

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

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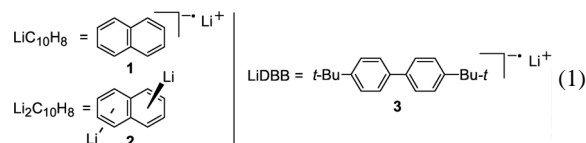
Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Bis(lithiomethyl)germanes, $R_2Ge(CH_2Li)_2$, tris(lithiomethyl)germanes, $RGe(CH_2Li)_3$, and tetrakis(lithiomethyl)germane, $Ge(CH_2Li)_4$, were prepared by the reductive C-S bond cleavage with lithium naphthalenide ($LiC_{10}H_8$) or lithium *p,p'*-di-*tert*-butylbiphenylide (LiDBB) and characterized by trapping with Bu_3SnCl . 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: Polyolithium 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 polyolithium organic compounds. Three recent reviews of poly-metalated 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, polyolithiated 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 polyolithium compounds. Since side reactions like the deprotonation and/or the decomposition of the polar solvent molecules increase at higher temperatures, the ideal polyolithiation reaction is a fast homogeneous reaction at low temperatures. In many cases, the synthesis of polyolithium organic compounds by successive deprotonation reactions is difficult, and the second deprotonation step is often kinetically hindered. In exchange reactions

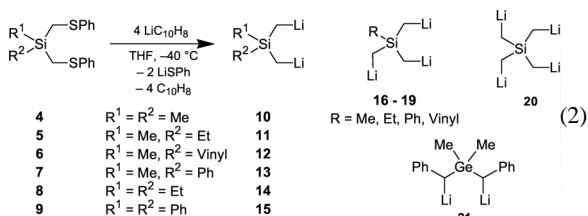


(halide-lithium, metal-lithium), the thermodynamic equilibrium can sometimes prevent the formation of the desired polyolithium compound. To circumvent these problems, thioether cleavage reactions (reductive carbon-sulfur bond cleavage) have successfully been applied to generate polyolithiated compounds [1]. While heterogeneous reactions with lithium metal are becoming too slow at low temperatures, lithium naphthalenide ($LiC_{10}H_8$, **1**) and especially lithium *p,p'*-di-*tert*-butylbiphenylide (LiDBB, **3**) can be employed as homogeneous THF solutions even at $-78\text{ }^{\circ}\text{C}$. The possibility to prepare $LiC_{10}H_8$ (**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 $0\text{ }^{\circ}\text{C}$. In a recent article of Yus and coworkers, the importance of a catalytic amount of DBB in polyolithiation reactions with metal-

lic lithium has been emphasised [2]. This has become even more important for $\text{LiC}_{10}\text{H}_8$ (**1**), since a large excess of lithium might produce the $\text{Li}_2\text{C}_{10}\text{H}_8$ 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-dilithiopropene decomposes at -60°C to give allyllithium) prevented their preparation [4].

As a part of our systematic studies on the structural unit “ $-\text{CR}_2-\text{M}-\text{CR}_2-$ ” [M = element of groups 14–16, partly with substituents ($\text{R} = \text{H}$, alkyl, aryl)] [5,6], we have investigated the synthesis of bis(lithiomethyl)silanes with the structural unit “ $\text{LiCH}_2-\text{SiR}_2-\text{CH}_2\text{Li}$ ” ($\text{M} = \text{SiR}_2$) [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 $\text{LiC}_{10}\text{H}_8$ or LiDBB. These were then derivatized by reactions with chlorostannanes and chlorosilanes.

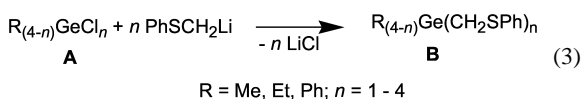


We report here the application of the reductive cleavage of C-S bonds with $\text{LiC}_{10}\text{H}_8$ and LiDBB in the synthesis of bis(lithiomethyl)germanes, tris(lithiomethyl)germanes and tetrakis(lithiomethyl)germane, as well as some of their synthetic conversion reactions. The germanium system **21** 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 chlorogermanes **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.

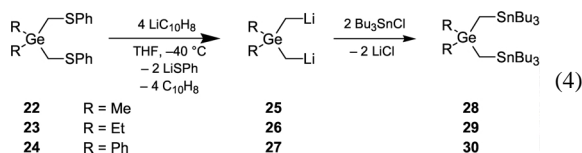


Single crystals of methyltris(phenylthiomethyl)germane (**31**) and tetrakis(phenylthiomethyl)germane (**40**) could be isolated by crystallization from a hexane solution at -35°C . Methyltris(phenylthiomethyl)germane (**31**) crystallizes in the monoclinic crystal system, space group *Cc* with two molecules 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-CH₂-Ge bond angles smaller than these in the methylgermane **31**.

