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Synthesis and structure of bis(thiomethyl)magnesium compounds $[Mg(CH_2SR)_2(thf)_3]$ (R = Me, Ph) - the first dimethylmagnesium compounds functionalized by a Lewis-basic heteroatom

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Abstract—Hg(CH₂SR)₂, (R = Me (1), R = Ph (2)), prepared by reaction of HgCl₂ with [Li₂(CH₂SR)₂(tmeda)₂], reacts with magnesium activated by mercury in boiling THF to give [Mg(CH₂SR)₂(thf)₃] (R = Me (3), R = Ph (4)). 3 readily splitts off THF in vacuo to give the solvate free complex [Mg(CH₂SMe)₂] (3'). The complexes 3' and 4 are fully characterized by microanalysis and NMR spectroscopy (¹H, ¹³C).

The X-ray structure analyses of **3** and **4** reveal mononuclear compounds with two symmetry independent molecules in the unit cell of **3**. In both complexes the coordination of Mg is trigonal–bipyramidal. The two apical positions are occupied by THF and the three equatorial positions by one THF and the two thiomethyl ligands. The C–Mg–C angles are slightly greater $(123.9(1)-131.0(2)^\circ)$ than the ideal angle for equatorial atoms in a trigonal–bipyramidal coordination. In neither case, the sulfur atoms are involved in the coordination of Mg. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: thiomethyl magnesium compounds; functionalized methyl magnesium compounds; mercurymagnesium transmetallation; crystal structures.

INTRODUCTION

The very low thermal stability ($T_{dec.} < -100^{\circ}$ C) and the carbenoid reactivity of Köbrich's (halogeno)methyl lithium compounds [1] had exhibited, that a Lewis-basic heteroatom may strongly influence the reactivity and stability of functionalized methyl lithium compounds. Since then, the influence of Lewisbasic heteroatoms Y on structure, reactivity and stability of organolithium complexes of the type LiCH₂ YR_n (A) (YR_n=NR₂, PR₂, OR, SR, Cl, ...) has been investigated thoroughly [2, 3]. X-ray structure investigations reveal a wide variety of solid state structures exhibiting a coordination Y \rightarrow Li in most cases [4]. The THF adducts, [Li(CH₂YR_n)(thf)_x] are polymeric (YR_n = SMe [5], PPh₂ [6]), tetrameric (YR_n = NC₅H₁₀ [7], NMe₂ [8]) or dimeric with a four-membered Li₂C₂ ring $(YR_n = SPh [5], NPh_2 [7])$. Monomeric compounds are not known at all.

Compared to the numerous lithium compounds **A**, there are far fewer examples of functionalized methyl Grignard compounds Mg(CH₂YR_n)X (**B**) with Lewisbasic heteroatoms Y (YR_n = OR, SR, X) [2, 9, 10]. To date, there have been no reports of functionalized dimethyl magnesium compounds Mg(CH₂YR_n)₂ (**C**). Although a lot of structures of organomagnesium compounds had been described [11], those of type **B** and **C** are not known at all.

We report here the synthesis of thiomethyl magnesium compounds $[Mg(CH_2SR)_2(thf)_3]$ (R = Me (3), R = Ph (4)) and their solid state structures being the first compounds of type C.

RESULTS AND DISCUSSION

The thiomethyl mercury complexes $Hg(CH_2SR)_2$ (R = Me (1), R = Ph (2)) were prepared by the reac-

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tion of $HgCl_2$ with $[Li_2(CH_2SR)_2(tmeda)_2]$ in THF, cf. Equation (1). The identities of **1** and **2** were confirmed by microanalysis and NMR spectroscopy (¹H and ¹³C). In the case of the complex **2** these values agree with the data given in the literature [12].

The organomercury compounds 1 and 2 undergo with magnesium in boiling THF a transmetallation reaction yielding the bis(thiomethyl)magnesium complexes [Mg(CH₂SR)₂(thf)₃] (R = Me (3), R = Ph (4)) that precipitate from the concentrated solutions at -40° C as well shaped colorless crystals, eq. (1).

$$HgCl_{2} \xrightarrow{[Li_{2}(CH_{2}SR)_{2}(tmeda)_{2}]} Hg(CH_{2}SR)_{2}$$

$$\xrightarrow{R \mid Me \ Ph} \\ \xrightarrow{+ Mg} [Mg(CH_{2}SR)_{2}(thf)_{3}] \\ \xrightarrow{R \mid Me \ Ph} \\ \xrightarrow{R \mid Me \ Ph}$$

There is an induction period of several hours. Activating the magnesium with one drop of mercury, the reactions take not more than three hours (degree of conversion >90%). The transmetallation of **2** with magnesium was proved to proceed also in boiling toluene and xylene with mercury activated magnesium (degree of conversion >80%). Within eight hours no reaction was observed in boiling ether, not even with magnesium activated by mercury.

