Bis-, Tris- and Tetrakis(lithiomethyl)germanes: New Building Blocks for Organogermanium Compounds

Carsten Strohmann and Eric Wack
Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
Reprint requests to Dr. C. Strohmann. E-mail: mail@carsten-strohmann.de

Z. Naturforsch. 59b, 1570 – 1578 (2004); received September 9, 2004

Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Bis(lithiomethyl)germanes, R₂Ge(CH₂Li)₂, tris(lithiomethyl)germanes, RGe(CH₂Li)₃, and tetrakis(lithiomethyl)germane, Ge(CH₂Li)₄, were prepared by the reductive C-S bond cleavage with lithium naphthalenide (LiC₁₀H₈) or lithium p,p'-di-tert-butylbiphenyldide (LiDBB) and characterized by trapping with Bu₃SnCl. The bis(lithiomethyl)germanes were used for the synthesis of 1,1-dimethyl-3,3-diphenyl-1-germa-3-silacyclobutane, 1,1-diethyl-3,3-diphenyl-1-germa-3-silacyclobutane, 1,1,3,3-tetraphenyl-1-germa-3-silacyclobutane and 1,1,3,3-tetraphenyl-1,3-digerma-cyclobutane. The single-crystal X-ray diffraction studies of methyltris(phenylthiomethyl)germane and tetrakis(phenylthiomethyl)germane, starting materials for the corresponding poly(lithiomethyl)germanes, indicate tetrahedrally arranged substituents at the germanium atoms.

Key words: Polylithium Compounds, Metalation, 1-Germa-3-silacyclobutane, 1,3-Dilithium, (Stannylmethyl)germanes

Introduction

Organic compounds containing two or more lithium atoms in one molecule are defined as polylithium organic compounds. Three recent reviews of polylmetalated compounds have been published by Maercker and our group [1]. Monolithiated compounds are mostly soluble in polar (ethers) as well as in non-polar solvents (hydrocarbons). In contrast, polylithiated systems are polyfunctional carbon nucleophiles and mostly soluble in polar solvents only and in some case totally insoluble. Thus, to avoid incomplete metalation reactions caused by precipitating partially lithiated intermediates, working in ethers is almost inevitable when synthesizing polylithium compounds. Since side reactions like the deprotonation and/or the decomposition of the polar solvent molecules increase at higher temperatures, the ideal polylithiation reaction is a fast homogeneous reaction at low temperatures. In many cases, the synthesis of polylithium organic compounds by successive deprotonation reactions is difficult, and the second deprotonation step is often kinetically hindered. In exchange reactions (halide-lithium, metal-lithium), the thermodynamic equilibrium can sometimes prevent the formation of the desired polylithium compound. To circumvent these problems, thioether cleavage reactions (reductive carbon-sulfur bond cleavage) have successfully been applied to generate polylithiated compounds [1]. While heterogeneous reactions with lithium metal are becoming too slow at low temperatures, lithium naphthalenide (LiC₁₀H₈, 1) and especially lithium p,p'-di-tert-butylbiphenyldide (LiDBB, 3) can employed as homogeneous THF solutions even at −78 °C. The possibility to prepare LiC₁₀H₈ (1) in THF solution even at room temperature has to be emphasised as a major advantage of this reagent, since LiDBB (3) decomposes at temperatures above 0 °C. In a recent article of Yus and coworkers, the importance of a catalytic amount of DBB in polylithiation reactions with metal-
lic lithium has been emphasised [2]. This has become even more important for LiC_{10}H_{8} (1), since a large excess of lithium might produce the Li_{2}C_{10}H_{8} dianion (2), which has a higher reduction potential [3].

Despite the large number of dilithioalkyl compounds, only a few examples of 1,3-dilithioalkyl compounds have been described [1]. These have great synthetic potential as bifunctional building blocks, e.g., for the synthesis of cyclobutane derivatives, but were not available, mainly due to the lack of appropriate synthetic routes. Also, their decomposition by β-elimination of LiH (e.g., 1,3-dilithiopropane decomposes at −60 °C to give allyllithium) prevented their preparation [4].

As a part of our systematic studies on the structural unit “-CR_{2}-M-CHR_{2}” [M = element of groups 14 – 16, partly with substituents (R = H, alkyl, aryl)] [5, 6], we have investigated the synthesis of bis(lithiomethyl) silanes with the structural unit “LiCH_{2}SiR_{2}-CH_{2}Li” (M = SiR_{2}) [7, 8]. We succeeded in preparing the first non-π-stabilized bis(lithiomethyl)silanes by reductive cleavage of C-S bonds with electron transfer reagents. Bis(phenylthiomethyl)silanes 10–15, tris(phenylthiomethyl)silanes 16–19 and tetrakis(phenylthiomethyl)silane 20, synthesized by reaction of chlorosilanes with (phenylthiomethyl) lithium, were converted to the corresponding (lithiomethyl)silanes 10–20 by reaction with LiC_{10}H_{8} or LiDBB. These were then derivatized by reactions with chlorostannanes and chlorosilanes.

