Peng, S.-M.Insertion Reactions of Isocyanates, Isothiocyanates, and Carbon Disulfide into Mg-C Bonds of Polynuclear Aluminum-Magnesium Compounds: Synthesis, **Characterization, and Crystal Structures**

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A number of insertion products, viz., $Me_2Al(\mu-i-Pr_2N)_2Mg[(t-Bu)NC(CH_3)S]$ (1), $Me_2Al(\mu-i-Pr_2N)_2Mg[(t-Bu)NC(EH_3)S]$ (1), $Me_2Al(\mu-i-Pr_2N)_2Mg[(t-Bu)$ i-Pr₂N)₂Mg[(Ph)NC(CH₃)S)] (**2**), Me₂Al(μ -Et₂N)₂Mg[(t-Bu)NC(CH₃)S] (**3**), Me₂Al(μ -Et₂N)₂Mg- $[(Ph)NC(CH_3)S]$ (4), $\{Me_2Al(\mu-Et_2N)_2Mg[(Ph)NC(CH_3)O]\}_2$ (5), and $Me_2Al(\mu-i-Pr_2N)_2Mg[SC-i-Pr_2N)_2Mg[SC-i-Pr_2N]_2$ (CH₃)S] (6) have been synthesized using polynuclear aluminum-magnesium compounds and various heteroannulenes such as isothiocyanates, isocyanates, and carbon disulfide. All the new compounds were characterized by ${}^{1}\dot{H}$ and ${}^{13}C$ NMR, IR, and elemental analysis. The structures of two of the above compounds, 1 and 5, have been determined by single-crystal X-ray diffraction technique.

Introduction

The insertion reactions of carbon dioxide¹ and its isoelectronic analogues, such as isocyanates,² isothiocyanates,³ and carbon disulfide,⁴ into M-X (X = C, N) bonds have been studied extensively. Carbon disulfide has extensive utility in both organic and organometallic chemistry.⁵ Recently, we reported the insertion reactions of isothiocyanates and carbodiimides into Mg-X (X = C, N) bonds of organomagnesium reagents.⁶ The

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insertion of carbodiimides $\{R'CN(R)NR'\}$ into the Mg-C bond of polynuclear aluminum-magnesium compounds represents a rare σ - σ bond formation between the nitrogen atoms of the carbodiimide and the Mg atom.⁷ In this paper, we report the synthesis, characterization, and crystal structures of the products obtained in the insertion reactions of isocyanates, isothiocyanates, and carbon disulfide into Mg-C bonds of dimeric and tetrameric aluminum-magnesium compounds.

Experimental Section

All experiments were carried out in a N₂-flushed glovebag, dry-box, or in vacuo using standard Schlenk techniques.⁸ All solvents were distilled and degassed prior to use. tert-Butyl isothiocyanate, phenyl isothiocyanate, phenyl isocyanate, and carbon disulfide were purchased from Aldrich and were used as received. ¹H, ¹³C, and ²⁷Al NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts are referred to either SiMe₄ ($^{\bar{1}}$ H) or C₆D₆ (1 H, δ 7.15; 13 C {1H}, δ 128.00), while ²⁷Al NMR spectra were referred to $[Al(H_2O)_6]^{3+}$. Mass spectral data were obtained on a VG-7025 GC/MS/MS spectrometer, IR spectra were recorded of Nujol mulls between KBr disks on a Bio-Rad FTS-40 FT-IR spectrometer. Elemental analyses (C, H, N) were performed at the Analytische Laboratorien, Lindlar, Germany. Deviations in the results from calculated values are attributed to the extremely airsensitive and hygroscopic nature and limited thermal stabilities of these compounds.

