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Syntheses and Crystal Structures of Polynuclear Organoaluminum–Magnesium Complexes and Their Oxidative Products

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This paper reports the syntheses of a number of aluminum–magnesium complexes. Reaction of $\{[(Me_3Si)_2N]_2Mg\}_2$-(1,4-dioxane) (**1**) with trimethylaluminum produces $[\{(R_2N)Mg(Me)\}_2\{Mg(NR_2)(NR_2AlMe_3)\}_2]$ ($R = SiMe_3$) (**2**) and $\{Me_2Al[N(SiMe_3)_2]\}_2$(1,4-dioxane) (**3**). Compound **2** is a dialuminum–tetramagnesium complex with unusual linear metal···methyl–metal bridge groups. Reactions of $Mg[N(i\text{-}Pr)_2]_2$ with $AlEt_3$ and $Mg[N(i\text{-}Bu)_2]_2$ with $AlMe_3$ also afford Al–Mg complexes. However, reaction of $Mg(NMe_2)_2$ and $Mg[N(n\text{-}Pr)_2]_2$ with $AlMe_3$ and reaction of $Mg(NEt_2)_2$ with $Al(i\text{-}Bu)_3$ produce dialuminum complexes. In order to understand why Al dimers formed rather than Al–Mg complexes, $\{Me_2Al(\mu\text{-}NEt_2)_2Mg(\mu\text{-}Me)\}_2$ (**A**) was heated to produce the dialuminum complex $[Me_2Al(\mu\text{-}NEt_2)]_2$. Insertion of O_2 into the Mg–R bond of Al–Mg complexes resulted in the formation of the magnesium alkoxide derivatives $\{R_2Al(\mu\text{-}NR'_2)_2Mg(\mu\text{-}OR)\}_2$ (**13**, R = Me, R′ = *i*-Pr; **14**, R = Et, R′ = Et; **15**, R = Me, R′ = Et; **16**, R = Me, R′ = *i*-Bu). The molecular structures of compounds **2**, **3**, and **13** were determined by X-ray diffraction. Compound **2** crystallizes in the triclinic space group $P1$ with unit cell parameters $a = 12.288(5)$ Å, $b = 12.698(6)$ Å, $c = 14.285(7)$ Å, $\alpha = 101.79(4)°$, $\beta = 90.07(3)°$, $\gamma = 111.57(3)°$, $V = 2022(2)$ Å^3, and $Z = 1$, compound **3** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 14.804(5)$ Å, $b = 7.475(3)$ Å, $c = 15.378(5)$ Å, $\beta = 100.77(3)°$, $V = 1672(1)$ Å^3, and $Z = 2$, and compound **13** crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 8.893(1)$ Å, $b = 13.995(2)$ Å, $c = 16.382(3)$ Å, $\beta = 96.60(1)°$, $V = 2025.6(6)$ Å^3, and $Z = 2$.

Introduction

Although polynuclear aluminum magnesium complexes have been of chemical interest for many years,[1] few papers on this subject exist. Initially, attention was directed to dialuminum magnesium complexes[2,3] owing to their catalytic role in polymerization.[4] Their structures were reported to exist in the solid state as an oligomer instead of a monomer.[5–8] Recently, we reported the first example of Mg···Me–Mg interactions in $\{[Me_2Al(\mu\text{-}N(i\text{-}C_3H_7)_2]_2Mg(\mu\text{-}Me)_4\}$ similar to those in $(LiR)_n$, where R = Me.[9] Instead of linear metal–methyl–metal bridge groups found in $LiB(Me_4)$,[10] this metal···methyl–metal bridge group is bent. In an attempt to prepare the aluminum magnesium monomer, we used the bulky group $N(SiMe_3)_2$ and different alkyl groups to stabilize the monomer. Reaction of bis(dialkylamido)magnesium with trialkylaluminum yielded dimeric complexes and a tetrameric aluminum–magnesium complex. The novel dimer $[\{(R_2N)Mg(Me)\}_2\{Mg(NR_2)(NR_2AlMe_3)\}_2]$ ($R = SiMe_3$) (**2**) contains unusual linear metal···methyl–metal bridge interactions. This paper focuses on the syntheses, characterization, and structures of compounds **2**, **3**, and a series of dimeric aluminum–magnesium complexes. Pyrolysis of these compounds and insertion of oxygen into the Mg–C bond are also examined.

Experimental Section

Apparatus and Materials. All procedures were carried out in a N_2-flushed glovebox, drybox, and vacuum system. Solvents were distilled and degassed by standard procedures before use. The ^1H-, ^{13}C-, and ^{27}Al-NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts were measured relative to TMS (^1H) or benzene-d_6 (^1H, δ 7.15; $^{13}C\{^1H\}$, δ 128.00). ^{27}Al-NMR spectra were referenced relative to $Al(H_2O)_6^{3+}$. Mass spectral data were obtained on a VG-7025 GC/MS/MS spectrometer. Elemental analyses (C, H, N) were performed at the Analytische Laboratorien of H. Malissa and G. Reuter GmbH (Germany). Deviations from the calculated values in the elemental analyses were attributed to the extremely air-sensitive and hygroscopic nature of these compounds.

The $AlMe_3$, $AlEt_3$, and $Al(i\text{-}Bu)_3$ reagents were purchased from Aldrich and used as received. Compound **1** and $Mg(NR_2)_2$ were prepared by following previous[12,13] procedures.

Synthesis of Compounds 2 and 3. $AlMe_3$ (34 mmol) in toluene (2 M, 17 mL) was added dropwise to a stirring solution of $\{[(Me_3Si)_2N]_2Mg\}_2$-(1,4-dioxane) (11.52 g, 14.9 mmol) in diethyl ether (100 mL) at room temperature under nitrogen. After 12 h, a pale yellow solution was obtained, which, after removal of diethyl ether and toluene under vacuum, gave a pale yellow viscous fluid. Two kinds of colorless crystals were produced by a gradient-temperature sublimator at 100 °C under vacuum. The more volatile crystal is $\{Me_2Al[N(SiMe_3)_2]\}_2$(1,4-dioxane) (**3**): Mp 129–130 °C; yield 30%; ^1H-NMR (C_6D_6) δ 0.257 (s, 36H, $Si(CH_3)_3$), −0.545 (s, 12H, $Al(CH_3)_2$), 3.498 (s, 8H, OCH_2); ^{13}C-NMR (C_6D_6) δ 66.891 (OCH_2), 5.796 ($Si(CH_3)_3$), −5.241 ($Al(CH_3)_2$); ^{27}Al-NMR (C_6D_6) δ 152 (broad); mass spectrum (EI, 30 eV) 10 most intense m/e peaks at 218, 452, 146, 147, 453, 220, 130, 454, 276, 148. Anal. Calc: C, 45.89; H, 10.79; N, 5.36. Found: C, 45.52; H, 10.55; N, 5.46. The less volatile crystal is $[\{(R_2N)Mg(Me)\}_2\{Mg(NR_2)(NR_2AlMe_3)\}_2]$ ($R = SiMe_3$) (**2**): Mp 124–127 °C; yield 50%; ^1H-NMR (C_6D_6) δ 0.246–0.355 (m,

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(1) Ziegler, K.; Holzkamp, Z. *Justus Liebigs Ann. Chem.* **1957**, *605*, 93.

(2) Atwood, J. L.; Stucky, G. D. *J. Organomet. Chem.* **1968**, *3*, 53.

(3) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 2538.

(4) Lynch, M. W.; Pullukat, T. J. U.S. Pat. 4 455 386, 1984. (*Chem. Abstr.* **1985**, *102*, 101152510h).

(5) Malpass, D. B.; Fannin, L. W. *J. Organomet. Chem.* **1975**, *93*, 1.