We report here the application of the reductive cleavage of C-S bonds with LiC_{10}H_{8} and LiDBB in the synthesis of bis(lithiomethyl)germanes, tris(lithiomethyl)germane and tetrakis(lithiomethyl)germane, as well as some of their synthetic conversion reactions. The germanium system 21 with stabilizing phenyl substituents on the metalated carbon centres, prepared by Bickelhaupt et al. [9], is the only described example of the class of title compounds.

Results and Discussion

Synthesis of bis(phenylthiomethyl)germane, tris(phenylthiomethyl)germane and tetrakis(phenylthiomethyl)germane compounds

The bis(phenylthiomethyl)germanes, tris(phenylthiomethyl)germanes and tetrakis(phenylthiomethyl)germane B used for reductive cleavage were prepared by reaction of (phenylthiomethyl)lithium with the corresponding chlorogermandes A (3). (Phenylthiomethyl)lithium was synthesized by reaction of thioanisole with n-BuLi in diethyl ether. The bis(phenylthiomethyl)germanes 22–24 and tris(phenylthiomethyl)germanes 31–33 were isolated by Kugelrohr distillation (22, 23, 32) in 44–74% yield or by crystallization (24, 31, 33) in 48–68% yield. Tetrakis(phenylthiomethyl)germane (40) was isolated by crystallization in 63% yield.

\[
\begin{align*}
R_{4(n)}GeCl_{n} + nPhCH_{2}Li & \rightarrow nLiCl + R_{4(n)}GeCH_{2}Ph_{n} \quad (3)
\end{align*}
\]

Single crystals of methyltris(phenylthiomethyl)germane (31) and tetrakis(phenylthiomethyl)germane (40) could be isolated by crystallization from a hexane solution at −35 °C. Methyltris(phenylthiomethyl)germane (31) crystallizes in the monoclinic crystal system, space group Cc with two molecules in the asymmetric unit. The Ge-C bond lengths of 1.933–1.960 Å are in the established range, indicating no strong influence of the sulfur substituent on these bond lengths. Tetrakis(phenylthiomethyl)germane (40) crystallizes in the monoclinic crystal system, space group C2/c with two molecules in the asymmetric unit. One of these molecules shows highly disordered phenylthiomethyl substituents. The disordered sulfur and carbon atoms were refined on split positions. The Ge-C bonds of 1.968–1.995 Å are slightly elongated and the S-CH_{2}-Ge bond angles smaller than these in the methylgermane 31.

Preparation of bis(lithiomethyl)germane, tris(lithiomethyl)germane and tetrakis(lithiomethyl)germane reagents

The use of electron transfer reagents such as LiC_{10}H_{8} or LiDBB results in a fast reductive C-S bond cleavage in a homogeneous phase. By the use of LiC_{10}H_{8} these reactions were effective in replacing the thiophenyl groups of bis(phenylthiomethyl)germanes.
22 – 24 with lithium to give the corresponding bis(lithiomethyl)germanes 25 – 27 as red solutions. The reactions proceed readily in THF at −40 °C. The R₂Ge(CH₂Li)₂ thus formed were derivatized with Bu₃SnCl [ > 95% overall yield by NMR of the crude product; 25 – 38% yield of isolated pure R₂Ge(CH₂SnBu₃)₂].

Tris- and tetrakis(lithiomethyl)germanes are accessible by using LiDBB as an electron transfer reagent. LiDBB is preferred since it has a higher reduction potential compared with LiC₁₀H₈, resulting in a cleaner reaction. Substituted tris(phenylthiomethyl)germanes 31 – 33 and tetrakis(phenylthiomethyl)germane (40) can be turned into the triply and quadruply lithiated organogermanes 34 – 36 and 41 by reaction with LiDBB at −50 °C. The compounds RGe(CH₂Li)₃ and Ge(CH₂Li)₄ formed in this way were derivatized with Bu₃SnCl [ > 90% overall yield by NMR of the crude product; 23 – 33% yield of isolated pure RGe(CH₂SnBu₃)₃ and Ge(CH₂SnBu₃)₄]. Use of LiC₁₀H₈ as electron transfer reagent resulted in the same products but required longer reaction times and gave lower yields. The use of LiC₁₀H₈ at higher temperatures or with longer reaction times resulted in partial deprotonation of the acidic GeCH₂SPh groups by the formed (lithiomethyl)germanes, leading to undesired byproducts. This side reaction is more distinctive for (phenylthiomethyl)germanes than for corresponding (phenylthiomethyl)silanes.

The presence of the bis-, tris- and tetrakis(lithiomethyl)germanes could not be detected by NMR studies of the reaction mixtures, and it was uncertain whether the poly(lithiomethyl)germanes...
Table 1. Crystal data, data collection, and structure refinement of the compounds 31 and 40.