The starting materials $[Me_2Al(\mu - i - Pr_2N)_2Mg(\mu - Me)]_4$ (A) and $[Me_2Al(\mu-Et_2N)_2Mg(\mu-Me)]_2$ (B) were prepared as described elsewhere.9

Synthesis of Me₂Al(µ-i-Pr₂N)₂Mg[(t-Bu)NC(CH₃)S] (1) and Me₂Al(µ-i-Pr₂N)₂Mg[(Ph)NC(CH₃)S)] (2). To a solution of A (1.20 g, 4 mmol) in pentane (40 mL) was added 0.5 g, 4 mmol of tert-butyl isothiocyanate (t-BuNCS) in pentane (20 mL). The reaction mixture was stirred for 2 h at room

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Table 1. Crystal and Intensity Collection Data for
Complexes 1 and 5

1	5
C ₂₀ H ₄₆ N ₃ SAlMg	C ₃₆ H ₆₈ N ₆ O ₂ Al ₂ Mg ₂
411.95	719.54
monoclinic	monoclinic
Rigaku AFC6S	Nonius
$P2_1/n$ (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
8.301(2)	11.152(3)
14.300(4)	13.727(5)
21.916(5)	14.599(6)
92.67(2)	100.53(3)
2598.6(9)	2197.2(13)
4	2
912.0	785.0
1.053	1.088
1.91	1.248
47.1	45.0
$0.33 \times 0.35 \times 0.40$	$0.40 \times 0.50 \times 0.60$
4381	2851
4066	2851
1988 $[(I > 3.0\sigma(I)]]$	1577 $[(I > 2.0\sigma(I)]]$
235	217
0.058; 0.057	0.064; 0.074
23	25
3.04	1.64
Μο Κα	Μο Κα
3	5
	$\begin{array}{c} 1 \\ \hline C_{20}H_{46}N_3SAlMg \\ 411.95 \\ monoclinic \\ Rigaku AFC6S \\ P2_1/n (No. 14) \\ 8.301(2) \\ 14.300(4) \\ 21.916(5) \\ 92.67(2) \\ 2598.6(9) \\ 4 \\ 912.0 \\ 1.053 \\ 1.91 \\ 47.1 \\ 0.33 \times 0.35 \times 0.40 \\ 4381 \\ 4066 \\ 1988 [(I > 3.0\sigma(I)] \\ 235 \\ 0.058; 0.057 \\ 23 \\ 3.04 \\ Mo \ K\alpha \\ 3 \end{array}$

temperature, and the reaction mixture then was centrifuged. Colorless crystals of 1 (1.4 g, 75%) were obtained upon cooling for 8 h. A procedure similar to that used for 1 was adopted for the preparation of 2 except for using phenyl isothiocyanate (PhNCS) in place of t-BuNCS. Compound 1. mp: 104 °C (dec). ¹H NMR (C₆D₆): δ -0.237 (s, 6H, Al(CH₃)), 1.08 (s, 9H, C(CH₃)₃), 1.31 (d, 24H, N(CH₃)₂), 2.28 (s, 3H, *t*-BuNC(CH₃)S), 3.66 (br, 4H, NCH(CH₃)₂. ¹³C NMR (C₆D₆): δ -4.23 (br, (Al-(CH₃)₂), 30.12 (t-BuNC(CH₃)S), 27.05 (NCH(CH₃)₂, 30.97 (C(CH₃)₃), 45.30 (NCH(CH₃)₂), 56.05 (CCH₃)₃), 196.42 (t-BuNC(CH₃)S)). ²⁷Al-NMR (C₆D₆): δ 140 (br). Mass spectrum (EI, 70 eV): 10 most intense *m*/*e* peaks 131, 41, 42, 57, 75, 58, 76, 59, 56, 55. IR (Nujol, cm⁻¹): 2917 (s), 2842 (s), 2718 (sh), 1620 (w), 1518 (m), 1470 (s), 1384 (s), 1176 (m), 1029 (w), 910 (w), 969 (m), 754 (m), 662 (m), 609 (m). Anal. Calcd for C₂₀H₄₆-N₃SMgAl: C, 58.30; H, 11.28; N, 10.20. Found: C, 58.09; H, 11.11; N, 10.30.

