New Bis(lithiomethyl)silanes: Building Blocks for Organosilanes

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The first high yield preparation of non π-stabilized bis(lithiomethyl)silanes was performed by the reductive cleavage of C–S bonds with electron transfer reagents. Bis[(phenylthio)methyl]silanes synthesized by the reaction of dichlorosilanes with [(phenylthio)methyl]lithium were transformed to the corresponding bis(lithiomethyl)silanes **7** by reaction with lithium naphthalenide ($LiC_{10}H_8$) or lithium *p,p'*-di-*tert*-butylbiphenylide (LiDBB) as an electron transfer reagent and were characterized by their reaction with Bu_3SnCl. The C–S bonds of bis[(phenylthio)methyl]silanes can be cleaved selectively making possible the introduction of two different groups. – The silicon atom plays a central role in the reactivity of the presented structural types. The bis(lithiomethyl)silanes are used as new building blocks for the preparation of organosilanes, Si–H-functionalized organosilanes, and 1,3-disilacyclobutanes containing $SiCH_2Si$ structural units.

Introduction

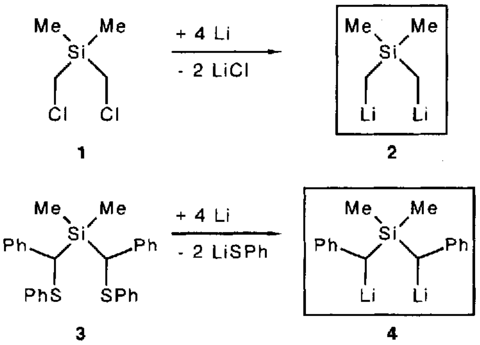
Dilithioalkanes can be classified as 1,1-, 1,2-, 1,3-, 1,4- etc. dilithio compounds by the position of the lithio substituents in the alkyl chain. In contrast to the large number of dilithioalkane compounds, only a few examples of 1,3-dilithioalkane compounds have been described[1]. The 1,3-dilithio compounds exhibit enormous synthetic potential as bifunctional building blocks, e.g., for the synthesis of cyclobutane derivatives. These important synthetic building blocks are not available mainly due to the lack of synthetic routes. Also the decomposition by β-elimination of LiH (e.g., 1,3-dilithiopropane decomposes at −60°C to allyllitihium[2]) prevented their preparation[1].

As a part of our systematic studies[1,3] on the structural unit "$-\mathbf{CR_2}-\mathbf{El}-\mathbf{CR_2}-$" (El = element of group 14–16, partly with substituents; R = H, alkyl, aryl) we have investigated the synthesis of bis(lithiomethyl)silanes with the structural unit "$\mathbf{LiCH_2}-\mathbf{SiR_2}-\mathbf{CH_2Li}$" ($SiR_2$ = El). The silicon atom stabilizes the lithio substituent in α-position[4] and prevents a β-elimination reaction.

Alkyllithium compounds can normally be prepared by[1]: 1. hydrogen-lithium exchange with lithium or lithium bases; 2. halogen-lithium exchange with lithium or lithium bases; 3. metal-lithium exchange with lithium or lithium bases; 4. reductive addition of lithium or lithium bases; 5. reductive cleavage of C–S bonds with lithium. Potential synthetic routes for the synthesis of 1,3-dilithiated compounds are the metal-lithium exchange and the reductive cleavage of C–S bonds.

For the synthesis of the two known bis(lithiomethyl)silanes, the halogen-lithium exchange (for **2**[5]) and the reductive cleavage of C–S bonds with lithium (for **4**[6]) have been used (see Scheme 1[7]). **2** was obtained only in 30% yield due to the elimination of LiCl after monometallation. The only high-yield preparation by Bickelhaupt[6] is for the derivative LiCHPh–$SiMe_2$–CHPhLi (**4**), which is π-stabilized by the phenyl groups on the lithiated carbon atoms. No general synthetic routes to non π-stabilized bis(lithiomethyl)silanes are known.

Scheme 1



We report herein on the synthetic potential of the reductive cleavage of C–S bonds with the electron transfer reagent lithium naphthalenide ($LiC_{10}H_8$) for the first high-yield synthesis of bis(lithiomethyl)silanes with the structural unit "$\mathbf{LiCH_2}-\mathbf{SiR_2}-\mathbf{CH_2Li}$" ($SiR_2$ = El). In addition, some examples of the synthetic potential of these new bifunctional reagents are shown.

Synthesis

The bis[(phenylthio)methyl]silanes used for reductive cleavage were prepared by the reaction of [(phenylthio)methyl]lithium with the corresponding chlorosilanes (Scheme 2).

[(Phenylthio)methyl]lithium was synthesized by two methods. *Method A:* Reaction of thioanisol, 1,4-diazabicyclo[2.2.2]octane (DABCO) and *n*BuLi in THF[8]. *Method B:* Reaction of thioanisol with *n*BuLi in diethyl ether[9]. [(Phenylthio)methyl]lithium prepared by *method B* was eas-

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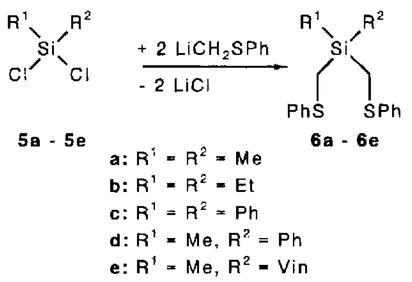
Scheme 2

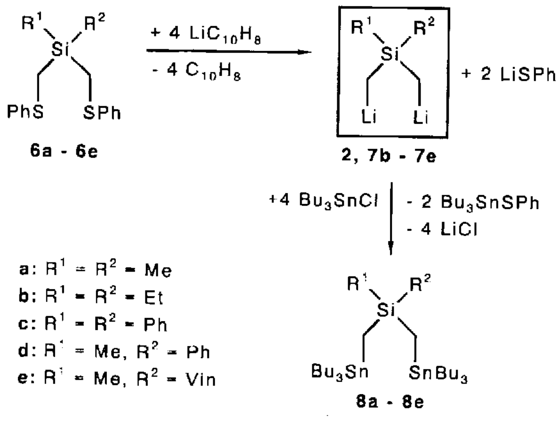


ier to handle as the reagent obtained by *method A* which decomposes at 0 °C.

