensitivity to air and hygroscopic nature of these compounds.

$AlMe_3$, pyrazole, LiPh and t-BuLi (Aldrich) were used as received. $Mg(NR_2)_2$, R = *i*Pr and $[(CH_3)_2Al\ (\mu\text{-}(N\textit{i}Pr_2)_2\text{-}MgCH_3]_4$ (**A**) were prepared according to the literature procedures.[6,9]

$[Me_2Al(\mu\text{-}N(\textit{i}\text{-}Pr)_2)_2Mg(pz)]_2$ 1

Pyrazole, (0.48 g, 7 mmol) in diethyl ether (30 mL) was added dropwise to a stirred solution of compound **A** (2.10 g, 1.7 mmol) in diethyl ether (100 mL) around 30 °C under nitrogen. After 8 h, a pale yellow solution was obtained, which after removal of diethyl ether under vacuum, gave a pale yellow viscous fluid. The crude product was recrystallized from a mixture of diethyl ether and hexane (1:1)

Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.

to yield a white microcrystalline solid. mp (dec) > 100 °C; IR (Nujol, cm^{-1}): 3742 (w), 3666 (m), 3641 (m), 3391 (m), 2968 (s), 2930 (s), 2708 (w), 1727 (m), 1650 (m), 1463 (s), 1389 (s). ^1H NMR (C_6D_6) δ -0.08 (s, 12H, $Al(C\underline{H}_3)_2$), 0.94 (d, 24H, $NCH(C\underline{H}_3)$, J = 6.6 Hz), 1.32 (d, 24H, $NCH(C\underline{H}_3)$, J = 6.3 Hz), 3.67 (sep, $NC\underline{H}(CH_3)$, J = 6.9 Hz), 6.27 (t, 2H, pz 4-H), J = 2.1 Hz), 7.84 (d, 4H, pz 3,5-H), J = 2.1 Hz) ppm; ^{13}C NMR (C_6D_6) δ -4.16 ($Al(\underline{C}H_3)_2$), 27.98 ($NCH(\underline{C}H_3)$), 28.55 ($NCH(\underline{C}H_3)$), 51.07 ($N\underline{C}H(CH_3)$, 107.01 (pz 4-C), 142.35 (pz 3,5-C) ppm; ^{27}Al NMR (C_6D_6) δ 155 (broad) ppm; mass spectrum (70eV, ten most intense features, *m/z*): 44, 88, 142, 57, 101, 70, 214, 299, 281, 681. Anal. calcd: C, 58.54; H, 10.69; N, 16.06; found: C, 58.44; H, 10.51; N, 16.16.

$[Me_2Al(\mu\text{-}pz)_2AlMe_2]_2$ 2 and $[Me_2Al(\mu\text{-}pz)_2Mg(\mu\text{-}pz)_2AlMe_2]$ 3

Pyrazole ($C_3N_2H_4$) (0.82 g, 12 mmol) dissolved in diethyl ether (50 mL) was added dropwise to a stirred solution of compound A (1. 20 g, 4 mmol) in diethyl ether (100 mL) around 30 °C under nitrogen. After 4 h, a pale yellow solution was obtained, which after removal of diethyl ether under vacuum gave a pale yellow viscous fluid. Sublimation at 70 °C under vacuum produced colorless crystals of two kinds. The more volatile crystal is $[Me_2Al(\mu\text{-}pz)_2AlMe_2]$ (**2**), mp 88-90 °C; IR (Nujol, cm^{-1}): 3788 (w), 3690 (w), 3397 (m), 2933 (s), 1675 (w), 1599 (m), 1493 (m), 1388 (m). ^1H NMR (C_6D_6) δ -0.26 (s, 12H, $Al(C\underline{H}_3)_2$), 5.86 (t, 2H, pz 4-H), J = 2.1 Hz), 7.34 (d, 4H, pz 3,5-H), J = 2.1 Hz) ppm; ^{13}C NMR (C_6D_6) δ -9.35 ($Al(\underline{C}H_3)_2$), 106.58 (pz 4-C), 140.41 (pz 3,5-C) ppm; ^{27}Al NMR (C_6D_6) δ 146 (broad) ppm; Mass spectrum (70 eV, ten most intense features, *m/z*): 233, 165, 109, 234, 217, 82, 176, 190, 150, 57. The less volatile crystal is $[Me_2Al(\mu\text{-}pz)_2Mg(\mu\text{-}pz)_2AlMe_2]$ (**3**). mp 96-99 °C; IR (Nujol, cm^{-1}): 3635 (m), 3404 (m), 3141 (m), 2936 (m), 2821 (w), 2541 (m), 2430 (m), 1743 (s), 1629 (m), 1502 (s), 1389 (m). ^1H NMR (C_6D_6) δ -0.234 (s, 12H, $Al(C\underline{H}_3)_2$), 6.00 (t, 4H, pz 4-H) J = 2.1 Hz), 7.31 (d, 4H, pz 3-H), J = 1.8 Hz, 7.67 (d, 4H, pz 5-H) J = 1.8 Hz) ppm; ^{13}C NMR (C_6D_6) δ -10.13 ($Al(\underline{C}H_3)_2$), 105.65 (pz 4-C), 139.31 (pz 3-C), 142.58 (pz 5-C) ppm; ^{27}Al NMR (C_6D_6) δ 148 (broad) ppm; mass spectrum (70 eV, ten most intense features, *m/z*): 267, 285, 391, 68, 109, 392, 172, 199, 41, 308. Anal. calcd: C, 47.25; H, 5.95; N, 27.55; found: C, 47.14; H, 5.87; N, 27.43.