Compound **2**. Yield: 65%. mp: 156 °C (dec). ¹H NMR (C₆D₆): δ -0.47 (s, 6H, Al(CH₃)), 1.26 (d,d, 24H, NCH(CH₃)₂), 2.04 (s, 3H, PhNC(CH₃)S), 3.48 (sep, 4H, NCH(CH₃)₂), 6.93, 6.70, 7.09 (m, 5H, C₆H₅). ¹³C NMR (C₆D₆): δ -4.16 (br, (Al-(CH₃)₂), 26.45 (NCH(CH₃)₂, 34.45 (PhNC(CH₃)S), 47.89 (NCH-(CH₃)₂), 123.87 (*o*-C, C₆H₅), 125.53 (ipso-C, C₆H₅), 129.32 (*m*-C, C₆H₅), 200.15 (PhNC(CH₃)S). ²⁷Al NMR (C₆D₆): δ 160 (br). Mass spectrum (EI, 70 eV) 10 most intense *m/e* peaks at 44, 77, 118, 135, 86, 58, 43, 51, 119, 42. IR (Nujol, cm⁻¹): 2049 (w), 1590 (m), 1466 (s), 1377 (m), 1277 (w), 1165 (m), 1072 (w), 1018 (w), 964 (w), 910 (w), 841 (sh), 749 (m), 690 (s). Anal. Calcd for C₂₂H₄₂N₃SMgAl: C, 61.11; H, 9.72; N, 9.72. Found: C, 58.09; H, 11.11; N, 10.30.

Synthesis of Me₂Al(μ -Et₂N)₂Mg[(t-Bu)NC(CH₃)S] (3) and Me₂Al(μ -Et₂N)₂Mg[(Ph)NC(CH₃)S] (4). To a solution of B (0.96 g, 4 mmol) in pentane (40 mL) was added a solution of t-BuNCS (0.5 g, 4 mmol) in pentane (20 mL), and the reaction mixture was stirred for 8 h. Compound 3 (0.87 g, 60%) was obtained as white solid upon cooling the reaction mixture for 8 h. A similar procedure was employed for the synthesis of 4 in diethyl ether solvent. Compound 3. mp: 210 °C (dec). ¹H NMR (C₆D₆): δ –0.43 (s, 6H, Al(CH₃)), 0.82 (s, 9H, C(CH₃)₃), 0.99 (t, 12H, NCH₂CH₃), 2.25 (s, 3H, t-BuNC-(CH₃)S), 2.92 (q, 8H, NCH₂CH₃). ¹³C NMR (C₆D₆): δ –9.70 (br, Al(CH₃)₂), 13.51 (NCH₂CH₃), 29.52 (t-BuNC(CH₃)S), 40.08 (NCH₂CH₃), 55.29 (C(CH₃)₃), 197.38 (t-BuNC(CH₃)S). ²⁷Al NMR (C₆D₆): δ 160 (br). Mass spectrum (EI, 70 eV): 10 most

