Solvent-free methylthiomethyllithium $[LiCH_2SMe]_\infty$: solid state structure and thermal decomposition†

Kai Ruth,[a] Robert E. Dinnebier,*[b] Stefan W. Tönnes,[c] Edith Alig,[a] Ingeborg Sänger,[a] Hans-Wolfram Lerner[a] and Matthias Wagner*[a]

Received (in Cambridge, UK) 12th April 2005, Accepted 16th May 2005
First published as an Advance Article on the web 9th June 2005
DOI: 10.1039/b505096k

Solvent-free $[LiCH_2SMe]_\infty$ forms a layer structure consisting of four- (Li_2C_2), five- (Li_2CS_2), and six-membered ($Li_2C_2S_2$) rings in the solid state; the compound violently explodes upon heating to $T = 160 \pm 5$ °C under an argon atmosphere.

The structures, stabilities and reactivities of sulfur-functionalized methyllithium compounds $LiCH_2SR$ have been subject to numerous studies in recent years. In part, this is due to the increasing interest in a new generation of tripodal scorpionate ligands of the type $[R'B(CH_2SR)_3]^-$, $R'Si(CH_2SR)_3$, and $R'Sn(CH_2SR)_3$.[1–3] These ligands, which are synthesized using organylthiomethyllithium derivatives, have already achieved considerable success in bioinorganic chemistry (*e.g.* development of acetyl CoA synthase models[4]) as well as in materials science (*e.g.* spherical assembly of gold nanoparticles[5]). Moreover, compounds $LiCH_2SR$ are also the reagents of choice for the preparation of homo- and heteroleptic organylthiomethyl metal complexes (*e.g.* $[Al(CH_2SMe)_3]_\infty$,[6] $Li_2[Ni(CH_2S^tBu)_4]$[7]).

$LiCH_2SMe$ is normally generated *in situ* by deprotonation of dimethyl sulfide with ^{n}BuLi in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)[8] and isolated as its (1 : 1) TMEDA adduct. Unfortunately, the presence of TMEDA can cause problems in the further synthesis steps by coordinating to the electrophilic reaction centre and by solubilizing lithium halide salts formed in the course of the substitution reactions. In many cases, it is thus of crucial importance to apply pure, solvent-free $LiCH_2SMe$,[9] which was first synthesized by Peterson[10] *via* the transmetalation of $^nBu_3SnCH_2SMe$ with ^{n}BuLi in hexane. Our group prefers to follow an alternative synthesis protocol giving access to $LiCH_2SMe$ directly from Me_2S and ^{n}BuLi–hexane in the absence of TMEDA.‡ The advantage of our procedure lies in the fact that synthesis and purification of $^nBu_3SnCH_2SMe$ is avoided. However, longer reaction times are required. As noted earlier,[9,11] pure solid $LiCH_2SMe$ spontaneously ignites in the presence of traces of oxygen. When we sealed microcrystalline $LiCH_2SMe$ in a capillary working in the glove box and using an electrically heated copper wire, we had to recognize that the compound may also explode violently upon warming under an inert gas atmosphere. This leads to the conclusion that donor-free $LiCH_2SMe$ is inherently unstable since an internal decomposition pathway with formation of a reactive carbene intermediate may be expected. Given this background, it is interesting to explore the solid state structure of solvent-free $LiCH_2SMe$ and to identify the products formed upon its thermolysis.

In the presence of tridentate *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdta), $LiCH_2SPh$ was found to exist as discrete monomers $[LiCH_2SPh\cdot pmdta]$ in the solid state.[12] The (1 : 1) TMEDA adducts of methylthiomethyllithium and phenylthiomethyllithium, $[LiCH_2SMe\cdot TMEDA)]_2$ (**1**) and $[LiCH_2SPh\cdot TMEDA]_2$ (**2**), crystallize as dimers characterized by four-membered Li_2C_2 rings and six-membered $Li_2C_2S_2$ rings, respectively (Fig. 1).[13] When the number of solvent donor atoms per formula unit is further reduced to one (*cf.* $[LiCH_2SMe\cdot THF]_\infty$ (**3**), Fig. 1), polymeric aggregates of edge-sharing four- and six-membered rings are formed thus combining the structural motifs