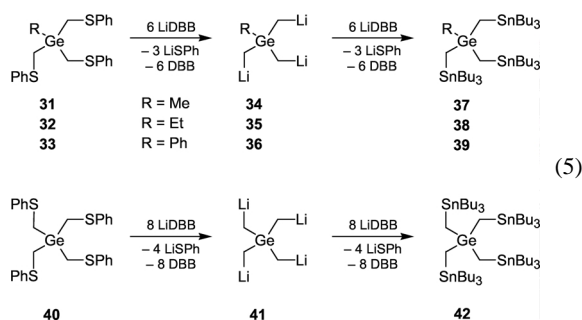
Preparation of bis(lithiomethyl)germane, tris(lithiomethyl)germane and tetrakis(lithiomethyl)germane reagents

The use of electron transfer reagents such as $\text{LiC}_{10}\text{H}_8$ or LiDBB results in a fast reductive C-S bond cleavage in a homogeneous phase. By the use of $\text{LiC}_{10}\text{H}_8$ 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 $-40\text{ }^{\circ}\text{C}$. The $\text{R}_2\text{Ge}(\text{CH}_2\text{Li})_2$ thus formed were derivatized with Bu_3SnCl [$> 95\%$ overall yield by NMR of the crude product; $25\text{--}38\%$ yield of isolated pure $\text{R}_2\text{Ge}(\text{CH}_2\text{SnBu}_3)_2$].



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 $\text{LiC}_{10}\text{H}_8$, 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 $-50\text{ }^{\circ}\text{C}$. The compounds $\text{RGe}(\text{CH}_2\text{Li})_3$ and $\text{Ge}(\text{CH}_2\text{Li})_4$ formed in this way were derivatized with Bu_3SnCl [$> 90\%$ overall yield by NMR of the crude product; $23\text{--}33\%$ yield of isolated pure $\text{RGe}(\text{CH}_2\text{SnBu}_3)_3$ and $\text{Ge}(\text{CH}_2\text{SnBu}_3)_4$. Use of $\text{LiC}_{10}\text{H}_8$ as electron transfer reagent resulted in the same products but required longer reaction times and gave lower yields. The use of $\text{LiC}_{10}\text{H}_8$ at higher temperatures or with longer reaction times resulted in partial deprotonation of the acidic GeCH_2SPh 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

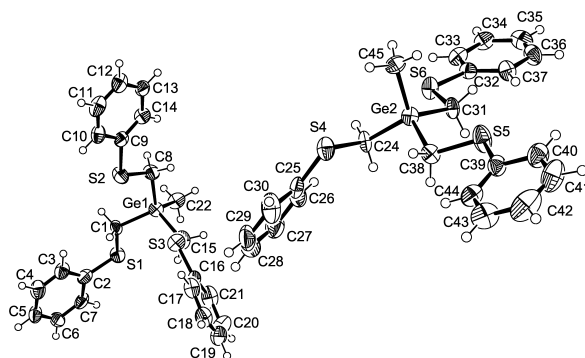


Fig. 1. The two independent molecules of **31** in the crystal (ORTEP, 50% probability ellipsoids, hydrogen atoms with arbitrary radii) with atomic numbering. Selected bond lengths [Å] and angles [°]: C(1)–S(1) 1.812(9), C(1)–Ge(1) 1.953(8), C(2)–S(1) 1.778(11), C(8)–S(2) 1.786(11), C(8)–Ge(1) 1.950(9), C(9)–S(2) 1.780(9), C(15)–S(3) 1.797(10), C(15)–Ge(1) 1.960(11), C(16)–S(3) 1.779(10), C(22)–Ge(1) 1.933(10), C(24)–S(4) 1.800(8), C(24)–Ge(2) 1.949(8), C(25)–S(4) 1.777(10), C(31)–S(6) 1.803(10), C(31)–Ge(2) 1.955(8), C(32)–S(6) 1.778(9), C(38)–S(5) 1.785(8), C(38)–Ge(2) 1.960(10), C(39)–S(5) 1.797(12), C(45)–Ge(2) 1.940(8); S(1)–C(1)–Ge(1) 109.6(4), S(2)–C(8)–Ge(1) 111.3(6), S(3)–C(15)–Ge(1) 111.9(5), S(4)–C(24)–Ge(2) 108.0(4), S(5)–C(38)–Ge(2) 107.8(5), S(6)–C(31)–Ge(2) 107.9(4).

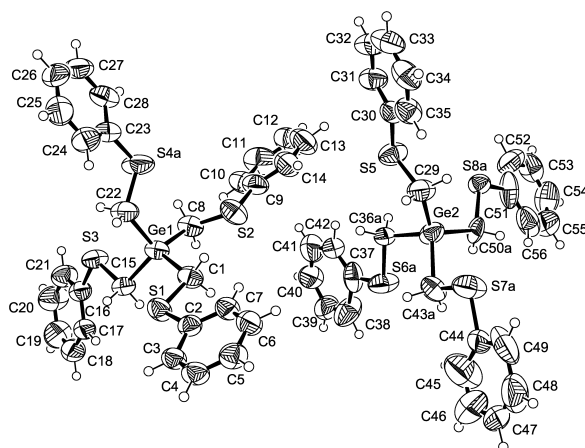


Fig. 2. The two independent molecules of **40** (only one of two disordered atoms shown) in the crystal (ORTEP, 50% probability ellipsoids, hydrogen atoms with arbitrary radii) with atomic numbering. Selected bond lengths [Å] and angles [°] for one molecule: C(1)–S(1) 1.793(6), C(1)–Ge(1) 1.978(6), C(2)–S(1) 1.769(6), C(9)–S(2) 1.770(7), C(8)–S(2) 1.773(7), C(15)–S(3) 1.803(6), C(16)–S(3) 1.776(6), C(15)–Ge(1) 1.968(6), C(8)–Ge(1) 1.995(6), C(22)–Ge(1) 1.970(7), C(23)–S(4A) 1.783(8); S(1)–C(1)–Ge(1) 108.4(3), S(2)–C(8)–Ge(1) 107.8(3), S(3)–C(15)–Ge(1) 107.7(3).