The bis[(phenylthio)methyl]silanes **6a**-**e** were isolated by Kugelrohr distillation (**6a**, **b**, **d**, **e**) or by crystallization (**6c**) in 49–78% yield. The diphenylsilane **6c** crystallizes from ethanol as **6c** and from diethyl ether as **6c** · 0.5 Et_2O. The diethyl ether can be removed in vacuo. Methyldiphenyl[(phenylthio)methyl]silane (**6f**) was prepared analogously and isolated in 65% yield.

The reductive cleavage of only one C–S bond with lithium or lithium naphthalenide ($LiC_{10}H_8$) yields mono(lithiomethyl)silanes. This transformation is well known and is used in the Peterson olefination reaction for the preparation of (lithiomethyl)trimethylsilane[10]. We employed it as a means of exchanging the phenylthio group in the bis[(phenylthio)methyl]silanes **6a**–**e** for lithium, thereby creating the corresponding bis(lithiomethyl)silanes **2** and **7b**–**e** (Scheme 3). $LiC_{10}H_8$ instead of lithium was used to avoid side reactions with the solvent or acidic groups in the reaction mixture by longer reaction times (see compound **10**).

Scheme 3



The bis(lithiomethyl)silanes were prepared by using $LiC_{10}H_8$ in THF as electron transfer reagent and characterized by their reactions with Bu_3SnCl [>95% overall yield by NMR; 42–81% yield of isolated pure (stannylmethyl)silanes] (Scheme 3). A longer reaction time (1 h) for the reaction of $LiC_{10}H_8$ with the diethylsilane **6b** compared to that of the diphenylsilane **6c** (reaction complete after 1 min) indicates low reactivity of alkyl-substituted silanes. Use of lithium *p,p*′-di-*tert*-butylbiphenylide (LiDBB) as electron transfer reagent provided the same products with shorter reaction times, especially in the case of **6b**.

We were not able to characterize the bis(lithiomethyl)silanes by NMR in the reaction mixture[11]. Therefore the question remains: Were the bis(lithiomethyl)silanes formed before or during the reaction with the trapping reagent Bu_3SnCl. Two observations indicate that the bis(lithiomethyl)silanes were formed before the addition of the trapping reagent:

i) The green or blue-green color of the electron transfer reagent had disappeared indicating completion of reaction.

ii) Only partly metallated species were formed at lower temperature or shorter reaction time and trapped with Bu_3SnCl.

The reaction mixtures decompose around 0 °C by hydrogen abstraction[12]. We and other groups were not able to prepare the carbon analogue of **2** (Si = C)[2] by reductive cleavage of C–S bonds[13]. LiSPh elimination was observed after monometallation starting from the carbon analogue of **6a** (Si = C). Therefore the silicon atom plays a central role in the reactivity of the presented structural types. By the addition of two equivalents of $LiC_{10}H_8$ to diphenylbis[(phenylthio)methyl]silane (**6c**) at −60 °C the monometallated species **9** was formed and trapped with Me_3SiCl. Diphenyl[(phenylthio)methyl][(trimethylsilyl)methyl]silane (**14**) was formed in an NMR yield of 90% and isolated after Kugelrohr distillation in a yield of 63%. Diphenyl[(phenylthio)methyl][(tributylstannyl)methyl]silane (**13**) was prepared by trapping **9** with Bu_3SnCl and isolated with a yield of 65%. This experiment indicates that monometallated compounds can be prepared at lower temperature and trapped with Me_3SiCl or Bu_3SnCl [see ii) above] (Scheme 4). At temperatures around −30 °C **10** was formed from **9** and trapped with Bu_3SnCl (**11**) and Me_3SiCl (**12**). For comparison **11** and **12** were prepared starting from (diphenylmethyl)[(phenylthio)methyl]silane (**6f**) (Scheme 5). Similar reactions were observed on addition of two equivalents of the electron transfer reagent to the bis[(phenylthio)methyl]silanes at −40 °C.

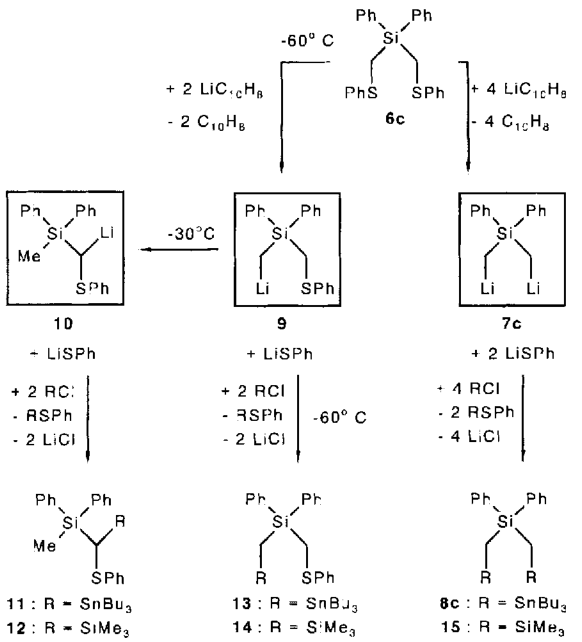
Diphenyl[(phenylthio)methyl][(trimethylsilyl)methyl]silane (**14**) was treated with two equivalents of $LiC_{10}H_8$, and the resulting (lithiomethyl)silane **16** was trapped with Bu_3SnCl. After workup diphenyl[(tributylstannyl)methyl][(trimethylsilyl)methyl]silane (**17**) was isolated in 69% yield (Scheme 6). This experiment shows the selective cleavage of C–S bonds facilitating the introduction of two different groups.

Some Reactions of Bis(lithiomethyl)diphenylsilane (7c)

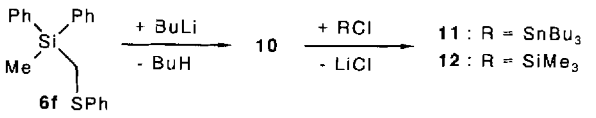
To demonstrate the synthetic potential of the new building blocks, the bifunctional reagent bis(lithiomethyl)diphenylsilane (**7c**) was used for some reactions with mono- and bifunctional substrates (Schemes 4 and 7).