(6) Veith, M.; Frand, W.; Töner, F.; Lange, H. *J. Organomet. Chem.* **1987**, *326*, 315.

(7) Chang, C. C.; Chang, M. Y.; Cheng, C. P. *J. Chin. Chem. Soc.* **1989**, *36*, 311.

(8) Her, T. Y.; Chang, C. C.; Liu, L. K. *Inorg. Chem.* **1992**, *31*, 2291.

(9) (a) Weiss, E.; Lucken, E. A. C. *J. Organomet. Chem.* **1964**, *2*, 197. (b) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265. (c) Dietrich, H. *Acta Crystallogr.* **1963**, *16*, 681.

(10) (a) Groves, D.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1971**, *93*, 1553. (b) Rhine, W.; Stucky, G. D.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401.

(11) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2547.

(12) Coates, G. E.; Ridley, D. *J. Chem. Soc. A* **1967**, 56.

(13) Her, T. Y.; Chang, C. C.; Peng, S. M.; Wang, Y.; Lee, G. H. *J. Chin. Chem. Soc.* **1993**, *40*, 315.

0020-1669/94/1333-0099$04.50/0

108H, all $Si(CH_3)_3$), –0.252 (s, 18H, $Al(CH_3)_2$), –0.720 (broad, 6H, $MgCH_3$); ^{13}C-NMR (C_6D_6) δ 5.065–6.603, –2.299 (broad); ^{27}Al-NMR (C_6D_6) δ 150 (broad); mass spectrum (EI, 30 eV) 10 most intense *m/e* peaks at 130, 202, 146, 184, 329, 275, 383, 331, 73, 203. Anal. Calc: C, 44.09; H, 11.11; N, 7.02. Found: C, 43.84; H, 10.77; N, 6.84.

Synthesis of $\{Et_2Al[\mu\text{-}N(SiMe_3)_2]Mg(\mu\text{-}Et)\}_2$ (4) and $\{Et_2[(Me_3Si)_2N]Al\}_2$(1,4-dioxane) (5). $AlEt_3$ (32.3 mmol) in toluene (1.9 M, 17 mL) was added dropwise to a stirring solution of $\{[(Me_3Si)_2N]_2Mg\}_2$(1,4-dioxane) (11.11 g, 14.3 mmol) in diethyl ether (100 mL) at room temperature under nitrogen. After 12 h, a pale yellow solution was obtained, which, after removal of diethyl ether and toluene under vacuum, gave a pale yellow viscous fluid. A volatile liquid and colorless crystals were produced by gradient-temperature sublimator at 65 °C under vacuum. The volatile liquid is the adduct of diethyl ether with $\{Et_2Al[\mu\text{-}N(SiMe_3)_2]Mg(\mu\text{-}Et)\}_2$ (**4**): Yield 40%; ^1H-NMR (C_6D_6) δ 3.507 (q, $OC\mathit{H}_2CH_3$), 1.318 (t, 6H, $MgCH_2C\mathit{H}_3$), 1.265 (t, 12H, $AlCH_2C\mathit{H}_3$), 0.805 (t, $OCH_2C\mathit{H}_3$), 0.292 (s, 72H, $Si(C\mathit{H}_3)_3$), –0.123 (t, 8H, $AlC\mathit{H}_2CH_3$), –0.092 (q, 4H, $MgC\mathit{H}_2CH_3$); ^{13}C-NMR (C_6D_6) δ 65.676 (OCH_2CH_3), 13.054 (OCH_2CH_3), 10.157 and 10.084 ($AlCH_2CH_3$ and $MgCH_2CH_3$), 5.030 ($Si(CH_3)_3$), 3.530 (broad, $AlCH_2CH_3$), 2.623 ($MgCH_2CH_3$); ^{27}Al-NMR (C_6D_6) δ 160 (broad); mass spectrum (EI, 70 eV) 10 most intense *m/e* peaks at 146, 130, 73, 246, 377, 260, 362, 232, 57, 319. The colorless crystal is $\{Et_2[(Me_3Si)_2N]Al\}_2$(1,4-dioxane) (**5**): Mp 78–81 °C; yield 30%; ^1H-NMR (C_6D_6) δ 3.416 (s, 8H, $O(C\mathit{H}_2C\mathit{H}_2)_2O$), 1.267 (t, 12H, $Al(CH_2C\mathit{H}_3)_2$), 0.271 (s, 36H, $Si(C\mathit{H}_3)_3$), 0.065 (q, 8H, $Al(C\mathit{H}_2CH_3)_2$); ^{13}C-NMR (C_6D_6) δ 67.157 (OCH_2), 9.906 ($Al(CH_2CH_3)_2$), 5.917 ($Si(CH_3)_3$), –2.793 ($Al(CH_2CH_3)_2$); ^{27}Al-NMR (C_6D_6) δ 160 (broad); mass spectrum (EI, 30 eV) 10 most intense *m/e* pe aks at 147, 73, 43, 45, 146, 59, 41, 277, 148, 75.

Synthesis of $\{Me_2Al[\mu\text{-}N(i\text{-}Bu)_2]_2Mg(\mu\text{-}Me)\}_2$ (6) and $\{Me_2Al[\mu\text{-}N(i\text{-}Bu)_2]\}_2$ (7). $Al(CH_3)_3$ (34 mmol) in toluene (2 M, 17 mL) was added dropwise to a stirring solution of $Mg[N(i\text{-}C_4H_9)_2]_2$ (9.52 g, 34 mmol) in diethyl ether (100 mL) at room temperature under nitrogen. After 12 h, a pale yellow solution was obtained, which, after removal of diethyl ether and toluene under vacuum, gave a pale yellow viscous fluid. Two colorless crystals were produced by gradient-temperature sublimator at 70 °C under vacuum. The more volatile crystal is $\{Me_2Al[\mu\text{-}N(i\text{-}Bu)_2]\}_2$ (**7**): Mp 65–68 °C; yield 40%; ^1H-NMR (C_6D_6) δ –0.284 (s, 12H, $Al(C\mathit{H}_3)$), 0.856 (d, 24H, $NCH_2CH(C\mathit{H}_3)_2$), 2.014 (sep, 4H, $NCH_2C\mathit{H}(CH_3)_2$), 2.794 (d, 8H, $NC\mathit{H}_2CH(CH_3)_2$); ^{13}C-NMR (C_6D_6) δ –6.521 ($AlCH_3$), 22.505 ($NCH_2CH(CH_3)_2$), 27.012 ($NCH_2CH(CH_3)_2$), 55.925 ($NCH_2CH(CH_3)_2$); ^{27}Al-NMR (C_6D_6) δ 166 (broad); mass spectrum (EI, 20 eV) 10 most intense *m/ e* peaks at 86, 242, 355, 184, 142, 170, 327, 243, 297, 356. Anal. Calc: C, 64.82; H, 13.06; N, 7.56. Found: C, 64.63; H, 12.98; N, 7.57. The less volatile crystal is $\{Me_2Al[\mu\text{-}N(i\text{-}Bu)_2]_2Mg(\mu\text{-}Me)\}_2$ (**6**): Mp_{dec} >112 °C; yield 40%; ^1H-NMR (C_6D_6) δ –0.528 (s, 6H, $MgC\mathit{H}_3$), –0.243 (s, 12H, $Al(C\mathit{H}_3)$), 0.926 (broad, 48H, $NCH_2CH(C\mathit{H}_3)_2$), 1.954 (m, 8H, $NCH_2C\mathit{H}(CH_3)_2$), 2.824 (d, 16H, $NC\mathit{H}_2CH(CH_3)_2$); ^{13}C-NMR (C_6D_6) δ –11.736 ($MgCH_3$), –7.771 ($AlCH_3$), 22.008 and 22.591 ($NCH_2CH(CH_3)_2$), 28.175 ($NCH_2CH(CH_3)_2$), 56.659 ($NCH_2CH(CH_3)_2$); ^{27}Al -NMR (C_6D_6) d 150 (broad); mass spectrum (EI, 70 eV) 10 most intense *m/e* peaks at 86, 57, 152, 166, 224, 168, 124, 170, 337, 70. Anal. Calcd: C, 64.67; H, 12.85; N, 7.94. Found: C, 64.36; H, 12.71; N, 7.80.