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**.

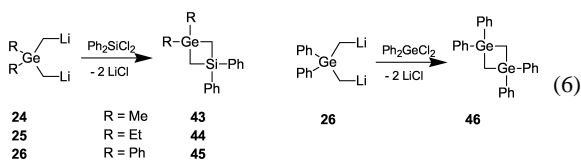
Compound	31	40
Empirical formula	C ₂₂ H ₂₄ GeS ₃	C ₂₈ H ₂₈ GeS ₄
Formula weight [g·mol ⁻¹]	457.18	565.33
Data collection	173(2)	173(2)
temperature <i>T</i> [K]		
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>Cc</i>	<i>C2/c</i>
<i>a</i> [Å]	6.305(2)	46.51(4)
<i>b</i> [Å]	25.819(8)	6.620(12)
<i>c</i> [Å]	26.557(7)	37.40(3)
β [°]	94.06(4)	108.77(10)
Cell volume [Å ³]	4313(2)	10903(24)
<i>Z</i>	8	16
Calculated density	1.408	1.378
ρ [g·cm ⁻³]		
Absorption coefficient	1.715	1.445
μ [mm ⁻¹]		
<i>F</i> (000)	1888	4672
Crystal size [mm]	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.10
Range for data collection 2θ [°]	4.40 – 50.00	6.60 – 50.00
Collected reflections	8936	31982
Independent reflections	5590	9536
<i>R</i> _{int}	0.0714	0.0649
Refinement method	— Full-matrix least-squares on <i>F</i> ² —	
Data	5590	9536
Restraints	2	0
Parameters	471	658
Goodness-of-fit on <i>F</i> ²	1.004	1.025
Final <i>R</i> indices [<i>I</i> > 2(<i>I</i>)]	<i>R</i> 1 = 0.0551, <i>wR</i> 2 = 0.1276	<i>R</i> 1 = 0.0615, <i>wR</i> 2 = 0.1617
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0737, <i>wR</i> 2 = 0.1352	<i>R</i> 1 = 0.1038, <i>wR</i> 2 = 0.1832
Absolute structure factor	−0.02(2)	—
Largest diff. peak and hole [e·Å ⁻³]	1.116 and −0.421	0.907 and −0.464

were present before the Bu₃SnCl was added or whether they were formed during the addition of Bu₃SnCl. However, two observations indicate that the poly(lithiomethyl)germanes were formed before the addition of the trapping reagent: (i) The green or blue-green colour of LiC₁₀H₈ 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 Bu₃SnCl. In earlier studies on the synthesis of bis(lithiomethyl)silanes we also isolated trapping products of partly metalated (*e.g.*, monometalated) compounds with Bu₃SnCl [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(lithiomethyl)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(lithiomethyl)diphenylgermane and dichlorodiphenylgermane 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-diphenylsilene and 1,1-diphenylgermene [12].



Summary and Perspective

Obviously, poly(lithiomethyl)silanes and poly(lithiomethyl)germanes are ideal precursors for the synthesis of ring systems. Polyolithiated organogermanes are now available by reductive C-S-bond cleavage in homogeneous phase with electron transfer reagents such as LiC₁₀H₈ 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 “-CR₂-M-CR₂-” [M = element of groups 14–16, partly with substituents (R = H, alkyl, aryl)].

Experimental Section

Melting points: Fa. Büchi, type 510. ^1H NMR [solvent CDCl_3 ; internal standard CHCl_3 ($\delta = 7.20$)]: Bruker AC-200P (200.13 MHz). ^{13}C NMR [solvent and internal standard CDCl_3 ($\delta = 77.05$)]: Bruker AC-200P (50.32 MHz). Assignment of the ^{13}C NMR data was supported by DEPT experiments and relative intensities of the resonance signals. ^{29}Si NMR (INEPT): [solvent CDCl_3 ; external standard TMS ($\delta = 0$)]: Bruker AC-200P (39.76 MHz). ^{119}Sn NMR: [solvent CDCl_3 ; external standard SnMe_4 ($\delta = 0$)]: Bruker AC-200P (74.63 MHz). EI-MS (70 eV): Finnigan-MAT 8430. The selected m/z values given refer to the isotopes ^1H , ^{12}C , ^{28}Si , ^{32}S , ^{74}Ge , ^{120}Sn . 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 oven 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 (phenylthiomethyl)lithium in 200 ml of diethyl ether/hexane, prepared from thioanisole and $n\text{-BuLi}$ in diethyl ether [13], was added to a solution of 0.08 mol of the appropriate trichlorosilane or 0.06 mol of SiCl_4 in 30 ml of diethyl ether. The reaction mixture was warmed to room temperature, 200 ml of Et_2O and then 50 ml of water were added, and the mixture was extracted three times with Et_2O . The combined organic solutions were washed three times with 0.5 N HCl and dried over Na_2SO_4 . The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation and/or crystallization to give the appropriate (phenylthiomethyl)germane.