Table 2. Selected Bond Distances (Å) and Angles(deg) for Compounds 1 and 5

(ut	<u>(5) 101 Com</u>	pounds 1 and 5		
$Me_2Al(\mu - i - Pr_2N)_2Mg[(t - Bu)NC(CH_3)S]$ (1)				
S(1)-Mg(1)	2.429(2)	S(1)-C(19)	1.737(6)	
Al(1) - N(1)	1.977(6)	Al(1) - N(2)	1.949(6)	
Al(1) - C(7)	1.989(8)	Al(1) - C(8)	1.990(7)	
Mg(1) - N(1)	2,132(6)	Mg(1) - N(2)	2.148(6)	
Mg(1) - N(3)	2.102(0) 2 150(4)	N(1) - C(1)	1.481(9)	
N(1) - C(4)	1 500(9)	N(2) - C(9)	1.401(0) 1.504(8)	
N(1) = C(12)	1.500(0) 1.508(0)	N(2) = C(15)	1.505(6)	
N(2) = C(12) N(2) = C(10)	1.000(0)	N(3) C(13)	1.505(0)	
N(3) = C(19)	1.292(0)			
Mg(1) - S(1) - C(1)	9) 76.5(2)	N(1) - Al(1) - N(2)	95.7(2)	
$N(1) = \Delta I(1) = C(7)$	109 4(3)	N(1) - Al(1) - C(8)	1147(2)	
N(1) = Al(1) = C(7) N(2) = Al(1) = C(7)	110 9(3)	N(2) - A(1) - C(8)	115.7(3)	
$N(L) = M_{\sigma}(1) = N(2)$	110.2(3) 1977(9)	$S(1) = M_{\sigma}(1) = N(1)$	198 0(9)	
N(1) = Mg(1) = N(2)	1 = 127.7(2)	S(1) = Mg(1) = N(1) $S(1) = M_{\pi}(1) = N(2)$	120.9(2)	
N(1) = Mg(1) = N(2)	$(2) 0 \mathbf$	S(1) = Mg(1) = N(3)	08.9(1)	
N(2) - Mg(1) - N(3)	120.1(2)	N(1) - Mg(1) - N(3)	126.0(2)	
AI(1) - N(1) - C(1)	114.8(5)	AI(1)-N(1)-Mg(1)) 87.9(2)	
Mg(1) - N(1) - C(1)) 106.4(4)	AI(1) - N(1) - C(4)	112.2(4)	
C(1) - N(1) - C(4)	117.4(6)	AI(1) - N(2) - Mg(1)) 114.3(5)	
Al(1)-N(2)-C(9)	113.2(5)	Al(1) - N(2) - C(12)	123.6(5)	
Mg(1) - N(2) - C(9)	106.1(4)	Mg(1)-N(2)-C(12)	2) 111.2(5)	
Mg(1) - N(3) - C(1)	9) 96.9(3)	Mg(1)-N(3)-C(15)	5) 139.5(4)	
N(3) - C(15) - C(1)	6) 105.1(5)	C(15)-N(3)-C(19) 123.6(5)	
N(3)-C(15)-C(1	8) 111.2(6)	N(1)-C(1)-C(3)	116.0(7)	
S(1) - C(19) - N(3)	117.6(4)	S(1) - C(19) - C(20)	113.2(4)	
N(3)-C(19)-C(20)	129.1(5)			
${Me_2A}$	Al(µ-Et ₂ N) ₂ Mg	[(Ph)NC(CH ₃)O]} ₂ (5	i)	
Al–Mg	2.865(3)	Mg-N(3)	2.181(6)	
Al-N(1)	1.922(8)	O–Mg	1.978(5)	
Al-N(2)	1.925(6)	O-C(11)	1.320(8)	
Al-C(1)	1.967(9)	N(1) - C(3)	1.494(10)	
Al-C(2)	1.972(8)	N(1) - C(5)	1.480(11)	
Mø-O	2,260(6)	N(2) - C(7)	1.484(10)	
Mg-O	1.978(5)	N(2) - C(9)	1.490(11)	
Mg = N(1)	2 134(6)	N(3) - C(11)	1.264(10)	
Mg = N(2)	2.101(0) 2 151(7)	N(3) - C(13)	1 421(9)	
ivig iv(2)	2.101(7)	14(3) C(13)	1.421(0)	
Mg-Al-N(1)	48.16(18)	Mg-O-Mg	103.61(22)	
Mg-Al-N(2)	48.64(21)	Mg = O - C(11)	89.0(4)	
$M\sigma - Al - C(1)$	110 6(3)	$M_{\sigma} = O = C(11)$	153 9(5)	
Mg-Al-C(2)	116 0(4)	$Al-N(1)-M\sigma$	89 7(3)	
N(1) - AI - N(2)	94 6(3)	Al - N(1) - C(3)	113 8(5)	
$N(1) - \Delta I - C(1)$	112 1(4)	Al - N(1) - C(5)	116.0(0) 116.1(5)	
$N(1) - \Delta l - C(2)$	110 9(4)	$M_{\sigma} - N(1) - C(3)$	108.5(4)	
N(1) = Al = C(2) N(2) = Al = C(1)	110.3(4) 110.6(2)	$M_{\sigma} = N(1) = C(5)$	100.3(4) 116 $4(5)$	
N(2) = AI = C(1) N(2) = AI = C(2)	110.0(3) 116 0(4)	C(2) N(1) - C(3)	110.4(3) 110.7(7)	
N(2) = AI = C(2)	110.0(4)	C(3) = IN(1) = C(3)	110.7(7)	
C(1) = AI = C(2)	111.0(4)	AI = N(2) = Mg	89.2(3)	
AI-Mg-O	150.37(17)	AI = N(2) = C(7)	114.7(5)	
AI-Mg-U	128.85(18)	AI = N(2) = C(9)	116.1(5)	
AI-Mg-N(I)	42.12(20)	Mg - N(2) - C(7)	111.9(5)	
AI-Mg-N(2)	42.20(17)	Mg - N(2) - C(9)	114.2(5)	
Al-Mg-N(3)	100.76(18)	C(7) - N(2) - C(9)	109.5(6)	
O-Mg-O	76.39(20)	Mg - N(3) - C(11)	94.1(4)	
O-Mg-N(1)	117.1(3)	Mg-N(3)-C(13)	144.3(5)	
O-Mg-N(2)	156.89(24)	C(11) - N(3) - C(13)	121.0(6)	
O-Mg-N(3)	129.79(23)	N(1)-C(3)-C(4)	116.0(7)	
N(1) - Mg - N(2)	82.5(3)	O - C(11) - N(3)	117.2(6)	
N(1)-Mg-N(3)	104.70(24)	O - C(11) - C(12)	117.4(6)	
N(2)-Mg-N(3)	105.56(25)	N(3) - C(11) - C(12)	125.3(7)	
		.,,		