The 1,3-dilithio compounds exhibit "normal" reactivity with monofunctional reagents (Schemes 4 and 7). 1,1- and 1,2-dilithio compounds do not always react in the expected way of an alkyllithium compound[1]. The synthesis of the (stannylmethyl)silane **8c**, the (silylmethyl)silane **15** and the

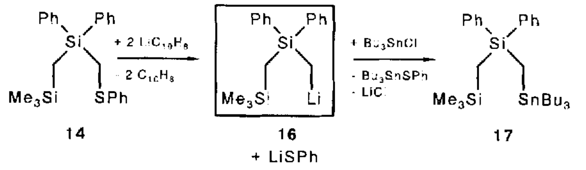
Scheme 4



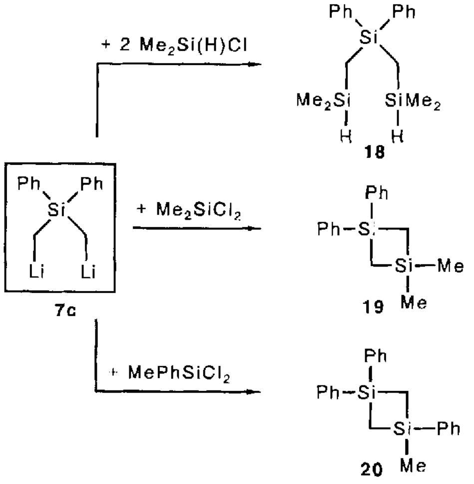
Scheme 5



Scheme 6



Scheme 7



hydridosilane **18** show that **7c** can be used for the synthesis of new organosilanes, which can be used for further reactions (e.g. the preparation of silicon-element bonds).

1,1-Dimethyl-3,3-diphenyl-1,3-disilacyclobutane[14,15] (**19**) and 1-methyl-1,3,3-triphenyl-1,3-disilacyclobutane[15] (**20**) were formed by the addition of dichlorodimethylsilane or dichloromethylphenylsilane at −50 °C to a freshly prepared solution of bis(lithiomethyl)diphenylsilane (**7c**) (Scheme 7). After warming up to 0 °C over a period of 20 minutes, the nucleophiles in the reaction mixture were trapped with Me_3SiCl. After aqueous workup the 1,3-disilacyclobutanes were isolated in 46% (**19**) and 42% (**20**) yield. Polymeric materials or higher ring systems were formed as byproducts reducing the yield. These reactions illustrate the synthetic potential of these new building blocks for the preparation of 1,3-disilacyclobutanes. The advantage over the known synthetic routes to 1,3-disilacyclobutanes is the selective preparation of non-symmetrical 1,3-disilacyclobutanes.

Conclusion

Alkyl-, aryl-, and vinyl-substituted bis(lithiomethyl)silanes were prepared by the reaction of bis[(phenylthio)methyl]silanes with electron transfer reagents. The new bis(lithiomethyl)silanes can be used as building blocks for organosilicon compounds.

Further related work including investigations of the reductive cleavage of C−S bonds and metal exchange reactions for the synthesis of other compounds with the structural unit "Li−$\mathbf{CR_2}$−El−$\mathbf{CR_2}$−Li" (El = element of group 14−16, partly with substituents; R = H, alkyl, aryl) is currently under progress.

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Experimental

Melting points: Melting point apparatus, Fa. Büchi, Typ 510. − ^1H NMR [solvent $CDCl_3$; internal standard $CHCl_3$ (δ = 7.20)]: Bruker AC-200P (200.13 MHz). − ^{13}C NMR [solvent and internal standard $CDCl_3$ (δ = 77.05): Bruker AC-200P (50.32 MHz). Assignment of the ^{13}C-NMR data was supported by DEPT experiments. − ^{29}Si NMR (INEPT) [solvent $CDCl_3$; external standard TMS (δ = 0)]: Bruker AC-200P (39.76 MHz). − ^{119}Sn NMR [solvent $CDCl_3$; external standard $SnMe_4$ (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, ^{12}C, ^{28}Si, ^{32}S, and ^{120}Sn. − Microanalyses: Fa. Beller, Göttingen; Institut for Inorganic Chemistry, Saarbrücken. − Kugelrohr distillation apparatus: GKR-501, Fa. Büchi, the b.p. given are oven temperatures. − All reactions were carried out under oxygen-free and dried argon. The solvents were dried according to common procedures.

1) *General Procedure for the Synthesis of* **6a–f**

Method A: At −40 °C a cooled solution of 0.24 mol of [(phenylthio)methyl]lithium in 250 ml of THF, prepared from thioanisol and DABCO and *n*BuLi by the method of Corey and Seebach[8], was added to a solution of 0.12 mol of the appropriate dichlorosilane in 30 ml THF. The reaction mixture was warmed to room temp., 200 ml of Et_2O and 50 ml of water were added, and the mixture was extracted 3 times with Et_2O. The combined organic solutions were washed three times with 0.5 N HCl and dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation to give the appropriate bis[(phenylthio)methyl]silane (**6a**, **d**, and **e**) or by crystallization (**6c**).

Method B: At −40 °C a cooled solution of 0.24 mol of [(phenylthio)methyl]lithium in 200 ml of diethyl ether/hexane, prepared from thioanisol and *n*BuLi in diethyl ether[9], was added to a solution of 0.12 mol of the appropriate dichlorosilane in 30 ml of diethyl ether. The reaction mixture was warmed to room temp. and filtered. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation to give the appropriate bis[(phenylthio)methyl]silanes (**6a**, **b**, and **e**) or by crystallization (**6c**). **6f** was prepared analogously.