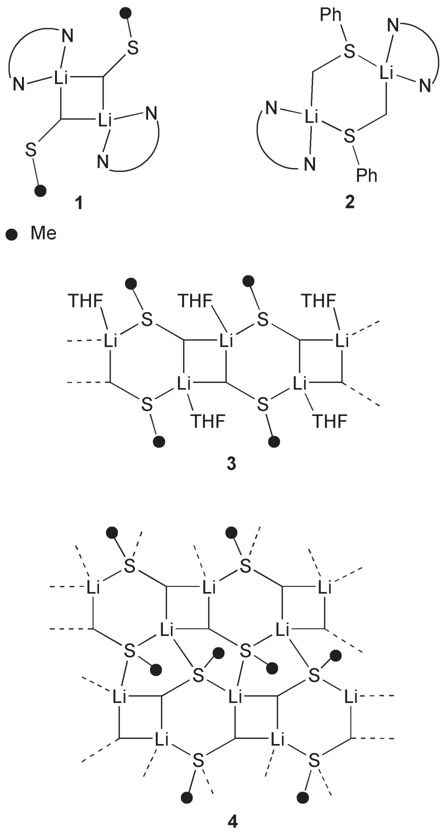

Fig. 1 Schematic drawings of the solid state structures of $[LiCH_2SMe\cdot TMEDA)]_2$ (**1**), $[LiCH_2SPh\cdot TMEDA]_2$ (**2**), $[LiCH_2SMe\cdot THF]_\infty$ (**3**) and $[LiCH_2SMe]_\infty$ (**4**).

---

† Electronic supplementary information (ESI) available: structure solution and refinement details, Rietveld plot (observed, calculated, and difference pattern). See http://dx.doi.org/10.1039/b505096k

*R.Dinnebier@fkf.mpg.de (Robert E. Dinnebier)
Matthias.Wagner@chemie.uni-frankfurt.de (Matthias Wagner)

of **1** and **2**.[11] The solid state structure of solvent-free $LiCH_2SMe$ (**4**)[14] was determined by high-resolution X-ray powder diffraction. The crystal lattice is built of infinite layers $[LiCH_2SMe]_\infty$ (Fig. 2).§ These layers can be regarded as being composed of parallel polymer strands **3** devoid of THF ligands but cross-linked *via* Li–S bonds to give distorted tetrahedral coordination at each Li^+ (S–Li–S = 92.2(4)°, CH_2–Li–CH_2 = 116.9(5)°). Thus, looking along each layer we see an alternating sequence of parallel chains featuring four- (Li_2C_2) and six-membered ($Li_2C_2S_2$) rings on one hand and five-membered Li_2CS_2 rings on the other (dihedral angles between adjacent four/six-membered rings: 65.1(3)°, between adjacent five-membered rings: 44.2(3)°). The Li_2C_2 fragments are planar; all $Li_2C_2S_2$ moieties adopt a chair conformation. Each $[CH_2SMe]^-$ unit bridges four Li^+ ions: two are bonded to the ligand's CH_2-group and two to its sulfur atom. The corresponding bond lengths (Li–CH_2 = 2.175(13)/2.216(12) Å, Li–S = 2.443(13)/2.662(12) Å) are in good agreement with those found in polymeric $[LiCH_2SMe\cdot THF]_\infty$ (**3**; Li–CH_2 = 2.225(5)/2.256(5) Å, Li–S = 2.531(5) Å) and in dimeric $[LiCH_2SMe\cdot TMEDA)]_2$ (**1**; Li–CH_2 bond lengths between 2.227(7) Å and 2.256(6) Å).

Base-free **4**, kept under argon in a glass capillary and electrically heated in a copper block, explodes at $T = 160 \pm 5$ °C with the capillary being shattered to powder. Such a behaviour is not observed for solvent-containing samples of $LiCH_2SMe$. For a closer investigation, the thermolysis was repeated within a thick-walled screw-capped vial.¶ The GC/MS analysis of the decomposition products revealed ethene, MeSH, and Me_2S as the major components in the gas space. As minor components, the sulfur-rich species MeS–SMe, MeS–S–SMe and MeS–CH_2–CH_2–SMe were identified. The formation of ethene and MeSH is likely to be due to an α-elimination reaction of $LiCH_2SMe$, yielding, in the first step, methylene (CH_2) and MeSLi. Quantum chemical calculations have revealed that this process requires the formation of an Li–C–S ring structure (*cf. ab initio* calculations on $LiCH_2SH$ by Schleyer *et al.*[15]). The fact, that such three-membered rings are not pre-formed in the solid state structure of **4** may be the reason why heating to T = 160 °C (with concomitant rearrangement of Li–S bonds) is required to induce internal degradation. It should, however, be noted that formation of MeS–S–SMe and MeS–CH_2–CH_2–SMe, as well as the presence of a dark grey insoluble solid residue, strongly suggests alternative degradation mechanisms to be operative as well (*e.g.* radical reactions). This does not come as a surprise given the fact that methylene, even though most likely expelled in its singlet state, is a diradical in its ground state (further theoretical investigations into the precise degradation mechanism of **4** are currently underway).

