Synthesis and molecular structure of the unsymmetrically substituted magnesium alkyl Mg(Bu^n){CH[SPh][SiPh$_2$(CH$_2$NC$_5$H$_{10}$)]}

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Received (in Basel, Switzerland) 12th January 2000, Accepted 10th April 2000

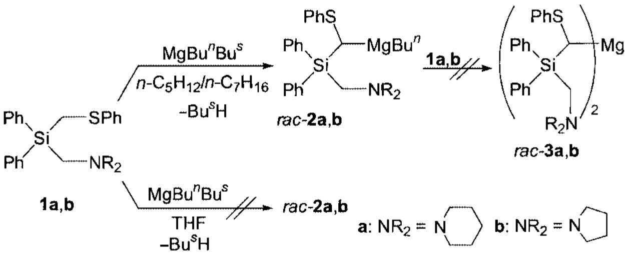
The unsymmetrically substituted magnesium alkyl Mg(Bu^n){CH[SPh][SiPh$_2$(CH$_2$NC$_5$H$_{10}$)]} (NC$_5$H$_{10}$ = 1-piperidyl) with a stereogenic metalated carbon atom is obtained by deprotonation of an (aminomethyl)[(phenylthio)methyl]silane with MgBu^{n}Bu^s and examined by single crystal X-ray diffraction analysis and theoretical methods.

In selective transformations, enantiomerically enriched metal alkyls can work as chiral alkyl-transfer reagents. Moreover, they are valuable tools for studies on the stereochemical course of transmetalation and protonation reactions. Stereogenic metalated carbon centres are usually generated by deprotonation using alkyllithium reagents, giving the corresponding enantiomerically enriched lithium alkyls. These molecules have been investigated intensively.[1] Despite the huge synthetic potential of magnesium alkyls, only one example of an enantiomerically enriched magnesium alkyl is described in the literature.[2]

In a few reported cases, organomagnesium compounds have been used to abstract aryl protons (*e.g.* as part of crown ether systems[3]) and to deprotonate C–H-acidic molecules, such as cyclopentadiene or fluorene.[4,5,6] To turn the nucleophilic magnesium reagent into a deprotonating agent, the metal must be fixed next to the reactive centre by coordinating donor groups. (Aminomethyl)silanes, such as **1a** and **1b**, which are established in our workgroup,[7] intramolecularly provide a coordinating amino group. These (aminomethyl)silanes can be deprotonated easily by *tert*-butyllithium in non-polar solvents leading to (aminomethyl)(lithiomethyl)silanes that form definite aggregates in the solid state.[8]

Here we report the formation and molecular structure of the unsymmetrically substituted magnesium alkyls *rac*-**2a** and *rac*-**2b** with metalated stereogenic centres. *Rac*-**2a**,**b** were generated by deprotonation reaction with the purchasable MgBu^{n}Bu^s in *n*-pentane/*n*-heptane (6 : 1) in racemic form.

The synthesis of *rac*-**2a**,**b**† was carried out in *n*-pentane, kinetically controlled at low temperatures (−78 °C), by treating **1a**,**b** with 1 equiv. of MgBu^{n}Bu^s (solution in *n*-heptane). To our surprise, all attempts of building up the symmetrically substituted bis{[(aminomethyl)diphenylsilyl]methyl}magnesium compounds *rac*-**3a**,**b** by treating **1a**,**b** with only 0.5 equiv. of MgBu^{n}Bu^s failed. In all of these experiments, *rac*-**2a**,**b** was obtained in *ca*. 50% yield, while half the starting material remained unreacted. Even when the reaction mixture was heated to reflux temperature, only mono substitution occured. Furthermore, neither a *sec*-butyl-substituted product, nor a mixture of *sec*-butyl- and *n*-butyl-substituted products were observed. In all reactions, exclusively the MgBu^n fragment was transferred to the (aminomethyl)silanes **1a**,**b** (Scheme 1).



