DOI: 10.1002/ejic.201000045

Magnesium Diimidosulfinates – Conformational Studies in the Solid State and in Solution

Thomas Schulz,[a] Stephan Deuerlein,[a] and Dietmar Stalke*[a]

Keywords: Sulfur / Imides / Magnesium / Grignard reaction / Structure elucidation

The magnesium diimidosulfinates [$(thf)_2MgX\{(NR)_2SR'\}$] (X = Cl, Br; R = *t*Bu, $SiMe_3$; R′ = Ph, Bz, Me, *n*Bu; **1**–**5**) have been synthesised by treating sulfur diimides with different Grignard reagents and characterized by X-ray crystallography and NMR spectroscopy. The structural analyses of compounds **1**–**5** show that they contain either monomeric or dimeric structural motifs, depending on the steric requirements of the sulfur-bound organic substituent. NMR experiments suggest a temperature-dependent dynamic equilibrium between different conformers for all compounds.

Introduction

Organomagnesium compounds, especially Grignard reagents, have been a rapidly developing field[1] ever since they were discovered by Barbier in 1899[2] and subsequently harnessed by Grignard in 1900.[3] Like their organolithium congeners, they play a central role in both preparative organic and organometallic chemistry.[4]

Sulfur diimido compounds are also widely used in organometallic chemistry[5] and have been intensively studied as their lithium and transition-metal complexes.[6] However, little is known about their reactions with Grignard reagents.[7] Although it was reported as long ago as 1976 that sulfur diimides react readily with Grignard reagents[8] and that this reaction can be used for titrating Grignard solutions, its chemical versatility has not been explored any further. To close this gap, herein we report on the reactivity of a range of sulfur diimides with various Grignard reagents. These reactions proceed smoothly to afford the desired magnesium diimidosulfinates in very good yields with high purity. The resulting reaction products **1**–**5** were analyzed by NMR spectroscopy and single-crystal diffraction experiments. Furthermore, they are valuable precursors for the synthesis of magnesium sulfur ylides in analogy to the lithium sulfur ylides $[(thf)Li_2\{H_2CS(NtBu)_2\}]_2$[9] and $[(TMEDA)_2Li_2H_2CS(NtBu)_3]$[10] previously synthesised in our group.

Sulfur ylides play an important role in organic synthesis[11] as R_2C-transfer reagents for one-step epoxidation, cyclopropanation or aziridination. In a reaction with an additional equivalent of the Grignard reagent, complexes **2**–**5** could be deprotonated at the sulfur-bound carbon C_α-atom to give the related magnesium sulfur ylides, which should be even more selective for C–C coupling reactions than their lithium analogues since their basicity is lower. Furthermore, deprotonation of **2**–**5** with an organolithium base was found to generate heterobimetallic sulfur ylides, which can act as precursors for heterobimetallic complexes known to be useful as catalysts for a variety of chemical reactions.[12] [$(thf)_2MgCl\{(NtBu)(NSiMe_3)SBz\}$] (**4**), which already contains a stereogenic sulfur atom, should prove particularly interesting in this respect as the second centre of symmetry introduced at the benzylic C_α-carbon atom upon deprotonation would make this compound especially useful in stereoselective reactions.

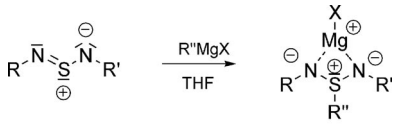
In contrast to the related lithium compounds, which normally form dimers in the solid state,[13] complexes **2**–**5** are monomeric with a fivefold coordinated magnesium atom. Only $[(thf)MgCl\{(NtBu)_2SPh\}]_2$ (**1**) forms a dimer by connecting two monomers through a four-membered Mg_2Cl_2 ring.

Another interesting feature of the magnesium sulfur diimides discussed herein is their behaviour in solution, as monitored by NMR spectroscopic experiments. Thus, compounds **1**–**5** exhibit a multiple set of resonances for the *tert*-butyl protons and those of the organic periphery. This observation was further investigated by various NMR experiments.

Results and Discussion

Complexes **1**–**5** (**1**: R,R′ = *t*Bu, R′′ = Ph, X = Cl; **2**: R,R′ = *t*Bu, R′′ = Methyl, X = Br; **3**: R,R′ = *t*Bu, R′′ = *n*Bu, X = Cl; **4**: R = *t*Bu, R′ = $SiMe_3$, R′′ = Bz, X = Cl; **5**: R,R′ = *t*Bu, R′′ = Bz, X = Cl) were easily prepared in both high yield and purity by adding the appropriate Grignard reagent R′′MgX to a sulfur diimide compound (Scheme 1). Storage of the solutions at –24 °C yielded colourless crystals suitable for X-ray structure analysis.

[a] Institut für Anorganische Chemie, Georg-August Universität Göttingen,
Tammannstr. 4, 37077 Göttingen, Germany
Fax: +49-551-393459
E-mail: dstalke@chemie.uni-goettingen.de



	1	2	3	4	5
R	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu
R'	*t*Bu	*t*Bu	*t*Bu	$SiMe_3$	*t*Bu
R"	Ph	Me	*n*Bu	Bz	Bz
X	Cl	Br	Cl	Cl	Cl

Scheme 1. Preparation of the magnesium sulfur diimides **1**–**5**.

Crystal Structures of 1–5

The metal diimidosulfinates reported to date have mostly crystallized as dimers.[14] Various other structural motifs were found, but the one thing they all had in common was their dimeric aggregation. Indeed, monomers could only be crystallized in the presence of a polydentate donor base such as TMEDA.[15] $[(thf)MgCl\{(N\textit{t}Bu)_2SPh\}]_2$ (**1**) is no exception to this rule of thumb as it crystallizes as a dimer with a central four-membered Mg_2Cl_2 ring (Figure 1).

