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Insertion Reactions of Carbon Disulfide into Mg-C and Mg-N Bonds: Syntheses and Structural Determinations of $Mg(S_2CY)_2(THF)_n$ ($Y=NEt_2$, N^iPr_2, ^iPr, Ph) and $BrMg(S_2CZ)(THF)_3$ (Z=Ph, ^iPr)

Chung-Cheng Chang[a]* (張宗仁), Kuo-Ching Yang[b] (楊國清), Jeng-Gong Guo[a] (郭政躬),
Leigh-May Huang[a] (黃麗美), Li-Chyung Wang[a] (王立群),
Gene-Hsiang Lee[c] (李錦祥) and Shie-Ming Peng[c] (彭旭明)
[a]*Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, R.O.C.*
[b]*Department of Chemical Engineering, Cheng-Shiu Institute of Technology, Kaohsiung, Taiwan, R.O.C.*
[c]*Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.*

The insertion reaction of CS_2 with $Mg(NR_2)_2$ (R= Et, ^{i}Pr), MgR'_2 (R′= Et, Ph) and $R''MgBr$ (R″= ^{i}Pr, Ph) respectively lead solid products, $Mg(S_2CNR_2)_2(THF)_n$ (**1**: R= Et, n=2; **2**: R= ^{i}Pr, n=1), $Mg(S_2C'R)_2(THF)_2$ (**3**: ′R= Et, **4**: ′R= Ph), $BrMg(S_2C''R)(THF)_3$ (**5**: ″R= ^{i}Pr, **6**: ″R= Ph) in which the inserted carbon disulfides act as terminal chelating ligands. These compounds were characterized with ^{1}H, ^{13}C NMR, IR spectroscopy, mass spectrometry, elemental analyses, and X-ray crystallography.

Keywords: Magnesium thiocarbamate; Magnesium thiocarboxylates; CS_2 insertion.

INTRODUCTION

The reaction between carbon dioxide and organometallic compounds is interesting because it provides one-carbon homologization of the organic group. A number of synthetic and mechanistic studies have been carried out on the insertion reactions of CO_2 into M-C, M-O, M-H and M-N bonds.[1-11] Recently we studied the CO_2 insertion reactions of aluminium-magnesium compounds.[12] We attributed the high reactivity of the magnesium center in comparison with that in Grignard reagents due to its more electropositive nature.[13-16] This interesting activity prompted us to investigate the reactivity of magnesium compounds towards CO_2 and analogues of CO_2 such as isothiocyanates and carbodiimides.[12,17] Evans et al. report the different bonding situation between organosamarium compounds with carbon dioxide and carbon disufide.[18] In magnesium compounds, the bonding modes between carbon dioxide and carbodiimides are different. The former acts as a bridging ligand[12,19,20] and the latter acts as a terminal chelating ligand. Herein we continue to explore the insertion reactions of carbon disulfide, another CO_2 analogue, with magnesium compounds.

RESULTS AND DISCUSSIONS

Syntheses and Characterization

$Mg(NR_2)_2$ reacted with carbon disulfide (1:1and 1:2 molar ratio) in tetrahydrofuran for 8 h at ambient temperature getting $Mg(S_2CNR_2)_2(THF)_n$ in good isolated yields (Eq 1). The reaction of MgR'_2 with carbon disulfide (1:1and 1:2 molar ratio) gave $Mg(S_2C'R_2)_2(THF)_2$ as shown in Eq 2. Similarly the reaction of $R''MgBr$ with carbon disulfide in 1:1 molar ratio yields $BrMg(S_2CR'')(THF)_3$ as shown in Eq 3.

$$Mg(NR_2)_2 \quad + \quad 2\ CS_2 \quad \xrightarrow[\text{[R= Et, n=2; R=}^{i}\text{Pr, n=1]}]{\text{THF}} \quad Mg(S_2CNR_2)_2(THF)_n \qquad \text{(Eq. 1)}$$

$$MgR'_2 \quad + \quad 2\ CS_2 \quad \xrightarrow[\text{[R'= Et, Ph]}]{\text{THF}} \quad Mg(S_2CR'_2)_2(THF)_2 \qquad \text{(Eq. 2)}$$

$$R''MgBr \quad + \quad 2\ CS_2 \quad \xrightarrow[\text{[R''= }^{i}\text{Pr, Ph]}]{\text{THF}} \quad BrMg(S_2CR''_2)(THF)_3 \qquad \text{(Eq. 3)}$$