intense *m/e* peaks at 57, 72, 58, 42, 114, 41, 44, 243, 128, 73. IR (Nujol, cm⁻¹): 1513 (m), 1459 (m), 1376 (m), 1191 (w), 1131 (m), 1039 (w), 991 (w), 845 (w), 781 (w), 670 (m). Anal. Calcd for $C_{16}H_{38}N_3SMgAl$: C, 53.93; H, 10.67; N, 11.80. Found: C, 53.24; H, 10.18; N, 11.26.

Compound **4**. Yield: 46%. mp: 121 °C. ¹H NMR (C₆D₆): δ -0.43 (s, 6H, Al(CH₃)₂), 1.04 (t, 12H, NCH₂CH₃), 2.13 (s, 3H, PhNC(CH₃)S); 2.90 (m, 8H, NCH₂CH₃), 6.74, 6.92, 7.05 (m, 5H, C₆H₅). ¹³C NMR (C₆D₆): δ -9.77 (br, Al(CH₃)₂), 14.08 (NCH₂CH₃), 27.67 (PhNC(CH₃)S), 41.00 (N*C*H₂CH₃), 122.99 (*o*-C, C₆H₅), 123.45 (ipso-C, C₆H₅), 129.35 (*m*-C, C₆H₅). ²⁷Al NMR (C₆D₆): δ 160 (br). Mass spectrum (EI, 70 ev): 10 most intense *m/e* peaks at 58, 360, 245, 231, 118, 174, 303, 77, 289, 375. IR (Nujol, cm⁻¹): 2055 (w), 1593 (m), 1456 (s), 1370 (m), 1280 (w), 1172 (m), 1055 (w), 970 (w), 908 (w), 825 (s), 790 (s),

CH₃

Scheme 1



688 (m). Anal. Calcd for C₁₈H₃₄N₃SMgAl: C, 57.44; H, 9.04; N, 11.17. Found: C, 58.09; H, 11.11; N, 10.30.

Synthesis of $\{Me_2Al(\mu-Et_2N)_2Mg[(Ph)NC(CH_3)O]\}_2$ (5). To a solution of **B**, (0.96 g, 4 mmol) in diethyl ether (40 mL) was added a solution of PhNCO (0.68 g, 4 mmol) in diethyl ether (20 mL). The solution was stirred for 8 h and centrifuged. Cooling the resultant supernatant solution yielded colorless crystals of 5 (0.91 g, 56%). Compound 5. mp: 153 °C. ¹H NMR (C₆D₆): δ -0.41 (s, 6H, Al(CH₃)₂), 1.00 (t, 12H, NCH₂CH₃), 1.72 (s, 3H, PhNC(CH₃)O), 2.934 (m, 8H, NCH₂-CH₃), 6.91, 6.97, 7.14 (m, 5H, C₆H₅). ¹³C NMR (C₆D₆): δ -9.49 (br, Al(CH₃)₂), 13.41 (NCH₂CH₃), 19.03 (PhNC(CH₃)O), 40.28 (NCH₂CH₃), 124.20 (o-C, C₆H₅), 125.31 (ipso-C, C₆H₅), 129.44 (*m*-C, C₆H₅). ²⁷Al NMR (C₆D₆): δ 160 (br). Mass spectrum (EI, 70 eV): 10 most intense *m*/*e* peaks at 229, 344, 287, 118, 215, 57, 58, 158, 114, 176. IR (Nujol, cm⁻¹): 2923 (s), 2853 (s), 2728 (sh), 2664 (sh), 1555 (w), 1459 (s), 1377 (s), 1303 (sh), 1249 (w), 1131 (w), 1023 (w), 958 (w), 721 (m), 662 (w), 593 (w). Anal. Calcd for C₃₆H₆₈N₆O₂Mg₂Al₂: C, 60.10; H, 9.47; N, 11.70. Found: C, 58.58; H, 9.10; N, 11.31.