2) *General Procedure for the Synthesis of* **8a–f**: At −40 °C 10 mmol of the appropriate bis[(phenylthio)methyl]silane was added to a freshly prepared solution of 42 mmol of $LiC_{10}H_8$ in 60 ml of THF and stirred for 1 h at −20 °C. 13.6 g (42 mmol) of Bu_3SnCl was added to the reaction mixture at −40 °C. After warming to room temp., 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)silane.

Dimethylbis[(phenylthio)methyl]silane (**6a**): 66% (method A), 76% (method B); b.p. 165 °C/10^{-3} Torr. – ^1H NMR: $\delta = 0.34$ (s, 6H; $SiCH_3$), 2.35 (s, 4H; $SiCH_2S$), 7.10–7.40 (m, 10H; SC_6H_5). – ^{13}C NMR: $\delta = -3.3$ (2 C, $SiCH_3$), 16.7 (2 C, $SiCH_2S$), 124.9 (2 C, C-4 von SC_6H_5), 126.3 (4 C), 128.7 (4 C), (C-2,6 and C-3,5 of SC_6H_5), 139.5 (2 C, C-1 of SC_6H_5). – ^{29}Si NMR: $\delta = 2.6$. – EI-MS, *m/z* (%): 304 (36) [M^+], 181 (100) [$M^+ - CH_2SC_6H_5$], 165 (66) [$M^+ - SC_6H_5 - 2\,CH_3$]. – $C_{16}H_{20}S_2Si$ (304.6): calcd. C 63.10, H 6.62; found C 63.0, H 6.7.

Diethylbis[(phenylthio)methyl]silane (**6b**): 49% (method B); b.p. 175 °C/10^{-3} Torr. – ^1H NMR: $\delta = 0.80$ [q, 4H, $^3J(H,H) = 7.8$ Hz; CH_2CH_3], 1.05 [t, 6H, $^3J(H,H) = 7.8$ Hz; CH_2CH_3], 2.32 [s, 4H, $^2J(H,Si) = 6.3$ Hz; CH_2S], 7.05–7.30 (m, 10H; SC_6H_5). – ^{13}C NMR: $\delta = 3.7$ (2 C, $SiCH_2CH_3$), 7.3 (2 C, $SiCH_2CH_3$), 13.8 (2 C, CH_2S), 124.9 (2 C, C-4 of SC_6H_5), 126.3 (4 C, C-2,6 or C-3,5 of SC_6H_5), 128.7 (4 C, C-2,6 or C-3,5 of SC_6H_5), 139.8 (2 C, C-1 of SC_6H_5). – ^{29}Si NMR: $\delta = 5.9$. – EI-MS, *m/z* (%): 332 (21) [M^+], 209 (100) [$M^+ - CH_2SC_6H_5$], 179 (29) [$M^+ - CH_2SC_6H_5 - CH_2CH_3 - H$], 151 (18) [$M^+ - CH_2SC_6H_5 - 2\,CH_2CH_3$]. – $C_{18}H_{24}S_2Si$ (332.6): calcd. C 65.00, H 7.27; found C 65.1, H 7.0.

Diphenylbis[(phenylthio)methyl]silane (**6c**): 52% (method A), 78% (method B); m.p. 63–64 °C (ethanol). – ^1H NMR: $\delta = 2.82$ (s, 4H; CH_2S), 7.0–7.45 (m, 20H; SC_6H_5, SiC_6H_5). – ^{13}C NMR: $\delta = 15.3$ (2 C, CH_2S), 125.1 (2 C, C-4 of SC_6H_5), 126.6 (4 C), 128.8 (4 C) (C-2,6 or C-3,5 of SC_6H_5), 128.2 (4 C), 135.2 (4 C) (C-2,6 or C-3,5 of SiC_6H_5), 130.5 (2 C, C-4 of SiC_6H_5), 132.3 (2 C, C-1 of SiC_6H_5), 140.1 (2 C, C-1 of SC_6H_5). – ^{29}Si NMR: $\delta = -11.3$. – EI-MS, *m/z* (%): 428 (1) [M^+], 305 (7) [$M^+ - CH_2SC_6H_5$], 199 (100) [$M^+ - 3\,C_6H_5 + 2H$], 123 (100) [$CH_2SC_6H_5^+$], 109 (36) [$SC_6H_5^+$]. – $C_{21}H_{22}S_2Si$ (428.7): calcd. C 72.85, H 5.64; found C 72.7, H 5.9.

Methylphenylbis[(phenylthio)methyl]silane (**6d**): 65% (method A); b.p. 195 °C/10^{-3} Torr. – ^1H NMR: $\delta = 0.61$ (s, 3H; CH_3), 2.59, 2.62 (AB system, 4H, $J_{AB} = 12.4$ Hz; CH_2S), 7.10–7.50, 7.65–7.75 (m, 15H; SiC_6H_5, SC_6H_5). – ^{13}C NMR: $\delta = -5.0$ (CH_3), 16.1 (2 C, CH_2S), 125.0 (2 C, C-4 of SC_6H_5), 126.5 (4 C), 128.7 (4 C) (C-2,6 and C-3,5 of SC_6H_5), 128.1 (2 C), 134.0 (2 C) (C-2,6 and C-3,5 of SiC_6H_5), 130.2 (C-4 of SiC_6H_5), 134.2 (C-1 of SiC_6H_5), 139.4 (2 C, C-1 of SC_6H_5). – ^{29}Si NMR: $\delta = -4.5$. – EI-MS, *m/z* (%): 366 (6) [M^+], 243 (39) [$M^+ - CH_2SC_6H_5$], 165 (30) [$M^+ - SC_6H_5 - CH_3 - C_6H_5$], 137 (100) [$SSiC_6H_5^+$]. – $C_{21}H_{22}S_2Si$ (366.6): calcd. C 68.80, H 6.04; found C 68.8, H 6.1.