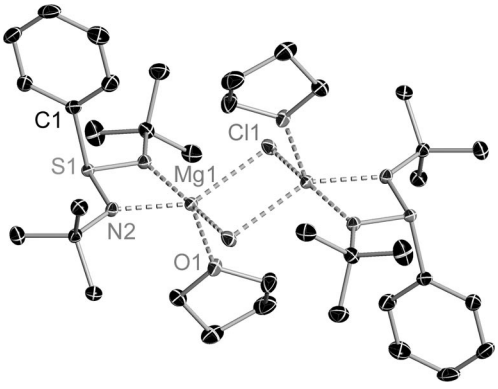


Figure 1. Molecular structure of $[(thf)_2MgCl\{(N\textit{t}Bu)_2SPh\}]$ (**1**). All hydrogen atoms have been omitted for clarity, and anisotropic displacement parameters are depicted at the 50% probability level.

Except for the central Mg_2X_2 ring, **1** exhibits essentially the same bond lengths and angles, within their standard deviation, as its heavier congener $[(thf)MgBr\{(NSiMe_3)_2SPh\}]_2$ (**6**).[7] The geometry of these two compounds is also very similar. The preferred fivefold coordination of the magnesium atom is achieved by two Mg–N contacts to the diimidosulfinate, the interactions with the two chlorine atoms and the coordination of one thf molecule. As a result of this geometry, the chlorine atoms are not positioned at the sterically favourable apex of the square-pyramidal environment of the magnesium atoms but reside in the base. As already observed for other compounds containing a central Mg_2X_2 ring, the Mg–Cl interactions show a distinct asymmetry [Δ(Mg–Cl) = 0.07 Å], which means that the electron density of the halogen anions is not shared equally between the magnesium atoms. Furthermore, the tertiary carbon atoms of the *t*Bu groups are nearly co-planar with the N–S–N plane, which is tilted 37° towards the central Mg_2X_2 ring.

In contrast to **1**, compounds **2**–**5** crystallize as monomers. Although the geometry formed by fivefold coordination at the magnesium is maintained, the structural motif shown by **2**–**5** is therefore totally different (Table 1). Thus, the four-membered Mg_2X_2 ring is not retained and a second thf molecule completes the coordination sphere at the metal ion. The square-pyramidal environment is preserved but with the halogen anion occupying the sterically favourable apex of the pyramid in the monomeric form.

In contrast to **1**, the tertiary carbon atoms of the *t*Bu groups point away from the magnesium atom and the C–N bonds form angles of 31° and 47°, respectively, with the N–S–N plane, thus providing enough space at the other side of this plane for two thf molecules and the organic substituent on the sulfur atom. The deviation of the *t*Bu groups (39.5° and 38.7°) is reasonably symmetric in **2** (Figure 2), whereas all other compounds, especially **3** (Figure 3), exhibit a distinct asymmetry (31.2° and 47.3°), with the larger angle being found on the side where the substituent at the sulfur atom is positioned.

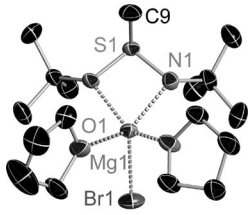


Figure 2. Molecular structure of $[(thf)_2MgBr\{(N\textit{t}Bu)_2SMe\}]$ (**2**). All hydrogen atoms have been omitted for clarity and anisotropic displacement parameters are depicted at the 50% probability level.

Table 1. Selected bond length [Å] and angles [°] for **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
S–N1	1.6089(17)	1.6201(59)	1.6277(12)	1.6285(13)	1.6186(15)
S–N2	1.6160(17)	1.6307(54)	1.6346(11)	1.6218(12)	1.6168(15)
S–C	1.8173(20)	1.8039(58)	1.8145(14)	1.8440(15)	1.8393(17)
N1–Mg	2.0815(17)	2.1263(61)	2.1042(12)	2.1021(14)	2.1118(17)
N2–Mg	2.0558(18)	2.0943(56)	2.1504(12)	2.1697(13)	2.1542(15)
Mg–Cl	2.4160(8)	Mg–Br	2.3474(6)	2.3430(7)	2.3407(7)
	2.4841(8)	2.4960(13)			
Mg–O1	2.0265(15)	2.1166(47)	2.0793(11)	2.1112(12)	2.0909(14)
Mg–O2		2.0736(56)	2.1116(11)	2.0854(12)	2.0866(14)
N–S–N	94.41(8)	99.44(15)	99.62(6)	99.65(7)	100.05(8)

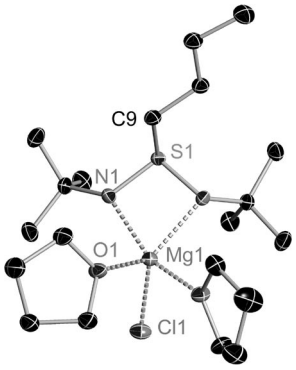


Figure 3. Molecular structure of $[(thf)_2MgCl\{(NtBu)_2SnBu\}]$ (**3**). All hydrogen atoms have been omitted for clarity and anisotropic displacement parameters are depicted at the 50% probability level.

It is clear from the structures of **1** and **5** that neither the nature of the halogen anions nor the organic substituents at the nitrogen atoms have an impact on the geometry. The reason for the formation of a monomer rather than a dimer must therefore be related to the organic substituent bound to the sulfur atom. Thus, the presence of a sterically demanding group at the sulfur atom means that there is not enough room for both this bulky group and an additional thf molecule on the same side of the N–S–N plane, as would be required for potential dimer formation, even if the *t*Bu groups at the nitrogen atoms are pointing to the adjacent side.

