4296 *Inorg. Chem.* **1995**, *34*, 4296−4298

Articles

Sterically Hindered Aluminum−Magnesium Bridged Complex: $\{Me_2Al[\mu\text{-}N(^iC_3H_7)_2]_2Mg\text{-}[O\text{-}2,6\text{-}(^tC_4H_9)_2\text{-}4\text{-}MeC_6H_2]\}$

Chung-Cheng Chang,*,† Tzong-Yih Her,† Mung-Dar Li,† Rodney Williamson,†
Gene-Hsiung Lee,‡ Shie-Ming Peng,‡ and Yu Wang‡

Departments of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, R.O.C., and
National Taiwan University, Taipei, Taiwan, R.O.C.

Received July 15, 1994®

The monomeric aluminum−magnesium bridged complex $Me_2Al[\mu\text{-}N(^iPr)_2]_2Mg(BHT)$, (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide) with a three-coordinate magnesium atom was prepared. Crystal data: space group $P2_1/n$; $a = 13.807(5)$, $b = 15.636(4)$, and $c = 14.905(3)$ Å, $\beta = 95.03(3)°$, $V = 3205(2)$ Å^3; $D_{calc} = 1.038$ g/cm^3, $Z = 4$, and $R = 0.056$. Fenske−Hall molecular orbital calculations are used to explain the bonding situation.

Introduction

A well-established feature of the organometallic chemistry of metals such as lithium, copper, beryllium, magnesium, and aluminum is the tendency of their alkyl and aryl derivatives to adopt associated structures with three-center or even four-center electron-pair bonds.[1] Recently we reported several bridged aluminum−magnesium tetrameric complexes[2−4] in which the $\{Me_2Al[\mu\text{-}N(^iPr)_2]_2MgMe\}_4$ moiety associates via weak interactions of magnesium atoms and methyl groups in the solid state. So far, there is no literature on the preparations of monomers of aluminum−magnesium complexes. We found that the bulky phenol and the above tetramer could undergo a metathesis reaction producing the title compound $Me_2Al[\mu\text{-}N(^iPr)_2]_2Mg(BHT)$ (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide). We report the synthesis and structural determination of this first example of a mixed aluminum−magnesium monomeric bridged complex with tricoordinated magnesium.

Experimental Section

All operations were carried out in a N_2-flushed glovebag, drybox, or vacuum system. All solvents were distilled prior to use. Infrared spectra (Nujol mull) were recorded on a Perkin-Elmer IR spectrophotometer, mass spectra were recorded on a VG 70-250S GC/MS spectrophotometer, and NMR spectra were recorded on a Varian VXR 300 MHz FT-NMR spectrometer with TMS as the internal standard. Elemental analyses were carried out at H. Malissa and G. Reuter GmbH, Germany.

Synthesis. $\{\mathbf{Me_2Al[\mu\text{-}N(^iC_3H_7)_2]_2Mg(BHT)}\}$. An ether solution (50 mL, 1.7 mmol) of $\{Me_2Al[\mu\text{-}N(^iPr)_2]_2MgCH_3\}_4$, prepared by following the previous method,[2] was added dropwise to a stirred ether solution of 6.8 mmol of 2,6-di-*tert*-butyl-4-methylphenol (BHT) at room temperature under a nitrogen atmosphere. The reaction took place immediately, and methane gas was released. After the reaction was complete and the ether was removed, the pale yellow solid was then recrystallized from toluene. Colorless crystals of **1** were obtained. Mp = 156−158 °C; yield, 80%. Anal. Calcd: C, 69.80; N, 5.61; H, 11.11. Found: C, 69.53; N, 5.45; H, 11.05. The ten most intense peaks of the mass spectral data of compound **1** (30 eV) are as follows (*m*/*e* (relative intensity, ion formula tentatively assigned): 142 (100, $[MeAlN(^iPr)_2]^+$), 44 (68, $[^iPrH]^+$), 124 (59, $[MgN(^iPr)_2]^+$), 86 (47, $[(^iPr)_2]^+$), 328 (45, $[M - (^tBu) - Me - N(^iPr)_2]^+$), 57 (37, $[AlMe_2]^+$), 205 (29, $[BHT - Me]^+$), 400 (28, $[M - N(^iPr)_2]^+$), 485 (25, $[M - Me]^+$), 299 (18, $[(BHT)Mg(N(^iPr)_2)_2 - {}^iPr]^+$), with a molecular ion 500 (10, $[M]^+$). The peaks are cut off at *m*/*e* 500.