$[Me_2Al(\mu\text{-}(N(i\text{-}Pr)_2)_2MgCl]_2$ 4

Chloroform (0.32 mL, 4 mmol) in benzene (30 mL) was added dropwise to a stirred solution of compound A (1.2 g, 4 mmol) in benzene (100 mL) around 30 °C under nitrogen. After 24 h a pale yellow solution was obtained, which after removal of benzene under vacuum, gave colorless crystals, $[Me_2Al(\mu\text{-}(N(i\text{-}Pr)_2)_2MgCl]_2$ (**4**). mp (dec) > 120 °C; Yield: 72 %; IR (Nujol, cm^{-1}): 2950 (s), 2915 (m), 2850 (m), 1450 (s), 1385 (s), 1200 (s), 1146 (m), 938 (m), 750 (m), 667 (m). ^1H NMR (C_6D_6) δ -0.18 (s, 12H, $Al(C\underline{H}_3)_3$), 1.28 (d-d, 48H, $NCH(C\underline{H}_3)_2$ J = 6.9 Hz), 3.56 (sep, 8H, $NC\underline{H}(CH_3)_2$ J = 6.6 Hz) ppm; ^{13}C NMR (C_6D_6) δ -3.65 ($Al(\underline{C}H_3)_3$), 26.84 ($NCH(\underline{C}H_3)_2$), 48.16 ($N\underline{C}H(CH_3)_2$) ppm; ^{27}Al NMR (C_6D_6) δ 140 (broad) ppm; Mass spectrum (70 eV, ten most intense features, *m/z*): 142, 44, 86, 301, 124, 243, 57, 100, 281, 316. Anal. calcd: C, 53.16; H, 10.83; N, 8.86; found: C, 53.05; H, 10.65, N, 8.70.

$[Me_2Al(N(i\text{-}Pr)_2)_2MgC(t\text{-}Bu)]$ 5 and $[Me_2Al(N\text{-}iPr_2)_2MgPh]_2$ 6

A solution of t-BuLi (2.23 mL, 3.8 mmol) in pentane was added dropwise to a stirred solution of compound **4** (1.2 g, 1.9 mmol) in toluene (100 mL) maintaining the temperature at -78 °C; under nitrogen. After 12 h, the precipitated LiCl was filtered off. The crude product after removal of solvent was recrystallized from diethyl ether to give a white solid, compound **5**. A similar procedure was adopted to prepare of compound **6** except to use PhLi (2.63 mL, 4.7 mmol) in cyclohexane and diethylether; the product was obtained upon sublimation at 89 °C. Compound **5** mp 104-106 °C; Yield: 43%; IR (Nujol, cm^{-1}): 2953 (m), 1475 (m), 1462 (m), 1395 (m), 1200 (m), 983 (m), 830 (m), 830 (m), 764 (m). ^1H NMR (C_6D_6) δ -0.32 (s, 6H, $Al(C\underline{H}_3)$), 1.08 (d, 24H, $NCH(C\underline{H}_3)_2$ J = 6.6 Hz) ppm, 1.27 (s, 9H, $C(C\underline{H}_3)_3$), 3.13 (sep, 4H, $NC\underline{H}(CH_3)_2$, J = 6.6 Hz); ^{13}C NMR (C_6D_6) δ -3.41 ($Al(\underline{C}H_3)_2$), 25.53 ($NCH(\underline{C}H_3)_2$), 14.93 ($C(\underline{C}H_3)_3$), 46.96 ($N\underline{C}H(CH_3)_2$) ppm, 34.68 ($\underline{C}(CH_3)_3$); ^{27}Al NMR (C_6D_6) δ 152 (broad) ppm; Mass spectrum (70 eV, ten most intense features, *m/z*): 124, 44, 138, 86, 57, 281, 142, 223, 180, 323. Anal. calcd: C, 63.90; H, 12.72; N, 8.28; found: C, 63.51; H, 12.45; N, 8.10.