Although a phenyl group is generally not considered to be sterically particularly demanding, its bulk is sufficient to bring the *ortho* carbon atom in close proximity to the magnesium atom, thus restricting the space available for both thf donor molecules. In contrast, the methyl group of **2** is less sterically demanding and the substituents of **3**–**5** all contain CH_2 spacers, thus meaning that they are able to bend the remaining organic substituent away and leave enough room for the thf molecules.

Since the thf oxygen atom is a better donor to magnesium than a halogen anion bridging two metal ions, the monomeric form is favoured for **2**–**5** and the Mg–N and Mg–O contacts are longer in **2**–**5** than in **1**. Only the Mg–X bond is shorter in **2**–**5** than in **1** as the halogen anion is not forced to share its electron density between two metal ions.

The structural differences between the monomeric compounds **2**–**5** are minimal (Figure 4), and even the asymmetric diimidosulfinate **4** (Figure 5) exhibits nearly the same bond lengths and angles as its symmetric congener **5**. Only the S–C bonds of **4** and **5** (1.84 Å) are clearly longer than those in **1**–**3** or other organyl diimidosulfinates (1.80 Å on average).[6] The phenyl substituents at the benzylic carbon atoms withdraw electron density from the S–C bonds, which are therefore destabilized and elongated. Although **4** possesses a stereogenic sulfur atom, it crystallizes as a racemate in the centrosymmetric space group $P2_1/c$. In addition, the *t*Bu groups and the $SiMe_3$ groups are disordered, thus making assignment of the isomers impossible.

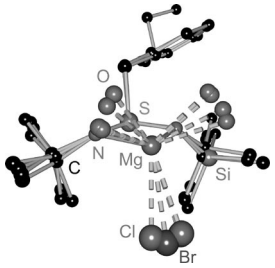


Figure 4. Molecular structure overlay of **2**–**5**. All hydrogen atoms and the carbon atoms of the thf molecules have been omitted for clarity.

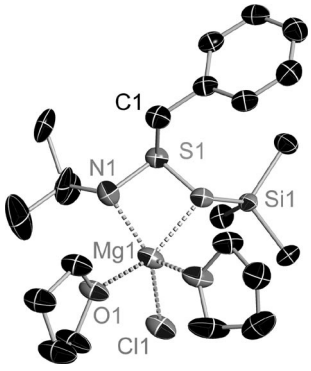


Figure 5. Molecular structure of $[(thf)_2MgCl\{(NtBu)(NSiMe_3)SBz\}]$ (**4**). All hydrogen atoms have been omitted for clarity and anisotropic displacement parameters are depicted at the 50% probability level.

The N–S–N bond angles in all the compounds presented here [94.41(8)–100.05(3)°] are more acute than those in alkali metal derivatives (104.2–110.7°),[6] but span almost the same range as in comparable compounds with Mg^{2+} or other dicationic metals (94.3–98.5°).[6] This is probably due to the higher charge at the magnesium dication, which leads to a stronger repulsion between the positively charged sulfur atom and the metal ion.

NMR Investigation

The ^1H and ^{13}C NMR spectra all exhibit a double set of signals for compounds **1**–**5**. Integration of all peaks showed that the peaks shifted to higher field in each double set of signals belong together. Figure 6 shows the spectra of **2**

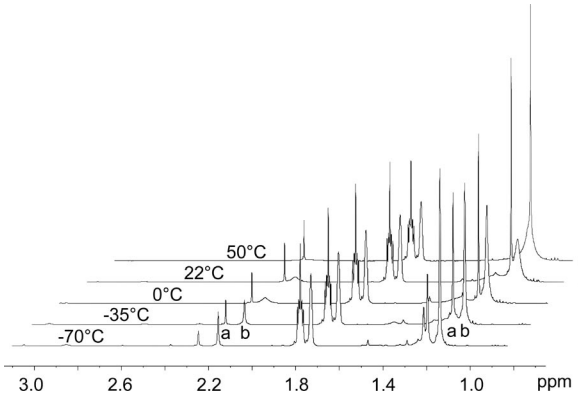
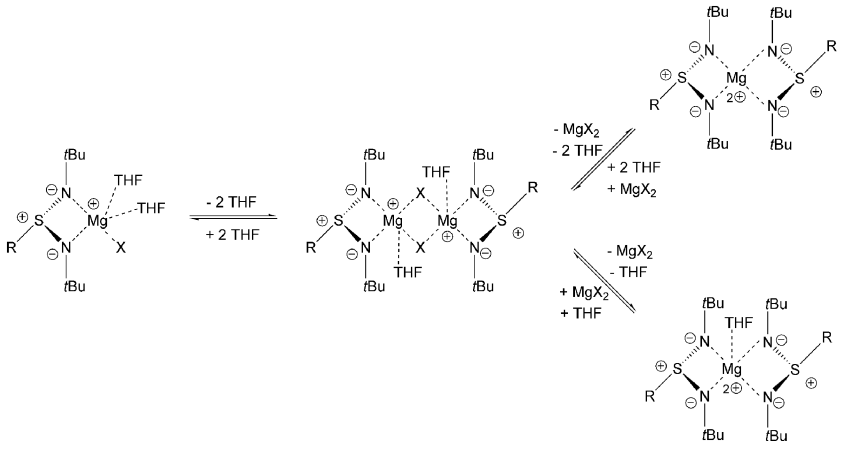


Figure 6. ^1H NMR spectra of **2** at different temperatures.