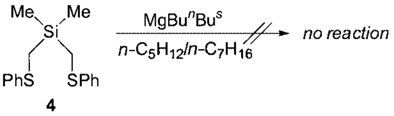
Scheme 1

Earlier results in reactions of organolithium reagents indicated that there is a significant solvent effect on the reactivity of such polar metal–carbon bonds.[7] No detectable amounts of *rac*-**2a**,**b** were obtained, when the reaction of **1a**,**b** with MgBu^{n}Bu^s was carried out in THF. This can be explained by the fact that vacant coordination sites, which are essential for the pre-coordination of the metal by the aminomethyl ligand, are then occupied by solvent molecules. The importance of this intramolecular activation is revealed by the result that dimethylbis[(phenylthio)methyl]silane (**4**) is not metalated by MgBu^{n}Bu^s under the same conditions (Scheme 2).

To the best of our knowledge, the only magnesium alkyls containing a sulfur–carbon–magnesium unit, (PhSCH$_2$)$_2$Mg(thf)$_3$ (**5**) and (MeSCH$_2$)$_2$Mg(thf)$_3$ (**6**), were obtained by transmetalation and crystallographically examined by Steinborn and coworkers.[9] In the monomeric molecular structures of **5** and **6**, the magnesium atom is coordinated by three THF molecules. The crystal data of *rac*-**2a**,‡ together with that of **5** and **6**, is important for examining the role of the sulfur atom with respect to aggregation and reactivity.

Compound *rac*-**2a** crystallised from *n*-pentane/*n*-heptane in the triclinic crystal system, space group $P\bar{1}$. We detected two symmetry independent dimers of *rac*-**2a** in the asymmetric unit (molecule A and B) that are different in the conformation of the *n*-butyl groups and the phenyl substituents (Fig. 1). The central six-membered ring of two carbon, two magnesium and two sulfur atoms is built up by the intermolecular S–Mg coordination, that leads to an S(1)–Mg(1) distance of 275.5(1) pm. The Mg(1)–C(1) bond, which is 223.2(3) pm long, is part of another five-membered ring, due to the intramolecular coordination of the aminomethyl substituent [N(1)–Mg(1) 221.4(2) pm]. In the crystal, the metal is surrounded by four different substituents, which makes *rac*-**2a** a magnesium alkyl with a stereogenic magnesium centre. The S(1)–C(1) distances of **5** [177.7(6) pm] and *rac*-**2a** [178.1(3) pm] are nearly identical. This is not true for the S(1)–C(2) distance, which is 176.6(5) pm for **5** and 179.4(3) pm for *rac*-**2a**, as a result of the S → Mg coordination for *rac*-**2a**. The second dimer (molecule B) of *rac*-**2a** may be described in the same way and will, therefore, not be discussed. The crystal data of both molecules A and B can be found in Table 1.

Despite the intensive theoretical studies on organolithium compounds, the corresponding magnesium alkyls have not been investigated to this extent.[10] Sulfur substituents at metalated carbon atoms can increase the stability of the configuration at this centre.[11] For α-lithiated organosulfanes the rotation around



Scheme 2

DOI: 10.1039/b000494o

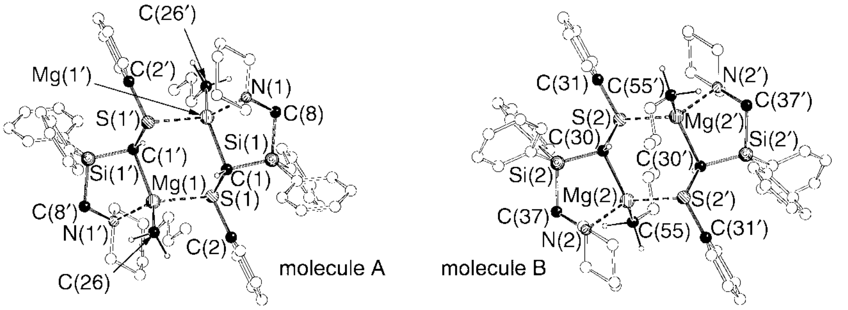


Fig. 1 Molecular structure and numbering scheme of the two crystallographically independent dimers A and B of *rac*-**2a** in the crystal.