Compound **6**. mp 112-114 °C; Yield: 56%; IR (Nujol, cm^{-1}): 3049 (s), 3000 (s), 1600 (m), 1500 (m), 1388 (s), 1357 (s), 1300 (m), 1223 (m), 1194 (s), 1138 (s), 1118 (s), 1061 (m), 969 (s), 908 (s), 837 (m), 785 (m), 704 (m), 653 (m), 612 (m). ^1H NMR (C_6D_6) δ -0.30 (s, 12H, $Al(C\underline{H}_3)_2$), 1.15 (d-d, 48H, $NCH(\underline{CH_3})_2$, J = 6.6 Hz), 3.20 (sep, 8H, $N\underline{CH}(CH_3)_2$, J = 6.3 Hz), 7.84 (d, 2H, $C_6\underline{H}_5$, J = 2.1 Hz), 7.43 (t, 2H, $C_6\underline{H}_5$, J = 2.1 Hz), 7.35 (t, 1H, $C_6\underline{H}_5$, J = 1.8 Hz) ppm; ^{13}C NMR (C_6D_6) δ -3.30 ($Al(\underline{C}H_3)_2$), 25.61 ($NCH(\underline{C}H_3)_2$), 46.68 ($N\underline{C}H(CH_3)_2$), 126.64 ($\underline{C}_6H_5$), 128.53 ($\underline{C}_6H_5$), 140.19 ($\underline{C}_6H_5$), 160.88 ($\underline{C}_6H_5$) ppm; ^{27}Al NMR (C_6D_6) δ 154 (broad) ppm; mass spectrum (70 eV, ten most intense features, *m/z*): 86, 124, 142, 78, 57, 281, 101, 100, 209, 156. Anal. calcd: C, 67.04; H, 10.89; N, 7.82; found: C, 66.60; H, 10.67, N, 7.72.

$[\mathrm{Me_2Al(\mu\text{-}N(}i\mathrm{\text{-}Pr)_2)(\mu\text{-}Me)Mg(\mu\text{-}N(}i\mathrm{\text{-}Pr)_2)(\mu\text{-}Me)AlMe_2]}$ 7

$\mathrm{AlMe_3}$ (2 M, 51 mL, 102 mmol) in toluene was added dropwise to a stirred solution of $\mathrm{Mg(N(}i\mathrm{\text{-}Pr)_2)_2}$ (7.62 g, 34 mmol) in diethyl ether (100 mL) around 30 °C under nitrogen. After 12 h, a pale yellow solution was obtained, which after removal of diethyl ether under vacuum, gave a pale yellow solid. The crude product was recrystallized from diethyl ether to field colorless crystals. mp 76-78 °C; ^{1}H NMR ($\mathrm{C_6D_6}$) δ -0.28 (s, 18H, $(\mu\text{-}\mathrm{C\underline{H}_3)Al(C\underline{H}_3)_2}$, 1.06 (d, 24H, $\mathrm{NCH(C\underline{H}_3)_2}$, $J = 6.6$ Hz), 3.28 (sep, 4H, $\mathrm{NC\underline{H}(CH_3)_2}$, $J = 6.6$ Hz) ppm; ^{13}C NMR ($\mathrm{C_6D_6}$) δ, -5.40 $(\mu\text{-}C\mathrm{H_3)Al\underline{C}H_3}$, 25.32 $\mathrm{(NCH(\underline{C}H_3)_2)}$, 47.73 $\mathrm{(N\underline{C}H(CH_3)_2)}$ ppm; ^{27}Al NMR ($\mathrm{C_6D_6}$), δ 155 (broad) ppm; mass spectrum (30 eV, ten most intense features, *m/z*): 142, 57 124, 196, 156, 84, 43, 157, 197, 198.

$[\mathrm{Me_2Al(\mu\text{-}N(}i\mathrm{\text{-}Pr)_2)_2Mg(\mu\text{-}Me)_2AlMe_2]}$ 8

$\mathrm{AlMe_3}$, (2 M, 3.40 mL, 6.8 mmol) in toluene was added dropwise to a stirred solution of **A** (2.00 g, 7 mmol) in toluene (100 mL) around 30 °C under nitrogen. After 8 h, a pale yellow solution was obtained, which after removal of toluene under vacuum, gave a pale yellow solid. The crude product was recrystallized from toluene to obtain a white solid. mp 69-72 °C; IR (Nujol, cm^{-1}): 2972 (m), 2878 (m), 1460 (m), 1374 (m), 1318 (w), 1227 (m), 1134 (m), 1060 (w), 969 (m), 910 (m), 835 (m), 789 (m), 760 (m), 699 (m), 577 (m). ^{1}H NMR ($\mathrm{C_6D_6}$) δ -0.38(s, 6H, $\mu\text{-}\mathrm{C\underline{H}_3}$), -0.27 (s, 12H, $\mathrm{Al(C\underline{H}_3)}$), 1.132 (d, 24H, $\mathrm{NCH(C\underline{H}_3)}$ $J = 6.6$ Hz), 3.36 (sep, 4H, $\mathrm{NC\underline{H}(CH_3)}$ $J = 6.6$ Hz) ppm; ^{13}C NMR ($\mathrm{C_6D_6}$) δ -6.64 ($\mu\text{-}\mathrm{\underline{C}H_3}$), -3.78 $\mathrm{(Al(\underline{C}H_3)_2)}$, 27.20 $\mathrm{(NCH(\underline{C}H_3))}$, 27.13 $\mathrm{(N\underline{C}H(CH_3)}$ ppm; ^{27}Al NMR ($\mathrm{C_6D_6}$) δ 152 (broad); mass spectrum (30 eV, the ten most intense features, *m/z*): 142, 44, 124, 86, 228, 57, 212, 281, 123, 339.