Bis(phenylthiomethyl)dimethylgermane (22)

B.p. $160^\circ\text{C}/10^{-3}$ mm (oven temperature); yield 60%. ^1H NMR (200.13 MHz, CDCl_3): $\delta = 0.40$ (s, 6 H, GeCH_3), 2.40 (s, 4 H, GeCH_2S), 7.0–7.30 (m, 10 H, SC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): $\delta = -3.4$ (GeCH_3), 16.5 (GeCH_2S), 125.0 (C-4 of SC_6H_5), 126.4, 128.7 (C-2/C-6 and C-3/C-5 of SC_6H_5), 139.8 (C-1 of SC_6H_5). – EI-MS (70 eV): m/z (%) = 350 (28, M^+), 227 (100, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5$), 211 (25, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5 - \text{CH}_3 - \text{H}$), 123 (20, $\text{CH}_2\text{SC}_6\text{H}_5^+$). Elemental analysis for $\text{C}_{16}\text{H}_{20}\text{GeS}_2$ (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. $180^\circ\text{C}/10^{-3}$ mm (oven temperature); yield 44%. ^1H NMR (200.13 MHz, CDCl_3): $\delta = 0.9 - 1.2$ (m, 10 H,

GeCH_2CH_3), 2.42 (s, 4 H, GeCH_2S), 7.0–7.35 (m, 10 H, SC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): $\delta = 5.2$ (GeCH_2CH_3), 8.8 (GeCH_2CH_3), 13.5 (GeCH_2S), 124.9 (C-4 of SC_6H_5), 126.2 (C-2/C-6 or C-3/C-5 of SC_6H_5), 128.7 (C-2/C-6 or C-3/C-5 of SC_6H_5), 140.2 (C-1 of SC_6H_5). – EI-MS (70 eV): m/z (%) = 378 (16, M^+), 349 (3, $\text{M}^+ - \text{C}_2\text{H}_5$), 255 (100, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5$), 123 (16, $\text{CH}_2\text{SC}_6\text{H}_5^+$). Elemental analysis for $\text{C}_{18}\text{H}_{24}\text{GeS}_2$ (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, CDCl_3): $\delta = 2.89$ (s, 4 H, GeCH_2S), 7.0–7.60 (m, 20 H, GeC_6H_5 and SC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): $\delta = 15.2$ (GeCH_2S), 125.1 (C-4 of SC_6H_5), 126.6 (4 C), 128.4, 128.8 (C-2/C-6 or C-3/C-5 of GeC_6H_5 or SC_6H_5), 129.8 (C-4 of GeC_6H_5), 134.2 (C-1 of GeC_6H_5), 134.5 (C-2/C-6 or C-3/C-5 of GeC_6H_5 or SC_6H_5), 139.6 (C-1 of SC_6H_5). – EI-MS (70 eV): m/z (%) = 474 (11, M^+), 351 (100, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5$), 273 (11, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5 - \text{C}_6\text{H}_5 - \text{H}$), 123 (33, $\text{CH}_2\text{SC}_6\text{H}_5^+$). Elemental analysis for $\text{C}_{26}\text{H}_{24}\text{GeS}_2$ (473.2 g mol^{-1}): calcd. C 66.00, H 5.11; found C 66.1, H 5.2.

Methyltris(phenylthiomethyl)germane (31)

B.p. (oven temperature): $225^\circ\text{C}/10^{-3}$ mm/m.p.: 50°C (hexane); yield 68%. ^1H NMR (200.13 MHz, CDCl_3): $\delta = 0.49$ (s, 3 H, GeCH_3), 2.52 (s, 6 H, GeCH_2S), 7.0–7.30 (m, 15 H, SC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): $\delta = -4.9$ (GeCH_3), 15.6 (GeCH_2S), 125.3 (C-4 of SC_6H_5), 126.8, 128.8 (C-2/C-6 and C-3/C-5 of SC_6H_5), 139.1 (C-1 of SC_6H_5). – EI-MS (70 eV): m/z (%) = 458 (27, M^+), 443 (3, $\text{M}^+ - \text{CH}_3$), 335 (100, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5$), 225 (46, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5 - \text{SC}_6\text{H}_5 - \text{H}$), 211 (39, $\text{M}^+ - 2 \text{CH}_2\text{SC}_6\text{H}_5 - \text{H}$), 123 (80, $\text{CH}_2\text{SC}_6\text{H}_5^+$). Elemental analysis for $\text{C}_{22}\text{H}_{24}\text{GeS}_3$ (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. $220^\circ\text{C}/10^{-3}$ mm (oven temperature); yield 74%. ^1H NMR (200.13 MHz, CDCl_3): $\delta = 1.15$ ("s" [broad signal], 5 H, GeCH_2CH_3), 2.55 (s, 6 H, GeCH_2S), 7.10–7.35 (m, 15 H, SC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): $\delta = 6.0$ (GeCH_2CH_3), 8.7 (GeCH_2CH_3), 14.2 (GeCH_2S), 125.2 (C-4 of SC_6H_5), 126.6, 128.8 (C-2/C-6 and C-3/C-5 of SC_6H_5), 139.3 (C-1 of SC_6H_5). – EI-MS (70 eV): m/z (%) = 472 (28, M^+), 349 (100, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5$), 239 (42, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5 - \text{SC}_6\text{H}_5 - \text{H}$), 123 (70, $\text{CH}_2\text{SC}_6\text{H}_5^+$). Elemental analysis for $\text{C}_{23}\text{H}_{26}\text{GeS}_3$ (471.2 g mol^{-1}): calcd. C 58.62, 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, CDCl_3): δ = 2.77 (s, 6 H, GeCH_2S), 7.0–7.60 (m, 20 H, GeC_6H_5 and SC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = 15.0 (GeCH_2S), 125.4 (C-4 of SC_6H_5), 126.9 (C-2/C-6 or C-3/C-5 of SC_6H_5), 128.5 (C-2/C-6 or C-3/C-5 of GeC_6H_5), 128.8 (C-2/C-6 or C-3/C-5 of SC_6H_5), 130.0 (C-4 of GeC_6H_5), 133.9 (C-2/C-6 or C-3/C-5 of GeC_6H_5), 134.4 (C-1 of GeC_6H_5), 139.1 (C-1 of SC_6H_5). – EI-MS (70 eV): m/z (%) = 520 (15, M^+), 397 (2, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5$), 319 (100, $\text{M}^+ - \text{C}_6\text{H}_5 - \text{CH}_2\text{SC}_6\text{H}_5 - \text{H}$), 273 (8, $\text{M}^+ - 2 \text{SC}_6\text{H}_5 - \text{H}$), 123 (68, $\text{CH}_2\text{SC}_6\text{H}_5^+$). Elemental analysis for $\text{C}_{27}\text{H}_{26}\text{GeS}_3$ (519.3 g mol^{-1}): calcd. C 62.45, H 5.05; found C 61.6, H 5.2%.