Syntheses of $\{Et_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}Et)\}_2$ (8) and $\{Et_2Al[\mu\text{-}N(i\text{-}Pr)_2]\}_2$ (9). $AlEt_3$ (32.3 mmol) in toluene (1.9 M, 17 mL) was added dropwise to a stirring solution of $Mg[N(i\text{-}C_3H_7)_2]_2$ (7.24 g, 32.3 mmol) in diethyl ether (100 mL) at room temperature under nitrogen. After 12 h, a pale yellow solution was obtained, which, after removal of diethyl ether and toluene under vacuum, gave a pale yellow viscous fluid. A solid was produced during sublimation at 50 °C under vacuum. This product is $\{Et_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}Et)\}_2$ (**8**): Mp near room temperature; yield 80%; ^1H-NMR (C_6D_6) δ 3.157 (sep, 8H, $NC\mathit{H}(CH_3)_2$), 1.583 (t, 6H, $MgCH_2C\mathit{H}_3$), 1.391 (t, 12H, $Al(CH_2C\mathit{H}_3)_2$), 1.109 (t(d of d), 48H, $NCH(C\mathit{H}_3)_2$), 0.245 (q, 8H, $Al(C\mathit{H}_2CH_3)_2$), –0.058 (q, 4H, $MgC\mathit{H}_2CH_3$); ^{13}C-NMR (C_6D_6) δ 46.498 ($NCH(CH_3)_2$), 25.880 and 25.143 ($NCH(CH_3)_2$), 12.852 ($MgCH_2CH_3$), 10.294 ($Al(CH_2CH_3)_2$), 4.000 ($Al(CH_2CH_3)_2$), 1.588 ($MgCH_2CH_3$); ^{27}Al-NMR (C_6D_6) δ 150 (broad). A colorless crystal was produced during sublimation at above 50 °C under vacuum, yield 10%. The crystal was characterized as $\{Et_2Al[\mu\text{-}N(i\text{-}Pr)_2]\}_2$ (**9**) and is in good agreement with published data.[14]

Reaction of $Mg(NEt_2)_2$ with $AlMe_3$. $AlMe_3$ (34 mmol) in toluene (2 M, 17 mL) was added dropwise to a stirring solution of $Mg(NMe_2)_2$ (3.80 g, 34 mmol) in diethyl ether (100 mL) at room temperature under nitrogen. The reaction mixture was refluxed for 12 h. A pale yellow solution was obtained, which, after removal of diethyl ether and toluene under vacuum, gave a pale yellow viscous fluid. A colorless crystal was produced during sublimation at 60 °C under vacuum. The crystal was characterized as $[Me_2Al(\mu\text{-}NMe_2)]_2$ (**10**) and is in good agreement with published data.[15]

Reaction of $Mg[N(n\text{-}Pr)_2]_2$ with $AlMe_3$. $AlMe_3$ (34 mmol) in toluene (2 M, 17 mL) was added dropwise to a stirring solution of $Mg[N(n\text{-}Pr)_2]_2$ (7.62 g, 34 mmol) in diethyl ether (100 mL) at room temperature under nitrogen. After 12 h, a pale yellow solution was obtained, which, after removal of diethyl ether and toluene under vacuum, gave a pale yellow viscous fluid. A colorless crystal was produced during sublimation at 60 °C under vacuum. The crystal is $\{Me_2Al[\mu\text{-}N(n\text{-}Pr_2)]\}_2$ (**11**): Mp 49–51 °C; yield 90%; ^1H-NMR (C_6D_6) δ 2.687 (m, 8H, $N(C\mathit{H}_2CH_2CH_3)_2$), 1.295 (m, 8H, $N(CH_2C\mathit{H}_2CH_3)_2$), 0.711 (t, 12H, $N(CH_2CH_2C\mathit{H}_3)_2$), –0.444 (s, 12H, $Al(C\mathit{H}_3)_2$); ^{13}C-NMR (C_6D_6) δ 49.225 ($N(CH_2CH_2CH_3)_2$), 20.620 ($N(CH_2CH_2CH_3)_2$), 11.686 ($N(CH_2CH_2CH_3)_2$), –10.276 ($Al(CH_3)_2$); ^{27}Al-NMR (C_6D_6) δ 165 (broad); mass spectrum (EI, 30 eV) 10 most intense *m/e* peaks at 72, 101, 43, 299, 214, 156, 241, 44, 142, 300.

Reaction of $Mg(NEt_2)_2$ with $Al(i\text{-}Bu)_3$. $Al(i\text{-}Bu)_3$ (8.56 mL, 34 mmol) (d = 0.786 g/mL) was added dropwise to a stirring solution of $Mg(NEt_2)_2$ (5.71 g, 34 mmol) in diethyl ether (100 mL) at room temperature under nitrogen. After 12 h, a pale yellow solution was obtained, which, after removal of diethyl ether under vacuum, gave a pale yellow viscous fluid. A colorless transparent liquid was produced during distillation at 60 °C under vacuum. The liquid is $[(i\text{-}Bu)_2Al(\mu\text{-}NEt_2)]_2$ (**12**): Yield 95%; ^1H-NMR (C_6D_6) δ 3.335 (q, 8H, $N(C\mathit{H}_2CH_3)_2$), 2.064 (sep, 4H, $CH_2C\mathit{H}(CH_3)_2$), 1.215 (d, 24H, $CH_2CH(C\mathit{H}_3)_2$), 0.689 (t, 12H, $N(CH_2C\mathit{H}_3)_2$), 0.155 (d, 8H, $C\mathit{H}_2CH(CH_3)_2$); ^{13}C-NMR (C_6D_6) δ 65.862, 28.955, 27.061, 23.913, 13.199; ^{27}Al-NMR (C_6D_6) δ 180 (broad); mass spectrum (EI, 70 eV) 10 most intense *m/e* peaks at 100, 313, 43, 369, 85, 128, 58, 141, 171, 227.

Preparation of $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}OMe)\}_2$ (13). During recrystallization of $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}Me)\}_4$, the solution was exposed to air, and a colorless needle crystal was obtained. The crystal is $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}OMe)\}_2$ (**13**): Mp 144–146 °C; yield 90%; ^1H-NMR (C_6D_6) δ 3.455 (sep, 8H, $NC\mathit{H}(CH_3)_2$), 3.375 (s, 6H, $OC\mathit{H}_3$), 1.292 (d, 48H, $NCH(C\mathit{H}_3)_2$), –0.182 (s, 12H, $Al(C\mathit{H}_3)_2$); ^{13}C-NMR (C_6D_6) δ 51.389 ($NCH(CH_3)_2$), 48.534 (OCH_3), 27.122 ($NCH(CH_3)_2$), –3.205 ($AlCH_3$); ^{27}Al-NMR (C_6D_6) δ 155 (broad); mass spectrum (EI, 30 eV) 10 most intense *m/e* peaks at 142, 385, 86, 124, 281 , 228, 212, 300, 455, 540. Anal. Calc: C, 57.55; H, 11.90; N, 8.95. Found: C, 57.29; H, 11.62; N, 8.76.