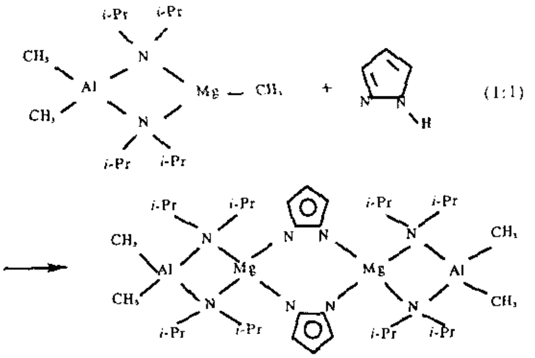
Structure Determination

Single crystals for xray measurements were sealed in glass capillaries. Intensity data were collected using a θ-2θ scan mode and corrected for absorption and decay. All structures were solved by a direct method and refined with full-matrix least-squares on F. In the final cycle all non-hydrogenic atoms were refined anisotropically and all hydrogen atoms fixed at idealized positions. Scattering factors for neutral atoms and anomalous scattering coefficients for non-hydrogen atoms were taken from the literature.[10] All calculations were carried out with either a computer (Micro VAX 3600) using the NRC VAX program package[11] for **7**, or a computer (SGI R4000) using the teXsan program package. Data collection and cryatal parameters are summarized in Table 1.

RESULTS AND DISCUSSION

Reactions of Compound A with Pyrazole

The reaction of compound **A** with pyrazole (in equimolar proportions) produced $[\mathrm{Me_2Al(\mu\text{-}N(}i\mathrm{\text{-}Pr_2)_2)_2Mg(\mu\text{-}Pz)]_2}$ **1** and methane through metathesis (eq. 1). The ^{1}H NMR spectrum displays chemical shifts δ = 7.84 (d) and 6.27 (t) ppm in the integral ratio 2:1, the ^{13}C NMR spectrum shows chemical shifts at δ = 107.01 and 142.35 ppm for $^{\beta}$C-H and $^{\alpha}$C-H of pyrazolide. The chemical shifts δ = 0.94 (d) and 1.32 (d) are due to methyl groups on isopropyl. The singlet at δ = -0.08 ppm is assigned to methyl groups attached to the aluminum atoms. Mass spectral data show a base-ion peak at *m/z* = 681 assigned to the dimer with cleavage of one methyl group. Hence the structure has retained the $\mathrm{Al_2Mg_2}$ framework.



(1)

On varying the molar ratio of compound **A** to pyrazole from 1:1 to 1:3, we obtained a pale yellow product distinct from the above product. The metathetical reactions occur not only at magnesium-alkyl bonds, but also at aminobridges accompanied by elimination of methane and amine. Upon sublimation, colorless crystals of two kinds were obtained and their structures were elucidated with xray diffraction analysis. The more volatile crystal was $[\mathrm{Me_2Al(\mu\text{-}pz)_2\text{-}AlMe_2]}$ **2**, and the other was $[\mathrm{Me_2Al(\mu\text{-}pz)_2Mg(\mu\text{-}pz)_2\text{-}AlMe_2]}$ **3**. Both compounds have an $\mathrm{Al_2Mg_2}$ framework with pyrazolides replacing amides as bridging ligands. In compound **2**, two pyrazolide groups serve as bridges between the two metals. A six-membered ring consists of $\mathrm{N_4}$ on these two pyrazolide groups and $\mathrm{Al_2}$. The six-membered

Table 1. Crystallographic Data and Refinement Results.

	2	**3**	**7**
formula	$Al_2C_{10}H_{18}N_4$	$Al_2MgC_{16}H_{24}N_8$	$Al_2MgC_{18}H_{46}N_2$
molar mass/g	248.24	406.69	368.84
Diffractometer	Rigaku AFC7S	Rigaku AFC6S	Enraf-Nonius
Crystal system	triclinic	triclinic	Monoclinic
Space Group	$P\bar{1}$(#2)	$P\bar{1}$(#2)	$P2_1/n$
a,/Å	9.071(2)	8.8584(8)	11.632(4)
b,/Å	12.367(2)	16.925(2)	14.003(3)
c,/Å	7.140(1)	8.2233(9)	15.741(4)
α,/deg	100.12(1)	97.88(1)	
β,/deg	104.78(1)	105.975(7)	102.43(2)
γ,/deg	100.89(2)	90.353(9)	
V,/$Å^3$	739.0(3)	1172.9(2)	2503.7(12)
Z	2	2	4
Dcalc,/gmL^{-1}	1.116	1.151	0.979
λ,/Å	0.71069 (M_o K_α)	1.54178 (Cu K_α)	0.70930 (Mo K_α)
F(000)	264.00	428.00	824
Crystal dimens ions./mmp	0.33 × 0.50 × 0.75	0.33 × 0.33 × 0.66	0.20 × 0.40 × 0.50
$2\theta_{max}$	50.0°	120.3°	45.0°
no.of meas. reflns	2798	3758	3340
no of obsed relfns	1736 [$I > 3.00\sigma(I)$]	2705 [$I>3.00\sigma(I)$]	1327 [$I>2.00\sigma(I)$]
no. of unique reflns	2615	3498	3271
R_f; R_w	0.042;0.052	0.044;0.044	0.065;0.052
Weight scheme	$1.0/\sigma^2(F_o)$	$1.0/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
Max peak in diff. map,/$eÅ^{-3}$	0.19	0.21	0.28
No. of Variables	145	244	209

ring has a boat-shaped conformation (Fig. 1). Selected bond distances and angles are listed in Table 2. Two Al atoms exist in a distorted tetrahedral environment; for example, bond angles around Al(1) of C(8)-Al(1)-C(10), C(8)-Al(1)-N(1), N(1)-Al(1)-N(3) and N(3)-Al(1)-C(10) are 118.8(1), 111.1(2), 99.28(5) and 106.95(6) deg, respectively.