Scheme 2. Possible interconversion of the magnesium diimidosulfinates in solution.

measured at different temperatures. The signals for the methyl groups occur between δ = 2.1 and 2.3 ppm while the *t*Bu protons resonate between δ = 1.1 and 1.3 ppm. The spectrum of **2** at –70 °C also displays an additional set of signals.

Further measurements were performed at different temperatures and different times after sample preparation. The concentration of the samples was also varied. These experiments showed that the equilibrium is time-, concentration- and temperature-dependent. It is clear from Figure 6 that even more species are generated at very low temperatures and that species **a** increases at the expense of species **b** as the temperature rises. In addition, the peak for **b** gets sharper. The ratio of the integrated intensity of **b** divided by the integrated intensity of **a** increases at higher sample concentrations but decreases when the time elapsed between preparing the sample and measuring the spectrum increases. In addition, the peak for **b** becomes broader as more time passes. Since the exchange between **a** and **b** is bidirectional, these findings confirm that these two species are interconvertible and that the double set of signals is not simply due to hydrolysis or ligand scrambling. In addition, the ^{15}N-HMBC spectrum shows two cross-peaks, for both *t*Bu signals with the signal of the nitrogen atoms, at δ = –270 and –272 ppm respectively. The proximity of these signals indicates that the chemical environment of the nitrogen atoms is the same for both species and, together with the absence of any amine proton, proves that hydrolysis is not responsible for the signal doubling. Our initial assumption was that the spectra reflect the equilibrium between the monomeric form shown in the solid state by **2**–**5** and a dimeric form similar that shown by **1** in the solid state, reminiscent of the Schlenk equilibrium species, therefore we recorded a DOSY spectrum to test this assumption.[16] To our surprise, the DOSY spectrum showed that both species move with nearly the same speed in solution, thus indicating that the size of both molecules and the number of atoms they contain should be almost the same. In light of these experiments, and from our earlier observations with magnesium imidosulfinates,[13,17] we suppose that the second species in solution might be [Mg{(N*t*Bu)$_2$SR}$_2$] or [(thf)Mg{(N*t*Bu)$_2$SR}$_2$]. All these three compounds are about the same size and should yield very similar peaks in their NMR spectra.

Additional evidence for this assumption was provided by a NOESY spectrum, which showed no distinct cross-peaks between both species, although cross-peaks were observed between both species and a very broad signal next to the *t*Bu peaks and the peaks for the methyl groups. This suggests that the exchange between both species **a** and **b** occurs via a short-lived intermediate that only produces a very small and broad signal (see Scheme 2). We believe that this intermediate is a dimeric form similar to the structure of **1** in the solid state, although definitive proof is still lacking.

Conclusions

Our experiments have shown that sulfur diimides react readily with different Grignard reagents to give highly pure products in high yields. Varying the steric demand of the substituent at the sulfur atom allows monomeric or dimeric molecules, which can be distinguished by X-ray structure determination in the solid state and show interesting features in solution, to be synthesised. The structural motifs of the monomer and the dimer are very different although, in contrast to their lithium counterparts, the monomeric and dimeric magnesium diimidosulfinates do not vary significantly. The NMR spectra of **1**–**5** all show a multiple set of signals. It has been determined that interconversion between the different species is temperature-, time- and concentration-dependent and a reasonable explanation for the signal doubling supported by different NMR experiments has been suggested, although an unequivocal assignment of a single process in solution has not proved possible. Further studies on the reactions of Grignard reagents with sulfur triimides are currently underway. To date, reactions of organolithium reagents with sulfur triimides have only proved possible with small organic substituents due to the electron distributions above and below the SN_3 plane. Our hope is that the application of a HSAB-soft Grignard nucleophile will allow this electronic shielding to be overcome as it matches the soft character of the sulfur atom.

Experimental Section

General Procedures: All experiments were carried out either under an atmosphere of purified, dry nitrogen or argon using modified Schlenk techniques or in an argon-filled drybox. All glassware was dried for several hours at 120 °C, assembled hot, and allowed to cooln under vacuum. Solvents were freshly distilled from potassium prior to use and degassed. All reagents were available commercially or were synthesized according to published procedures [$S(N\mathit{t}Bu)_2$[18]].

NMR spectra were recorded on Bruker Avance 400 or 500 spectrometers. The measurement frequencies are given with the analyses. Chemical shifts are given in ppm, with positive values for low-field shifts, relative to tetramethylsilane as external standard.

Elemental analyses were performed by the Mikroanalytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen with an elementar Vario EL3 apparatus. Some values deviate more than usual from the calculated ones as the substances are highly sensitive to oxygen and moisture.

Mass spectra were recorded using the electron ionization method (EI-MS: 70 eV) on a Finnigan MAT 95 spectrometer. The mass-to-charge ratios (*m*/*z*) of the fragment ions are based on the molecular masses of the isotopes with the highest natural abundance. The molecular peak is defined as the compound with no coordinated solvent. Some spectra were unspecific as the ionic nature and lability of the synthesized compounds made measurement difficult. No electron spray ionization (ESI-MS) or fast atom bombardment (FAB-MS) mass spectra could be recorded due to the reactivity and solubility of the compounds.

Synthesis and Analysis: $S(N\mathit{t}Bu)_2$ [5.0 mmol; $S(NSiMe_3)(N\mathit{t}Bu)$ was used for the synthesis of **4**] was dissolved in 20 mL of thf and a solution of RMgX in thf (5.0 mmol; X = Cl or Br; R = Ph, Me, *n*Bu or benzyl) was added to this solution at –78 °C over 15 min. The mixture was then allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo, the residual solids re-dissolved in an *n*-hexane/THF mixture and the precipitate filtered off. The resulting solution was stored at –24 °C to yield colourless crystals suitable for X-ray structure analyses after 1–3 days.