Tetrakis(phenylthiomethyl)germane (40)

M. p. 57 °C (acetone/hexane 1:2), yield 63%. ^1H NMR (200.13 MHz, CDCl_3): δ = 2.60 (s, 8 H, GeCH_2S), 7.00–7.30 (m, 20 H, SC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = 14.8 (GeCH_2S), 125.6 (C-4 of SC_6H_5), 127.2, 128.9 (C-2/C-6 and C-3/C-5 of SC_6H_5), 138.6 (C-1 of SC_6H_5). – EI-MS (70 eV): m/z (%) = 566 (42, M^+), 443 (100, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5$), 333 (90, $\text{M}^+ - \text{CH}_2\text{SC}_6\text{H}_5 - \text{SC}_6\text{H}_5 - \text{H}$), 319 (34, $\text{M}^+ - 2 \text{CH}_2\text{SC}_6\text{H}_5 - \text{H}$), 183 (22, $\text{M}^+ - 3 \text{CH}_2\text{SC}_6\text{H}_5 - \text{CH}_2$), 123 (100, $\text{CH}_2\text{SC}_6\text{H}_5^+$). Elemental analysis for $\text{C}_{28}\text{H}_{28}\text{GeS}_4$ (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 $\text{LiC}_{10}\text{H}_8$ in 30 ml of THF and stirred for 2 h at -40 °C. Bu_3SnCl (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. C_{10}H_8 and Bu_3SnSPh were removed at 60 and $100-120$ °C/ 10^{-3} mbar, and the high-boiling (stannylmethyl)germanes were isolated at the temperatures listed below.

General procedure for the synthesis of 34–36 and 41 and transformation to 37–39 and 42

At -60 °C 5 mmol of the appropriate tris(phenylthiomethyl)germane in 3 ml of THF was added to a freshly prepared solution of 32 mmol of LiDBB in 40 ml of THF and stirred for 6 h at -50 °C. Bu_3SnCl (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 Bu_3SnSPh 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 LiDBB, reaction time 8 h at -50 °C, 42 mmol Bu_3SnCl).

Bis(tributylstannylmethyl)dimethylgermane (28)

B. p. 165 °C/ 10^{-3} mm (oven temperature); yield 25%. ^1H NMR (200.13 MHz, CDCl_3): δ = -0.22 (s, $^2J(\text{H}, ^{119/117}\text{Sn}) = 59.2/56.7$ Hz, 4 H, GeCH_2Sn), 0.10 (s, 6 H, GeCH_3), 0.55–1.60 (m, 54 H, SnCH_2C , CCH_2C , CCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = -5.7 ($^1J(\text{C}, ^{119/117}\text{Sn}) = 221.2/211.5$ Hz, $^3J(\text{C}, \text{Sn}) = 16.9$ Hz; GeCH_2Sn), 2.6 ($^3J(\text{C}, \text{Sn}) = 10.2$ Hz; GeCH_3), 10.4 ($^1J(\text{C}, ^{119/117}\text{Sn}) = 322.3/307.9$ Hz; SnCH_2C), 13.8 (CCH_3), 27.5 ($^3J(\text{C}, ^{119/117}\text{Sn}) = 57.0/54.6$ Hz; CCH_2CH_3), 29.3 ($^2J(\text{C}, \text{Sn}) = 19.4$ Hz; $\text{SnCH}_2\text{CH}_2\text{C}$). – ^{119}Sn NMR (74.63 MHz, CDCl_3): δ = 4.2. – EI-MS (70 eV): m/z (%) = 653 (100, $\text{M}^+ - \text{C}_4\text{H}_9$; $\text{M}^+ = \text{C}_{28}\text{H}_{64}^{72}\text{Ge}^{120}\text{Sn}^{118}\text{Sn}$), 597 (38, $\text{M}^+ - 2 \text{C}_4\text{H}_9 + \text{H}$), 539 (30, $\text{M}^+ - 3 \text{C}_4\text{H}_9$), 481 (30, $\text{M}^+ - 4 \text{C}_4\text{H}_9 - \text{H}$), 291 (76, $^{120}\text{Sn}(\text{C}_4\text{H}_9)_3^+$). Elemental analysis for $\text{C}_{28}\text{H}_{64}\text{GeSn}_2$ (710.8 g mol^{-1}): calcd. C 47.32, H 9.08; found C 47.6, H 9.1%.