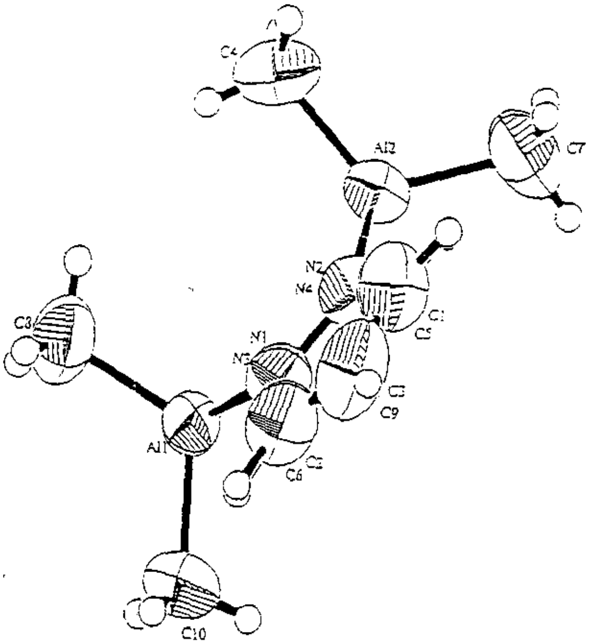


Fig. 1. Side view of $[Me_2Al(\mu\text{-}pz)_2AlMe_2]$ (**2**).

The structure of compound **3** is illustrated in Fig. 2. Both six-membered rings have a distorted boat conformation. The Al and Mg atoms also exist in a distorted tetrahedral environment. Selected bond distances and angles are shown in Table 2.

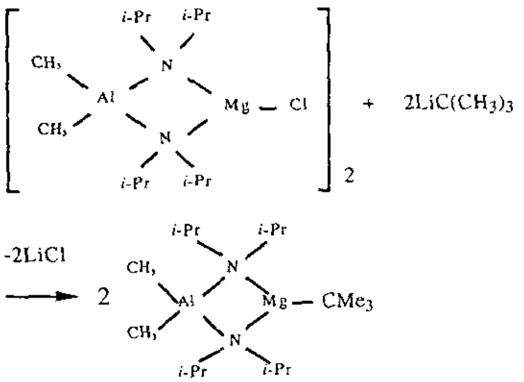
Reaction of Compound 4 with LiR (R = Ph, t-Bu)

Compound A reacted with chloroform to produce a crystalline product characterized by elemental and spectral analyses to be $[Me_2Al(\mu\text{-}N(i\text{-}Pr)_2)_2MgCl]_2$ **4**. Compound **4** reacted with *t*-BuLi to produce compound **5** and LiCl according to eq (**2**). Single crystals of compound **5** were not obtained. The structure is consistent with elemental and spectral data; ^1H NMR spectra contained chemical shifts at δ = -0.32 (s, 6H) 1.08 (d, 24H), 1.27 (s, 9H), 3.13 (sep, 4H) ppm assigned to the methyl group attached to aluminum atoms, methyl groups of isopropyl amine, methyl groups of t-butyl, and the methine group of isopropyl amine respectively. Mass spectral data contain the base ion peak *m/z* at