The products **1~6** having insertion carbon disulfides into Mg-C and Mg-N bonds have been fully characterized by ^{1}H, ^{13}C NMR, IR spectroscopy, mass spectrometry, and elemental analyses, while some of them have been further characterized structurally by single-crystal X-ray diffraction. The IR spectra for all the products showed bands between 1141-1178 cm^{-1} and 1018-1039 cm^{-1} which are assignable to symmetric and asymmetric stretching frequencies of the CS_2-containing fragment, η^2-S_2CR formed by CS_2 insertion into M-R bonds. In the ^{1}H NMR spectrum of compound **1**, two broad signals at δ = 1.35, and 3.83 ppm were assigned to the methylene protons of the coordinated tetrahydrofuran ligands, a triplete δ = 1.04 and a quartet at δ = 3.71 were respectively assigned to the methyl protons and the methylene protons of the ethyl groups. ^{13}C NMR spectrum showed the chemical shift δ = 206.84 ppm assigned to the quaternary carbon of CS_2 groups. For compound **6** one set of multiplete δ = 7.11 and a triplet δ = 8.96 which were assigned to the aromatic protons. The corresponding aromatic carbon in ^{13}C NMR spectrum appeared at δ = 127.87, 132.00, 132.57, 147.15, and the chemical shift of the quaternary carbon of the CS_2 group is δ = 250.95 ppm. Those ^1H NMR data showed that the chemical shifts (δ = 1.04-1.33, δ = 3.69-3.84 ppm) as the coordinated tetrahydrofuran away from that of the free tetrahydrofuran δ = 1.43 and δ = 3.57 ppm, and the chemical shifts of their ^{13}C NMR data of the inserted CS_2 groups appeared at δ = 206.84-273.67 ppm far away from that (δ = 192.80 ppm) of the free CS_2. ^1H NMR spectrum of compound **2** at room temperature showed one kind environment of isopropyl groups at δ = 1.01(d) and 2.77(m) assigned to methyl protons and methylene protons, respectively. However two kinds of environments of isopropyl groups were observed for compound **2** at -70 °C, through ^1H NMR (C_4D_8O) spectrum δ = 1.15(d), 1.65(d) for the methyl protons, and δ = 3.63 (m), 3.90 (m) for the methylene protons. The non-equivalency of the isopropyl groups at low temperature might be due to the coordination of THF slow exchange with free THF, which would destroy the S_2MgS_2 effective plane of symmetry. The reaction of $Mg(NR_2)_2$, MgR'_2, and $R''MgBr$ with carbon disulfide yielded the magnesium thiocarbamate and magnesium thiocarboxylates consisting of the four member rings, in which the carbon disulfide acted as a terminal chelating ligand. The results are quite different from those of reacting with carbon dioxide. The magnesium compounds reacted with carbon dioxide to form linear and cage magnesium carboxylates, $Mg_n(O_2CY)_{2n}$ (n=2, 3, 6),[12,19] in which carbon dioxide acted as bridging ligand to constitute the eight-member rings. The reason why magnesium thiocarbamates and magnesium carboxylates exhibit different bonding modes is that the former favors a four-member ring configuration due to the large radius of the sulfur atom whereas the larger angle strain precludes the formation of a four-member ring for the latter. Those data were in accordance with the work by W. J. Evans etc.[18] They reported that the samarium compounds were inserted by carbon disulfide and carbon dioxide to form the chelating four-member rings and eight-member rings, respectively. Here it is also interesting to mention that the insertion reaction of carbon sulfides, carbodiimides, and carbon dioxide into Mg-Br hasn't been found.

X-ray Crystal Structures of Magnesium Thiocarbamates and Magnesium Thiocarboxylates

Compounds **1**, **2**, **5** and **6** possess similar structure features. ORTEP views of the compounds **1**, **2**, **5** and **6** are shown in Figs. 1~ 4. The selected bond distances and bond angles are listed in Table 1, and crystal data are listed in Table 2.