Infrared spectra (Nujol mull) showed the following absorptions: 3653 (m), 2994 (m), 2914 (m), 2853 (m), 1461 (m), 1417 (s), 1389 (m), 1355 (m), 1276 (s), 1195 (m), 1150 (m), 962 (m), 908 (m), 846 (m), 804 (w), 763 (m), 665 (s), 607 (m), 569 (w), and 432 (m) cm^{-1}.

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 ($\lambda = 0.710\,73$ Å). Intensity data were collected by using a $\theta-2\theta$ scan mode for $2\theta \leq 45°$ and corrected for absorption and decay. Both structures were solved by MULTAN and refined by full-matrix least-squares analyses on F with $w = 1.0/[\sigma^2(F_o) + 0.0001F_o^2]$. In the final cycles, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at idealized positions ($d_{C-H} = 1.00$ Å) calculated during the anisotropic convergence stage. Scattering factors for the neutral atoms and anomalous scattering coefficients for non-hydrogen atoms were taken from the literature.[5] All calculations were carried out with a Micro VAX 3600 computer using the NRC VAX program package.[6] A summary of data collected on the crystal structure is given in Table I. Selected bond angles and distances are listed in Table 3, and an ORTEP view of the complex is given in Figure 1.

Results and Discussion

The reaction of $\{Me_2Al[\mu\text{-}N(^iPr)_2]_2MgCH_3\}_4$ with 2,6-di-*tert*-butyl-4-methylphenol in a 1:4 ratio gives methane and the colorless crystal $Me_2Al[\mu\text{-}NR_2]_2Mg(BHT)$ (**1**). The structure

---

† National Sun Yat-Sen University.

‡ National Taiwan University.

® Abstract published in *Advance ACS Abstracts*, July 1, 1995.

(1) O'Neill, M. E.; Wade K. *Comprehensive Organometallic Chemistry*; Pergamon Press: London, 1982; Vol. 1, Chapter 1 and references cited therein.

(2) Her, T. Y.; Chang, C. C.; Liu, L. K. *Inorg. Chem.* **1992**, *31*, 2219.

(3) Her, T. Y.; Chang, C. C.; Lee, G. H.; Peng, S. M.; Wang, Y. *Inorg. Chem.* **1994**, *33*, 99.

(4) Chang, C. C.; Lee, W. H.; Her, T. Y.; Lee, G. H.; Peng, S. M.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1994**, 315.

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

(6) 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, 1985; p 167.

0020-1669/95/1334-4296$09.00/0

Table 1. Crystal Data, Conditions for Crystallographic Data Collection, and Structure Refinement[a]

formula	$C_{29}H_{57}ON_2AlMg$
fw	501.06
space group	monoclinic $P2_1/n$
a (Å)	13.807(5)
b (Å)	15.636(4)
c (Å)	14.905(3)
β (deg)	95.03(3)
V (Å^3)	3205(2)
Z	4
D_{calc} (g cm^{-3})	1.038
λ (Å)	0.71073
2θ limits (deg)	19.0–30.0
μ (cm^{-1})	0.997
crystal size (mm)	0.50 × 0.60 × 0.60
temp (°C)	25.0
no. of meas reflns	4208
no. of obsvd reflns ($I > 2.0\sigma(I)$)	2830
no. of unique reflns	4176
no. of refined params	308 (2830 out of 4176 refines)
R; R_w	0.056; 0.056
GoF	2.60
refinement program	NRCVAX
(D-map) max; min (e/Å^3)	−0.240; 0.220

[a] $R = \sum(F_o - F_c)/\sum(F_o)$. $R_w = [\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$. GoF $= [\sum(w(F_o - F_c)^2)/(\text{no. of reflns} - \text{no. of params})]^{1/2}$.