1: Yield 1.55 g (81%). ^{1}H NMR (500.132 MHz, [D$_8$]THF): major compound: δ = 1.31 [s, 18 H, C(CH_3)$_3$], 1.77 (m, 8 H, OCH$_2$CH_2), 3.62 (m, 8 H, OCH_2CH$_2$), 7.38 (m, 3 H, H$_{meta/para}$/C$_6H_5$), 7.83 (d, 2 H, H$_{ortho}$/C$_6H_5$) ppm. ^{13}C NMR (125.772 MHz, [D$_8$]THF): δ = 25.3 (OCH$_2$*C*H$_2$), 32.5 [C(*C*H$_3$)$_3$], 53.0 [*C*(CH$_3$)$_3$], 67.4 (O*C*H$_2$CH$_2$), 128.2 (C$_{ortho}$/C$_6$H$_5$), 128.7 (C$_{para}$/C$_6$H$_5$), 129.3 (C$_{meta}$/C$_6$H$_5$), 156.8 (C$_{ipso}$/C$_6$H$_5$) ppm; minor compound: ^{1}H NMR (500.132 MHz, [D$_8$]THF): δ = 1.16 [s, 18 H, C(CH_3)$_3$], 1.77 (m, 8 H, OCH$_2$CH_2), 3.62 (m, 8 H, OCH_2CH$_2$), 7.34 (m, 3 H, H$_{meta/para}$/C$_6H_5$), 7.78 (d, 2 H, H$_{ortho}$/C$_6H_5$) ppm. ^{13}C NMR (125.772 MHz, [D$_8$]THF): δ = 25.3 (OCH$_2$*C*H$_2$), 33.8 [C(*C*H$_3$)$_3$], 55.2 [*C*(CH$_3$)$_3$], 67.4 (OCH$_2$CH$_2$), 125.9 (C$_{ortho}$/C$_6$H$_5$), 129.5 (C$_{para}$/C$_6$H$_5$), 130.7 (C$_{meta}$/C$_6$H$_5$), 156.8 (C$_{ipso}$/C$_6$H$_5$) ppm. $C_{36}H_{62}Cl_2Mg_2N_4O_2S_2$ (798.52): calcd. C 56.40, H 8.20, N 7.30, S 8.40; found C 56.00, H 7.80, N 7.30, S 8.50.

2: Yield 1.86 g (85%). ^{1}H NMR (500.132 MHz, [D$_8$]THF): major compound: δ = 1.17 [s, 18 H, C(*C*H$_3$)$_3$], 1.77 (m, 8 H, OCH$_2$CH_2), 2.18 (s, 3 H, SCH_3), 3.62 (m, 8 H, OCH_2CH$_2$) ppm. ^{13}C NMR (125.772 MHz, [D$_8$]THF): δ = 25.3 (OCH$_2$*C*H$_2$), 32.8 [C(*C*H$_3$)$_3$], 52.0 (S*C*H$_3$), 52.7 [*C*(CH$_3$)$_3$] 67.4 (O*C*H$_2$CH$_2$) ppm. ^{15}N NMR (40.548 MHz, [D$_8$]THF): δ = –270.0 [NC(CH$_3$)$_3$] ppm; minor compound: ^{1}H NMR (500.132 MHz, [D$_8$]THF): δ = 1.22 [s, 18 H, C(CH_3)$_3$], 1.77 (m, 8 H, OCH$_2$CH_2), 2.26 (s, 3 H, SCH_3), 3.62 (m, 8 H, OCH_2CH$_2$) ppm. ^{13}C NMR (125.772 MHz, [D$_8$]THF): δ = 25.3 (OCH$_2$*C*H$_2$), 33.6 [C(*C*H$_3$)$_3$], 53.2 (S*C*H$_3$), 53.4 [*C*(CH$_3$)$_3$], 67.4 (OCH$_2$CH$_2$) ppm. ^{15}N NMR (40.548 MHz, [D$_8$]THF): δ = –271.8 [NC(CH$_3$)$_3$] ppm. $C_{17}H_{37}BrMgN_2O_2S$ (437.77): calcd. C 46.68, H 8.47, N 6.41, S 7.32; found C 45.40, H 8.24, N 6.86, S 7.55.