<table>
<thead>
<tr>
<th>Compound</th>
<th>31</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{C}<em>{22}\text{H}</em>{24}\text{GeS}_{3}$</td>
<td>$\text{C}<em>{28}\text{H}</em>{28}\text{GeS}_{4}$</td>
</tr>
<tr>
<td>Weight [g mol$^{-1}$]</td>
<td>547.18</td>
<td>565.33</td>
</tr>
<tr>
<td>Data collection</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>Temperature $T$ [K]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wavelength [Å]</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$C_{2}$</td>
<td>$C_{2}$/c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>6.305(8)</td>
<td>6.620(12)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>25.819(8)</td>
<td>26.557(7)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>6.305(2)</td>
<td>37.40(3)</td>
</tr>
<tr>
<td>空間 volume [Å$^3$]</td>
<td>4313(2)</td>
<td>10903(24)</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.408</td>
<td>1.378</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.715</td>
<td>1.445</td>
</tr>
<tr>
<td>ρ [g cm$^{-3}$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F(000)$</td>
<td>1888</td>
<td>4672</td>
</tr>
<tr>
<td>Crystal size [mm]</td>
<td>0.30 $\times$ 0.20 $\times$ 0.20</td>
<td>0.20 $\times$ 0.20 $\times$ 0.10</td>
</tr>
<tr>
<td>Range for data</td>
<td>4.40 $-$ 50.00</td>
<td>6.60 $-$ 50.00</td>
</tr>
<tr>
<td>Collection 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collected reflections</td>
<td>8936</td>
<td>31982</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5590</td>
<td>9536</td>
</tr>
<tr>
<td>$R_{	ext{int}}$</td>
<td>0.0714</td>
<td>0.0649</td>
</tr>
<tr>
<td>Refinement method</td>
<td>— Full-matrix least-squares on $F^2$ —</td>
<td></td>
</tr>
<tr>
<td>Data</td>
<td>5590</td>
<td>9536</td>
</tr>
<tr>
<td>Restraints</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Parameters</td>
<td>471</td>
<td>658</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.004</td>
<td>1.025</td>
</tr>
<tr>
<td>Final $R$ indices [I &gt; 2σ(I)]</td>
<td>$R_1 = 0.0551$</td>
<td>$R_1 = 0.0615$</td>
</tr>
<tr>
<td>$wR_2 = 0.1276$</td>
<td>$wR_2 = 0.1617$</td>
<td></td>
</tr>
<tr>
<td>$R$ Indices (all data)</td>
<td>$R_1 = 0.0737$, $wR_2 = 0.1352$</td>
<td>$R_1 = 0.1038$, $wR_2 = 0.1832$</td>
</tr>
<tr>
<td>Absolute structure factor</td>
<td>$-0.02(2)$</td>
<td>—</td>
</tr>
<tr>
<td>Largest diff. peak and hole [e Å$^{-3}$]</td>
<td>1.16 and $-0.421$</td>
<td>0.907 and $-0.464$</td>
</tr>
</tbody>
</table>

were present before the Bu$_3$SnCl was added or whether they were formed during the addition of Bu$_3$SnCl. However, two observations indicate that the poly(lithiometlyl)germanes were formed before the addition of the trapping reagent: (i) The green or blue-green colour of LiC$_{10}$H$_8$ or LiDBB had disappeared on addition of the (phenylthiomethyl)germanes, indicating completion of reaction. (ii) Partly metalated species were formed at lower temperatures or after shorter reaction times and trapped with Bu$_3$SnCl. In earlier studies on the synthesis of bis(lithiometlyl)silanes we also isolated trapping products of partly metalated (e.g., monometalated) compounds with Bu$_3$SnCl [7]. The reaction mixtures began to decompose around 0 °C by proton abstraction caused by the lithium bases.

Preparation of 1,1,3,3-tetraphenyl-1,3-digermacyclobutane and 1-germa-3-silacyclobutanes

Cyclic carbosilanes are of interest as starting materials for the preparation of carbosilane polymers and/or Si-C ceramics on pyrolysis of such polymers [10]. Polymeric linear carbosilanes can be produced by ring-opening reactions of 1,3-disilacyclobutanes or thermal rearrangement of polysilanes [11]. 1-Germa-3-silacyclobutanes and 1,3-digermacyclobutanes would be interesting and potentially useful monomers for corresponding polymers, but, to date, selective synthetic routes to non-symmetric cycles are extremely limited. Bis(lithiometlyl)germanes 25–27 served well in the synthesis of the 1-germa-3-silacyclobutanes 43–45 in a reaction with dichlorodiphenylsilane at $-50$ °C. As the reaction mixture was allowed to warm, at 0 °C we added chlorotrimethylsilane to intercept the formed S-nucleophiles and unreacted C-nucleophiles before they could react with 43–45. Kugelrohr distillation gave the 1-germa-3-silacyclobutanes 43 and 44 as colorless liquids (30 and 31% yield) and 45 after additional crystallization from hexane (32% yield). 1,1,3,3-Tetraphenyl-1,3-digermacyclobutane (46) was synthesized analogous starting from bis(lithiometlyl)diphenygermane and dichlorodiphenygermane in 28% yield as colorless crystals. 45 and 46 were also synthesized by Leigh et al. by homo- and cross-[2+2]-cycloaddition of 1,1-diphenyilsilene and 1,1-diphenylergmen [12].