$Mg(S_2CNEt_2)_2(THF)_2$, 1

Compound **1** was recrystallized from a mixed solution of tetrahydrofuran and ether. The compound is described as having a distorted octahedral geometry around magnesium, which are bonded through sulfur and nitrogen atoms of the ligands and two cis-coordinated molecules of tetrahydrofuran. One of the coor-dinated tetrahydrofuran is disordered with the twisted five-membered ring. The C_{15}, C_{15}', C_{18}, C_{18}' atoms have the half occupancies. The Mg, S_2, C_1, S_1, atoms and Mg, S_3, C_2, S_4 atoms constitute the four-membered coplanar rings. The dihedral angle between the planes is 95.97(6)°. The Mg-S distances between 2.552 and 2.574 Å in hexacoordinated magnesium compounds being as typical of

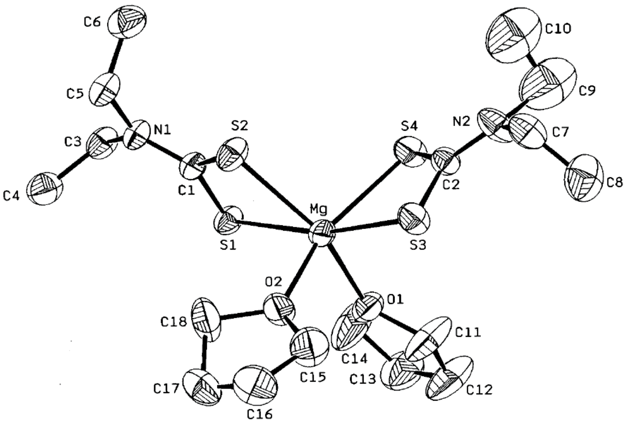

Fig. 1. ORTEP view of the molecule $Mg(S_2CNEt_2)_2$-$(THF)_2$, **1**.

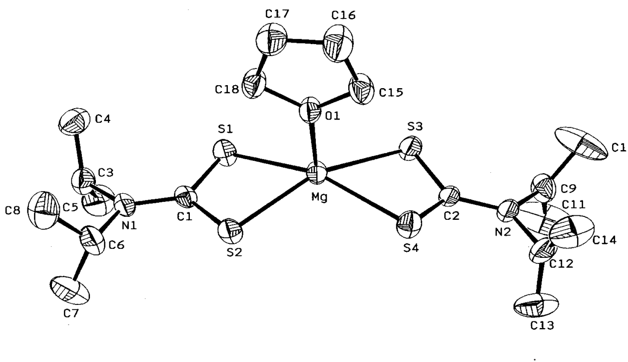

Fig. 2. ORTEP view of the molecule $Mg(S_2CN^iPr_2)_2$-(THF), **2**.

σ-bonding are reasonably longer than the mean value 2.427 Å of Mg-S distances in tetracoodinated magnesium compounds.[22,23] The C(1)-S(1) and C(1)-N(1) bond lengths, 1.724(4) and 1.321(5) Å, respectively (Table 1), are between single and double bond values, C-S 1.81 and 1.61, C-N 1.51 and 1.26 Å. This data with the summation of the internal angle of the MgSCS cycle supported that the C(1) atoms possesses *sp*^{2} character and delocalization of the moieties NCS_2.

$Mg(S_2CN^iPr_2)_2(THF)$, 2

Compound **2** was also recrytallized from a mixed solution of tetrahydrofuran and ether. It possesses square bipyramidal geometry around magnesium. The diisopropylamino-thiocarbamate ligands act as bidentate chelates forming the basal plane and the solvent tetrahydrofuran occupies the axial position. The Mg, S_2, C_1, S_1 atoms and Mg, S_3, C_2, S_4 atoms constitute the four-membered coplanar rings. The dihedral angle between the basal planes is 149.7(1)° which is larger than 96.0 (1)° in compound **1**, because there is one less coordinated tetrahydrofuran than that in compound **1**, hence a larger dihedral angle resulted from less repulsion from the tetrahydrofuran molecule. The structure contains a crystallographic two-fold axis passing through O(1) and Mg. An ORTEP view of the compound **2** is given in Fig. 2. Analogous to Compound **1**, the Mg-S distance between 2.466 and 2.496 Å are typical of σ bonding. The bond lengths of Mg-S and Mg-O for the pentacoordinated are noticeably shorter than those for the hexacoordinated and longer than those for tetracoordinated. The C(1)-S(1) and C(1)-N(1) bond lengths, 1.719(4) and 1.326(6) Å, respectively, are partial double bond.