Ethenylmethylbis[(phenylthio)methyl]silane (**6e**): 55% (method A), 73% (method B); b.p. 150 °C/10^{-3} Torr. – ^1H NMR: $\delta = 0.41$ [s, 3H, $^2J(H,Si) = 6.7$ Hz; CH_3], 2.41 [s, 4H, $^2J(H,Si) = 6.5$ Hz; CH_2S), 5.90–6.40 (m, 3H; $CH{=}CH_2$), 7.05–7.40 (m, 10H; SC_6H_5). – ^{13}C NMR: $\delta = -5.4$ (CH_3), 15.7 (2 C, CH_2S), 125.0 (2 C, C-4 of SC_6H_5), 126.5 (4 C), 128.7 (4 C) (C-2,6 and C-3,5 of SC_6H_5), 133.7 ($SiCHCH_2$), 135.2 ($SiCHCH_2$), 139.4 (2 C, C-1 of SC_6H_5). – ^{29}Si NMR: $\delta = -6.8$. – EI-MS, *m/z* (%): 316 (22) [M^+], 193 (94) [$M^+ - CH_2SC_6H_5$], 165 (100) [$M^+ - SC_6H_5 - CH_3 - CHCH_2$]. – $C_{17}H_{20}S_2Si$ (316.6): calcd. C 64.50, H 6.37; found C 64.5, H 6.5.

Methyldiphenyl[(phenylthio)methyl]silane (**6f**): 65% (method B); b.p. 155 °C/10^{-3} Torr. – ^1H NMR: $\delta = 0.70$ (s, 3H; CH_3), 2.68 (s, 2H; CH_2S), 7.00–7.70 (m, 15H; SC_6H_5, SiC_6H_5). – ^{13}C NMR: $\delta = -4.3$ (CH_3), 16.5 (CH_2S), 124.8 (C-4 of SC_6H_5), 126.2 (2 C, C-2,6 or C-3,5 of SC_6H_5), 128.0 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 128.7 (2 C, C-2,6 or C-3,5 of SC_6H_5), 129.8 (2 C, C-4 of SiC_6H_5), 134.6 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 135.2 (2 C, C-1 of SiC_6H_5), 140.0 (C-1 of SC_6H_5). – ^{29}Si NMR: $\delta = -9.0$. – EI-MS, *m/z* (%): 320 (16) [M^+], 197 (100) [$M^+ - CH_2SC_6H_5$], 120 (18) [$M^+ - C_6H_5 - CH_2SC_6H_5$], 105 (29) [$M^+ - CH_2SC_6H_5 - C_6H_5 - CH_3$]. – $C_{20}H_{20}SSi$ (320.5): calcd. C 74.95, H 6.29; found C 75.0, II 6.2.

Dimethylbis[(tributylstannyl)methyl]silane (**8a**): 46%; b.p. 160 °C/10^{-3} Torr. – ^1H NMR: $\delta = -0.34$ [s, 4H; $^2J(H,^{119/117}Sn) = 67.2/64.5$ Hz; $SiCH_2Sn$], −0.04 (s, 6H; $SiCH_3$), 0.65–1.0, 1.2–1.65 (m, 54H; $SnCH_2C$, CCH_2C, CCH_2CH_3, CCH_3). – ^{13}C NMR: $\delta = -5.1$ [2 C, $^1J(C,^{119/117}Sn) = 200.4/191.6$, $^3J(C,Sn) = 17.5$ Hz; CH_2Sn], 3.1 [2 C, $^3J(C,Sn) = 10.8$ Hz; $SiCH_3$], 10.4 [6 C, $^1J(C,^{119/117}Sn) = 323.1/308.7$ Hz; $SnCH_2C$], 13.8 (6 C, CCH_3), 27.0 [6 C, $^3J(C,^{119/117}Sn) = 57.5/55.2$ Hz; CCH_2CH_3], 29.3 [6 C, $^2J(C,Sn) = 19.4$ Hz; $SnCH_2CH_2C$]. – ^{29}Si NMR: $\delta = 5.2$ [$^2J(Si,Sn) = 22.2$ Hz]. – ^{119}Sn NMR: $\delta = 0.3$. – EI-MS, *m/z* (%): 609 (30) [$M^+ - C_4H_9$, $M^+ = C_{28}H_{64}Si^{118}Sn^{120}Sn$], 553 (3) [$M^+ - 2\,C_4H_9 + H$], 291 (100) [$Sn(C_4H_9)_3^+$], 235 (66) [$SnH(C_4H_9)_2^+$], 179 (20) [$SnH_2(C_4H_9)^+$]. – $C_{28}H_{64}SiSn_2$ (666.3): calcd. C 50.48, H 9.68; found C 50.9, H 9.7.

Diethylbis[(tributylstannyl)methyl]silane (**8b**): 55%; b.p. 165 °C/10^{-3} Torr. – ^1H NMR: $\delta = -0.40$ [s, 4H, $^2J(H,^{119/117}Sn) = 68.3/65.4$, $^2J(H,Si) = 6.7$ Hz; $SiCH_2Sn$], 0.38 [q, 4H, $^3J(H,H) = 8.1$ Hz; $SiCH_2CH_3$], 0.59–1.56 (m, 60H; $SnCH_2C$, CCH_2C, CCH_2CH_3, CCH_3). – ^{13}C NMR: $\delta = -9.7$ [2 C, $^1J(C,^{119/117}Sn) = 202.5/193.0$, $^3J(C,Sn) = 15.9$ Hz; $SiCH_2Sn$], 8.0 (2 C, $SiCH_2CH_3$), 9.1 [2 C, $^3J(C,Sn) = 11.3$ Hz; $SiCH_2C$], 10.5 [2 C, $^1J(C,^{119/117}Sn) = 330.2/308.5$ Hz; $SnCH_2CH_2C$], 13.7 (2 C, $SnCH_2CH_2CH_2CH_3$), 27.5 [2 C, $^3J(C,^{119/117}Sn) = 58.3/55.7$ Hz; CCH_2CH_3], 29.3 [2 C, $^2J(C,Sn) = 19.3$ Hz; $SnCH_2CH_2C$]. – ^{29}Si NMR: $\delta = 10.2$ [$^2J(Si,Sn) = 23.0$ Hz]. – ^{119}Sn NMR: $\delta = 0.4$. – EI-MS, *m/z* (%): 637 (37) [$M^+ - C_4H_9$, $M^+ = C_{30}H_{68}Si^{118}Sn^{120}Sn$], 581 (7) [$M^+ - 2\,C_4H_9 + H$], 291 (100) [$Sn(C_4H_9)_3^+$]. – $C_{30}H_{68}SiSn_2$ (694.3): calcd. C 51.90, H 9.87; found C 52.8, H 10.0.