Bis(tributylstannylmethyl)diethylgermane (29)

B. p. 165 °C/ 10^{-3} mm (oven temperature); yield 31%. ^1H NMR (200.13 MHz, CDCl_3): δ = -0.27 (s, $^2J(\text{H}, ^{119/117}\text{Sn}) = 60.5/57.8$ Hz, 4 H, GeCH_2Sn), 0.55–1.55 (m, 64 H, GeCH_2CH_3 and SnCH_2C , CCH_2C , CCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = -10.7 ($^1J(\text{C}, ^{119/117}\text{Sn}) = 217.8/210.1$ Hz, $^3J(\text{C}, \text{Sn}) = 15.8$ Hz; GeCH_2Sn), 9.1 (GeCH_2CH_3), 9.7 ($^3J(\text{C}, \text{Sn}) = 10.5$ Hz; GeCH_2CH_3), 10.5 ($^1J(\text{C}, ^{119/117}\text{Sn}) = 311.3/302.8$ Hz; SnCH_2C), 13.7 (CCH_2CH_3), 27.5 ($^3J(\text{C}, ^{119/117}\text{Sn}) = 57.5/55.0$ Hz; CCH_2CH_3), 29.3 ($^2J(\text{C}, \text{Sn}) = 19.2$ Hz; $\text{SnCH}_2\text{CH}_2\text{C}$). – ^{119}Sn NMR (74.63 MHz, CDCl_3): δ = 4.8. – EI-MS (70 eV): m/z (%) = 681 (76, $\text{M}^+ - \text{C}_4\text{H}_9$; $\text{M}^+ = \text{C}_{30}\text{H}_{68}^{72}\text{Ge}^{120}\text{Sn}^{118}\text{Sn}$), 625 (28, $\text{M}^+ - 2 \text{C}_4\text{H}_9 + \text{H}$), 501 (100), 291 (55, $\text{Sn}(\text{C}_4\text{H}_9)_3^+$). Elemental analysis for $\text{C}_{30}\text{H}_{68}\text{GeSn}_2$ (738.8 g mol^{-1}): calcd. C 48.77, H 9.28; found C 49.1, H 8.9%.

Bis(tributylstannylmethyl)diphenylgermane (30)

B. p. (oven temperature); 220 °C. 10^{-3} mm; yield 38%. ^1H NMR (200.13 MHz, CDCl_3): δ = 0.01 (s, $^2J(\text{H}, \text{Sn}) = 43.0$ Hz, $^3J(\text{H}, \text{Sn}) = 7.4$ Hz, 4 H, GeCH_2Sn),

0.5–1.6 (m, 54 H, $\text{Sn}(\text{C}_4\text{H}_9)_3$), 6.80–7.40 (m, 10 H, GeC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = –9.0 (GeCH_2Sn), 13.7 (SnCH_2C), 14.3 (CCH_3), 27.0 (CCH_2CH_3), 28.5 ($\text{SnCH}_2\text{CH}_2\text{C}$), 125.7 (C-4 of GeC_6H_5), 128.5, 134.7 (C-2/C-6 and C-3/C-5 of GeC_6H_5), 139.7 (C-4 of GeC_6H_5). – ^{119}Sn NMR (74.63 MHz, CDCl_3): δ = 3.9. Elemental analysis for $\text{C}_{38}\text{H}_{68}\text{GeSn}_2$ (834.9 g mol $^{-1}$): calcd. C 54.67, H 8.21; found C 54.9, H 8.1.

Tris(tributylstannylmethyl)methylgermane (37)

B.p. 230 °C/10 $^{-3}$ mm (oven temperature); yield: 23%. ^1H NMR (200.13 MHz, CDCl_3): δ = –0.20 (s, $^2J(\text{H}, ^{119/117}\text{Sn})$ = 59.6/57.1 Hz, 6 H, GeCH_2Sn), 0.07 (s, 3 H, GeCH_3), 0.70–1.55 (m, 81 H, SnCH_2C , CCH_2C , CCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = –3.9 ($^1J(\text{C}, ^{119/117}\text{Sn})$ = 221.8/212.1 Hz, $^3J(\text{C}, \text{Sn})$ = 15.1 Hz; GeCH_2Sn), 3.9 ($^3J(\text{C}, \text{Sn})$ = 8.8 Hz; GeCH_3), 10.5 ($^1J(\text{C}, ^{119/117}\text{Sn})$ = 321.6/307.2 Hz; SnCH_2C), 13.7 (CCH_3), 27.5 ($^3J(\text{C}, ^{119/117}\text{Sn})$ = 57.3/54.9 Hz; CCH_2CH_3), 29.3 ($^2J(\text{C}, \text{Sn})$ = 19.2 Hz; $\text{SnCH}_2\text{CH}_2\text{C}$). – ^{119}Sn NMR (74.63 MHz, CDCl_3): δ = 3.2. Elemental analysis for $\text{C}_{40}\text{H}_{90}\text{GeSn}_3$ (999.8 g mol $^{-1}$): calcd. C 48.05, H 9.07; found C 48.4, H 8.9.