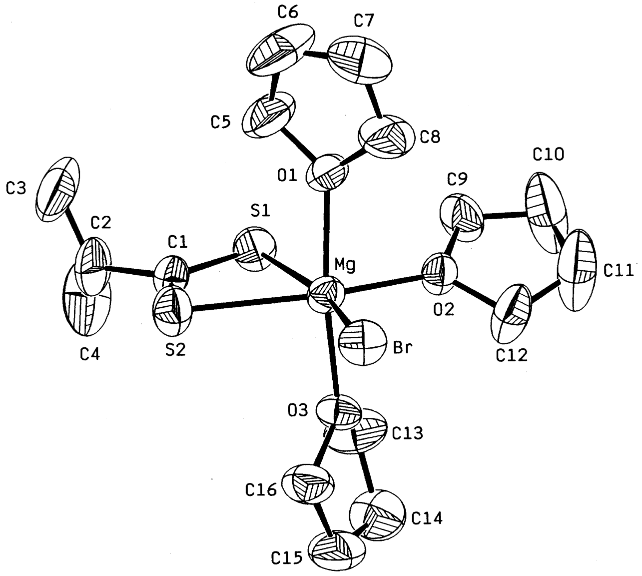

Fig. 3. ORTEP view of the molecule $BrMg(S_2C^iPr)(THF)_3$, **5**.

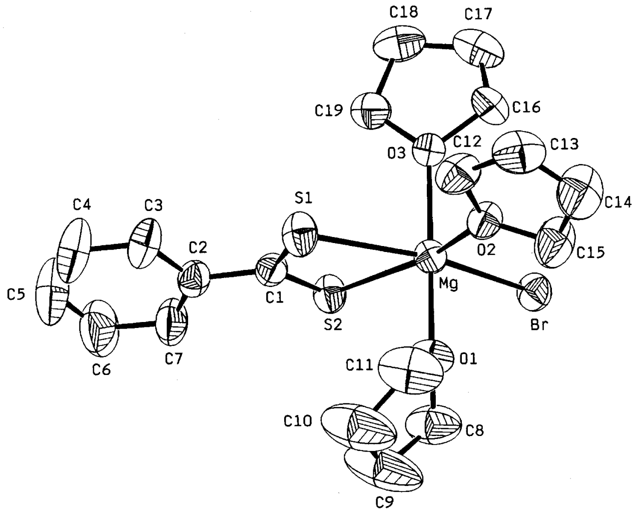

Fig. 4. ORTEP view of the molecule $BrMg(S_2CPh)(THF)_3$ **6**.

$BrMg(S_2CR'')(THF)_3$, ($R''= {}^iPr$, 5 or Ph, 6)

Both compounds are described as meridional structures. The axial coordination sites are occupied by the oxygen atoms of the two tetrahydrofuran molecules. The Mg-O axial bonds are nearly perpendicular to the average equatorial plane. It is obvious to mention that the trans-influence of bromide to induce the Mg-S_1 distance is much longer than the Mg-S_2 distance (In compound **5**, 2.656(3) Å > 2.596(3) Å and in compound **6**, 2.708(3) Å > 2.574(3) Å). Those Mg-S_1 distances of compound **5** and compound **6** are much longer than those of the previous compounds. The observed C-S distances between 1.667(8) and 1.683(6) Å, were shorter than the C-S distances of compound **2**. It seems to support a more localized double-bond character, which is in accordance with the C-S stretching frequencies data. It may be due to the electronic donating property of the isopropyl group. In compound **5**, one of the methyl group in the isopropyl group is disordered with the tertiary hydrogen atom. C_4, C_4', H_2 and H_2' have the half occupancies.

Pyrolysis of Insertion Products

The reactions of carbon disulfide and carbon dioxide with freshly prepared $Mg(C_6H_5)_2$ were carried out to obtain the products, $Mg(S_2CPh)_2(THF)_3$ and $Mg_3(O_2CPh)_6(THF)_2$;[19] while heating the $Mg(S_2CPh)_2(THF)_3$ over 80 °C, it decomposed to get the sublimed biphenyl $C_6H_5C_6H_5$. However when the same procedure to purify the $Mg_3(O_2CPh)_6(THF)_2$ was used,[19] it decomposed to get the sublimed products, the