Preparation of $\{Et_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}OEt)\}_2$ (14), $\{Me_2Al[\mu\text{-}NEt_2]_2Mg(\mu\text{-}OMe)\}_2$ (15), and $\{Me_2Al[\mu\text{-}N(i\text{-}Bu)_2]_2Mg(\mu\text{-}OMe)\}_2$ (16). Compounds **14**–**16** were prepared in a manner analogous to that of compound **13**. Compound **14** is white powder, characterized as follows: Mp >400 °C; yield 90%; ^1H-NMR (C_6D_6) δ 3.778 (q, 4H, $OC\mathit{H}_2CH_3$), 3.587 (sep, 8H, $NC\mathit{H}(CH_3)_2$), 1.545 (t, 12H, $Al(CH_2C\mathit{H}_3)_2$), 1.344 (d, 48H, $NCH(C\mathit{H}_3)_2$), 1.194 (t, 6H, $OCH_2C\mathit{H}_3$), 0.429 (q, 8H, $Al(C\mathit{H}_2CH_3)_2$); ^{13}C-NMR (C_6D_6) δ 59.022 (OCH_2CH_3), 49.069 ($NCH(CH_3)_2$), 28.903 and 27.786 ($NCH(CH_3)_2$), 20.633 (OCH_2CH_3), 11.084 ($Al(CH_2CH_3)_2$), 5.000 (A $l(CH_2CH_3)_2$); ^{27}Al-NMR (C_6D_6) δ 152 (broad). Anal. Calc: C, 61.01; H, 12.19; N, 7.64. Found: C, 60.68; H, 12.16; N, 7.64.

Compounds **15** and **16** were detected by NMR. Data for compound **15**: ^1H-NMR (C_6D_6) δ 3.385 (s, 6H, $OC\mathit{H}_3$), 2.877 and 2.787 (m, 16H, $N(C\mathit{H}_2CH_3)_2$), 0.990 (t, 24H, $N(CH_2C\mathit{H}_3)_2$), –0.402 (s, 12H, $Al(C\mathit{H}_3)_2$); ^{13}C-NMR (C_6D_6) δ 51.369 (OCH_3), 39.935 ($N(CH_2CH_3)_2$), 13.483 ($N(CH_2(CH_3)_2$), –10.219 ($Al(CH_3)_2$); ^{27}Al-NMR (C_6D_6) δ 156 (broad).

Data for compound **16**: ^1H-NMR (C_6D_6) δ 3.557 (s, 6H, $OC\mathit{H}_3$), 2.855 (broad, 16H, $NCH_2CH(CH_3)_2$), 1.950 (sep, 8H, $NCH_2C\mathit{H}(CH_3)_2$), 0.987 (broad, 48H, $NCH_2CH(C\mathit{H}_3)_2$), –0.266 (s, 12H, $Al(C\mathit{H}_3)_2$); ^{13}C-NMR (C_6D_6) δ 56.627 (OCH_3), 52.338 ($NCH_2CH(CH_3)_2$), 29.243 ($NCH_2CH(CH_3)_2$), 22.494 and 22.484 ($CH_2CH(CH_3)_2$), –7.625 ($Al(CH_3)_2$); ^{27}Al-NMR (C_6D_6) δ 150 (broad).

Structure Determination. Crystals 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 $2\theta \leq 45$ °C and corrected for absorption and decay. Both structures were solved by MULTAN and refined with full-matrix least-squares on F with w =

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(14) Her, T. Y.; Chang, C. C.; Liu, L. K.; Chang, H. C.; Chen, J. H.; Tsai, J. O.; Lai, Y. Y. *Polyhedron* **1993**, *12*, 731.

(15) (a) Cocco, L.; Eyman, D. P. *J. Organomet. Chem.* **1979**, *179*, 1. (b) Hess, V. H.; Hinderer, A.; Steinhauser, S. *Z. Anorg. Allg. Chem.* **1970**, *377*, 1.

Table 1. Crystallographic Data nad Refinement Results

	2	3	13
formula	$Al_2Mg_4Si_{12}C_{44}H_{130}N_2$	$Al_2Si_4N_2C_{20}H_{56}O_2$	$C_{30}H_{74}O_6N_4Mg_2Al_2$
cryst syst	triclinic	monoclinic	monoclinic
space group	$P1$	$P2_1/c$	$P2_1/n$
a, Å	12.288(5)	14.804(5)	8.893(1)
b, Å	12.698(6)	7.475(3)	13.995(2)
c, Å	14.285(7)	15.378(5)	16.382(3)
α, deg	101.79(4)		
β, deg	90.07(3)	100.77(3)	96.60(2)
γ, deg	111.57(3)		
cell vol, Å^3	2022(2)	1672(1)	2025.5(6)
mol wt	1197.48	522.98	625.51
Z	1	2	2
$F(000)$	739.82	575.89	695.82
D_{calc}, g/cm^3	0.983	1.039	1.026
μ, mm^{-1}	0.27	0.24	0.13
λ, Å	0.710 73	0.710 73	0.710 73
2θ(max), deg	45	45	45
cryst dimens, mm	0.20 × 0.45 × 0.50	0.30 × 0.30 × 0.60	0.45 × 0.55 × 0.60
diffractometer	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4
mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
no. of measd reflns	5288	2169	2640
no. of unique reflns	5276	2169	2640
no. of observns [$I > 2.0\sigma(I)$]	2307	1257	1441
no. of atoms	87	43	52
no. of params	362	137	200
weight	$1.0/[\sigma^2(F_o) + 0.0001F_o^2]$	$1.0/[\sigma^2(F_o) + 0.0001F_o^2]$	$1.0/[\sigma^2(F_o) + 0.0001F_o^2]$
R	0.081	0.076	0.072
R_w	0.091	0.085	0.083
Gof	1.48	1.63	1.88
highest peak in diff map, e/Å^3	0.330	0.330	0.470

$1.0/[\sigma^2(F_o) + 0.0001F_o^2]$. In the final cycle all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at idealized positions (d_{C-H} = 1.00 Å) as calculated at the anisotropic convergence stage. Scattering factors for the neutral atoms and scattering anomalous coefficients for non-hydrogen atoms were taken from the literature.[16] All calculations were carried out with a Micro VAX 3600 computer using the NRC VAX program package.[17] A summary of data collection and structure solution is given in Table 1. Selected bond distances and angles are shown in Table 2. The final position parameters of the refined atoms are listed in Table 3.

Results and Discussion

Preparation and Structural Description of the Various Aluminum–Magnesium Complexes. The aluminum–magnesium dimer, $\{Me_2Al[\mu\text{-}NEt_2]_2Mg(\mu\text{-}Me)\}_2$ (**A**), and tetramer, $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}Me)\}_4$ (**B**), were obtained, as mentioned previously, through the reaction of $Mg(NR_2)_2$ (R = Et, *i*-Pr) with $AlMe_3$. In the continuous search for those elusive aluminum magnesium monomeric species, we used the bulky group $N(SiMe_3)_2$ and different alkyl groups to stabilize the monomer. The reactions and the products are shown in Scheme 1.