3: Yield 1.65 g (76%). ^{1}H NMR (500.132 MHz, [D$_8$]THF): major compound: δ = 0.92 (m, 3 H, SCH$_2$CH$_2$CH$_2$CH_3), 1.17 [s, 18 H, C(CH_3)$_3$], 1.39 (m, 2 H, SCH$_2$CH$_2$CH_2CH$_3$), 1.62 (m, 2 H, SCH$_2$CH_2CH$_2$CH$_3$), 1.77 (m, 8 H, OCH$_2$CH_2), 2.23 (t, 2 H, SCH_2CH$_2$CH$_2$CH$_3$), 3.62 (m, 8 H, OCH_2CH$_2$) ppm. ^{13}C NMR (125.757 MHz, [D$_8$]THF): δ = 14.26 (SCH$_2$CH$_2$CH$_2$*C*H$_3$), 22.58 (SCH$_2$CH$_2$*C*H$_2$CH$_3$), 23.11 (SCH$_2$*C*H$_2$CH$_2$CH$_3$), 25.30 (OCH$_2$*C*H$_2$), 33.89 [C(*C*H$_3$)$_3$], 53.51 [*C*(CH$_3$)$_3$], 63.83 (S*C*H$_2$CH$_2$*C*H$_2$CH$_3$), 67.43 (O*C*H$_2$CH$_2$) ppm; minor compound: ^{1}H NMR (500.132 MHz, [D$_8$]THF): δ = 0.92 (m, 3 H, SCH$_2$CH$_2$CH$_2$CH_3), 1.22 [s, 18 H, C(CH_3)$_3$], 1.39 (m, 2 H, SCH$_2$CH$_2$CH_2CH$_3$), 1.67 (m, 2 H, SCH$_2$CH_2CH$_2$CH$_3$), 1.77 (m, 8 H, OCH$_2$CH_2), 2.36 (t, 2 H, SCH_2CH$_2$CH$_2$CH$_3$), 3.62 (m, 8 H, OCH_2CH$_2$) ppm. ^{13}C NMR (125.757 MHz, [D$_8$]THF): δ = 14.29 (SCH$_2$CH$_2$CH$_2$*C*H$_3$), 22.58 (SCH$_2$CH$_2$*C*H$_2$CH$_3$), 23.26 (SCH$_2$*C*H$_2$CH$_2$CH$_3$), 25.30 (OCH$_2$*C*H$_2$), 33.26 [C(*C*H$_3$)$_3$], 52.97 [*C*(CH$_3$)$_3$], 61.30 (S*C*H$_2$CH$_2$*C*H$_2$CH$_3$), 67.43 (O*C*H$_2$CH$_2$) ppm. $C_{20}H_{43}ClMgN_2O_2S$ (435.38): calcd. C 55.24, H 9.90, N 6.44, S 7.36; found C 54.32, H 10.00, N 6.84, S 7.79.

4: Yield 1.99 g (82%). ^{1}H NMR (500.134 MHz, [D$_8$]THF): major compound: δ = –0.12 [s, 9 H, Si(CH_3)$_3$], 1.15 [s, 9 H, C(CH_3)$_3$] 1.77 (m, 8 H, OCH$_2$CH_2), 3.27 (d, 1 H, SCH_2), 3.62 (m, 8 H, OCH_2CH$_2$), 3.66 (d, 1 H, SCH_2), 7.16–7.30 (m, 5 H, C$_6H_5$) ppm. ^{13}C NMR (125.757, [D$_8$]THF): δ = 1.66 [Si(*C*H$_3$)$_3$], 24.66 (OCH$_2$*C*H$_2$), 32.36 [C(*C*H$_3$)$_3$], 52.71 [*C*(CH$_3$)$_3$], 66.79 (O*C*H$_2$CH$_2$), 72.29 (S*C*H$_2$Ph), 126.96 (C$_{para}$/C$_6$H$_5$), 128.16 (C$_{meta}$/C$_6$H$_5$), 130.87 (C$_{ortho}$/C$_6$H$_5$), 133.24 (C$_{ipso}$/C$_6$H$_5$) ppm; minor compound: ^{1}H NMR (500.132 MHz, [D$_8$]THF): δ = –0.08 [s, 9 H, Si(CH_3)$_3$], 1.17 [s, 9 H, C(CH_3)$_3$] 1.77 (m, 8 H, OCH$_2$CH_2), 3.53 (d, 1 H, SCH_2), 3.62 (m, 8 H, OCH_2CH$_2$), 3.92 (d, 1 H, SCH_2), 7.16–7.30 (m, 5 H, C$_6H_5$) ppm. ^{13}C NMR (125.757 MHz, [D$_8$]THF): δ = 2.06 [Si(CH_3)$_3$]: δ = 24.66 (OCH$_2$*C*H$_2$), 33.35 [C(*C*H$_3$)$_3$], 52.48 [*C*(CH$_3$)$_3$], 66.79 (O*C*H$_2$CH$_2$), 75.07 (S*C*H$_2$Ph), 127.28 (C$_{para}$/C$_6$H$_5$), 128.48 (C$_{meta}$/C$_6$H$_5$), 130.56 (C$_{ortho}$/C$_6$H$_5$), 133.47 (C$_{ipso}$/C$_6$H$_5$) ppm. $C_{22}H_{41}ClMgN_2O_2SSi$ (485.48): calcd. C 54.49, H 8.46, N 5.78; found C 53.84, H 8.41, N 5.65.

5: Yield 1.83 g (78%). ^{1}H NMR (500.134 MHz, [D$_8$]THF): major compound: δ = 1.09 [s, 18 H, C(CH_3)$_3$], 1.77 (m, 8 H, OCH$_2$CH_2), 3.49 (br., 2 H, SCH_2), 3.62 (m, 8 H, OCH_2CH$_2$), 7.17 (m, 1 H, H$_{para}$/C$_6H_5$) 7.23–7.26 (br., 4 H, H$_{meta/ortho}$/C$_6H_5$) ppm. ^{13}C NMR (125.757 MHz, [D$_8$]THF): δ = 25.29 (OCH$_2$*C*H$_2$), 33.06 [C(*C*H$_3$)$_3$], 53.35 [*C*(CH$_3$)$_3$], 67.43 (O*C*H$_2$CH$_2$), 70.79 (S*C*H$_2$Ph), 127.43 (C$_{para}$/C$_6$H$_5$), 128.59 (C$_{meta}$/C$_6$H$_5$), 131.43 (C$_{ortho}$/C$_6$H$_5$), 134.20 (C$_{ipso}$/C$_6$H$_5$) ppm; minor compound: ^{1}H NMR (500.132 MHz, [D$_8$]-THF): δ = 1.11 [s, 18 H, C(CH_3)$_3$], 1.77 (m, 8 H, OCH$_2$CH_2), 3.49 (br., 2 H, SCH_2), 3.62 (m, 8 H, OCH_2CH$_2$), 7.17 (m, 1 H, H$_{para}$/C$_6H_5$) 7.23–7.26 (br., 4 H, H$_{meta/ortho}$/C$_6H_5$) ppm. ^{13}C NMR (125.757 MHz, [D$_8$]THF): δ = 25.29 (OCH$_2$*C*H$_2$), 33.86 [C(*C*H$_3$)$_3$], 53.75 [*C*(CH$_3$)$_3$], 67.43 (O*C*H$_2$CH$_2$), 74.15 (S*C*H$_2$Ph), 127.93 (C$_{para}$/C$_6$H$_5$), 128.92 (C$_{meta}$/C$_6$H$_5$), 131.73 (C$_{ortho}$/C$_6$H$_5$), 134.31 (C$_{ipso}$/C$_6$H$_5$) ppm. $C_{23}H_{41}ClMgN_2O_2S$ (469.40): calcd. C 58.90, H 8.80, N 6.00, S 6.80; found C 56.10, H 7.70, N 6.40, S 8.00.