Table 2. Selected bond Distances/Å and Angles/deg

[$Me_2Al(\mu$-Pz)]$_2$ (**2**)			
Al(1)-N(1)	1.923(1)	C(1)-C(3)	1.363(3)
Al(1)-C(8)	1.939(3)	C(2)-C(3)	1.37(1)
Al(2)-N(2)	1.914(1)	Al(1)-N(3)	1.920(2)
Al(2)-C(4)	1.939(6)	Al(1)-C(10)	1.953(1)
N(1)-N(2)	1.369(1)	Al(2)-N(4)	1.927(4)
N(2)-C(1)	1.344(5)	A1(2)-C(7)	1.950(4)
N(3)-C(6)	1.347(7)	N(1)-C(2)	1.339(5)
N(1)-Al(1)-N(3)	99.3(1)	N(3)-Al(1)-C(8)	110.3(1)
N(1)-Al(1)-C(10)	108.7(1)	C(8)-Al(1)-C(10)	118.8(1)
N(3)-Al(1)-C(10)	107.0(1)	Al(1)-N(1)-C(2)	126.7(3)
Al(1)-N(1)-N(2)	126.2(1)	Al(2)-N(2)-N(1)	125.9(1)
N(2)-N(1)-C(2)	107.1(3)	N(1)-N(2)-C(1)	107.0(1)
Al(1)-N(3)-N(4)	126.7(1)	Al(1)-N(3)-C(6)	126.5(2)
N(2)-C(1)-C(3)	110.7(6)	N(1)-C(2)-C(3)	110.7(6)
N(1)-Al(1)-C(8)	111.1(2)	C(1)-C(3)-C(2)	104.4(7)
[$Me_2Al(\mu$-Pz)$_2$Mg(μ-Pz)$_2AlMe_2$] (**3**)			
Al(1)-N(1)	1.923(3)	Al(1)-N(8)	1.920(3)
Al(1)-C(13)	1.943(4)	Al(1)-C(14)	1.951(4)
Mg(1)-N(2)	2.047(3)	Mg(1)-N(7)	2.039(3)
N(1)-N(2)	1.365(3)	N(1)-C(1)	1.336(4)
N(2)-C(3)	1.332(4)	N(7)-N(8)	1.363(3)
N(7)-C(10)	1.335(4)	N(8)-C(12)	1.341(4)
C(1)-C(2)	1.371(5)	C(10)-C(11)	1.369(5)
C(2)-C(3)	1.354(5)	C(11)-C(12)	1.361(5)
N(1)-Al(1)-N(8)	102.2(1)	N(1)-C(1)-C(2)	109.9(4)
N(1)-Al(1)-C(14)	108.6(2)	N(2)-C(3)-C(2)	111.5(4)
N(8)-Al(1)-C(14)	108.0(2)	N(8)-C(12)-C(11)	109.9(4)
N(1)-Al(1)-C(13)	108.3(2)	C(10)-C(11)-C(12)	104.1(4)
N(8)-Al(1)-C(13)	107.4(1)	N(2)-Mg(1)-N(6)	116.7(1)
C(13)-Al(1)-C(14)	120.8(2)	N(6)-Mg(1)-N(7)	113.3(1)
N(2)-Mg(1)-N(3)	108.4(1)	Al(1)-N(1)-C(1)	127.1(3)
N(2)-Mg(1)-N(7)	101.4(1)	Mg(1)-N(2)-N(1)	124.9(2)
N(3)-Mg(1)-N(7)	116.0(1)	N(1)-N(2)-C(3)	106.5(3)
Al(1)-N(1)-N(2)	124.7(2)	Mg(1)-N(7)-C(10)	127.8(3)
N(2)-N(1)-C(1)	107.8(3)	Al(1)-N(8)-N(7)	123.6(2)
Mg(1)-N(2)-C(3)	128.0(3)	N(7)-N(8)-C(12)	108.4(3)
Mg(1)-N(7)-N(8)	125.3(2)	N(7)-N(10)-C(11)	111.5(4)
N(8)-N(7)-C(10)	106.0(3)	C(1)-C(2)-C(3)	104.3(3)
Al(1)-N(8)-C(12)	126.6(3)		
{Me_2Al[μ-N(i-Pr)$_2$] (μ-Me)Mg[μ-N(i-Pr)$_2$](μ-Me)$AlMe_2$} (**7**)			
Mg···Al(1)	2.804(4)	Al(1)-C(3)	1.966(9)
Mg···Al(2)	2.791(4)	Al(1)-C(4)	1.958(8)
Mg-N(1)	2.102(6)	Al(2)-N(2)	1.953(6)
Mg-N(2)	2.114(6)	Al(2)-C(2)	2.048(9)
Mg-C(1)	2.316(8)	Al(2)-C(5)	1.968(9)
Mg-C(2)	2.271(8)	N(1)-C(7)	1.499(8)
Al(1)-N(1)	1.980(6)	C(7)-C(8)	1.51(1)
Al(1)-C(1)	2.122(8)	C(16)-C(17)	1.52(1)
N(1)-Mg-N(2)	150.4(2)	Mg-N(1)-Al(1)	86.7(2)
N(1)-Mg-C(1)	91.3(2)	Mg-N(1)-C(7)	122.0(4)
N(1)-Mg-C(2)	109.8(3)	Mg-N(1)-C(10)	113.0(4)
N(2)-Mg-C(1)	105.7(3)	Al(1)-N(1)-C(7)	107.4(4)
N(2)-Mg-C(2)	89.2(3)	Al(1)-N(1)-C(10)	110.8(4)
C(1)-Mg-C(2)	105.6(3)	C(7)-N(1)-C(10)	113.2(5)
N(1)-Al(1)-C(1)	100.9(3)	Mg-C(1)-Al(1)	78.2(3)
N(1)-Al(1)-C(3)	114.2(3)	Mg-C(2)-Al(2)	80.3(3)
N(1)-Al(1)-C(4)	112.8(3)	N(1)-C(7)-C8)	117.2(6)
C(1)-Al(1)-C(3)	109.1(3)	N(1)-C(7)-C(9)	113.7(6)
C(1)-Al(1)-C(4)	106.2(4)	C(8)-C(7)-C(9)	110.5(6)
C(3)-Al(1)-C(4)	112.6(4)		

323 assigned to monomer less one methyl group. As the t-butyl group is bulky, it is expected that the compound can exist as a monomer.