Treatment of compound **1** with $AlMe_3$ produces compounds **2** and **3**. The structure of compound **2**, determined by X-ray diffraction measurements, is illustrated in Figure 1. Note that compound **2** contains two monomeric $Me_3Al\{\mu\text{-}N(SiMe_3)_2\}Mg\{N(SiMe_3)_2\}$ molecules bound through Mg atoms to the methyl groups of $MeMg\{\mu\text{-}N(SiMe_3)_2\}_2MgMe$. The unstable $Me_3Al\{\mu\text{-}N(SiMe_3)_2\}Mg\{N(SiMe_3)_2\}$ monomer is probably stabilized by $MeMg\{\mu\text{-}N(SiMe_3)_2\}_2MgMe$. Compound **2** possesses a center of inversion related to the two equivalent fragments. The Mg(1)–C(1) distance of 2.16(1) Å is normal for a δ bond. However, the Mg(2)···C(1) distance of 2.43(1) Å is longer than expected for a σ bond but shorter than the Mg···C interaction in $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}Me)\}_4$,[8] indicating a weak interaction between Mg(2) and C(1). This weak interaction gives rise to the observed Mg(1)–C(1)···Mg(2) angle of nearly 180°. This unusual linear metal···methyl–metal bridge group is similar to that of $LiB(Me_4)$[10] but different from the bent metal···methyl–metal bridge groups of compound **B**.[8] Because the Mg(2)···C(2) distance of 2.40(2) Å is also slightly longer than a δ bond and similar to the Mg(2)···C(1) bond length, the interaction between Mg(2) and C(2) may be weak. The Al–C(2) bond distance is 0.09 Å longer than the Al–(3) and Al–(4) bond distances, which may infer that the C(2) methyl group is interacting agostically with Mg(2). The Mg(1), N(1), Mg(1′), and N(1′) atoms form a coplanar heterocyclic four-membered ring. The respective angles of Si(3)–N(2)–Si(4) and the Si(1)–N(1)–Si(2) are 120.2(6) and 119.2(6)°, while the bond lengths of Si(4)–N(2) and Si(2)–N(1) are 1.687(9) and 1.72(1) Å respectively. Note that the Mg(2)–N(2) and Si(4)–N(2) bond lengths are slightly shorter than expected for σ bonds. The geometry suggests that a lone pair at N(2) atom should be sp^2 hybridized to have a trigonal-planar coordination geometry and that there may be partial π interactions among the Si(4), N(2), and Mg(2) atoms. The coordination geometries about the Mg(2), Mg(1), and Al atoms are linear (quasi-two-coordinate), triangular, and distorted tetrahedral, respectively. If the Mg(2)···C(1) and Mg(2)···C(2) interactions are included, the geometry about the Mg(2) will be pseudotetrahedral.

The structure of compound **3**, determined by X-ray diffraction measurements, is illustrated in Figure 2. Compound **3** consists of a pair of $Me_2\{(Me_3Si)_2N\}Al$ moieties linked by a common dioxane molecule with an inversion center located at the center of the dioxane molecule. The dioxane moiety is in the chair conformation, with the four carbon atoms residing in a plane, while the two oxygen atoms sit above and below this plane. The oxygen atoms have a three-coordinated triangular geometry. The O, Al, C(1′), and C(2) atoms are roughly coplanar with C(1′)–O–Al, C(1′)–O–C(2), and Al–O–C(2) angles of 121.4(6), 111.4(7), and 126.2(5)°, respectively. The aluminum atoms exist in distorted tetrahedral environments. The Si–N–Si angle is 121.4(4)° with a Si–N bond length of 1.715(8) Å, corresponding to a σ bond.[11] The Al–N distance of 1.848(8) Å is much shorter

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(16) Ibers, J. A.; Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Tables 2.2B and 2.3.1.

(17) Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon: Oxford, 1985; p 167.

(18) Cree-Uchiyama, M.; Shapley, J. R.; George, G. M. St. *J. Am. Chem. Soc.* **1986**, *108*, 1316.

Table 2. Selected Bond Distances (Å) and Angles (deg)

$[\{(R_2N)Mg(Me)\}_2\{Mg(NR_2)(NR_2AlMe_3)\}_2]$ (R = $SiMe_3$) (**2**)			
Distances			
Al···Mg(2)	2.838(6)	Mg(2)–N(3)	2.169(9)
Al–N(3)	2.00(1)	Mg(2)···C(1)	2.43(1)
Al–C(2)	2.05(2)	Mg(2)···C(2)	2.40(2)
Al–C(3)	1.96(2)	Si(1)–N(1)	1.76(1)
Al–C(4)	1.96(2)	Si(2)–N(1)	1.72(1)
Mg(1)···Mg(1′)	2.856(8)	Si(3)–N(2)	1.712(9)
Mg(1)–N(1)	2.076(9)	Si(4)–N(2)	1.687(9)
Mg(1)–N(1′)	2.08(1)	Si(5)–N(3)	1.75(1)
Mg(1)–C(1)	2.16(1)	Si(6)–N(3)	1.756(9)
Mg(2)–N(2)	1.98(1)		
Angles			
N(3)–Al–C(2)	102.2(5)	Mg(1)–N(1)–Mg(1′)	86.7(4)
N(3)–Al–C(3)	113.1(9)	Mg(1)–N(1)–Si(1)	109.5(5)
N(3)–Al–C(4)	116.6(6)	Mg(1)–N(1)–Si(2)	112.4(5)
C(2)–Al–C(3)	105.4(9)	Si(1)–N(1)–Si(2)	119.2(6)
C(2)–Al–C(4)	108.7(8)	Mg(2)–N(2)–Si(3)	124.6(5)
C(3)–Al–C(4)	109.9(8)	Mg(2)–N(2)–Si(4)	114.5(5)
N(1)–Mg(1)–N(1′)	93.3(4)	Si(3)–N(2)–Si(4)	120.2(6)
N(1)–Mg(1)–C(1)	129.7(5)	Al–N(3)–Mg(2)	85.6(4)
N(1′)–Mg(1)–C(1)	136.8(4)	Al–N(3)–Si(5)	110.8(5)
N(2)–Mg(2)–N(3)	132.8(4)	Al–N(3)–Si(6)	111.2(5)
N(2)–Mg(2)–C(1)	103.4(4)	Mg(2)–N(3)–Si(5)	108.4(5)
N(2)–Mg(2)–C(2)	114.9(5)	Mg(2)–N(3)–Si(6)	123.0(5)
N(3)–Mg(2)–C(1)	117.1(4)	Si(5)–N(3)–Si(6)	114.2(5)
N(3)–Mg(2)–C(2)	87.2(5)	Mg(1)–C(1)–Mg(2)	178.6(6)
C(1)–Mg(2)–C(2)	93.0(5)	Al–C(1)–Mg(2)	79.0
$\{Me_2Al[N(SiMe_3)_2]\}_2$(1,4-dioxane) (**3**)			
Distances			
Al–N	1.848(8)	N–Si(1)	1.733(7)
Al–O	2.001(6)	O–C(1)	1.457(9)
Al–C(3)	1.95(1)	O–C(2)	1.44(1)
Al–C(4)	1.96(1)	C(1)–C(2)	1.53(1)
Si(2)–N	1.715(8)		
Angles			
Al–O–C(1)	121.4(6)	N–Al–C(3)	120.4(4)
C(1′)–O–C(2)	111.4(7)	O–Al–C(3)	101.9(4)
Al–O–C(2)	126.2(5)	O–Al–C(4)	98.8(4)
N–Al–O	99.9(3)	C(3)–Al–C(4)	110.5(5)
N–Al–C(4)	119.8(4)	Si(1)–N–Si(2)	121.4(4)
$\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}OMe)\}_2$ (**13**)			
Distances			
Al···Mg	2.869(4)	N(2)–C(9)	1.50(1)
Mg···Mg	2.957(5)	N(2)–C(12)	1.53(1)
Mg–O	1.957(5)	C(3)–C(4)	1.55(2)
Mg–O′	1.968(5)	C(3)–C(5)	1.43(2)^a
Al–N(1)	1.953(8)	C(6)–C(7)	1.51(2)
Al–N(2)	1.972(9)	C(6)–C(8)	1.34(2)^a
Al–C(1)	1.98(1)	C(9)–C(10)	1.52(2)
Al–C(2)	1.97(1)	C(9)–C(11)	1.55(2)
Mg–N(1)	2.152(7)	C(12)–C(13)	1.71(3)^a
Mg–N(2)	2.157(7)	C(12)–C(13′)	1.51(3)^a
O–C(15)	1.41(1)	C(12)–C(14)	1.46(3)^a
N(1)–C(3)	1.50(1)	C(12)–C(14′)	1.18(3)^a
N(1)–C(6)	1.49(1)	C(13)–C(13′)	0.89(4)^a
C(14)–C(14′)	1.41(4)^a		
Angles			
Mg′–Mg–Al	165.5(1)	Mg–N(2)–C(12)	110.2(6)
O–Mg–O′	82.2(2)	C(9)–N(2)–C(12)	116.0(8)
O–Mg–N(1)	127.8(3)	N(1)–C(3)–C(4)	116.0(9)
O–Mg–N(2)	127.9(3)	N(1)–C(3)–C(5)	119.7(9)
O′–Mg–N(1)	119.8(3)	C(4)–C(3)–C(5)	111(1)
O′–Mg–N(2)	117.9(3)	N(1)–C(6)–C(7)	116(1)
N(1)–Al–N(2)	96.3(3)	N(1)–C(6)–C(8)	119(1)
N(1)–Al–C(1)	115.6(5)	C(7)–C(6)–C(8)	111(1)
N(1)–Al–C(2)	111.0(5)	N(2)–C(9)–C(10)	114.7(9)
N(2)–Al–C(1)	114.0(5)	N(2)–C(9)–C(11)	117.5(9)
N(2)–Al–C(2)	111.5(5)	C(10)–C(9)–C(11)	118(1)
C(1)–Al–C(2)	108.1(6)	N(2)–C(12)–C(13)	104(1)
N(1)–Mg–N(2)	85.5(3)	N(2)–C(12)–C(13′)	120(1)
Mg–O–Mg′	97.8(2)	N(2)–C(12)–C(14)	113(1)
Mg–O–C(15)	134.4(5)	N(2)–C(12)–C(14′)	131(2)
Mg′–O–C(15)	127.8(5)	C(13)–C(12)–C(13′)	31(1)
Al–N(1)–Mg	88.5(3)	C(13)–C(12)–C(14)	112(2)
Al–N(1)–C(3)	111.6(6)	C(13)–C(12)–C(14′)	124(2)
Al–N(1)–C(6)	113.2(6)	C(13′)–C(12)–C(14)	120(1)
Mg–N(1)–C(3)	108.1(5)	C(13′)–C(12)–C(14′)	98(2)
Mg–N(1)–C(6)	110.2(6)	C(14)–C(12)–C(14′)	63(2)
C(3)–N(1)–C(6)	120.4(9)	C(12)–C(13)–C(13′)	62(2)
Al–N(2)–Mg	87.9(3)	C(12)–C(13′)–C(13)	87(2)
Al–N(2)–C(9)	111.6(6)	C(12)–C(14)–C(14′)	49(1)
Al–N(2)–C(12)	119.8(8)	C(12)–C(14′)–C(14)	68(2)
Mg–N(2)–C(9)	107.1(5)		