Synthesis of Me₂Al(µ-i-Pr₂N)₂Mg[SC(CH₃)S] (6). To a solution of A (1.20 g, 4 mmol) in pentane (40 mL) was added CS₂ in excess (5 mL). The reaction took place immediately.

The solvent was removed in vacuo, and the crude product was recrystallized from pentane to yield 6. Yield: 0.45 g; 30%. mp: 65 °C (dec). ¹H NMR (C₆D₆): δ -0.25 (s, 6H, Al(CH₃)₂), 1.22 (d, 24H, NCH(CH₃)₂), 2.77 (s, 3H, SC(CH₃)S), 3.46 (sep, NCH(CH₃)₂). ¹³C NMR (C₆D₆): δ -3.59 (br, Al(CH₃)₂), 26.56 (NCH(CH₃)₂, 44.55 (SC(CH₃)S), 48.02 (NCH(CH₃)₂), 264.39 (SC(CH₃)S). ²⁷Al NMR (C₆D₆): δ 160 (br). Mass spectrum (EI, 70 eV): 10 most intense *m*/*e* peaks at 44, 86, 200, 43, 42, 51, 57, 214, 115, 58. IR (Nujol, cm⁻¹): 2922 (s), 2847 (s), 1453 (s), 1378 (s), 1260 (w), 1142 (m), 1017 (w), 969 (w), 958 (w), 872 (w), 797 (w). Anal. Calcd for C₁₆H₃₇N₂S₂MgAl: C, 51.61; H, 9.95; N, 7.53. Found: C, 49.31; H, 9.22; N, 6.96.

Structure Determination. Suitable single crystals of complexes 1 and 5 were sealed in glass capillaries for X-ray diffraction study. Preliminary examination and intensity data collection were carried out with either a Rigaku AFC6S diffractometer (for 1) or an Enraf-Nonius CAD-4 automatic diffractometer (for 5) using graphite-monochromatized Mo K $\!\alpha$ $(\lambda = 0.710 69 \text{ Å})$ radiation. Intensity data were collected using the θ -2 θ scan mode and corrected for absorption and decay. The structures were solved by SIR92¹⁰ (for 1) or by MULTAN¹¹ (for 5) and refined with full-matrix least squares on F. In the final cycles, all non-hydrogen atoms were refined anisotropi-

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cally and all hydrogen atoms were fixed at idealized positions. All calculations were carried out with a SGI R4000 computer using the teXsan program package¹² (for 1) or a Microvax 3600 computer using the NRCVAX program package¹³ (for 5). A summary of the data collection and structure solution is given in Table 1; selected bond lengths and angles are given in Table 2.

Results and Discussion

Synthesis, Characterization, and Spectral Data. Compounds **1–6** were obtained by the straightforward reaction between the reagents *tert*-butyl, and phenyl isothiocyanate, phenyl isocyanate, and carbon disulfide with the respective polynuclear aluminum-magnesium precursor compounds, A and B. Except in the case of the reaction of **B** with phenyl isocyanate, in which case a tetranuclear compound was obtained, all other reactions yielded only dinuclear insertion products (see Schemes 1 and 2). In the case of **1**, a distinct change in the NMR pattern of the product compared to that of the starting A was noticed after the insertion of *tert*-butyl isothiocyanate. The Mg-CH₃ signal had shifted downfield to δ 2.285 ppm, indicating the migration of the methyl group from Mg to the carbon atom of the NCS unit. A change in CH₃ chemical shift of similar magnitude also was noticed in the case of 2-6. The ¹³C NMR resonance associated with the carbon of the inserted CS₂ group was observed at δ 264 ppm for **6**.