Summary and Perspective

Obviously, poly(lithiometlyl)silanes and poly (lithiometlyl)germanes are ideal precursors for the synthesis of ring systems. Polyliithiated organoger- manes are now available by reductive C-S-bond cleavage in homogeneous phase with electron transfer reagents such as LiC$_{10}$H$_8$ or LiDBB. Further studies are related to the synthesis of germa- and silacycles by the use of bi- or multifunctional building blocks with the structural unit “-$\text{CR}_2$-$\text{M}$-$\text{CR}_2$” (M = element of groups 14–16, partly with substituents (R = H, alkyl, aryl)).
Experimental Section

Melting points: Fa. Büchi, type 510. 1H NMR [solvent CDCl3; internal standard CHCl3 (δ = 7.20)]: Bruker AC-200P (200.13 MHz), 13C NMR [solvent and internal standard CDCl3 (δ = 77.05)]: Bruker AC-200P (50.32 MHz). Assignment of the 13C NMR data was supported by DEPT experiments and relative intensities of the resonances. 29Si NMR (INEPT): [solvent CDCl3; external standard TMS (δ = 0)]: Bruker AC-200P (39.76 MHz). 119Sn NMR: [solvent CDCl3; external standard SnMe4 (δ = 0)]: Bruker AC-200P (74.63 MHz). EI-MS (70 eV): Finnigan-MAT 8430. The selected m/z values given refer to the isotopes 1H, 12C, 28Si, 32S, 74Ge, 120Sn. Microanalyses: Fa. Beller, Göttingen; Leco Elemental Analyser CHN 900, Institute of Inorganic Chemistry, Saarbrücken. Kugelrohr distillation: GKR-501, Fa. Büchi, the boiling points given are over temperatures. All reactions were carried out under oxygen-free and dried argon. The solvents were dried according to common procedures.

General procedure for the synthesis of 22 – 24, 31 – 33 and 40

At −40 °C a cooled solution of 0.24 mol of (phenylthio)methylluminolithium in 200 ml of diethyl ether/hexane, prepared from thioanisole and n-BuLi in diethyl ether [13], was added to a solution of 0.08 mol of the appropriate trichlorosilane or 0.06 mol of SiCl4 in 30 ml of diethyl ether. The reaction mixture was warmed to room temperature, 200 ml of Et2O and then 50 ml of water were added, and the mixture was extracted three times with Et2O. The combined organic solutions were washed three times with 0.5 N HCl and dried over Na2SO4. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation and/or crystallization to give the appropriate (phenylthio)methylgermane.

Bis(phenylthiomethyl)dimethylgermane (22)

B. p. 160 °C/10−3 mm (oven temperature); yield 60%. 1H NMR (200.13 MHz, CDCl3): δ = 0.40 (s, 6 H, GeCH3), 2.40 (s, 4 H, GeCH2S), 7.0 – 7.30 (m, 10 H, SC6H5). 13C NMR (50.32 MHz, CDCl3): δ = −3.4 (GeCH3), 16.5 (GeCH2S), 125.0 (C-4 of SC6H5), 126.4, 128.7 (C-2/C-6 and C-3/C-5 of SC6H5), 139.8 (C-1 of SC6H5). – EI-MS (70 eV): m/z (%) = 350 (28, M+), 227 (100, M+ - CH2SC6H5), 211 (25, M+ - CH2SC4H5 - CH3 - H), 123 (20, CH2SC4H5+). Elemental analysis for C16H20GeS2 (349.0 g mol−1): calcd. C 55.06, H 5.78; found C 55.1, H 6.0%.

Bis(phenylthiomethyl)diethylgermane (23)

B. p. 180 °C/10−3 mm (oven temperature); yield 44%. 1H NMR (200.13 MHz, CDCl3): δ = 0.9 – 1.2 (m, 10 H, GeCH2CH3), 2.42 (s, 4 H, GeCH2S), 7.0 – 7.35 (m, 10 H, SC6H5). 13C NMR (50.32 MHz, CDCl3): δ = 5.2 (GeCH2CH3), 8.8 (GeCH2CH3), 13.5 (GeCH2S), 124.9 (C-4 of SC6H5), 126.2 (C-2/C-6 or C-3/C-5 of SC6H5), 128.7 (C-2/C-6 or C-3/C-5 of SC6H5), 140.2 (C-1 of SC6H5). – EI-MS (70 eV): m/z (%) = 376 (16, M+), 349 (3, M+ - CH3 - C6H5), 255 (100, M+ - CH2SC6H5), 123 (16, CH2SC4H5+). Elemental analysis for C18H24GeS2 (377.1 g mol−1): calcd. C 57.33, H 6.41; found C 57.4, H 6.7%.