Tris(tributylstannylmethyl)ethylgermane (38)

B.p. 210 °C/10 $^{-3}$ mm (oven temperature); yield 28%. ^1H NMR (200.13 MHz, CDCl_3): δ = –0.23 (s, $^2J(\text{H}, ^{119/117}\text{Sn})$ = 61.7/55.9 Hz, 6 H, GeCH_2Sn), 0.60–1.55 (m, 86 H, SnCH_2C , GeCH_2C , CCH_2C , CCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = –6.0 ($^1J(\text{C}, ^{119/117}\text{Sn})$ = 217.6/207.7 Hz, $^3J(\text{C}, \text{Sn})$ = 14.8 Hz; GeCH_2Sn), 9.2 (GeCH_2CH_3), 10.6 ($^1J(\text{C}, ^{119/117}\text{Sn})$ = 321.1/306.9 Hz; SnCH_2C), 12.6 ($^3J(\text{C}, \text{Sn})$ = 9.1 Hz; GeCH_2CH_3), 13.7 (CCH_3), 27.5 ($^3J(\text{C}, ^{119/117}\text{Sn})$ = 57.5/55.0 Hz; CCH_2CH_3), 29.3 ($^2J(\text{C}, ^{119/117}\text{Sn})$ = 19.2 Hz; $\text{SnCH}_2\text{CH}_2\text{C}$). – ^{119}Sn NMR (74.63 MHz, CDCl_3): δ = 3.2. – EI-MS (70 eV): m/z (%) = 667 (33, $\text{M}^+ - ^{120}\text{Sn}(\text{C}_4\text{H}_9)_3 - \text{C}_4\text{H}_9 + \text{H}$, $\text{M}^+ = \text{C}_{41}\text{H}_{92}^{72}\text{Ge}^{118}\text{Sn}^{120}\text{Sn}_2$), 637 (50, $\text{M}^+ - ^{120}\text{Sn}(\text{C}_4\text{H}_9)_3 - \text{C}_4\text{H}_9 - \text{CH}_2\text{CH}_3$), 609 (100, $\text{M}^+ - ^{120}\text{Sn}(\text{C}_4\text{H}_9)_3 - 2 \text{C}_4\text{H}_9$), 291 (34, $^{120}\text{Sn}(\text{C}_4\text{H}_9)_3^+$), 289 (25, $^{118}\text{Sn}(\text{C}_4\text{H}_9)_3^+$). Elemental analysis for $\text{C}_{41}\text{H}_{92}\text{GeSn}_3$ (1013.8 g mol $^{-1}$): calcd. C 48.57, H 9.15; found C 49.8, H 9.0%.

Tris(tributylstannylmethyl)phenylgermane (39)

B.p. (oven temperature): 230 °C/10 $^{-3}$ mm; yield 25%. ^1H NMR (200.13 MHz, CDCl_3): δ = 0.04 (s, 6 H, GeCH_2Sn), 0.80–1.55 (m, 81 H, SnCH_2C , CCH_2C , CCH_3), 6.8–7.4 (m, 5 H, GeC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = –5.5 (GeCH_2Sn), 10.5 (SnCH_2C), 13.7 (CCH_3), 27.4 (CCH_2CH_3), 29.2 ($\text{SnCH}_2\text{CH}_2\text{C}$), 125.7 (C-4 of GeC_6H_5), 127.8, 132.9 (C-2/C-6 and C-3/C-5 of GeC_6H_5), 144.8 (C-1 of

GeC_6H_5). – ^{119}Sn NMR (74.63 MHz, CDCl_3): δ = 2.1. – EI-MS (70 eV): m/z (%) = 1006 (2.5, $\text{M}^+ - \text{C}_4\text{H}_9 + \text{H}$; $\text{M}^+ = \text{C}_{45}\text{H}_{92}^{72}\text{Ge}^{118}\text{Sn}^{120}\text{Sn}_2$), 890 (2.5, $\text{M}^+ - 3 \text{C}_4\text{H}_9 - \text{H}$), 811 (3.5, $\text{M}^+ - 3 \text{C}_4\text{H}_9 - \text{C}_6\text{H}_5 - 3 \text{H}$), 715 (100, $\text{M}^+ - ^{120}\text{Sn}(\text{C}_4\text{H}_9)_3 - \text{C}_4\text{H}_9 + \text{H}$), 657 (30, $\text{M}^+ - ^{120}\text{Sn}(\text{C}_4\text{H}_9)_3 - 2 \text{C}_4\text{H}_9$). Elemental analysis for $\text{C}_{45}\text{H}_{92}\text{GeSn}_3$ (1061.9 g mol $^{-1}$): calcd. C 50.90, H 8.73; found C 50.5, H 8.9.