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds **1, 2, 5, 6**

$Mg(S_2CNEt_2)_2(THF)_2$, **1**							
Mg-S1	2.552(2)	Mg-O1	2.126(3)	S3-C2	1.705(4)	N1-C5	1.458(5)
Mg-S2	2.566(2)	Mg-O2	2.114(3)	S4-C2	1.712(4)	N2-C2	1.326(5)
Mg-S3	2.555(2)	S1-C1	1.724(4)	N1-C1	1.321(5)	N2-C7	1.460(6)
Mg-S4	2.574(2)	S2-C1	1.714(4)	N1-C3	1.467(5)	N2-C9	1.696(1)
S1-Mg-S2	70.4(1)	S2-Mg-O2	92.6(1)	Mg-S2-C1	85.6(1)	C7-N2-C9	110.8(4)
S1-Mg-S3	167.2(1)	S3-Mg-S4	69.9(1)	Mg-S3-C2	85.8(1)	S1-C1-S2	118.1(2)
S1-Mg-S4	102.2(1)	S3-Mg-O1	99.5(1)	Mg-S4-C2	85.1(2)	S1-C1-N1	120.8(3)
S1-Mg-O1	90.8(1)	S3-Mg-O2	91.4(1)	C1-N1-C3	122.7(3)	S2-C1-N1	121.1(3)
S1-Mg-O2	97.6(1)	S4-Mg-O1	92.4(1)	C1-N1-C5	122.7(3)	S3-C2-S4	118.6(2)
S2-Mg-S3	100.2(1)	S4-Mg-O2	159.8(1)	C3-N1-C5	114.6(3)	S3-C2-N2	119.1(3)
S2-Mg-S4	98.0(1)	O1-Mg-O2	83.1(1)	C2-N2-C7	124.1(4)	S4-C2-N2	122.3(3)
S2-Mg-O1	160.0(1)	Mg-S1-C1	85.8(1)	C2-N2-C9	122.7(4)		
$Mg(S_2CN^iPr_2)_2(THF)$, **2**							
Mg-S1	2.496(2)	Mg-O1	2.039(4)	S4-C2	1.701(5)	N2-C2	1.326(5)
Mg-S2	2.466(2)	S1-C1	1.719(4)	N1-C1	1.326(6)	N2-C9	1.470(7)
Mg-S3	2.495(2)	S2-C1	1.727(5)	N1-C3	1.479(6)	N2-C12	1.470(7)
Mg-S4	2.488(2)	S3-C2	1.721(4)	N1-C6	1.483(6)		
S1-Mg-S2	72.3(1)	S3-Mg-S4	71.6(1)	C1-N1-C3	124.3(4)	S1-C1-S2	123.3(3)
S1-Mg-S3	104.6(1)	S3-Mg-O1	102.7(1)	C1-N1-C6	121.1(4)	S2-C1-N1	120.4(3)
S1-Mg-S4	156.4(1)	S4-Mg-O1	103.5(1)	C3-N1-C6	114.6(4)	S3-C2-S4	116.7(3)
S1-Mg-O1	100.1(1)	Mg-S1-C1	85.0(2)	C2-N2-C9	123.9(4)	S3-C2-N2	120.9(3)
S2-Mg-S3	154.4(1)	Mg-S2-C1	85.7(2)	C2-N2-C12	122.1(4)	S4-C2-N2	122.4(3)
S2-Mg-S4	100.8(1)	Mg-S3-C2	85.4(2)	C9-N2-C12	114.0(4)		
S2-Mg-O1	102.8(1)	Mg-S4-C2	86.0(2)	S1-C1-N1	116.4(3)		
$BrMg(S_2C^iPr)(THF)_3$, **5**							
Mg-Br	2.547(3)	Mg-S2	2.596(3)	Mg-O2	2.076(5)	S1-C1	1.679(8)
Mg-S1	2.656(3)	Mg-O1	2.124(5)	Mg-O3	2.124(5)	S2-C1	1.667(8)
Br-Mg-S1	167.4(1)	S1-Mg-S2	67.6(1)	S2-Mg-O2	160.8(2)	Mg-S1-C1	84.2(3)
Br-Mg-S2	99.8(1)	S1-Mg-O1	88.8(2)	S2-Mg-O3	91.2(2)	Mg-S2-C1	86.4(3)
Br-Mg-O1	91.7(2)	S1-Mg-O2	93.4(2)	O1-Mg-O2	86.1(2)	S1-C1-S2	121.8(4)
Br-Mg-O2	99.2(2)	S1-Mg-O3	88.5(2)	O1-Mg-O3	171.0(2)	S1-C1-C2	119.0(6)
Br-Mg-O3	92.8(2)	S2-Mg-O1	95.7(2)	O2-Mg-O3	85.5(2)	S2-C1-C2	119.2(6)
$BrMg(S_2CPh)(THF)_3$, **6**							
Mg-Br	2.550(2)	Mg-S2	2.574(3)	Mg-O2	2.065(4)	S1-C1	1.673(6)
Mg-S1	2.708(3)	Mg-O1	2.111(4)	Mg-O3	2.099(4)	S2-C1	1.683(6)
C1-C2	1.495(8)						
Br-Mg-S1	164.5(1)	S1-Mg-S2	66.8(1)	S2-Mg-O2	162.0(2)	Mg-S1-C1	84.3(2)
Br-Mg-S2	97.7(1)	S1-Mg-O1	88.1(1)	S2-Mg-O3	93.8(1)	Mg-S2-C1	88.5(2)
Br-Mg-O1	92.1(1)	S1-Mg-O2	95.2(1)	O1-Mg-O2	85.1(2)	S1-C1-S2	120.4(4)
Br-Mg-O2	100.2(1)	S1-Mg-O3	87.7(1)	O1-Mg-O3	169.9(2)	S1-C1-C2	120.0(4)
Br-Mg-O3	94.5(1)	S2-Mg-O1	92.9(1)	O2-Mg-O3	86.2(2)	S2-C1-C2	119.6(5)