(2)

The reaction of compound **4** with LiPh yielded the solid product **6** that is well characterized by elemental and spectral analyses. In IR spectra, νC=C is observed at 1601 and 1501 cm^{-1} and some overtones of phenyl rings appear at 1937, 1865, 1810 and 1744 cm^{-1}. The ^{1}H NMR spectrum shows and phenyl signals $\delta = 7.842$ (m, 2H), 7.432 (m, 2H) and 7.356 (m, 1H) ppm. The structure is expected to be the

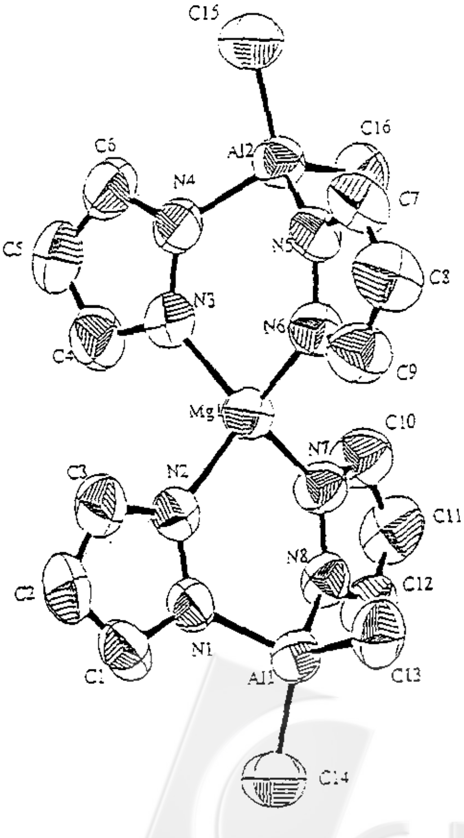


Fig. 2. ORTEP drawing of [$Me_2Al(\mu$-pz)$_2$Mg(μ-pz)$_2$-$AlMe_2$] (3).

dimer with $MgPh_2$.[12]

Reaction of Compound A with $AlMe_3$

In previous investigations we demonstrated that $[Mg(N\text{-}iPr_2)_2]$ reacted with $AlMe_3$ in the ratio 1:1 to give compound (**A**), which exists as a dimer in solution.[6] When the stoichiometry of $[Mg(N\text{-}iPr_2)_2]$ to $AlMe_3$ was varied to 1:3, compound **7** was obtained. Compound **8**, a geometrical isomer of **7** was further synthesized by the reaction of compound **A** with $AlMe_3$ in a molar ratio 1:1. Temperature-dependent NMR experiments were performed in order to probe the fluxionality of methyl groups in $[Me_2Al(\mu\text{-}NiPr_2)(\mu\text{-}Me)Mg(\mu\text{-}NiPr_2)(\mu\text{-}Me)AlMe_2]$ **7** (vide supra). The molecular structure of compound **7** was determined by xray diffraction; an ORTEP diagram appears in Fig. 3. Both the amido and methyl groups act as bridging ligands between aluminium and magnesium atoms. Al(1), N(1), Mg and C(1) and Al(2), N(2), Mg and C(2) respectively make up two nonplanar heterocyclic four-membered rings in a spiro form. As the amido ligands stretch outward due to the bulky isopropyl groups, the Al-Mg-Al angle deviates from linear Al-Mg-Al to 139°.[8] The distance between Al(1) and C(1) at 2.122(8)Å is greater than that of Al(1)-C(3), 1.966(9)Å, due to the electron-deficient nature of bridging methyl ligands. The bond distances Mg-C(1) and Mg-C(2) at 2.316(8) and 2.271(8)Å respectively are within the typical range of a Mg-C bond in a bridging mode. Selected bond distances and angle of **2**, **3** and **7** are presented in Table 2.

Variable-temperature NMR spectra recorded for compound **7** are shown in Fig. 4. Upon cooling to -30 °C the septet due to methine protons of the isopropyl group splits gradually. By -50 °C, the signal splits into two sets of septets. The methyl protons of isopropyl that show a doublet initially split into an octet (expected to arise from a doublet of quartets) and became broader due to poor resolution at low temperature. This behaviour is expected to result from the distinct chemical enviroments among four methyl groups of two isopropyls on each nitrogen or four isopropyl groups on two nitrogen atoms.

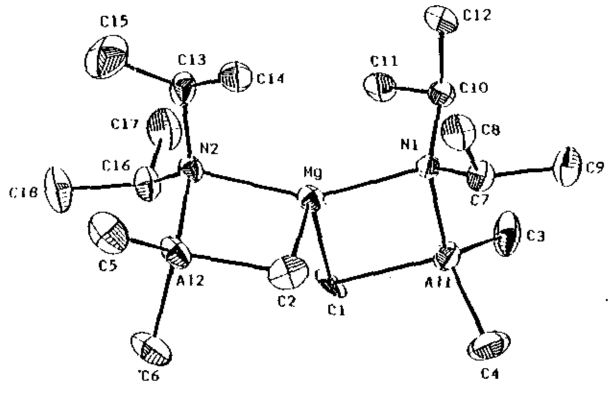


Fig. 3. ORTEP drawing of $[Me_2Al(\mu\text{-}N(iPr_2))(\mu\text{-}Me)\text{-}Mg(\mu\text{-}N(iPr_2))(\mu\text{-}Me)AlMe_2]$ (**7**).