Bis(phenylthiomethyl)diphenylgermane (24)

M. p. 62 °C (hexane/diethylether 2:1); yield 56%. 1H NMR (200.13 MHz, CDCl3): δ = 2.89 (s, 4 H, GeCH2S), 7.0 – 7.60 (m, 20 H, GeC6H5 and SC6H5). 13C NMR (50.32 MHz, CDCl3): δ = 15.2 (GeCH2S), 125.1 (C-4 of SC6H5), 126.6 (4 C), 128.4, 128.8 (C-2/C-6 or C-3/C-5 of GeC6H5 or SC6H5), 129.8 (C-4 of GeC6H5), 134.2 (C-1 of GeC6H5). – EI-MS (70 eV): m/z (%) = 474 (11, M+), 351 (100, M+ - CH2SC6H5), 273 (11, M+ - CH2SC6H5 - C6H5 - H), 123 (33, CH2SC4H5+). Elemental analysis for C26H26GeS2 (473.2 g mol−1): calcd. C 66.0, H 5.11; found C 66.1, H 5.2.

Methyltris(phenylthiomethyl)germane (31)

B. p. (oven temperature): 225 °C/10−3 mm/m.p.: 50 °C (hexane); yield 68%. 1H NMR (200.13 MHz, CDCl3): δ = 0.49 (s, 3 H, GeCH3), 2.52 (s, 6 H, GeCH2S), 7.0 – 7.30 (m, 15 H, SC6H5). 13C NMR (50.32 MHz, CDCl3): δ = −4.9 (GeCH3), 15.6 (GeCH2S), 125.3 (C-4 of SC6H5), 126.8, 128.8 (C-2/C-6 and C-3/C-5 of SC6H5), 139.1 (C-1 of SC6H5). – EI-MS (70 eV): m/z (%) = 458 (27, M+), 443 (3, M+ - CH3), 335 (100, M+ - CH2SC6H5), 225 (46, M+ - CH2SC6H5 - C6H5 - H), 211 (39, M+ - 2 CH2SC6H5 - H), 123 (80, CH2SC4H5+). Elemental analysis for C22H22GeS3 (457.2 g mol−1): calcd. C 57.80, H 5.29; found C 57.9, H 5.2%.

Ethyltris(phenylthiomethyl)germane (32)

B. p. 220 °C/10−3 mm (oven temperature); yield 74%. 1H NMR (200.13 MHz, CDCl3): δ = 1.15 “s” [broad signal], 5 H, GeCH2CH3), 2.55 (s, 6 H, GeCH2S), 7.0 – 7.35 (m, 15 H, SC6H5). 13C NMR (50.32 MHz, CDCl3): δ = 6.0 (GeCH2CH3), 8.7 (GeCH2CH3), 14.2 (GeCH2S), 125.2 (C-4 of SC6H5), 126.6, 128.8 (C-2/C-6 and C-3/C-5 of SC6H5), 139.3 (C-1 of SC6H5). – EI-MS (70 eV): m/z (%) = 472 (28, M+), 349 (100, M+ - CH2SC6H5), 239 (42, M+ - CH2SC6H5 - SC6H5 - H), 123 (70, CH2SC4H5+). Elemental analysis for C23H24GeS3 (471.2 g mol−1): calcd. C 58.52, H 5.56; found C 58.7, H 5.9%.
Phenyltris(phenylthiomethyl)germane (33)

M. p. 58 °C (hexane); yield 48%. 1H NMR (200.13 MHz, CDC13): δ = 2.77 (s, 6 H, GeCH2S), 7.00–7.60 (m, 20 H, GeC6H5 and SC6H5). – 13C1H NMR (50.32 MHz, CDC13): δ = 15.0 (GeCH2S), 125.4 (C-4 of SC6H5), 126.9 (C-2/C-6 or C-3/C-5 of SC6H5), 128.5 (C-2/C-6 or C-3/C-5 of GeCH2H5), 128.8 (C-2/C-6 or C-3/C-5 of SC6H5), 130.0 (C-4 of GeC6H5), 133.9 (C-2/C-6 or C-3/C-5 of GeCH2H5), 134.4 (C-1 of GeCH3), 139.1 (C-1 of SC6H5). – 13C NMR (C-2/C-6 or C-3/C-5 of SC6H5), 128.5 (C-2/C-6 or C-3/C-5 of GeCH2H5), 131.0 (100, M+ - C6H5 - CH2SC6H5 - H), 273 (8, M+ - 2 SC6H5 - H), 123 (68, CH2SC6H5+). Elemental analysis for C27H26GeS (519.3 g mol–1): calcd. C 62.45, H 5.05; found C 61.6, H 5.2%.