Diphenylbis[(tributylstannyl)methyl]silane (**8c**): 81%; b.p. 200°C/10^{-3} Torr. – ^{1}H NMR: $\delta = 0.18$ [s, 4H, $^{2}J(\mathrm{H},^{119/117}\mathrm{Sn}) = 65.1/62.2$ Hz; $\mathrm{SiCH_2Sn}$], 0.45–0.95, 1.1–1.45 [m, 54H; $\mathrm{SnCH_2C}$, $\mathrm{CCH_2C}$, $\mathrm{CC}H_2\mathrm{CH_3}$, $\mathrm{CCH_3}$], 7.15–7.3, 7.4–7.5 (m, 10H; $\mathrm{SiC_6H_5}$). – ^{13}C NMR: $\delta = -8.6$ [2 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 190.0/181.7$, $^{3}J(\mathrm{C,Sn}) = 7.5$ Hz; $\mathrm{SiCH_2Sn}$], 10.4 [6 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 327.8/313.3$ Hz; $\mathrm{SnCH_2C}$], 13.6 (6 C, $\mathrm{CCH_3}$), 27.4 [6 C, $^{3}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 60.4/57.8$ Hz; $\mathrm{C}C\mathrm{H_2CH_3}$], 29.1 [6 C, $^{2}J(\mathrm{C,Sn}) = 19.4$ Hz; $\mathrm{SnCH_2}C\mathrm{H_2C}$], 127.6 (4 C), 133.4 (4 C) (C-2,6 and C-3,5 of $\mathrm{SiC_6H_5}$), 128.7 (2 C, C-4 of $\mathrm{SiC_6H_5}$), 140.9 [2 C, $^{3}J(\mathrm{C,Sn}) = 38.5$ Hz; C-1 of $\mathrm{SiC_6H_5}$]. – ^{29}Si NMR: $\delta = -3.3$ [$^{2}J(\mathrm{Si,Sn}) = 19.0$ Hz]. – ^{119}Sn NMR: $\delta = -1.2$. – EI-MS, *m/z* (%): 789 (1) [$\mathrm{M^+ - H}$; $\mathrm{M^+ = C_{38}H_{68}Si^{118}Sn^{120}Sn}$], 733 (100) [$\mathrm{M^+ - C_4H_9}$], 677 (9) [$\mathrm{M^+ - 2\,C_4H_9 + H}$], 445 (20) [$\mathrm{M^+ - {}^{118}Sn(C_4H_9)_3 - C_4H_9 + H}$], 291 (66) [$\mathrm{Sn(C_4H_9)_3^+}$], 235 (48) [$\mathrm{SnH(C_4H_9)_2^+}$], 179 (48) [$\mathrm{SnH_2(C_4H_9)^+}$]. – $\mathrm{C_{38}H_{68}SiSn_2}$ (790.4): calcd. C 57.74, H 8.67; found C 57.8, H 8.7.

Methylphenylbis[(tributylstannyl)methyl]silane (**8d**): 42%; b.p. 175°C/10^{-3} Torr. – ^{1}H NMR: $\delta = 0.07$, 0.12 [AB system, 4H, $J_{\mathrm{AB}} = 13.0$, $^{2}J(\mathrm{H},^{119/117}\mathrm{Sn}) = 65.7/63.1$ Hz; $\mathrm{SiCH_2Sn}$], 0.25 (s, 3H; $\mathrm{SiCH_3}$), 0.50–0.90, 1.10–1.50 (m, 54H; $\mathrm{SnCH_2C}$, $\mathrm{SnCH_2C}H_2\mathrm{C}$, $\mathrm{CC}H_2\mathrm{CH_3}$, $\mathrm{CCH_3}$), 7.20–7.30, 7.40–7.50 (m, 5H; $\mathrm{SiC_6H_5}$). – ^{13}C NMR: $\delta = -6.2$ [2 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 194.5/185.8$, $^{3}J(\mathrm{C,Sn}) = 13.4$ Hz; $\mathrm{SiCH_2Sn}$], 1.0 [$^{3}J(\mathrm{C,Sn}) = 8.4$ Hz; $\mathrm{SiCH_3}$], 10.4 [6 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 325.2/310.7$ Hz; $\mathrm{SnCH_2C}$], 13.7 (6 C, $\mathrm{CCH_3}$), 27.5 [6 C, $^{3}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 58.6/56.2$ Hz; $\mathrm{C}C\mathrm{H_2CH_3}$], 29.2 [6 C, $^{2}J(\mathrm{C,Sn}) = 19.5$ Hz; $\mathrm{SnCH_2}C\mathrm{H_2C}$], 127.6 (2 C), 133.2 (2 C) (C-2,6 and C-3,5 of $\mathrm{SiC_6H_5}$), 128.5 (C-4 of $\mathrm{SiC_6H_5}$), 142.8 [$^{3}J(\mathrm{C,Sn}) = 12.0$ Hz; C-1 of $\mathrm{SiC_6H_5}$]. – ^{29}Si NMR: $\delta = 0.6$ [$^{2}J(\mathrm{Si},^{119/117}\mathrm{Sn}) = 22.0/21.1$ Hz]. – ^{119}Sn NMR: $\delta = -0.6$. – EI-MS, *m/z* (%): 713 (0.3) [$\mathrm{M^+ - CH_3}$, $\mathrm{M^+ = C_{33}H_{66}Si^{118}Sn^{120}Sn}$], 671 (100) [$\mathrm{M^+ - C_4H_9}$], 615 (11) [$\mathrm{M^+ - 2\,C_4H_9 + H}$], 311 (88) [$\mathrm{M^+ - CH_3 - {}^{118}Sn(C_4H_9)_3 - 2\,C_4H_9 + H}$], 291 (88) [$\mathrm{Sn(C_4H_9)_3^+}$], 235 (43) [$\mathrm{SnH(C_4H_9)_2^+}$], 179 (20) [$\mathrm{SnH_2(C_4H_9)^+}$]. – $\mathrm{C_{33}H_{66}SiSn_2}$ (728.4): calcd. C 54.42, H 9.13; found C 55.3, H 9.1.