major product of $C_6H_5C_6H_5$ and the minor product of $C_6H_5C(O)C_6H_5$. The biphenyl was characterized with ^{1}H, ^{13}C NMR, IR spectroscopy, and elemental analyses; the mixed products were separated and identified by GC/MS. It indicates that the cleavage of the C-Ph bonds is expected.

EXPERIMENTAL SECTION

All experiments were carried out in an N_2-flushed glovebag, in a drybox, or in vacuum using schlenk tube techniques. All solvents were distilled and degassed prior to use.

Table 2. Crystal and Intensity Collection Data for Compounds **1, 2, 5, 6**

Formula	$C_{18}H_{36}N_2O_2S_4Mg$	$C_{18}H_{36}N_2OS_4Mg$	$C_{16}H_{31}O_3S_2MgBr$	$C_{19}H_{29}O_3S_2MgBr$
Fw	465.03	449.04	439.74	473.76
Space group	Monoclinic *P*2$_1$/c	Monoclinic *P*2$_1$/c	Orthorthombic *P bca*	Monoclinic *P*2$_1$/c
a, Å	11.3406(16)	14.173(3)	14.7260(20)	11.991(3)
b, Å	9.0380(14)	12.034(3)	16.591(4)	15.229(3)
c, Å	25.186(3)	14.745(3)	18.048(4)	13.196(3)
α, deg				
β, deg	93.067(15)	97.793(22)		107.264(22)
γ, deg				
V, Å^3	2577.7(6)	2491.7(10)	4409.4(16)	2301.1(9)
Z	4	4	8	4
F(000)	1002	970	1840	984
D_{calc}, g/cm^3	1.198	1.197	1.325	1.368
μ, cm^{-1}	3.914	4	20.5	19.828
2θ(max), deg	50	50	45	50
Crystal size, mm	0.50 × 0.50 × 0.40	0.50 × 0.50 × 0.40	0.65 × 0.50 × 0.45	0.70 × 0.50 × 0.35
No. of meas. rflns	4527	4382	2897	4058
No. of unique. rflns	4527	4382	2897	4058
No. of obs. rflns [I>2ó(I)]	2637	2315	1201	1954
R_f, R^w	0.050; 0.049	0.045; 0.045	0.040; 0.039	0.048; 0.047
GOF	2.31	1.18	1.49	1.86
T, °C	22	22	22	22

All ^1H, ^{13}C NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts are referenced to either TMS(^1H) or C_6D_6 {^1H, δ 7.15; ^{13}C, δ 128.00}. Mass spectral data were obtained on a VG-7025S GC/MS/MS spectrometer; IR spectra were obtained as nujol mulls between KBr disks on a Bio-Rad FT-40 FT-IR spectrometer. Elemental analyses were performed at the Analysche Laboratories of H. Malissa and G. Reuter GmbH, Germany. Deviations in the results from calculated values are attributed to the extremely air-sensitive and hygroscopic nature of these compounds. The starting materials $Mg(NR_2)_2$ (R = Et, ^iPr), MgR'_2 (R′= Et, Ph) and R″MgBr (R″= ^iPr, Ph) were prepared according to previous reports.[13,14,22]

Synthesis of $Mg(S_2CNR_2)_2(THF)_n$, (R = Et, 1 or ^{i}Pr, 2)

A solution of carbon disulfide (2.04 mL, 27 mmol) in tetrahydrofuran (10 mL) was added dropwise to a two neck round bottomed flask containing a tetrahydrofuran solution (80 mL) of $Mg(NR_2)_2$ (27 mmol) under nitrogen atmosphere. The clear solution changed to yellow immediately; the reaction mixture was stirred till the solution turned to a deep red brown color. After removal of solvent, then the deep red powder was recrystallized with a mixed solution of tetrahydrofuran and ether to obtain the colorless crystal.