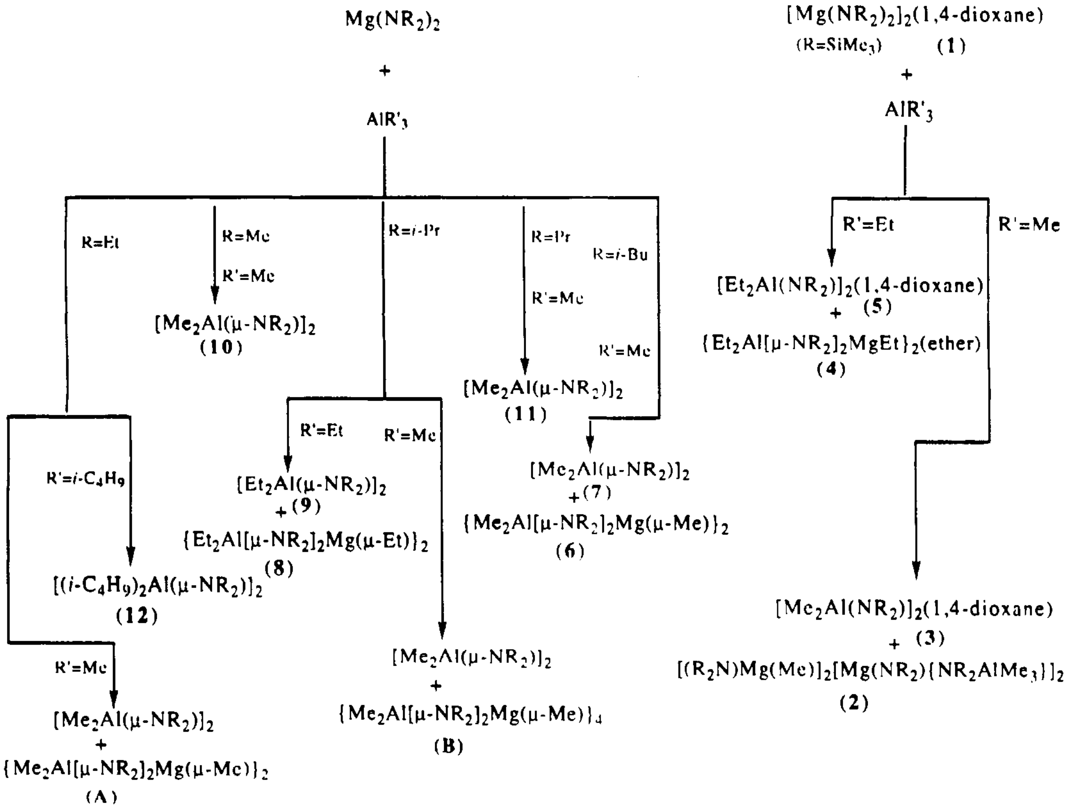
[a] These values are attributed to disorder.