For Hg–Mg transmetallation reactions, a wide range of reactivity was described in the literature: Me₂Hg was found to react with magnesium immediately in a strong exothermic reaction [13]. On the other hand, transmetallation reactions of aryl mercury compounds take up to two weeks in THF at room temperature [14]. An activation of the Hg–Mg transmetallation with HgCl₂ was observed [15], but the isolation of R₂Mg in a pure state might be difficult due to the Schlenk equilibrium. The thiomethyl magnesium complexes 3 and 4 are very sensitive against air and moisture. The (methylthio)methyl complex 3 loses the coordinated THF very easily in vacuo to give the solvate free complex $[Mg(CH_2SMe)_2]$ (3'). 3 and 4 are well soluble in THF and ether and insoluble in aromatic and aliphatic hydrocarbons. The identities of 3' and 4 were confirmed by microanalysis and NMR spectroscopy (¹H and ¹³C).

Table 1 shows the resonances of the methylene group in **3**, **4** and in related lithium complexes. Compared with their lithium analogues, the ¹H resonances of **3** and **4** are shifted downfield because of the magnesium is less electropositive. The difference $\Delta\delta(^{1}\text{H}) = 0.20 \text{ ppm}$ between **3** and **4** should be caused by the electronic effect of the phenyl substituent. As in the (phenylthio)methyl lithium compounds, there is an unusual high field shift of the methylene carbon in **4**. The coupling constants $^{1}J(^{13}\text{C},^{1}\text{H})$ for the CH₂ groups of all compounds in Table 1 are in the expected range exhibiting no unusual bonding relationships.

Structures of $[Mg(CH_2SMe)_2(thf)_3]$ (3) and $[Mg(CH_2SPh)_2(thf)_3]$ (4)

The molecular structures of complexes **3** and **4** along with the atom numbering schemes are shown in Figs 1 and 2. Selected bond lengths and angles are listed in Table 2.

The two structures consist of monomeric molecules without any unusal intermolecular interactions. The unit cell of complex **3** contains two symmetry independent molecules (**3** and **3a**); one of them (**3a**) exhibits a crystallographically imposed C_2 symmetry. Related bond lengths of **3** and **3a** differ less than 1% while related bond angles show noteable differences (up to 5–6%).

Both in 3 and in 4, the magnesium displays a distorted trigonal-bipyramidal coordination. As usual for trigonal-bipyramidal structures [18], the more electronegative ligands (THF) occupy the apical positions. These Mg–O bonds are longer than that to the

Table 1. ¹H and ¹³C NMR resonances (in ppm) and ¹J(¹³C, ¹H) coupling constants (in Hz) of the methylene group in thiomethyl magnesium and lithium complexes

Compound ^a	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\text{C})$	${}^{1}J({}^{13}C, {}^{1}H)$	Ref.
$[Mg(CH_2SMe)_2(thf)_3] (3)$	0.66	12.9	121.3	b
$[Mg(CH_2SPh)_2(thf)_3]$ (4)	0.86	4.9	121.7	b
[Li ₂ (CH ₂ SMe) ₂ (tmeda) ₂]	0.38	15.3	116.4	с
[Li ₂ (CH ₂ SPh) ₂ (tmeda) ₂]	0.36	4.1	121.0	с
[{Li(CH ₂ SMe)(thf)} _m]	0.36	14.8	116.0	[5]
$[Li_2(CH_2SPh)_2(thf)_4]$	0.31	3.8	121.0	[5]

^aFormulae refer to aggregation in solid state.

^bThis work.

^cOwn measurements, prepared according to the literature [16, 17].

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Fig. 1. Molecular structure and numbering scheme of the two crystallographically independent molecules **3** (above) and **3a** (below). To make the correspondence between them clear, the atoms are numbered in the same way, but 'a' was added to independent atoms of **3a**; ''' refers to symmetry related atoms of **3a**. Ellipsoids are drawn at 50% probability.