Tetras(phenylthiomethyl)germane (40)

M. p. 57 °C (acetone/hexane 1:2); yield 63%. 1H NMR (200.13 MHz, CDC13): δ = 2.60 (s, 8 H, GeCH2S), 7.00–7.30 (m, 20 H, GeC6H5). – 13C1H NMR (50.32 MHz, CDC13): δ = 14.8 (GeCH2S), 125.6 (C-4 of SC6H5), 127.2, 128.9 (C-2/C-6 and C-3/C-5 of SC6H5), 138.6 (C-1 of SC6H5). – 13C NMR (C-2/C-6 and C-3/C-5 of SC6H5), 128.5 (C-2/C-6 and C-3/C-5 of GeCH2H5), 131.0 (100, M+ - C6H5 - CH2SC6H5 - H), 273 (8, M+ - 2 SC6H5 - H), 123 (68, CH2SC6H5+). Elemental analysis for C28H26GeS4 (565.4 g mol–1): calcd. C 59.49, H 4.99; found C 59.2, H 5.1%.

General procedure for the synthesis of 25 – 27 and transformation to 28 – 30

At –60 °C 5 mmol of the appropriate bis(phenylthiomethyl)germane in 3 ml of THF was added to a freshly prepared solution of 21 mmol of LiC6H5 in 30 ml of THF and stirred for 2 h at –40 °C. Bu3SnCl (6.8 g, 21 mmol) was added to the reaction mixture at –78 °C. After warming to room temperature the solvent was evaporated in vacuo and the residue was extracted with hexane and filtered. After evaporating the solvent the residue was purified by Kugelrohr distillation to give the appropriate bis(stannylmethyl)germane. C10H8 and Bu3SnSPh were isolated at the temperatures listed below.

At –60 °C 5 mmol of the appropriate bis(phenylthiomethyl)germane in 3 ml of THF was added to a freshly prepared solution of 32 mmol of LiDDBB in 40 ml of THF and stirred for 6 h at –50 °C. Bu3SnCl (10.4 g, 32 mmol) was added to the reaction mixture at –78 °C.

After warming to room temperature the solvent was evaporated in vacuo and the residue was extracted with hexane and filtered. After evaporating the solvent the residue was purified by Kugelrohr distillation to give the appropriate tris(stannylmethyl)germane. DBB and Bu3SnSHs were removed at 100–120 °C/10–3 mbar, and the high-boiling (stannylmethyl)germanes were isolated at the temperatures listed below. 42 was prepared analogously (5 mmol of 41, 42 mmol of LiDDBB, reaction time 8 h at –50 °C, 42 mmol Bu3SnCl).

Bis(butylstannylmethyl)dimethylgermane (28)

B. p. 165 °C/10–3 mm (oven temperature); yield 25%. 1H NMR (200.13 MHz, CDC13): δ = 0.22 (s, 21H, 119/117Sn) = 59.2/56.7 Hz, 4 H, GeCH2Sn), 0.10 (s, 6 H, GeCH3), 0.55–1.60 (m, 54 H, SnC4H9, CCH3, GeCH3, CCH3) – 119/117Sn NMR (50.32 MHz, CDC13): δ = –3.7 (J(C, 119/117Sn) = 221.2/211.5 Hz, 12 H, GeCH3), 10.4 (J(C, 119/117Sn) = 322.3/327.9 Hz; SnC4H9, 13.6 (CCH3), 27.5 (J(C, 119/117Sn) = 57.0/54.6 Hz; CCH3), 29.3 (J(C, Sn) = 19.4 Hz; SnC2H5C2H5). – 119Sn NMR (74.63 MHz, CDC13): δ = –4.2. – 119Sn NMR (70 eV): m/z (%) = 653 (100, M+ - C6H5 - M+ - C2H5Sn, M+ = C2H5Sn2Ge118Sn120), 579 (38, M+ - 2 C4H9 + H), 539 (30, M+ - 3 C4H9), 481 (30, M+ - 4 C2H5 + H), 291 (76, 120Sn(C4H9)3). Elemental analysis for C39H58GeSn2 (710.8 g mol–1): calcd. C 47.32, H 9.08; found C 47.6, H 9.1%.