In the IR spectra for 1-4, there was no band at ca. 2150 cm⁻¹ attributable to asymmetric stretching frequency of -N=C=S and the bands that were observed are similar to the characteristic bands observed for N-methylthioacetamide (1550, 1200, and 720 cm^{-1}).¹⁴ The IR spectrum of 5 displayed a carbonyl stretch at 1555 cm⁻¹ for the PhNCO group. The CS₂ insertion product **6** has been formulated as having η^2 -S₂CR ligands on the basis of its Nujol mull IR spectrum, which showed two bands at 1142 and 1017 cm⁻¹, which are assignable to the symmetric and asymmetric stretching frequencies of the CS₂-containing fragments. These values are comparable to those exhibited by closely related CS₂ insertion products, Cp*W(NO)(η^2 -S₂CN-HCMe₃)(OCMe₃)¹⁵ and Cp*W(NO)(η^2 -S₂CPh)(Ph).¹⁶ A number of trithiocarbonato complexes contain bands corresponding to the ν (C=S) and ν (C-S) modes in the 990-1054 and 850-885 cm⁻¹ regions.¹⁷

Description of Structures. Compound **1** possesses an interlinked bicyclic structure as shown in Figure 1. Selected bond lengths and angles are listed in Table 2. As seen in Figure 1, one of the rings is formed by Al,

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Figure 1. ORTEP view of the complex Me₂Al(*µ*-*i*-Pr₂N)₂-Mg[(*t*-Bu)NC(CH₃)S] (1). Thermal ellipsoids are drawn at 50% probability level.



Figure 2. ORTEP view of the complex $\{Me_2Al(\mu-Et_2N)_2-Mg[(Ph)NC(CH_3)O]\}_2$ (5). Thermal ellipsoids are drawn at 50% probability level.

Mg, and the amide nitrogen atoms of the two $(i-Pr_2)N$ ligands while the other is formed by a Mg atom and carbon, sulfur, and nitrogen atoms of the methylmigrated *tert*-butyl isothiocyanate moiety. These two rings are connected through the magnesium atom. Each of the rings is nearly coplanar and approximately perpendicular to each other. The observed C(19)–N(3) and C(19)–S(1) bond distances of 1.292 (6) and 1.737 (6) Å fall between single- and double- bond values.^{18,19}

Compound **5** consists of an interlinked tricyclic structure similar to that of its parent compound as shown in Figure 2. Selected bond distances and angles are listed in Table 2. The molecule possesses crystallographic inversion center symmetry at the center of the Mg_2O_2 ring.

The two symmetrically related terminal rings are formed by Al, Mg, and amide nitrogen atoms of the (Et₂N) groups. The structural features of the rings are comparable to those of the terminal rings in the parent compound **B**.¹⁰ The middle ring is defined by two sets

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of symmetrically related Mg and oxygen atoms and is planar with alternating Mg-O distances of 1.978(5) and 2.260(6) Å. The O-Mg-O and Mg-O-Mg angles are 76.39(20) and 103.60(22)°, respectively, and the intermetallic Mg-Mg distance is 3.335(5) Å. The Mg-Al distance in the present compound is comparable to that in the parent compound, as could be expected. The observed C-N and C-O bond distances associated with the sp carbon atom of 1.264(10) and 1.320(8) Å are commensurate with C=N and C-O, respectively. The observation of two dissimilar Mg-O distances in the middle ring reveals that the tetranuclear arrangement is due largely to both the ability of the ligating oxy group to interact with the neighboring magnesium center and the small bite angle of the PhNC(CH₃)O ligand species, 59.54(21)°.

In the case of **1**, since the *tert*-butyl group is disposed away from the Mg center, a similar tetranuclear arrangment as in **5** could not be expected. We assume that the considerably longer Mg-S distance of 2.429(2) Å and larger bite angle of the *t*-BuNC(CH₃)S ligand, 68.9(1)°, preclude such a tetranuclear arrangement. Our recent report on a magnesium dimer similar to **5**, in which the two magnesium atoms are bridged by the sulfur atoms of the phenyl isothiocyanate, can serve as an additional case for comparison.⁶

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Supporting Information Available: ORTEP drawings and tables of crystal data, atomic coordinates, temperature factors, hydrogen coordinates, and intramolecular bond distances and angles for 1 and 5 (26 pages). Tables of observed and calculated structure factors can be obtained from the authors upon request. Ordering information is given on any current masthead page.

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