Hydrogen atoms are omitted for clarity.

equatorially bonded THF molecule $(d(Mg-O_{ap}) = 2.140(4)-2.236(4) \text{ Å}$ vs. $d(Mg-O_{eq}) = 2.087(4)-2.107(2) \text{ Å}$.

The distortions of the coordination polyhedron around Mg are relatively small: The angles O_{ap} -Mg– O_{ap} are between 163.40(8)° and 169.6(1)° and the sum of angles in the equatorial planes is between 359.6(4)° and 360.0(2)°. The less electronegative organo ligands are more space-demanding as can be seen at the widening of the C–Mg–C angles (123.9(1)–131.0(2)°) and at the lowering of the O_{ap} -Mg– O_{eq} angles (81.4(2)– 84.79(6)°).

	3 (R = Me)	$3\mathbf{a} (\mathbf{R} = \mathbf{M}\mathbf{e})^{\mathbf{a}}$	$4\left(R=Ph\right)$
Mg1–C1	2.178(3)	2.196(3)	2.168(6)
Mg1–C2	2.191(3)		2.195(6)
C1-S1	1.757(3)	1.775(3)	1.777(6)
C2-S2	1.770(3)		1.767(6)
S1-C15	1.803(4)	1.811(3)	1.766(5)
S2-C16	1.811(4)		1.773(6)
Mg1–O1	2.095(2)	2.107(2)	2.087(4)
Mg1–O2	2.178(2)	2.189(2)	2.236(4)
Mg1–O3	2.185(2)		2.140(4)
Cl-Mgl-C2	123.9(1)	131.0(2) ^b	128.4(3)
Cl-Mgl-Ol	118.1(1)	114.49(7)	110.8(2)
C2–Mg1–O1	118.0(1)		120.4(2)
C1–Mg1–O2	94.7(1)	91.62(9)	90.6(2)
C2–Mg1–O3	95.1(1)		93.9(2)
C1–Mg1–O3	92.3(1)	92.69(9)°	97.2(2)
C2–Mg1–O2	93.5(1)		91.1(2)
O1–Mg1–O2	81.59(7)	84.79(6)	81.4(2)
O1–Mg1–O3	81.83(7)		84.2(2)
O2–Mg1–O3	163.40(8)	$169.6(1)^{d}$	165.2(2)
Mg1–C1–S1	115.1(2)	111.7(1)	113.9(3)
Mg1–C2–S2	112.0(1)		114.6(3)
C1-S1-C15	106.4(2)	107.0(2)	108.4(3)
C2-S2-C16	107.7(2)		108.9(3)

Table 2. Selected bond lengths (in Å) and angles (in °) for [Mg(CH₂SR)₂(thf)₃]

^aSymmetry transformations used to generate equivalent atoms: ': -x, y, -z+1/2.

^bCla–Mgla–Cl′. ^cCla–Mgla–O2′.

^dO2a-Mg1a-O2'.

The Mg–C bond lengths in **3** and **4** (d(Mg–C) = 2.168(6)–2.196(3)Å) are in the range for Mg–C bond lengths of other monomeric five-coordinate dialkylmagnesium compounds such as [MgR₂ (pmdta)] [19] (R = Me, Et; pmdta = N, N, N', N'', pentamethyldiethylenetriamine) (d(Mg–C) = 2.158(5)–2.223(9)Å).

The CH₂–S distances (d(C-S) = 1.757(3)-1.777(6)Å) are substantially shorter than the S–CH₃ distances in **3** (d(C-S) = 1.803(4)-1.811(4)Å). They are in the same range as the S–C_{Ph} distances in **4** (d(C-S) = 1.766(5) and 1.773(6)Å) in spite of the smaller covalent radii of sp² hybridized carbons in comparison with sp³ hybridized ones [18]. This indicates a stabilizing influence on the carbanionoid centre of sulfur by polarization.