Table 2. Atomic Parameters x, y, z, and B_{eq}. ESDs Refer to the Last Digit Printed[a]

	x	y	z	B_{eq}
Al	0.2038(1)	0.2214(1)	0.1165(1)	3.6(1)
Mg	0.4023(1)	0.2156(1)	0.0998(1)	3.3(1)
N(1)	0.2776(2)	0.1610(2)	0.0295(2)	3.3(1)
N(2)	0.3068(2)	0.3068(2)	0.1470(2)	3.3(2)
O	0.5277(2)	0.1933(2)	0.1381(2)	3.4(1)
C(1)	0.2000(3)	0.1450(3)	0.2223(3)	5.0(2)
C(2)	0.0721(3)	0.2620(3)	0.0770(3)	6.0(3)
C(3)	0.2695(3)	0.0658(3)	0.0362(3)	4.4(2)
C(4)	0.1683(4)	0.0296(3)	0.0127(3)	6.6(3)
C(5)	0.3432(4)	0.0164(3)	−0.0128(3)	6.8(3)
C(6)	0.2679(3)	0.1943(4)	−0.0655(3)	6.7(3)
C(7)	0.1802(4)	0.1902(4)	−0.1208(3)	9.1(4)
C(8)	0.3584(3)	0.2076(3)	−0.1082(3)	6.9(3)
C(9)	0.3249(3)	0.3209(3)	0.2465(3)	4.4(2)
C(10)	0.2425(3)	0.3664(3)	0.2888(3)	5.7(2)
C(11)	0.4214(3)	0.3618(3)	0.2772(3)	6.7(3)
C(12)	0.3051(3)	0.3853(3)	0.0904(4)	7.3(3)
C(13)	0.2253(4)	0.4394(4)	0.0797(4)	9.7(4)
C(14)	0.3926(3)	0.4052(3)	0.0471(3)	7.0(3)
C(15)	0.6170(2)	0.1642(2)	0.1654(2)	2.8(2)
C(16)	0.6999(2)	0.1996(2)	0.1272(2)	3.0(2)
C(17)	0.7910(3)	0.1670(2)	0.1573(3)	3.8(2)
C(18)	0.8055(3)	0.1033(3)	0.2205(3)	4.1(2)
C(19)	0.7247(3)	0.0714(3)	0.2566(3)	3.9(2)
C(20)	0.6306(2)	0.0992(2)	0.2310(2)	3.3(2)
C(21)	0.9071(3)	0.0706(3)	0.2502(3)	6.5(3)
C(22)	0.6917(3)	0.2741(3)	0.0606(3)	3.9(2)
C(23)	0.6199(3)	0.2554(3)	−0.0209(3)	5.4(3)
C(24)	0.6616(3)	0.3542(3)	0.1102(3)	5.6(3)
C(25)	0.7899(3)	0.2952(3)	0.0230(3)	5.8(3)
C(26)	0.5446(3)	0.0586(3)	0.2742(3)	4.0(2)
C(27)	0.4888(3)	0.1245(3)	0.3230(3)	6.5(3)
C(28)	0.4775(3)	0.0139(3)	0.2029(3)	6.4(3)
C(29)	0.5759(3)	−0.0107(3)	0.3433(3)	8.1(3)

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

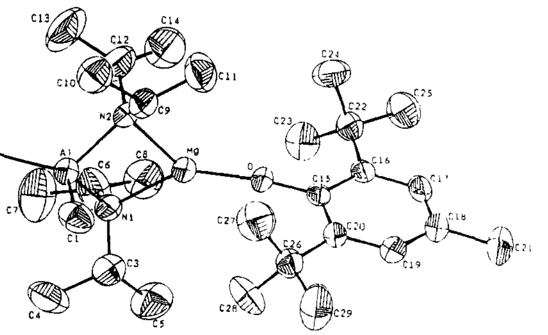

Figure 1. ORTEP drawing of $Me_2Al[\mu\text{-}N(^iPr)_2]_2Mg(BHT)$.

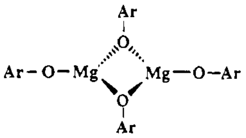

Figure 2. The skeleton of the dimagnesium complex of Ittel et al., Ar = BHT.