Ethenylmethylbis[(tributylstannyl)methyl]silane (**8e**): 48%; b.p. 160°C/10^{-3} Torr. – ^{1}H NMR: $\delta = -0.30$ [s, 4H, $^{2}J(\mathrm{H,Sn}) = 65.1$ Hz; $\mathrm{SiCH_2Sn}$], 0.03 (s, 3H; $\mathrm{SiCH_3}$), 0.5–1.0, 1.1–1.6 (m, 54H; $\mathrm{SnCH_2C}$, $\mathrm{CCH_2C}$, $\mathrm{CC}H_2\mathrm{CH_3}$, $\mathrm{CCH_3}$), 5.56 [dd, 1H, $^{3}J(\mathrm{H,H}) = 19.8$, $^{2}J(\mathrm{H,H}) = 4.3$ Hz; $\mathrm{CH{=}C}H_2$, H_{cis}], 5.82 [dd, 1H, $^{3}J(\mathrm{H,H}) = 14.6$, $^{2}J(\mathrm{H,H}) = 4.3$ Hz; $\mathrm{CH{=}C}H_2$, H_{trans}], 6.12 [dd, 1H, $^{3}J(\mathrm{H,H}_{cis}) = 19.8$, $^{3}J(\mathrm{H,H}_{trans}) = 14.6$ Hz; $\mathrm{C}H\mathrm{{=}CH_2}$]. – ^{13}C NMR: $\delta = -6.8$ [2 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 197.0/188.2$, $^{3}J(\mathrm{C,Sn}) = 16.1$ Hz; $\mathrm{SiCH_2Sn}$], 0.9 [3C, $^{3}J(\mathrm{C,Sn}) = 9.6$ Hz; $\mathrm{SiCH_3}$], 10.5 [6 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 324.8/310.5$ Hz; $\mathrm{SnCH_2C}$], 13.7 (6 C, $\mathrm{CCH_3}$), 27.5 [6 C, $^{3}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 58.0/55.6$ Hz; $\mathrm{C}C\mathrm{H_2CH_3}$], 29.3 [6 C, $^{2}J(\mathrm{C,Sn}) = 19.4$ Hz; $\mathrm{SnCH_2}C\mathrm{H_2C}$], 130.0 ($C\mathrm{H{=}CH_2}$), 142.9 [$^{4}J(\mathrm{C,Sn}) = 12.6$ Hz; $\mathrm{CH{=}}C\mathrm{H_2}$]. – ^{19}Si NMR: $\delta = -2.0$ [$^{2}J(\mathrm{Si,Sn}) = 21.6$ Hz]. – ^{119}Sn NMR: $\delta = 0.1$. – EI-MS, *m/z* (%): 621 (18) [$\mathrm{M^+ - C_4H_9}$, $\mathrm{M^+ = C_{29}H_{64}Si^{118}Sn^{120}Sn}$], 565 (100) [$\mathrm{M^+ - 2\,C_4H_9 + H}$], 509 (100) [$\mathrm{M^+ - 3\,C_4H_9 + 2H}$], 291 (52) [$\mathrm{Sn(C_4H_9)_3^+}$], 235 (43) [$\mathrm{SnH(C_4H_9)_2^+}$], 179 (20) [$\mathrm{SnH_2(C_4H_9)^+}$]. – $\mathrm{C_{29}H_{64}SiSn_2}$ (678.3): calcd. C 51.35, H 9.51; found C 51.4, H 9.4.

Methyldiphenyl[(phenylthio)(tributylstannyl)methyl]silane (**11**): a) At −60°C 7.7 g (18 mmol) of **6c** was added to a freshly prepared solution of 36 mmol of $\mathrm{LiC_{10}H_8}$ in 60 ml of THF, and the solution was stirred for 5 min at −60°C. The reaction mixture was warmed to −30°C and stirred for 1 h at this temp. 11.7 g (36 mmol) of $\mathrm{Bu_3SnCl}$ was added to the reaction mixture at −78°C. After warming to room temp. 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 7.2 g of **11** (90% pure).