The complexes **3** and **4** are the first functionalized dimethylmagnesium complexes $Mg(CH_2YR_n)_2$ with a Lewis-basic heteroatomic centre Y. Unexpectedly, the sulfur is not involved in the coordination sphere of magnesium. Furthermore, for the first time a trigonal-bipyramidal coordination around magnesium was found with monodentate coligands L ([MgR_2L_3]). To date, monomeric five-coordinate diorganomagnesium compounds were observed only with tridentate co-



Fig. 2. Molecular structure and numbering scheme of complex **4**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

ligands ([MgR₂L₃]; R=alkyl, aryl; L₃=pmdta, diglyme, tetraglyme) [19, 20]. With mono- and oligodentate coligands, tetrahedral complexes [MgR₂L₂] (R = alkyl, aryl; L = THF, quinuclidine; L₂ = TMEDA) [19, 21–26] and octahedral complexes [MgR₂L₄] (R = alkyl, alkynyl; L₂ = TMEDA, L₄ = crown ether) [20, 27–29] are formed.

EXPERIMENTAL

General comments

All reactions and manipulations were carried out under purified argon using standard Schlenk techniques. *n*-Hexane, *n*-pentane, TMEDA and THF-d₈ were dried with LiAlH₄. Toluene, xylene, THF and diethyl ether were distilled from sodium benzophenone ketyl. NMR spectra were recorded on Varian Unity 500 spectrometer using the protio impurities and ¹³C resonances of the deuterated solvents as references for ¹H and ¹³C NMR spectroscopy, respectively. Microanalyses (C, H, S) were obtained from the microanalytical laboratory of the Department of Chemistry. A CP9000 (Chrompack) was used for gaschromatographic analyses. [Li₂(CH₂SR)₂(tmeda)₂] (R = Me, Ph) was prepared according to the literature [16, 17].

Synthesis of $Hg(CH_2SR)_2$ (R = Me(I), R = Ph(2))

To a solution of HgCl₂ (6.5 g, 24 mmol) in THF (50 ml), $[Li_2(CH_2SR)_2(tmeda)_2]$ (R = Me, Ph) (48 mmol) in THF (50 ml) was added dropwise at

-78°C. After stirring for 1 h and warming up to r.t. water (100 ml) was added. The half of the solvent was removed in vacuo and the colorless precipitate formed was filtered off, washed with water and cold methanol and dried in vacuo. Yields: **1** (5.6 g, 75%); **2** (9.7 g, 90%).

Anal. Calcd for 1: C, 14.88; H, 3.12; S, 19.86. Found: C, 15.24; H, 3.20; S, 18.74. ¹H NMR (500 MHz, THF- d_8): δ 2.27 (s, 4H. ${}^{2}J({}^{199}\text{Hg},{}^{1}\text{H}) = 104.0 \text{ Hz}, \text{C}H_{2}), 2.15 \text{ (s, 6H, C}H_{3}\text{)}. {}^{13}\text{C}$ NMR (125 MHz, THF-d₈): δ 43.1 (s+d, ${}^{1}J({}^{199}\text{Hg}, {}^{13}\text{C}) = 820.1 \text{ Hz},$ CH₂), 22.8 (s+d, ${}^{3}J({}^{199}\text{Hg}, {}^{13}\text{C}) = 137.0 \text{ Hz}, CH_{3}).$

Anal. Calcd for **2**: C, 37.62; H, 3.16; S, 14.35. Found: C, 38.13; H, 3.22; S, 14.08. ¹H NMR (500 MHz, THF-d₈): δ 2.60 (s, 4H, ²*J*(¹⁹⁹Hg, ¹H) = 107.3 Hz, C*H*₂), 7.06–7.46 (m, 10H, *Ph*). ¹³C NMR (125 MHz, THF-d₈): δ 39.2 (s+d, ¹*J*(¹⁹⁹Hg, ¹³C) = 855.4 Hz, CH₂), 124.9 (*p*-C), 125.9 (*o*-C), 128.3 (*m*-C), 142.0 (*i*-C).

Synthesis of $[Mg(CH_2SR)_2(thf)_3]$ (R = Me (3), R = Ph (4))

A mixture of Hg(CH₂SR)₂ (R = Me (1), R = Ph (2)) (3.4 mmol), powdered magnesium (0.75 g, 31 mmol) and mercury (about 0.1 g, 0.5 mmol) in THF (10 ml) was refluxed under vigorous stirring for about 3 h. The amalgam formed was filtered off and the solution was concentrated in vacuo up to about 5 ml. At -40° C, 3 and 4 precipitated in well shaped crystals which were filtered off, washed with hexane and dried in vacuo. Yield: 3' (0.3 g, 60%); 4 (1.1 g, 65%). To