Table 3. Selected Bond Distances and Bond Angles

Al···Mg	2.775(2)	Mg–O	1.808(3)
Al–N(1)	1.960(3)	N(1)–C(3)	1.496(5)
Al–N(2)	1.973(3)	N(1)–C(6)	1.503(5)
Al–C(1)	1.983(4)	N(2)–C(9)	1.499(5)
Al–C(2)	1.967(4)	N(2)–C(12)	1.491(5)
Mg–N(1)	2.117(3)	O–C(15)	1.344(4)
Mg–N(2)	2.104(3)		
Mg···Al–N(1)	49.5(1)	Mg–N(1)–C(6)	109.2(2)
Mg···Al–N(2)	49.1(1)	C(3)–N(1)–C(6)	114.0(3)
Mg···Al–C(1)	98.4(1)	Al–N(2)–Mg	85.8(1)
Mg···Al–C(2)	151.4(2)	Al–N(2)–C(9)	112.5(2)
N(1)–Al–N(2)	94.2(1)	Al–N(2)–C(12)	116.8(3)
N(1)–Al–C(1)	106.7(2)	Mg–N(2)–C(9)	112.1(2)
N(1)–Al–C(2)	118.5(2)	Mg–N(2)–C(12)	110.3(2)
N(2)–Al–C(1)	107.0(2)	C(9)–N(2)–C(12)	115.6(3)
N(2)–Al–C(2)	118.7(2)	Mg–O–C(15)	171.4(2)
C(1)–Al–C(2)	110.1(2)	N(1)–C(3)–C(4)	115.3(3)
Al–Mg–N(1)	44.8(1)	N(1)–C(3)–C(5)	114.7(4)
Al–Mg–N(2)	45.2(1)	N(1)–C(6)–C(7)	122.5(4)
Al–Mg–O	154.6(1)	N(1)–C(6)–C(8)	116.7(4)
N(1)–Mg–N(2)	86.1(1)	N(2)–C(9)–C(10)	114.4(3)
N(1)–Mg–O	142.5(1)	N(2)–C(9)–C(11)	115.3(3)
N(2)–Mg–O	129.5(1)	N(2)–C(12)–C(13)	122.7(4)
Al–N(1)–Mg	85.7(1)	N(2)–C(12)–C(14)	117.2(4)
Al–N(1)–C(3)	112.9(2)	O–C(15)–C(16)	119.6(3)
Al–N(1)–C(6)	116.6(3)	O–C(15)–C(20)	121.0(3)
Mg–N(1)–C(3)	115.5(2)		

determined by X-ray is consistent with the data obtained from ^1H, ^{13}C, and ^{27}Al NMR spectroscopy, mass spectroscopy, and elemental analyses.

X-ray Structure. Selected bond angles and bond lengths are shown in Table 3. The structure exists as a monomer, which is the first example of a Mg···Al monomeric bridged complex. The triply coordinated magnesium of the compound is quite rare[7,8] and is caused by the bulkiness of the BHT ligand. Normal coordination numbers for magnesium are four or six. Unlike the starting material, $\{Me_2Al[\mu\text{-}N(^iPr_2)_2]MgCH_3\}_4$, the four-membered ring of Al, N(1), Mg, and N(2) does not exhibit the coplanar feature. The angle of 171.4° for Mg–O–C is almost linear, and the Mg–O bond distance is 1.808(3) Å. The Mg–O bond distance in this system is 0.015 Å shorter than that of the dimagnesium compound of Ittel et al.[7] (Figure 2). It is plausible to suggest that in the case of compound **1** {AlMgBHT} the oxygen atom adjacent to the magnesium is more electron donating than that of $\{MgBHT\}_2$, the complex of Ittel et al. Although the results of Fenske–Hall calculations[14]

---

(7) Calabrese, J.; Cushing, M. A.; Ittel, S. D. *Inorg. Chem.* **1988**, *27*, 867.

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

(9) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575.

(10) Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995.

showed a small decrease in the electron density of the magnesium atom for the Al••Mg complex in comparison to the electron density of the magnesium atoms of the complex of Ittel et al., this small difference could result in significant changes in bond length.

Spectral Data. All mass spectral data are well established with independent fragmentation. The NMR spectral data are in good agreement with the X-ray data. For compound **1**, the ^{1}H NMR spectrum (in C_6D_6) showed a triplet (doublet of doublets) at $\sigma = 1.19$ (24H) and a septet at $\sigma = 3.31$ (4H), which are due to the methyl protons and methine protons of the isopropyl groups, respectively. The chemical shifts at $\sigma = 0.25$ (s, 6H), 1.55 (s, 18H), 2.42 (s, 3H), and 7.25 (s, 2H) are due to the methyl protons attached to the aluminum atom, the methyl protons in the butyl groups, the methyl protons on the phenyl, and the protons of the phenyl group, respectively. The chemical shifts in the ^{13}C NMR spectra (in C_6D_6) at 158.475, 137.338, 126.058, and 123.290 are assigned to the phenyl carbons.