The reaction of compound **A** with $AlMe_3$ in a 1:1 molar ratio involves formation of $[Me_2Al(\mu\text{-}N(i\text{-}Pr)_2)_2Mg(\mu\text{-}Me)_2AlMe_2]$ **8** considered as an isomer of compound **7**. Compound **8** was thermally unstable and readily converted to compound **7** either on heating or on standing for a few days. Compound **8** on attempted recrystallization from diethyl ether readered the starting material compound **A**. ^1H NMR spectra contain chemical shifts δ at -0.38 (s, 6H), -0.27 (s, 12H), 1.13 (d, 24H) and 3.36 (sep, 4H) ppm, assigned to the bridging methyl group between Al and Mg, the terminal methyl group attached to the Al atom, the methyl in isopropyl groups, and the methine group respectively. ^1H NMR spectra of compound **8** at varied temperatures (Fig. 5) show that, when the temperature is increased gradually from 25 °C to 80 °C, two signals that correspond to distinct methyl groups merged into a singlet characteristic of compound **7**. Hence compounds **8** and **7** may be geometrical isomers.

Careful scrutiny of mass spectral data revealed two major differences between compound **7** and **8**. The line at *m/z* 281 assigned to the ion fragment of $[Me_2Al[N(i\text{-}Pr_2)]_2Mg]^+$ in compound **8** is not found in compound **7**; conversely, the live at *m/z* 196 assigned to the fragment of $[Me_2Al(\mu\text{-}Me)N(i\text{-}Pr_2)Mg]^+$ in compound **7** is absent from the spectrum of compound **8**. On the basis of this evidence

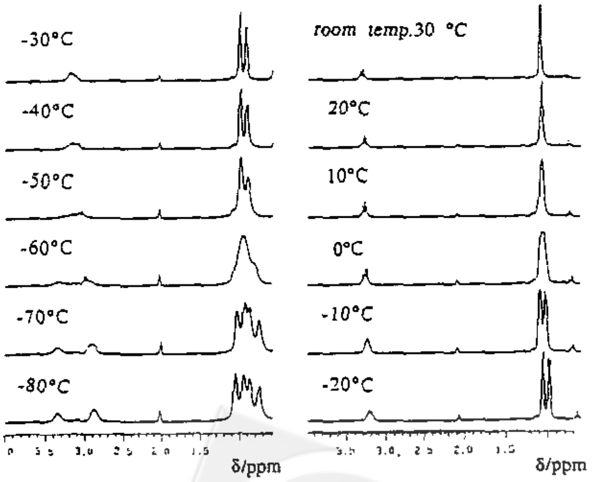


Fig. 4. Temperature dependent ^1H NMR spectrum for $[Me_2Al(\mu\text{-}N(iPr_2))(\mu\text{-}Me)Mg(\mu\text{-}N(iPr_2))(\mu\text{-}Me)AlMe_2]$ (**7**).

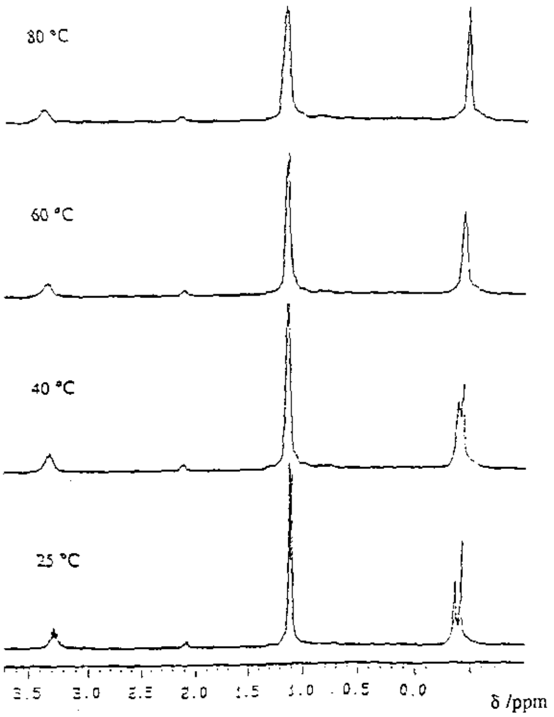


Fig. 5. Temperature-dependent ^1H NMR spectra for $[Me_2Al(\mu\text{-}N(iPr_2))_2Mg(\mu\text{-}Me)_2AlMe_2]$ (**8**).

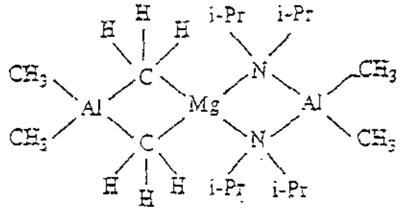


Fig. 6. Structure of $[Me_2Al(\mu\text{-}Me)_2Mg(\mu\text{-}N(iPr_2))_2AlMe_2]$ **8**.

and possible cracking models, we propose that the compound **8** has the structure shown in Fig. 6.

CONCLUSION

As we demonstrated previously,[8] whatever nucleophilic or electrophilic reagent is used for reaction with compound A, activation at the bridging magnesium-carbon bond is more pronounced than at the bridging aluminum-nitrogen bond. In the present set of compounds, we noticed the same phenomenon.

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Key Words

Synthesis; Aluminum magnesium compounds.

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