X-ray Crystal Structure Determinations: Data for **1**–**5** were collected from shock-cooled crystals at 100 (**1**, **3** and **4**), 133 (**5**) or 170 K (**2**). Data for **1**–**4** were collected on a Bruker SMART-APEX II

Table 2. Crystallographic data for compounds **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{36}H_{62}Cl_2Mg_2N_4O_2S_2$	$C_{17}H_{37}BrMgN_2O_2S$	$C_{20}H_{43}ClMgN_2O_2S$	$C_{22}H_{41}ClMgN_2O_2SSi$	$C_{23}H_{41}ClMgN_2O_2S$
M	798.52	437.77	435.38	485.48	469.40
T [K]	100	170	100	100	133
Space group	$P\bar{1}$	Pc	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	10.129(2)	9.763(4)	7.320(1)	10.197(1)	10.116(2)
b [Å]	10.299(2)	16.860(3)	32.936(4)	18.029(1)	18.081(4)
c [Å]	11.824 (2)	7.371(2)	10.384(2)	14.983(1)	14.635(3)
α [°]	88.27(1)	90.0	90.0	90.0	90.0
β [°]	69.40(1)	111.02(2)	96.42(1)	98.12(1)	97.38(3)
γ [°]	64.53(1)	90.0	90.0	90.0	90.0
V [Å^3]	1031.6(3)	1132.5(6)	2487.9(5)	2727.2(3)	2654.7(9)
Z	2	2	4	4	4
θ range [°]	2.40–25.07	2.24–26.04	2.33–26.73	2.54–26.55	1.8–24.71
Data	15492	20492	44906	28930	40812
Unique data	3637	4439	5064	5564	4666
R_{int}	0.0325	0.0356	0.0230	0.0246	0.0375
R_1	0.0460	0.0416	0.0349	0.0427	0.0325
wR_2	0.0957	0.0977	0.0783	0.1050	0.0790
Parameters	223	225	271	366	287
GooF	1.098	1.046	1.093	1.050	1.034
Peak/hole [e/Å^3]	0.51/–0.22	0.69/–0.40	0.31/–0.34	0.42/–0.44	0.28/–0.22
Flack parameter	–	0.0818(85)	–	–	–

(APEX I for **1**) diffractometer fitted with a D8 goniometer. A sealed-tube X-ray source was used for data collection for **1** and **4**, an Incoatec microfocus source for **3**[19] and a Bruker TXS-Mo rotating anode for **2**. Data for **5** were recorded on a Stoe IPDS II diffractometer with a sealed tube and an image plate detector. All diffractometers were equipped with a low-temperature device[20] and used monochromated Mo-K_α radiation (λ = 0.71073 Å). The Bruker TXS-Mo rotating anode and the Incoatec microfocus source used mirror optics as radiation monochromator, whereas the sealed-tube devices used a graphite monochromator. Data for **1**–**4** were integrated with SAINT,[21] and an empirical absorption correction (SADABS) was applied.[22] Data collection and data reduction for **5** were performed with X-Area.[23] All structures were solved by direct methods (SHELXS-97)[24] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically at calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond-length restraints and isotropic displacement parameter restraints. Further details can be found in Table 2.[26]

CCDC-738499 (for **1**), 738500 (for **2**), 738501 (for **3**) and 724648 (for **4**) and 738502 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the priority program 1178 ("Experimental charge density as the key to understanding chemical interactions") and Chemetall GmbH (Frankfurt and Langelsheim).

[1] a) H. Ila, O. Baron, A. J. Wagner, P. Knochel, *Chem. Commun.* **2006**, *6*, 583–593; b) P. Knochel, W. Dohle, N. Gommermann, F. F. Kneisel, F. Kopp, T. Korn, I. Sapountzis, V. A. Vu, *Angew. Chem. Int. Ed.* **2003**, *42*, 4302–4320; c) F. M. Bickelhaupt, *Chem. Soc. Rev.* **1999**, *28*, 17–23; d) F. Bickelhaupt, *J. Organomet. Chem.* **1994**, *475*, 1–14.

[2] M. Barbier, *C. R. Acad. Sci.* **1899**, *128*, 110–111.

[3] V. Grignard, *C. R. Acad. Sci.* **1900**, *130*, 1322–1324.

[4] a) T. Murai, F. Asai, *J. Am. Chem. Soc.* **2007**, *129*, 780–781; b) D. Seyferth, *Organometallics* **2009**, *28*, 2–33; c) D. Seyferth, *Organometallics* **2006**, *25*, 2–24.