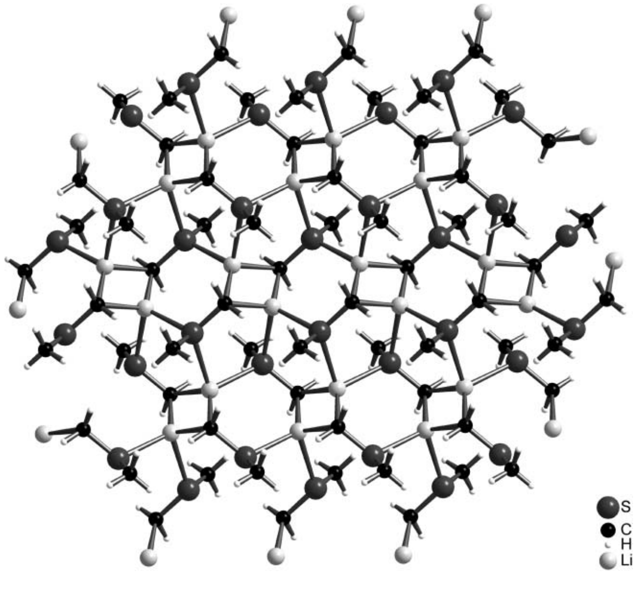

Fig. 2 Structure of solvent-free $[LiCH_2SMe]_\infty$ (**4**) in the solid state; orientation along the *a*-axis. Selected atom–atom distances [Å], angles [°], and dihedral angles between best planes [°]: Li–CH_2 = 2.175(13)/2.216(12), Li–S = 2.443(13)/2.662(12), CH_2–S = 1.809(1), CH_3–S = 1.812(1); CH_2–Li–CH_2 = 116.9(5), S–Li–S = 92.2(4), Li–CH_2–Li = 63.1(5), Li–CH_2–S = 110.6(4)/113.7(3), Li–S–Li = 106.9(4), Li–S–CH_2 = 115.8(4)/118.9(3), CH_2–S–CH_3 = 106.1(2); Li_2C_2–$Li_2C_2S_2$ = 65.1(3), Li_2CS_2–Li_2CS_2 = 44.2(3), Li_2C_2–Li_2CS_2 = 72.1(3), $Li_2C_2S_2$–Li_2CS_2 = 60.6(1).

M.W. is grateful to the "Deutsche Forschungsgemeinschaft" (DFG) for financial support and to Chemetall GmbH for generous gifts of organolithium compounds.

Kai Ruth,[a] Robert E. Dinnebier,*[b] Stefan W. Tönnes,[c] Edith Alig,[a] Ingeborg Sänger,[a] Hans-Wolfram Lerner[a] and Matthias Wagner*[a]
[a] *Institut für Anorganische Chemie, J.W. Goethe-Universität Frankfurt, Marie-Curie-Strasse 11, D-60439, Frankfurt (Main), Germany. E-mail: Matthias.Wagner@chemie.uni-frankfurt.de; Fax: +49 69 798 29260*
[b] *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569, Stuttgart, Germany. E-mail: R.Dinnebier@fkf.mpg.de; Fax: +49 711 689 1502*
[c] *Institut für Forensische Toxikologie, Zentrum der Rechtsmedizin, J.W. Goethe-Universität Frankfurt, Kennedyallee 104, D-60596, Frankfurt (Main), Germany*

Notes and references

‡ *Synthesis of* $[LiCH_2SMe]_\infty$ ***4****:* A solution of ^{n}BuLi in hexane (1.6 M, 15 ml, 24.0 mmol) was added to dimethyl sulfide (25 ml) at r.t. *via* syringe. The resulting mixture was kept at reflux temperature for 5 days, during which a colourless precipitate formed. After all volatiles had been removed *in vacuo*, analytically pure **4** remained as a white microcrystalline solid in essentially quantitative yield. The ^{1}H- and ^{13}C-NMR spectra (d_8-THF) of the product are in full agreement with literature data.[11]