Table 1 Selected bond lengths (pm) and angles (°) of the two molecules A and B of *rac*-**2a**, compared with the B3LYP/6-31+G(d)-optimized structure **7**

Molecule A/molecule B	Molecular structure	B3LYP [6-31 + G(d)]
S(1)–C(1)/S(2)–C(30)	178.1(3)/176.8(3)	180.4
S(1)–C(2)/S(2)–C(31)	179.4(3)/178.5(3)	184.4
Mg(1)–S(1)/Mg(2)–S(2)	257.4(1)/257.8(1)	262.0
Mg(1)–C(1)′/Mg(2)–C(30)	223.3(3)/224.7(3)	224.3
Mg(1)–N(1)′/Mg(2)–N(2)	221.4(2)/219.4(3)	223.5
C(1)′–Mg(1)–C(26)/C(30)–Mg(2)–C(55)	129.2(1)/129.2(2)	133.0
N(1)′–Mg(1)–S(1)/N(2)–Mg(2)–S(2)′	115.5(1)/114.8(1)	112.4

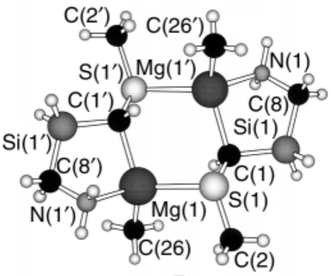


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Fig. 2 B3LYP/6-31 + G(d)-optimized structure of a model system for *ab initio* studies on *rac*-**2a** (numbering scheme adopted from Fig. 1).

the C–S bond is the rate-determining step of the racemisation process. We tried to reproduce the molecular structure of *rac*-**2a** by applying density functional calculations [at the B3LYP/ 6-31+G(d) level] to the model system **7** (Fig. 2).[12]

Structural features, such as the shortened $C–S_{alkyl}$ distance and the longer $C–S_{aryl}$ bond, as well as the antiperiplanar conformation of the C–S–C–Mg unit, could be reproduced by our density functional calculations. Further studies on model systems of sulfur-substituted organomagnesium and organolithium compounds are currently in progress.

In order to build up enantiomerically enriched magnesium alkyls, which have a stereogenic carbon centre, systems of defined aggregation are necessary. The facile generation of unsymmetrically substituted dialkylmagnesium compounds like *rac*-**2a**,**b** opens up a new route to enantiomerically enriched (magnesiomethyl)silanes by using optically active aminomethyl substituents as chiral auxillaries. This has already been successfully demonstrated in the case of enantiomerically enriched (lithiomethyl)silanes.[7,13]

We gratefully acknowledge the Deutsche Forschungsgemeinschaft (DFG), the Sonderforschungsbereich (SFB) 347, and the Fonds der Chemischen Industrie (FCI) for financial support. B. C. A., D. S. and K. S. thank the FCI for the grant of three scholarships.