Table 3. Fractional Coordinates and Isotropic Thermal Parameters

	x	y	z	B_{eq},^{a} Å^2
Compound **2**				
Al	0.7423(5)	0.0195(4)	0.3339(4)	8.7(3)
Mg(1)	0.5577(4)	–0.4241(3)	0.4388(3)	5.1(2)
Mg(2)	0.7739(3)	–0.1881(3)	0.2469(3)	4.7(2)
Si(1)	0.7135(5)	–0.5214(5)	0.5418(5)	12.6(5)
Si(2)	0.6446(5)	–0.3351(5)	0.6591(4)	11.3(3)
Si(3)	1.0143(3)	–0.2429(3)	0.2297(3)	6.6(3)
Si(4)	0.8038(4)	–0.3875(4)	0.0980(3)	7.3(3)
Si(5)	0.7933(4)	–0.0032(4)	0.1204(3)	7.1(2)
Si(6)	0.5500(4)	–0.1177(5)	0.1655(5)	10.5(4)
N(1)	0.6120(8)	–0.4536(8)	0.5653(6)	5.6(6)
N(2)	0.8741(8)	–0.2706(8)	0.1868(6)	5.1(5)
N(3)	0.7002(7)	–0.0751(7)	0.1990(7)	5.1(5)
C(1)	0.657(1)	–0.314(1)	0.3473(8)	5.3(7)
C(2)	0.868(2)	–0.031(1)	0.382(1)	10(1)
C(3)	0.614(2)	–0.025(2)	0.417(2)	18(2)
C(4)	0.808(2)	0.1882(2)	0.349(1)	13(2)
C(11)	0.765(3)	–0.527(4)	0.677(3)	13(3)
C(12)	0.593(3)	–0.700(2)	0.506(3)	11(2)
C(13)	0.804(3)	–0.490(3)	0.461(3)	14(3)
C(11′)	0.889(3)	–0.396(4)	0.570(3)	15(3)
C(12′)	0.726(3)	–0.549(3)	0.393(2)	9(2)
C(13′)	0.714(3)	–0.636(4)	0.581(3)	13(3)
C(21)	0.588(4)	–0.341(3)	0.771(2)	14(3)
C(22)	0.573(3)	–0.229(2)	0.601(2)	10(2)
C(23)	0.805(3)	–0.237(3)	0.652(3)	13(2)
C(21′)	0.734(5)	–0.384(4)	0.766(3)	19(4)
C(22′)	0.511(3)	–0.362(3)	0.723(2)	12(2)
C(23′)	0.729(4)	–0.198(3)	0.654(3)	14(3)
C(31)	1.025(2)	–0.244(3)	0.353(2)	24(3)
C(32)	1.077(2)	–0.347(2)	0.173(3)	29(3)
C(33)	1.126(1)	–0.111(2)	0.210(2)	20(2)
C(41)	0.780(2)	–0.531(1)	0.127(1)	12(1)
C(42)	0.872(2)	–0.386(2)	–0.018(1)	14(2)
C(43)	0.654(1)	–0.395(1)	0.073(1)	10(1)
C(51)	0.946(1)	0.061(2)	0.171(1)	11(1)
C(52)	0.798(2)	–0.104(2)	0.006(1)	14(2)
C(53)	0.758(2)	0.116(1)	0.090(1)	11(1)
C(61)	0.454(1)	–0.244(2)	0.211(2)	14(2)
C(62)	0.500(2)	0.006(2)	0.201(2)	15(2)
C(63)	0.512(2)	–0.169(2)	0.031(2)	16(2)
Compound **3**				
Al	0.6611(2)	0.2225(4)	0.6261(2)	3.9(1)
Si(1)	0.8443(2)	0.0810(5)	0.5874(2)	4.8(2)
Si(2)	0.7717(2)	–0.0675(4)	0.7426(2)	4.3(1)
N	0.7586(4)	0.065(1)	0.6500(4)	3.6(4)
O	0.5599(4)	0.0526(9)	0.5771(4)	8.6(3)
C(1)	0.4637(5)	0.107(2)	0.5627(6)	5.1(5)
C(2)	0.5705(7)	–0.119(1)	0.5377(7)	4.8(5)
C(3)	0.6132(7)	0.335(2)	0.7226(7)	5.7(6)
C(4)	0.6506(7)	0.386(2)	0.5248(8)	6.2(6)
C(5)	0.8017(8)	0.003(2)	0.4736(8)	7.8(8)
C(6)	0.8885(7)	0.312(2)	0.5840(8)	7.1(7)
C(7)	0.9482(8)	–0.055(3)	0.629(1)	11(1)
C(8)	0.8091(9)	–0.299(2)	0.7235(9)	7.9(8)
C(9)	0.8537(8)	0.033(2)	0.8363(8)	8.0(8)
C(10)	0.6618(8)	–0.105(2)	0.7818(8)	6.7(7)
Compound **13**				
Mg	0.4923(3)	0.0874(2)	0.4490(2)	4.3(1)
Al	0.5538(3)	0.2635(2)	0.3696(2)	7.3(2)
O	0.3641(5)	–0.0217(3)	0.4694(3)	4.4(2)
N(1)	0.4449(7)	0.2368(4)	0.4639(4)	5.4(3)
N(2)	0.5708(8)	0.1295(6)	0.3345(4)	6.4(4)
C(1)	0.448(2)	0.348(1)	0.2842(8)	12.5(9)
C(2)	0.754(1)	0.3196(9)	0.4048(9)	11.9(9)
C(3)	0.532(2)	0.2700(7)	0.5426(7)	9.7(7)
C(4)	0.542(2)	0.3798(8)	0.5554(9)	13(1)
C(5)	0.512(2)	0.2228(8)	0.6177(7)	10.9(8)
C(6)	0.280(1)	0.2546(8)	0.4474(9)	11.8(8)
C(7)	0.231(2)	0.358(1)	0.445(1)	17(1)
C(8)	0.185(2)	0.201(1)	0.487(1)	19(2)
C(9)	0.732(1)	0.0989(8)	0.3380(6)	8.4(6)
C(10)	0.756(2)	–0.008(1)	0.3399(8)	11.5(8)
C(11)	0.826(2)	0.141(1)	0.2729(8)	14(1)
C(12)	0.464(1)	0.091(1)	0.2622(6)	13(1)
C(13)	0.500(3)	0.163(2)	0.182(1)	11(2)
C(13′)	0.507(3)	0.100(2)	0.176(1)	12(2)
C(14)	0.305(2)	0.095(2)	0.276(1)	9(1)
C(14′)	0.396(4)	0.019(2)	0.254(1)	13(2)
C(15)	0.216(1)	–0.0509(7)	0.4383(6)	6.9(5)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Scheme 1



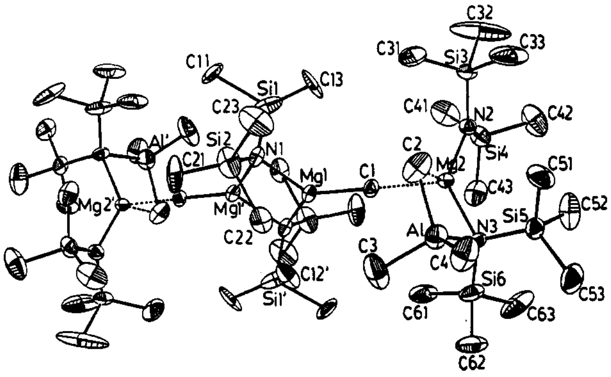


Figure 1. ORTEP drawing of $[\{R_2N)Mg(Me)\}_2\{Mg(NR_2)(NR_2AlMe_3)\}_2]$ (R = $SiMe_3$) (2).

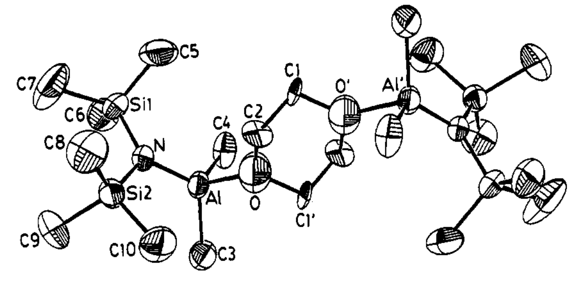
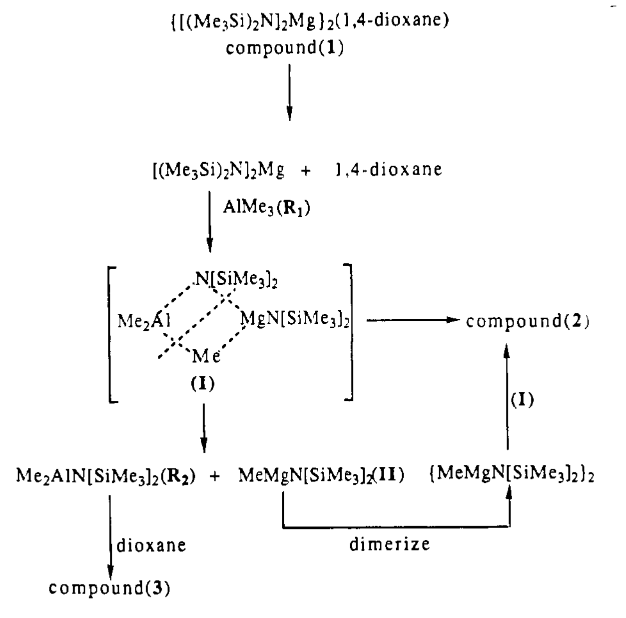


Figure 2. ORTEP drawing of $\{Me_2Al[N(SiMe_3)_2]\}_2(1,4\text{-dioxane})$ (3).

than a σ bond, indicating possible π interactions between the nitrogen and aluminum atoms.[19] On the basis of a comparison with published data, the Al–O distance of 2.001(6) Å is expected to be a σ bond.[20] The N–Al–O and O–Al–C(4) bond angles are 20.5 and 21.6° less than the N–Al–C bond angle, respectively, and 10.6 and 11.7° less than the O–Al–C(4) bond angle, respectively.