§ *Crystal data of* $[LiCH_2SMe]_\infty$ ***4****:* C_2H_5LiS, M = 68.06 g mol^{-1}, ρ = 1.115 g cm^{-3}, monoclinic, a = 8.3285(3) Å, b = 5.0376(1) Å, c = 9.8245(2) Å, β = 100.38(1)°, V = 405.45(3) Å^3, T = 293 K, space group $P2_1/c$, Z = 4, μ(Cu-Kα) = 4.929 mm^{-1}. The final R-values were R-p = 3.52%; R-wp = 4.85%; R-F^2 = 11.65% (162 reflections); χ^2 = 4.56 (47 variables); min./max. residual electron density −0.34/+0.38 e Å^{-3}; see the ESI for more details of the structure solution.† CCDC 267441. See http://dx.doi.org/10.1039/b505096k for crystallographic data in CIF or other electronic format.

¶ The capillaries were dried by repeated cycles of heating followed by application of a dynamic vacuum and subsequent storage of the capillary *in vacuo* overnight. Since the screw-cap of the vial was made of plastic, higher temperatures could not be applied such that the drying conditions were less rigorous in this case. Some of the Me_2S detected by our GC/MS measurements may thus be due to hydrolysis of $LiCH_2SMe$ prior to the explosion. For the analysis of degradation products, the gas space within the vial was investigated before and after the addition of HCl–^{i}PrOH. The solid residue was extracted with C_6D_6 and d_8-THF and the extracts were investigated by NMR spectroscopy.

1 P. Ge, B. S. Haggerty, A. L. Rheingold and C. G. Riordan, *J. Am. Chem. Soc.*, 1994, **116**, 8406.
2 H. W. Yim, L. M. Tran, E. D. Dobbin, D. Rabinovich, L. M. Liable-Sands, C. D. Incarvito, K.-C. Lam and A. L. Rheingold, *Inorg. Chem.*, 1999, **38**, 2211.
3 D. Morales, J. Pérez, L. Riera, V. Riera and D. Miguel, *Organometallics*, 2001, **20**, 4517.

4 R. Krishnan, J. K. Voo, C. G. Riordan, L. Zahkarov and A. L. Rheingold, *J. Am. Chem. Soc.*, 2003, **125**, 4422.
5 M. M. Maye, S. C. Chun, L. Han, D. Rabinovich and C.-J. Zhong, *J. Am. Chem. Soc.*, 2002, **124**, 4958.
6 T. Rüffer, C. Bruhn, E. Rusanov, K. Nordhoff and D. Steinborn, *Z. Anorg. Allg. Chem.*, 2002, **628**, 421.
7 F. Becke, T. Rüffer, R. Boese, D. Bläser and D. Steinborn, *J. Organomet. Chem.*, 1997, **545–546**, 169.
8 D. J. Peterson, *J. Org. Chem.*, 1967, **32**, 1717.
9 C. Lustig and N. W. Mitzel, *Organometallics*, 2002, **21**, 3471.
10 D. J. Peterson, *J. Organomet. Chem.*, 1971, **26**, 215.
11 F. Becke, F. W. Heinemann and D. Steinborn, *Organometallics*, 1997, **16**, 2736.
12 T. Rüffer, C. Bruhn, A. H. Maulitz, D. Ströhl and D. Steinborn, *Organometallics*, 2000, **19**, 2829.
13 R. Amstutz, T. Laube, W. B. Schweizer, D. Seebach and J. D. Dunitz, *Helv. Chim. Acta*, 1984, **67**, 224.
14 Only a few other solvent-free organolithium compounds have been structurally characterized; see: T. Kottke and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 580; R. E. Dinnebier, U. Behrens and F. Olbrich, *J. Am. Chem. Soc.*, 1998, **120**, 1430; X. Tian, M. Woski, C. Lustig, T. Pape, R. Fröhlich, D. Le Van, K. Bergander and N. W. Mitzel, *Organometallics*, 2005, **24**, 82.
15 P. v. R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk and N. G. Rondan, *J. Am. Chem. Soc.*, 1984, **106**, 6467.