Notes and references

† *Synthesis of rac*-**2a**,**b**: a colourless solution of 0.50 mmol **1a**,**b** in *n*-pentane (3 ml) was cooled to −78 °C. 0.50 ml (0.50 mmol) of $MgBu^nBu^s$ (1.0 M in *n*-heptane) was added and the reaction mixture was allowed to warm to room temperature. After 6 to 72 h, single crystals of *rac*-**2a**,**b** could be isolated that were suitable for single crystal X-ray structural studies. *Spectroscopic data* for *rac*-**2a**: δ_H(200.1 MHz, C_6D_6) 0.50–2.20 [m, 18 H, SiC(SPh)*H*Mg, $NCCC\mathit{H}_2C$, $NCC\mathit{H}_2C$, $SiC\mathit{H}_2N$, $MgC\mathit{H}_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_3$], 2.40–3.10 (m, 4 H, $NC\mathit{H}_2C$), 6.80–7.50, 7.80–8.10 [m, 15 H, $Si(C_6\mathit{H}_5)_2$, $S(C_6\mathit{H}_5)$]; δ_C(50.3 MHz, C_6D_6): 0.1 [Si*C*(SPh)HMg], 8.3 ($Mg\mathit{C}H_2C$), 13.9 ($C\mathit{C}H_2CH_3$), 14.8 ($\mathit{C}H_3$), 17.4 ($MgC\mathit{C}H_2C$), 22.3 ($NCC\mathit{C}H_2C$), 25.1 ($NC\mathit{C}H_2C$), 40.4 ($Si\mathit{C}H_2N$), 59.8 ($N\mathit{C}H_2C$), 127.1 (C-*p*), 128.2 [C-*p* (S*Ph*)], 128.3 (C-*m*), 129.3 [C-*m* (S*Ph*)], 135.4 [C-*o* (S*Ph*)], 136.5 (C-*i*), 139.8 (C-*o*), 142.3 [C-*i* (S*Ph*)]; δ_{Si}(39.8 MHz, C_6D_6) −7.2. *Spectroscopic data* for *rac*-**2b**: δ_H(300.1 MHz, C_6D_6) 0.06–2.20 [s, 1 H, SiC(SPh)*H*Mg], 0.35–0.55 (m, 2 H, $MgC\mathit{H}_2C$), 0.80–3.40 (m, 17 H, $NCC\mathit{H}_2C$, $NC\mathit{H}_2C$, $SiC\mathit{H}_2N$, $MgCH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_3$), 6.65–8.20 [m, 15 H, $Si(C_6\mathit{H}_5)_2$, $S(C_6\mathit{H}_5)$]; δ_C(75.5 MHz, C_6D_6) 0.4 [Si*C*(SPh)HMg], 8.0 ($Mg\mathit{C}H_2C$], 14.9 ($\mathit{C}H_3$), 22.4, 23.1 ($\mathit{C}H_2$), 33.0, 34.4 ($NC\mathit{C}H_2C$), 47.6 ($Si\mathit{C}H_2N$), 57.4, 61.9 ($N\mathit{C}H_2C$), 125.8 (C-*p*), 126.1 [C-*p* (S*Ph*)], 128.6 (C-*m*), 129.0 [C-*m* (S*Ph*)], 130.0 [C-*o* (S*Ph*)], 135.3 (C-*i*), 135.8 (C-*o*), 140.7 [C-*i* (S*Ph*)]; δ_{Si}(59.6 MHz, C_6D_6) −12.4.

‡ *Crystal data* for *rac*-**2a** (colourless crystals from *n*-pentane/*n*-heptane, 0.40 × 0.40 × 0.20 mm³): $C_{29}H_{37}MgNSSi$, $M = 464.06$, triclinic, space group $P\bar{1}$, $a = 12.053(3)$, $b = 13.678(3)$, $c = 18.810(4)$ Å, $\alpha = 89.84(2)$, $\beta = 81.13(2)$, $\gamma = 68.37(2)°$, $V = 2843.5(11)$ Å³, $Z = 4$, $D_c = 1.131$ Mg m^{-3}, Type of radiation: Mo-Kα, $\lambda = 0.71073$ Å, $\mu = 0.195$ mm^{-1}. Measurements: Stoe IPDS diffractometer, $T = 293$ K. The structure was solved using direct and Fourier methods. 22 940 reflections measured with θ in the range 1.89–24°, 8437 unique reflections; 6024 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-93); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions, except H(1), H(26a), H(26b), H(30), H(55a), H(55b), which were refined isotropic; $R = 0.0493$ [$I > 2\sigma(I)$], $wR_2 = 0.1519$ (all data). SHELXS-86 and SHELXL-93 computer programs were used. CCDC 182/1598. See http://www.rsc.org/suppdata/cc/b0/b000494o/ for crystallographic files in .cif format.

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