Scheme 2



The reaction of $AlMe_3$ with compound **1** may occur through the lone pair on the nitrogen atom of compound **1** coordinated to the aluminum atom of $AlMe_3$ to give the associative intermediate **I** (see Scheme 2). This intermediate is expected to be thermally unstable, and it decomposes to R_2 and a second intermediate, $\{Mg[N(SiMe_3)_2]_2\}_2$ (**II**). Then intermediate **II** dimerizes and reacts further with intermediate **I** to give compound **2**. The R_2 compound reacts with dioxane yielding compound **3**.

Reaction of compound **1** with $AlEt_3$ produces $\{Et_2Al[\mu\text{-}N(SiMe_3)_2]Mg(\mu\text{-}Et)\}_2$ (**4**) and $\{Et_2[(Me_3Si)_2N]Al\}_2(1,4\text{-dioxane})$ (**5**). Compounds **4** and **5** were characterized by mass spectrometry. The marked difference between compound **2** and **4** is probably due to steric hinderence of the ethyl group of

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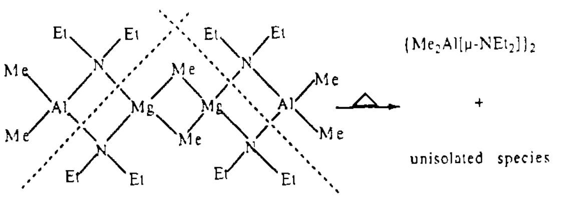
(19) Choquette, D. M.; Timm, M. J.; Hobbs, J. L.; Rahim, M. M.; Ahmed, K. J.; Planalp, R. P. *Organometallics* **1992**, *11*, 529.

(20) Mehrotra, R. C.; Rai, A. K. *Polyhedron* **1991**, *10*, 1967.

(21) (a) Han, R.; Parkin, G. *Organometallics* **1991**, *10*, 1010. (b) Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 748.

compound **4** to form a bridge. $\{Me_2Al[\mu\text{-}N(i\text{-}Bu)_2]_2Mg(\mu\text{-}Me)\}_2$ (**6**) and $\{Et_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}Et)\}_2$ (**8**) were synthesized and characterized by NMR and mass spectrometry. $\{Me_2Al[\mu\text{-}N(i\text{-}Bu)_2]\}_2$ (**7**) and $\{Et_2Al[\mu\text{-}N(i\text{-}Pr)_2]\}_2$ (**9**) were the pyrolysis products of compounds **6** and **8**, respectively (see below). Molecular weight determinations suggest that **4**, **6**, and **8** exist as dimers. However, reaction of $Mg(NMe_2)_2$ and $Mg(NEt_2)_2$ with $AlMe_3$ and reaction of $Mg(NEt_2)_2$ with $Al(i\text{-}Bu)_3$ only produce dialuminum complexes (compounds **10**–**12**). We think that the predicted products (aluminum–magnesium complexes) are very thermally unstable and decomposed to produce dialuminum complexes during the reaction or purification.

Pyrolysis of Aluminum–Magnesium Complexes. The reaction of bis(dialkylamido)magnesium with AlR_3 produced primarily aluminum–magnesium complexes and some dialuminum complexes. We believe that the dialuminum complexes were obtained from the thermal decomposition of aluminum–magnesium complexes, and when heated to 140 °C, $\{Me_2Al(\mu\text{-}NEt_2)_2Mg(\mu\text{-}Me)\}_2$ produces $[Me_2Al(\mu\text{-}NEt_2)]_2$ and an unisolated species shown in eq 1. The unisolated species could be a polymer of $MeMg(NEt_2)$.



(1)

Insertion of Oxygen into the Mg–C Bond. These complexes are extremely air-sensitive and hygroscopic. They oxidize quickly to form an insoluble white powder. However, during recrystallization of $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}Me)\}_4$, when the solution was exposed to a small amount of air, colorless needle crystals were obtained. These crystals were determined to be the dimer $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}OMe)\}_2$ (**13**), shown in Figure 3. The monomer fragment of the dimer, $Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(OMe)$, has C_2 symmetry. The Al, N(1), Mg, and N(2) atoms form a nonplanar heterocyclic four-membered ring with Al–N(1), Al–N(2), Mg–N(1), and Mg–N(2) bond lengths of 1.953(8), 1.972(9), 2.152(7), and 2.157(7) Å, respectively. The Mg, O, Mg′, and O′ atoms form a nearly symmetrical four-membered ring with nearly equal Mg–O, Mg–O′, Mg′–O, and Mg′–O′ bond distances. Analogous compounds **14**–**16** were found when compounds **8**, **B**, and **6** were recrystallized by exposure to a small amount of air.

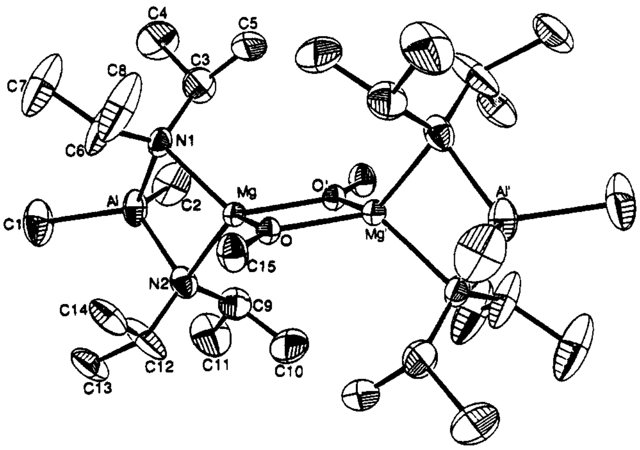


Figure 3. ORTEP drawing of $\{Me_2Al[\mu\text{-}N(i\text{-}Pr)_2]_2Mg(\mu\text{-}OMe)\}_2$ (**13**).

Parkins reported that the insertion of O_2 into the Mg–R bond of $\{^3\eta\text{-}HB(3\text{-}Bu\text{-}t\text{-}Pz)_3\}MgR$ (R = Me, Et, *i*-Pr, *t*-Bu) complexes results in the formation of the corresponding alkyl peroxo derivative $\{^3\eta\text{-}HB(3\text{-}Bu\text{-}t\text{-}Pz)_3\}MgOOR$, which is different from our results.

Conclusions

Although we were not successful in the synthesis of a monoaluminum magnesium complex, the reaction of AlR_3 (R = Me, Et, *i*-Bu) with $Mg[NR'_2]_2$ (R′ = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu) only produced aluminum–magnesium dimers or a tetramer and aluminum dimers. However, reaction of compound **1** with $AlMe_3$ produced compounds **2** and **3**. Compound **2** is the unstable monomer of $Me_3Al\{\mu\text{-}N(SiMe_3)_2\}Mg\{N(SiMe_3)_2\}$ stabilized by $MeMg\{\mu\text{-}N(SiMe_3)_2\}_2MgMe$. Some of the aluminum–magnesium dimers were found to be thermally unstable, with pyrolysis producing dialuminum complexes. Insertion of O_2 into the Mg–R bond of the Al–Mg complexes resulted in the formation of the alkoxide derivatives.

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Supplementary Material Available: Tables of crystal data, distances and angles, final fractional coordinates, and thermal parameters (7 pages). Ordering information is given on any current masthead page.