Bis(butylstannylmethyl)diethylgermane (29)

B. p. 165 °C/10–3 mm (oven temperature); yield 31%. 1H NMR (200.13 MHz, CDC13): δ = –0.27 (s, 21H, 119/117Sn) = 60.5/57.8 Hz, 4 H, GeCH2Sn), 0.55–1.55 (m, 64 H, GeCH3C2H5 and SnC4H9, CCH3C2H5, CCH3) – 119/117Sn NMR (50.32 MHz, CDC13): δ = –10.7 (J(C, 119/117Sn) = 217.8/211.0 Hz, 21H, C (Sn) = 15.8 Hz; GeCH3Sn, 9.1 (GeCH2CH3), 9.7 (J(C, Sn) = 10.5 Hz; GeCH2CH3), 10.5 (J(C, 119/117Sn) = 311.3/302.8 Hz; SnC4H9, 13.7 (CCH3), 27.5 (J(C, 119/117Sn) = 57.5/55.0 Hz; CCH3), 29.3 (J(C, Sn) = 19.2 Hz; SnC2H5C2H5). – 119Sn NMR (74.63 MHz, CDC13): δ = 4.8. – 119Sn NMR (70 eV): m/z (%) = 661 (76, M+ - C4H9, M+ = C30H68Ge118Sn120, 625 (28, M+ - 2 C4H9 + H), 501 (100), 291 (55, SnC2H5C2H5)). Elemental analysis for C30H68GeSn2 (738.8 g mol–1): calcd. C 48.77, H 9.28; found C 49.1, H 8.9%.

Bis(butylstannylmethyl)diethylgermane (30)

B. p. (oven temperature): 220 °C/10–3 mm; yield 38%. 1H NMR (200.13 MHz, CDC13): δ = 0.01 (s, 21H, Sn) = 43.0 Hz, 4 H, GeCH2Sn),

C. Strohmann – E. Wack - Bis-, Tris- and Tetrakis(lithiomethyl)germanes

1575
0.5 – 1.6 (m, 54 H, Sn(C₂H₅)₂), 6.80 – 7.40 (m, 10 H, GeC₅H₅). - ¹³C [¹H] NMR (50.32 MHz, CDCl₃): δ = -9.0 (GeCH₂Sn), 13.7 (SnCH₂C), 14.3 (CCH₂CH₃), 27.0 (C(CH₂CH₃)₂), 28.5 (SnCH₂CH₃), 125.7 (C=O of GeC₅H₅), 128.5, 134.7 (C=2-C=6 and C=3-C=5 of GeC₅H₅), 139.7 (C=4 of GeC₅H₅). - ¹¹⁹Sn NMR (74.63 MHz, CDCl₃): δ = 3.9. Elemental analysis for C₃₉H₆₀GeSn₃ (834.9 g mol⁻¹): calcd. C 54.67, H 8.21; found C 54.9, H 8.1.

**Tris(butylstannylmethyl)methylgermane (37)**

B. p. 230 °C/10⁻³ mm (oven temperature); yield: 23%. ¹H NMR (200.13 MHz, CDCl₃): δ = -0.20 (s, 2J(H, ¹¹⁹Sn) = 59.65/71. Hz, 6 H, GeCH₂Sn), 0.07 (s, 3 H, GeCH₃), 0.70 – 1.55 (m, 81 H, SnCH₂C, CCH₂C, CCH₃), - ¹³C [¹H] NMR (50.32 MHz, CDCl₃): δ = -3.9 (³J(C, ¹¹⁹Sn) = 222.8/221.2 Hz, ³J(C, Sn) = 15.1 Hz; GeCH₃Sn), 3.9 (³J(C, Sn) = 8.8 Hz; GeCH₃), 10.5 (³J(C, ¹¹⁹Sn) = 321.6/307.2 Hz; SnCH₂C), 13.7 (CCH₂C), 27.5 (³J(C, ¹¹⁹Sn) = 57.3/54.9 Hz, CCH₂CH₃), 29.3 (³J(C, Sn) = 19.2 Hz; SnCH₂CH₃). - ¹¹⁹Sn NMR (74.63 MHz, CDCl₃): δ = 3.2. Elemental analysis for C₃₉H₄₀GeSn (999.8 g mol⁻¹): calcd. C 48.05, H 9.07; found C 48.4, H 8.9.

**Tetrakis(butylstannylmethyl)methylgermane (42)**

B. p. 250 °C/10⁻³ mm (oven temperature); yield: 33%. ¹H NMR (200.13 MHz, CDCl₃): δ = -0.19 (s, 2J(H, Sn) = 60.2 Hz, 8 H, GeCH₂Sn), 0.55 – 1.65 (m, 108 H, Sn(C₂H₅)₂), - ¹³C [¹H] NMR (50.32 MHz, CDCl₃): δ = -2.3 (³J(C, Sn) = 13.6 Hz; GeCH₃Sn), 10.7 (³J(C, ¹¹⁹Sn) = 321.0/306.6 Hz; SnCH₂C), 13.7 (CCH₂C), 27.5 (³J(C, ¹¹⁹Sn) = 57.9/55.3 Hz; CCH₂CH₃), 29.4 (³J(C, Sn) = 5.5 Hz; SnCH₂CH₃). - ¹¹⁹Sn NMR (74.63 MHz, CDCl₃): δ = 2.1. Elemental analysis for C₄₃H₃₆GeSn₄ (1288.8 g mol⁻¹): calcd. C 48.46, H 9.07; found C 48.2, H 9.2.