$Mg(S_2CNEt_2)_2(THF)_2$, 1: $mp_{(dec)}$ > 134 °C; yield: 40%; NMR (C_6D_6): ^1H, δ 1.04 (t, $CH_2\underline{CH_3}$), 1.35 (m, 3, 4-thf-H), 3.71 (q, $\underline{CH_2}CH_3$), 3.83 (m, 2, 5-thf-H); ^{13}C, δ 12.77 ($CH\underline{C}H_3$), 25.98 (3, 4-thf-C), 48.93 ($\underline{C}H_2CH_3$), 69.09 (2, 5-thf-C), 207.00 ($\underline{C}S_2$). Mass spectrum (30 eV, the eight most intense peaks): *m/z* 58, 72, 116, 88, 172, 149, 320, 259.

$Mg(S_2CN^iPr_2)_2(THF)$, 2: mp 122.5-125.5 °C; yield: 40%; NMR (C_6D_6): ^1H, δ 1.01 [d, $CH(C\underline{H_3})_2$], 1.35 (br, 3, 4-thf-H), 2.77 [sep, $C\underline{H}(CH_3)_2$], 3.71 (br, 2, 5-thf-H); ^{13}C, δ 23.58 [$CH(\underline{C}H_3)_2$], 26.03 (2, 5-thf-C), 46.01 [$\underline{C}H(CH_3)_2$], 68.64 (2, 5-thf-C), 206.84 ($\underline{C}S_2$). Mass spectrum (electron spray, 3000v-4000v, the eight most intense peaks): *m/z* 30, 43, 73, 102, 178, 235, 279, 380. IR (Nujol): 2925s, 2855s, 1462s, 1377s, 1307m, 1148m, 1074w, 1039w, 847w. Anal. Calcd: C, 48.88; H, 8.03. Found: C, 49.95; H, 8.29.

Synthesis of $Mg(S_2CR)_2(THF)_2$, (R= Et, 3 or Ph, 4)

A solution of carbon disulfide (1.85 mL, 24 mmol) in tetrahydrofuran (10 mL) was added dropwise via a funnel to a two neck round-bottomed flask containing a tetrahydrofuran solution (50 mL) of MgR_2 (24 mmol) under nitrogen atmosphere; the reaction took place while releasing heat immediately and was stirred till the solution turned to a red brown color. After removal of solvent, the impuries were washed with diethylether, then it was recrystallized with a mixed solvent of tetrahydrofuran and n-hexane; a light yellow solid was obtained.

$Mg(S_2CEt)_2(THF)_2$, 3: $mp_{(dec)}$ > 169 °C; yield: 56%;

NMR ($\mathrm{C_6D_6}$): ^{1}H, δ 1.31 (br, 3, 4-thf-H), 1.48 (t, $\mathrm{CH_2C\underline{H}_3}$), 3.32 (q, $\mathrm{C\underline{H}_2CH_3}$), 3.69 (br, 2, 5-thf-H); ^{13}C, δ 16.58 ($\mathrm{CH_2\underline{C}H_3}$), 25.82 (3, 4-thf-C), 51.02 ($\mathrm{\underline{C}H_2CH_3}$), 69.13 (2, 5-thf-C), 268.52 ($\mathrm{\underline{C}S_2}$). Mass spectrum (30 eV, the eight most intense peaks): *m/z* 42, 76, 73, 176, 57, 111, 106, 144. IR (Nujol): 2927s, 2870s, 1460s, 1344s, 1141m, 1092w, 1031m, 963w, 935m, 723w. Anal. Calcd: C, 44.44; H, 6.87; S, 33.86. Found: C, 43.54; H, 6.46; S, 33.17.