Tetrakis(tributylstannylmethyl)germane (42)

B.p. 250 °C/10 $^{-3}$ mm (oven temperature); yield 33%. ^1H NMR (200.13 MHz, CDCl_3): δ = –0.19 (s, $^2J(\text{H}, \text{Sn})$ = 60.2 Hz, 8 H, GeCH_2Sn), 0.55–1.65 (m, 108 H, $\text{Sn}(\text{C}_4\text{H}_9)_3$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = –2.3 ($^3J(\text{C}, \text{Sn})$ = 13.6 Hz; GeCH_2Sn), 10.7 ($^1J(\text{C}, ^{117/119}\text{Sn})$ = 321.0/306.6 Hz; SnCH_2C), 13.7 (CCH_3), 27.5 ($^3J(\text{C}, ^{117/119}\text{Sn})$ = 57.9/55.3 Hz; CCH_2CH_3), 29.4 ($^2J(\text{C}, \text{Sn})$ = 5.5 Hz; $\text{SnCH}_2\text{CH}_2\text{C}$). – ^{119}Sn NMR (74.63 MHz, CDCl_3): δ = 2.1. Elemental analysis for $\text{C}_{52}\text{H}_{116}\text{GeSn}_4$ (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-methyl)germane in 3 ml of THF was added to a freshly prepared solution of 21 mmol of $\text{LiC}_{10}\text{H}_8$ in 30 ml of THF and stirred for 2 h at –40 °C. Bu_3SnCl (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 Me_3SiCl was added. Hydrolysis and extraction with Et_2O , drying of the organic phase over sodium sulfate, and evaporation of the solution yielded a residue. C_{10}H_8 and Bu_3SnSPh 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-silacyclobutane (43)

B.p. 130 °C/10 $^{-3}$ mm (oven temperature); yield 31%. ^1H NMR (200.13 MHz, CDCl_3): δ = 0.46 (s, 6 H, GeCH_3), 0.82 (s, $^2J(\text{H}, \text{Si})$ = 5.1 Hz, 4 H, SiCH_2Ge), 7.20–7.65 (m, 10 H, SiC_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = 2.0 (GeCH_3), 4.4 (SiCH_2Ge), 127.8 (C-2/C-6 or C-3/C-5 of SiC_6H_5), 129.2 (C-4 of SiC_6H_5), 134.0 (C-2/C-6 or C-3/C-5 of SiC_6H_5), 139.0 (C-1 of SiC_6H_5). – ^{29}Si NMR (39.76 MHz, CDCl_3): δ = –3.0. – EI-MS (70 eV): m/z (%) = 314 (26, M^+), 299 (100, $\text{M}^+ - \text{CH}_3$), 223 (58, $\text{M}^+ - \text{C}_6\text{H}_5 - \text{CH}_2$), 211 (41, $\text{M}^+ - \text{Ge}(\text{CH}_3)_2 + \text{H}$). Elemental analysis for $\text{C}_{16}\text{H}_{20}\text{GeSi}$ (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, ²J(H, Si) = 5.4 Hz, 4 H, GeCH₂Si), 0.85–1.15 (m, 10 H, GeC₂H₅), 7.25–7.7 (m, 10 H, SiC₆H₅). – ¹³C{¹H} NMR (50.32 MHz, CDCl₃): δ = –0.4 (GeCH₂Si), 8.8 (GeCH₂CH₃), 9.2 (GeCH₂CH₃), 127.8 (C-2/C-6 or C-3/C-5 of SiC₆H₅), 129.1 (C-4 of SiC₆H₅), 134.0 (C-2/C-6 or C-3/C-5 of SiC₆H₅), 139.0 (C-1 of SiC₆H₅). – ²⁹Si NMR (39.76 MHz, CDCl₃): δ = –2.7. – EI-MS (70 eV): *m/z* (%) = 342 (10, M⁺), 313 (100, M⁺ – C₂H₅), 285 (38, M⁺ – 2 C₂H₅ + H), 197 (44, (C₆H₅SiCH₃)⁺). Elemental analysis for C₁₈H₂₄GeSi (341.1 g mol⁻¹): calcd. C 63.39, H 7.09; found C 63.5, H 7.0%.

1,1,3,3-Tetraphenyl-1-german-3-silacyclobutane (45) [12]

M. p. 98 °C (hexane); yield 32%. ¹H NMR (200.13 MHz, CDCl₃): δ = 1.30 (s, ²J(H, Si) = 5.7 Hz, 4 H, SiCH₂Ge), 7.2–7.60 (m, 20 H, SiC₆H₅ and GeC₆H₅). – ¹³C{¹H} NMR (50.32 MHz, CDCl₃): δ = 3.8 (SiCH₂Ge), 127.9, 128.3 (C-2/C-6 or C-3/C-5 of SiC₆H₅ or GeC₆H₅), 129.0, 129.4 (C-4 of SiC₆H₅ or GeC₆H₅), 133.8, 134.2 (C-2/C-6 or C-3/C-5 of SiC₆H₅ or GeC₆H₅), 137.8, 139.0 (C-1 of SiC₆H₅ or GeC₆H₅). – ²⁹Si NMR (39.76 MHz, CDCl₃): 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 C₂₆H₂₄GeSi (437.2 g mol⁻¹): calcd. C 71.44, H 5.53; found C 71.5, H 5.6%.

1,1,3,3-Tetraphenyl-1,3-digermacyclobutane (46) [12]

M. p. 50 °C (hexane); yield 28%. ¹H NMR (200.13 MHz, CDCl₃): δ = 1.58 (s, 4 H, GeCH₂Ge), 7.20–7.6 (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-K_α radiation. The structures were solved by direct methods and refined by full-matrix least-squares methods on *F*² [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**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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