[5] a) F. T. Edelmann, S. Blaurock, V. Lorenz, T. Chivers, *Z. Anorg. Allg. Chem.* **2008**, *634*, 413–415; b) C. Hubrich, A. Schulz, A. Villinger, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2362–2366; c) G. M. Aspinall, M. C. Copsey, A. P. Leedham, C. R. Russell, *Coord. Chem. Rev.* **2002**, *227*, 217–232; d) J. K. Brask, T. Chivers, *Angew. Chem. Int. Ed.* **2001**, *40*, 3960–3976; e) D. Stalke, *Proc. Ind. Acad. Sci.* **2000**, *112*, 155–170; f) M. A. Beswick, D. S. Wright, *Coord. Chem. Rev.* **1998**, *176*, 373–406.

[6] a) D. Leusser, J. Henn, N. Kocher, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, *126*, 1781–1793; b) D. Leusser, B. Walfort, D. Stalke, *Angew. Chem. Int. Ed.* **2002**, *41*, 2079–2082; c) B. Walfort, T. Auth, B. Degel, H. Helten, D. Stalke, *Organometallics* **2002**, *21*, 2208–2214; d) B. Walfort, A. P. Leedham, C. R. Russell, D. Stalke, *Inorg. Chem.* **2001**, *40*, 5668–5674; e) B. Walfort, S. K. Pandey, D. Stalke, *Chem. Commun.* **2001**, 1640–1641; f) D. Ilge, D. S. Wright, D. Stalke, *Chem. Eur. J.* **1998**, *4*, 2275–2279; g) R. Fleischer, B. Walfort, A. Gbureck, P. Scholz, W. Kiefer, D. Stalke, *Chem. Eur. J.* **1998**, *4*, 2266–2279; h) F. T. Edelmann, F. Knösel, F. Pauer, D. Stalke, W. Bauer, *J. Organomet. Chem.* **1992**, *438*, 1–10; i) F. Pauer, J. Rocha, D. Stalke, *J. Chem. Soc., Chem. Commun.* **1991**, 1477–1479; j) F. Pauer, D. Stalke, *J. Organomet. Chem.* **1991**, *418*, 127–128; k) D. Hänssgen, R. Steffens, *Z. Naturforsch., Teil B* **1985**, *40*, 919–922; l) D. Hänssgen, R. Steffens, *J. Organomet. Chem.* **1982**, *236*, 53–60.

[7] S. Freitag, W. Kolodziejski, F. Pauer, D. Stalke, *J. Chem. Soc., Dalton Trans.* **1993**, 3479–3488.

[8] J. Kuyper, P. C. Keijzer, K. Vrieze, *J. Organomet. Chem.* **1976**, *116*, 1–13.

[9] a) S. Deuerlein, D. Leusser, U. Flierler, H. Ott, D. Stalke, *Organometallics* **2008**, *27*, 2306–2315; b) B. Walfort, R. Bertermann, D. Stalke, *Chem. Eur. J.* **2001**, *7*, 1424–1430.

[10] B. Walfort, D. Stalke, *Angew. Chem. Int. Ed.* **2001**, *40*, 3846–3849.

[11] a) F. A. Carey, R. J. Sundberg, in: *Advanced Organic Chemistry, Part A*, Plenum Press, New York, **1984**; b) K. P. C. Vollhardt, N. E. Schore, in: *Organic Chemistry*, Freeman & Co Ltd., San Francisco, **1994**, vol. 2; c) J. March, in: *Advanced Organic Chemistry*, Wiley-Interscience, New York, **1992**, vol. 4.
[12] a) S. Handa, K. Nagawa, Y. Sohtome, S. Matsunaga, M. Shibasaki, *Angew. Chem. Int. Ed.* **2008**, *47*, 3230–3233; b) S. Podder, J. Choudhury, S. Roy, *J. Org. Chem.* **2007**, *72*, 3129; c) G. Bai, S. Singh, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *J. Am. Chem. Soc.* **2005**, *127*, 3449–3455.
[13] R. Fleischer, D. Stalke, *Coord. Chem. Rev.* **1998**, *176*, 431–450.
[14] R. Fleischer, D. Stalke, *J. Organomet. Chem.* **1998**, *550*, 173–182.
[15] C. Selinka, S. Deuerlein, T. Häuser, D. Stalke, *Inorg. Chim. Acta* **2004**, *357*, 1873–1880.
[16] a) I. Fernández, E. Martínez-Viviente, F. Breher, P. S. Pregosin, *Chem. Eur. J.* **2005**, *11*, 1495–1506; b) H. Barjat, G. A. Morris, S. Smart, A. G. Swanson, S. C. R. Williams, *J. Magn. Reson., Ser. B* **1995**, *B108*, 170–172.
[17] T. Schulz, D. Stalke, *Eur. J. Inorg. Chem.* **2010**, 2185–2192, following paper.
[18] O. J. Scherer, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1977**, *432*, 173–176.
[19] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, *42*, 885–891.
[20] T. Kottke, R. J. Lagow, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465–468.
[21] SAINT, v7.34A, Bruker AXS Inc., Madison, WI, USA, **2005**.
[22] G. M. Sheldrick, SADABS v**2008**/2, Göttingen, **2008**.
[23] *X-AREA*, Stoe & Cie GmbH, Darmstadt, **2002**.
[24] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[25] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[26] P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya, in: *IUCR Texts on Crystallography* (Eds.: P. Müller), Oxford University Press, Oxford, **2006**, vol. 8.

Received: January 18, 2010
Published Online: April 7, 2010