Mg(S$_2$CPh)$_2$(THF)$_2$, 4: mp 135-138 °C; yield: 49%; NMR ($\mathrm{C_6D_6}$): ^{1}H, δ 1.22 (br, 3, 4-thf-H), 3.77 (br, 2, 5-thf-H), 7.10 (m, $\mathrm{C_6H_5}$: *p*, *m*-H), 8.97 (d, $\mathrm{C_6H_5}$: *o*-H); ^{13}C, δ 25.37 (3, 4-thf-C), 69.42 (2, 5-thf-C), 127.58 ($\mathrm{C_6H_5}$: *m*-C), 127.77 ($\mathrm{C_6H_5}$: *p*-C), 132.28 ($\mathrm{C_6H_5}$: *o*-C), 146.89 ($\mathrm{C_6H_5}$: *m*-C), 250.74 ($\mathrm{\underline{C}S_2}$). Mass spectrum (30 eV, the eight most intense peaks): *m/z* 121, 77, 154, 11, 210, 178, 332, 255. IR (Nujol): 2960s, 2800s, 1456s, 1375s, 1214m, 1173m, 1018s, 990s, 918m, 763m.

Synthesis of BrMg(S$_2$CR)(THF)$_3$, (R=^{i}Pr, 5 or Ph, 6)

A solution of carbon disulfide (3.04 mL, 41 mmol) in tetrahydrofuran (10 mL) was added dropwise to a two neck round bottomed flask containing a tetrahydrofuran solution (80 mL) of RMgBr (41 mmol) under nitrogen atmosphere; the gray solution changed to yellow while releasing heat. The reaction mixture was stirred for 8 h till the solution turned to a deep red brown color. Then the precipitate was decanted by centrifugation, the solution was pumped to dryness, and the colloid was recrystallized with tetrahydrofuran to obtain the colorless crystals.

BrMg(S$_2$C^{i}Pr)(THF)$_3$, 5: mp 49-52 °C; yield: 45%; NMR ($\mathrm{C_6D_6}$): ^{1}H, δ 1.43 (br, 3, 4-thf-H) 1.45 (t, $\mathrm{CHC\underline{H}_3}$), 3.73 [br, $\mathrm{C\underline{H}(CH_3)_2}$], 3.87 (t, 2, 5-thf-H); ^{13}C, δ 25.27 [$\mathrm{CH(\underline{C}H_3)_2}$], 26.78 (3, 4-thf-C), 54.43 [$\mathrm{\underline{C}H(CH_3)_2}$], 69.87 (2, 5-thf-C), 273.67 ($\mathrm{\underline{C}S_2}$). IR (Nujol): 2961s, 2847s, 1462, 1377m, 1242w, 1178w, 1150m, 1031m, 961m.

BrMg(S$_2$CC$_6$H$_5$)(THF)$_3$, 6: mp 65-67 °C; yield: 60%; NMR ($\mathrm{C_6D_6}$): ^{1}H, δ 1.33 (br, 3, 4-thf-H), 3.84 (br, 2, 5-thf-H), 7.11 (m, $\mathrm{C_6H_6}$: *p*, *m*-H), 8.96 (t, $\mathrm{C_6H_5}$: *o*-H); ^{13}C; 25.65 (3, 4-thf-C), 69.72 (2, 5-thf-C), 127.87 ($\mathrm{\underline{C_6}H_5}$), 132.00 ($\mathrm{\underline{C_6}H_5}$), 132.57 ($\mathrm{\underline{C_6}H_5}$), 147.15 ($\mathrm{C_6H_5}$, *ispo*-C), 250.95 ($\mathrm{\underline{C}S_2}$). IR (Nujol): 2921s, 2859s, 2724w, 1459s, 1347s, 1297m, 1165m, 1073m, 1018m, 910w, 717s. Anal. Calcd: C, 48.18; H, 6.12. Found: C, 47.72; H, 6.05.

Structure Determination

Suitable single crystals of compounds **1, 2, 5, 6** 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 ($\lambda = 0.71073$ Å). Intensity data were collected using the θ-2θ scan mode for $2\theta < 45°$ and were corrected for absorption and decay. Both structures were solved by MULTAN and refined by full-matrix least-squares analyses on F with $\omega = 1.0[\sigma^2(F_0) + 0.000lF^2]$. Scattering factors for the neutral atoms and anomalous scattering coefficients for non-hydrogen atoms were taken from the literature.[24] All calculations were carried out with a Micro Vax 3600 computer using the NRC VAX program package.[25] Selected bond distances and angles are listed in Table 1. A summary of the data collected in the crystal structures is given in Table 2.

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