The most downfield peak is the carbon attached to the oxygen atom. The other absorptions, at 46.66, 35.38, 31.77, and 21.51, are due to the methine carbon of the isopropyl group, the tertiary carbon of the *tert*-butyl group, the primary carbons of the *tert*-butyl group, and the methyl carbon on the phenyl group, respectively. The peaks at 26.83 and 25.54 are due to the methyl carbons of the diastereotopic isopropyl group. ^{27}Al NMR spectra (in C_6D_6) showed a typical four-coordinated environment at $\sigma = 158$ ppm.[15]

Calculations

A Fenske–Hall[11–13] molecular orbital calculation, an approximate self-consistent field (SCF) method, was carried out for the aluminum–magnesium complex. The Fenske–Hall method was chosen because of the simplicity of use and accuracy of results. The basis set was made up of Slater-type orbitals. Assumptions were made about the structure of the Al–Mg complex in the MO calculation. The bond angles and bond lengths of symmetry-equivalent atoms were averaged. The Al, N(1), N(2), and Mg were on the same plane, the Al, Mg, and O were arranged on a line, and the phenyl ring of BHT was vertical with the AlN_2Mg plane. The calculation did not converge when the Mg–O–C(15) angle was 180°; however, when the angle was reduced to the experimental 172°, the calculation converged. The Mulliken atomic charges of Mg and Al were 1.87 and 1.77, respectively. Although the dative bond of the amino group were considered in the calculation, the ionic character of the Al••Mg complex is dominant and it makes the monomer stable. A selected MO diagram is shown in Figure 3. It is noteworthy that the HOMO is composed of contributions from O (55%), C18 (17%), C16 (12%) and C20 (12%), and evidence of the C–O distance from X-ray data supports the existence of a partial double bond between O and C(15).

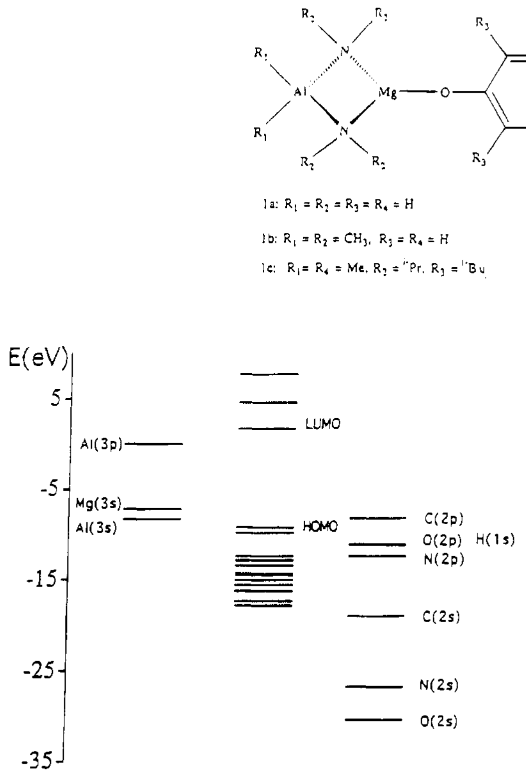

Figure 3. Computer-simulated MO diagram of model **1a** for complex **1**.

Acknowledgment. We thank the National Science Council, R.O.C., for financial support.

Supporting Information Available: Tables of crystallographic data, anisotropic displacement coefficients for non-hydrogen atoms, fractional coordinates, isotropic displacement coefficients of H atoms, and a complete list of the bond distances and angles for the compound $\{Me_2Al[\mu\text{-}N(^iPr)_2]_2Mg[O\text{-}2,6\text{-}(^tBu)_2\text{-}4\text{-}MeC_6H_2]\}$ (6 pages). Ordering information is given on any current masthead page. A list of structure factors is available from the author upon request.

IC940840C

---

(11) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(12) Bursten, E.; Fenske, R. F. *J. Chem. Phys.* **1977**, *67*, 3138.

(13) Bursten, E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320.

(14) The Mulliken atomic charges for the magnesium atom of model **1b** (Figure 3) of the Al••Mg bridged complex and the model of the complex of Ittel et al. are 1.71 and 1.73, respectively. The atomic charge for the compound of Ittel et al. was calculated by substituting Ar with methyl in the complex shown in Figure 2.

(15) Benn, R.; Rufinsky, B.; Lehmkuhl, H.; Jansseu, E.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *10*, 779.