	3	4
Empirical formula	$C_{16}H_{34}MgO_{3}S_{2}$	$C_{26}H_{38}MgO_3S_2$
tw	362.88	487.02
Crystal system/space group	orthorhombic/P b c n	triclinic/P1
a, b, c (Å)	10.387(2), 17.213(3), 35.355(8)	9.563(2), 12.344(3), 12.800(4)
α, β, γ (deg)	90, 90, 90	115.08(2), 98.38(4), 91.36(3)
$V(Å^3)$	6321(2)	1347.7(6)
Z	12	2
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.144	1.200
μ (MoK α) (mm ⁻¹)	0.291	0.245
<i>F</i> (000)	2376	524
Scan range (deg)	$2.27 < \theta < 24.06$	$1.78 < \theta < 22.50$
Index ranges	$-11 \leqslant h \leqslant 11, -18 \leqslant k \leqslant 19,$	$-10 \leqslant h \leqslant 10, -13 \leqslant k \leqslant 13,$
	$-40 \leq l \leq 40$	$-13 \leq l \leq 13$
Reflections collected	25569	5990
Independent reflections	$4895 (R_{int} = 0.1044)$	$3526 (R_{int} = 0.1156)$
Observed reflections $[I > 2 \sigma(I)]$	3837	1725
Parameters refined	479	441
Goodness-of-fit on F^2	1.088	1.014
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0512, wR2 = 0.1210^{a}$	$R1 = 0.0583, wR2 = 0.0748^{b}$
R indices (all data)	$R1 = 0.0669 \ wR2 = 0.1300^{a}$	$R1 = 0.1639 \ wR2 = 0.0998^{b}$
Largest diff. peak and hole (e Å ⁻³)	0.325 and -0.168	0.303 and -0.281

Table 3. Crystal data and structure refinement for 3 and 4

^a $w = 1/[(\sigma^2/F_o^2) + (0.0723P)^2 + 1.9927P]; P = (F_o^2 + 2F_c^2)/3.$ ^b $w = 1/[(\sigma^2/F_o^2).$

determine the degree of conversion, in separate experiments MeOH/THF (1/4; 0.5 ml) was added dropwise at -78° C to the reaction mixture. The yield of MeSR was determined by gaschromatography using naph-thalene as internal standard. Degree of conversion: **3** (THF, 93%), **4** (THF, 97%; toluene, 83%; xylene, 93%).

Anal. Calcd for **3**': C, 32.78; H, 6.88. Found: C, 33.20; H, 6,82. ¹H NMR (500 MHz, THF-d₈): δ 0.66 (s, 4H, CH₂), 1.89 (s, 6H, CH₃). ¹³C NMR (125 MHz, THF-d₈): δ 12.9 (CH₃), 27.2 (CH₃).

Anal. Calcd for 4: C, 64.12; H, 7.86. Found: C, 63.38; H, 7.02. ¹H NMR (500 MHz, THF-d₈): δ 0.86 (s, 4H, CH₂), 6.79–6.91 (m, 2H, *p*-H), 7.05–7.08 (m, 4H, *m*-H), 7.22–7.24 (m, 4H, *o*-H). ¹³C NMR (125 MHz, THF-d₈): δ 4.9 (CH₂), 122.4 (*p*-C), 128.3 (*m*-C), 124.1 (*o*-C), 151.8 (*i*-C). (Due to partial hydrolysis a small amount ot MeSPh was detected in the spectra.)

X-ray structure determinations of 3 and 4

Suitable single crystals of **3** ($0.4 \times 0.3 \times 0.3$ mm) and **4** ($0.8 \times 0.2 \times 0.1$ mm) were obtained from pentane/ THF solution at -40° C. X-ray measurements were performed on a Stoe IPDS (**3**) and on a Stoe STADI 4 diffractometer (**4**), respectively, with Mo_{Ka} radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS86 [30]) and refined using fullmatrix least-squares procedures on F^2 (SHELXL93 [31]). Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were found in the Fourier list and refined isotropically, except of some in **3**, which were placed in calculated positions. Crystal data, details of data collections, structure solutions and refinements are summarized in Table 3. Complete tables of the atomic coordinates, H-atom parameters, bond distances, bond angles and anisotropic displacement parameters atoms have been deposited with the Editor as supplementary material.

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