**General procedure for the synthesis of 43 – 46**

At ~60 °C 5 mmol of the appropriate bis(phenylthio)methylgermane in 3 ml of THF was added to a freshly prepared solution of 21 mmol of LiC₅H₄Sn in 30 ml of THF and stirred for 2 h at ~40 °C. Bu₃SnCl (6.8 g, 21 mmol) was added to the reaction mixture at ~78 °C. 5 mmol of the appropriate dichlorosilane or dichlorodiphenylgermane was added to the reaction mixture at ~78 °C and after warming to ~0 °C over a period of 20 min 10 mmol of Me₂SiCl was added. Hydrolysis and extraction with Et₂O, drying of the organic phase over sodium sulfate, and evaporation of the solution yielded a residue. C₁₀H₄₄ and Bu₃SnPh were removed at 60 and 100 – 120 °C/10⁻³ mbar, and 43 and 44 were isolated at the temperatures listed below. Recrystallization from hexane gave 45 and 46 as colorless crystals.

1.1-Dimethyl-3,3-diphenyl-1-germa-3-silacyclopentane (43)

B. p. 130 °C/10⁻³ mm (oven temperature); yield: 31%. ¹H NMR (200.13 MHz, CDCl₃): δ = 0.46 (s, 6 H, GeCH₃), 0.82 (s, 2J(H, Si) = 5.1 Hz, 4 H, SiCH₂Ge), 7.20 – 7.65 (m, 10 H, SiC₅H₄). - ¹³C [¹H] NMR (50.32 MHz, CDCl₃): δ = 2.0 (GeCH₃), 4.4 (SiCH₂Ge), 127.8 (C=2-C=6 or C=3-C=5 of SiC₅H₄), 129.2 (C=4 of SiC₅H₄), 134.0 (C=2-C=6 or C=3-C=5 of SiC₅H₄), 139.0 (C=1 of SiC₅H₄). - ²⁹Si NMR (39.76 MHz, CDCl₃): δ = -3.0. - EI-MS (70 eV): m/z (%) = 314 (26, M⁺), 299 (100, M⁺ - CH₃), 223 (58, M⁺ - C₆H₅ - CH₂), 211 (41, M⁺ - Ge(CH₂)₃ + H). Elemental analysis for C₁₅H₂₀GeSi (313.0 g mol⁻¹): calcd. C 61.40, H 6.44; found C 62.0, H 6.3%.
1,1-Diethyl-3,3-diphenyl-1-germa-3-silacyclobutane (44)

B.p. 135 °C/10−3 mm (oven temperature); yield 30%. 1H NMR (200.13 MHz, CDCl3): δ = 0.73 (s, 6H, SiC 6H5 and GeC 6H5). 13C NMR (50.32 MHz, CDCl3): δ = 129.4 (C-4 of SiC 6H5 or GeC 6H5), 133.8, 134.2 (C-2/C-6 or C-3/C-5 of SiC 6H5 or GeC 6H5), 128.3 (C-2/C-6 or C-3/C-5 of SiC 6H5 or GeC 6H5), 129.0, 129.1 (C-1 of SiC 6H5). – 29Si NMR (39.76 MHz, CDCl 3): δ = -2.6. – EI-MS (70 eV): m/z (%) = 438 (3, M+), 423 (2, M+ - CH3), 269 (18, M+ - 2 C6H5 - CH3), 197 (18, (C6H5)2SiCH3), 128 (100, M+ - 4 C6H5 - 2 H). Elemental analysis for C18H24GeSi: calcd. C 64.84, H 5.02; found C 65.0, H 5.53; yield 57%. 1H NMR (50.32 MHz, CDCl3): δ = 1.58 (s, 4H, GeCH2Ge), 7.20 – 7.60 (m, 20 H, GeC6H5). – 13C (1H) NMR (50.32 MHz, CDCl3): δ = 7.7 (GeCH2Ge), 128.3 (C-2/C-6 or C-3/C-5 of GeC6H5), 129.0 (C-4 of GeC6H5), 133.7 (C-2/C-6 or C-3/C-5 of GeC6H5), 139.6 (C-1 of GeC6H5). Elemental analysis for C26H24Ge2: (481.7 g mol−1): calcd. C 64.84, H 5.02; found C 65.0, H 4.9.

Crystal structure determination

Single crystals of compounds 31 and 40 were obtained by cooling of a saturated solution in hexane to −35 °C. Data collections were performed on a STOE IPDS diffractometer employing graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares methods on F2 [14]. The hydrogen atoms were calculated on ideal positions and refined by the riding model. Some phenylthiomethyl groups of 40 are disordered; corresponding sulfur and carbon atoms were refined on split positions. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. The crystallographic data of 31 and 40 (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre, CCDC-247123 (40) and CCDC-247124 (31).

Acknowledgements

We gratefully acknowledge the generous financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Prof. M. Veith (University Saarbrücken) for supporting this work.


[8] The illustrations of polylithiated compounds are not indicative of the real structure of these compounds in solution or the solid state.