b) At −20°C 10 ml (16 mmol) of 1.6 M *n*BuLi in hexane was added to a solution of 5.2 g (16 mmol) of **6f** in 60 ml of THF, and the solution was stirred for 15 min at this temp. 5.2 g (16 mmol) of $\mathrm{Bu_3SnCl}$ was added to the reaction mixture at −78°C. After warming to room temp. 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 **11**. Yield 75%, b.p. 190°C/10^{-3} Torr. – ^{1}H NMR: $\delta = 0.75$ (s, 3H; $\mathrm{SiCH_3}$), 0.60–1.50 (m, 27H; $\mathrm{SnCH_2C}$, $\mathrm{CCH_2C}$, $\mathrm{CC}H_2\mathrm{CH_3}$, $\mathrm{CCH_3}$), 2.66 [s, 1H, $^{2}J(\mathrm{H},^{119/117}\mathrm{Sn}) = 55.0/52.8$, $^{2}J(\mathrm{H,Si}) = 6.3$ Hz; SiCHSnS], 7.0–7.75 (m, 15H; $\mathrm{SC_6H_5}$, $\mathrm{SiC_6H_5}$). – ^{13}C NMR: $\delta = -3.1$ [$^{3}J(\mathrm{C,Sn}) = 53.8$ Hz; $\mathrm{SiCH_3}$], 10.1 [$^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 150.2/146.7$ Hz; SiCHSnS], 11.1 [3 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 323.6/309.7$ Hz; $\mathrm{SnCH_2C}$], 13.6 (3 C, $\mathrm{CCH_3}$), 27.3 [3 C, $^{3}J(\mathrm{C,Sn}) = 37.4$ Hz; $\mathrm{C}C\mathrm{H_2CH_3}$], 29.0 [3 C, $^{2}J(\mathrm{C,Sn}) = 19.0$ Hz; $\mathrm{SnCH_2}C\mathrm{H_2C}$], 124.8 (C-4 of $\mathrm{SC_6H_5}$), 127.5 (2 C), 127.6 (2 C), 127.8 (2 C), 128.3 (2 C) (C-2,6 or C-3,5 of $\mathrm{SiC_6H_5}$ and C-2,6 and C-3,5 of $\mathrm{SiC_6H_5}$), 129.1, 129.3 (C-4 of $\mathrm{SiC_6H_5}$), 134.6 (2 C), 134.7 (2 C) (C-2,6 or C-3,5 of $\mathrm{SiC_6H_5}$), 137.1 [$^{3}J(\mathrm{C,Sn}) = 12.2$ Hz; C-1 of $\mathrm{SiC_6H_5}$], 137.2 [$^{3}J(\mathrm{C,Sn}) = 6.0$ Hz; C-1 of $\mathrm{SiC_6H_5}$], 140.5 [$^{3}J(\mathrm{C,Sn}) = 19.0$ Hz; C-1 of $\mathrm{SC_6H_5}$]. – ^{29}Si NMR: $\delta = -8.4$ [$^{2}J(\mathrm{Si,Sn}) = 2.4$ Hz]. – ^{119}Sn NMR: $\delta = 0.7$. – EI-MS, *m/z* (%): 610 (0.6) [$\mathrm{M^+}$], 553 (3.5) [$\mathrm{M^+ - C_4H_9}$], 357 (10) [$\mathrm{M^+ - (C_6H_5)_2SiCH_3 - C_4H_9 + H}$], 291 (79) [$\mathrm{Sn(C_4H_9)_3^+}$], 199 (100) [$\mathrm{C_6H_5SCHC_6H_5^+}$], 197 (25) [$\mathrm{(C_6H_5)_2SiCH_3^+}$], 110 (33) [$\mathrm{C_6H_5SH}$]. – $\mathrm{C_{32}H_{46}SSiSn}$ (609.6): calcd. C 63.05, H 7.61; found C 62.6, H 7.8.

Methyldiphenyl[(phenylthio)(trimethylsilyl)methyl]silane (**12**)

a) Preparation analogous to **11** (starting from **6c**) by reaction of **10** with $\mathrm{Me_3SiCl}$. 61%; b.p. 150°C/10^{-3} Torr.

b) Preparation analogous to **11** (starting from **6f**) by reaction of **10** with $\mathrm{Me_3SiCl}$. 67%. – ^{1}H NMR: $\delta = -0.10$ (s, 9H; $\mathrm{SiCH_3}$), 0.70 (s, 3H; $\mathrm{SiCH_3}$), 2.10 (s, 1H; $\mathrm{Si_2CHS}$), 6.90–7.35, 7.5–7.6 (m, 15H; $\mathrm{SC_6H_5}$, $\mathrm{SiC_6H_5}$). – ^{13}C NMR: $\delta = -3.3$ ($\mathrm{SiCH_3}$), −0.2 (3 C, $\mathrm{SiCH_3}$), 17.3 ($\mathrm{Si_2CHS}$), 125.1 (C-4 of $\mathrm{SC_6H_5}$), 127.6 (2 C), 127.8 (2 C), 128.2 (2 C), 128.5 (2 C) (C-2,6 or C-3,5 of $\mathrm{SiC_6H_5}$ and C-2,6 and C-3,5 of $\mathrm{SC_6H_5}$), 129.2, 129.4 (C-4 of $\mathrm{SiC_6H_5}$), 134.8 (2 C), 134.9 (2 C) (C-2,6 or C-3,5 of $\mathrm{SiC_6H_5}$), 136.4, 136.9 (C-1 of $\mathrm{SiC_6H_5}$), 139.6 (C-1 of $\mathrm{SC_6H_5}$). – ^{29}Si NMR: $\delta = -9.3$ [$\mathrm{C_2Si(C_6H_5)_2}$], 4.1 [$\mathrm{CSi(CH_3)_3}$]. – EI-MS, *m/z* (%): 392 (26) [$\mathrm{M^+}$], 377 (4) [$\mathrm{M^+ - CH_3}$], 197 (100) [$\mathrm{(C_6H_5)_2SiCH_3^+}$], 165 (25) [$\mathrm{M^+ - Si(CH_3)_3 - 2\,C_6H_5}$], 73 (11) [$\mathrm{Si(CH_3)_3^+}$]. – $\mathrm{C_{23}H_{28}SSi_2}$ (392.7): calcd. C 70.35, H 7.19; found C 70.3, H 7.2.

Diphenyl[(phenylthio)methyl][(tributylstannyl)methyl]silane (**13**): At −60°C 7.7 g (18 mmol) of **6c** was added to a freshly prepared solution of 36 mmol of $\mathrm{LiC_{10}H_8}$ in 60 ml of THF, and the solution was stirred for 5 min at −60°C. 11.7 g (36 mmol) of $\mathrm{Bu_3SnCl}$ was added to the reaction mixture at −78°C. After warming to room temp. 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 **13**. Yield 65%; b.p. 195°C/10^{-3} Torr. – ^{1}H NMR: $\delta = 0.43$ [s, 2H, $^{2}J(\mathrm{H},^{119/117}\mathrm{Sn}) = 63.2/60.6$, $^{2}J(\mathrm{H,Si}) = 7.3$ Hz; $\mathrm{SiCH_2Sn}$], 0.5–1.6 (m, 27H; $\mathrm{SnCH_2C}$, $\mathrm{CCH_2C}$, $\mathrm{CC}H_2\mathrm{CH_3}$, $\mathrm{CCH_3}$), 2.72 [s, 2H, $^{2}J(\mathrm{H,Si}) = 6.3$ Hz; $\mathrm{SiCH_2S}$], 7.0–7.6 (m, 15H; $\mathrm{SC_6H_5}$, $\mathrm{SiC_6H_5}$). – ^{13}C NMR: $\delta = -11.9$ [$^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 177.0/169.3$ Hz; $\mathrm{SiCH_2Sn}$], 10.6 [3 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 331.8/317.3$ Hz; $\mathrm{SnCH_2C}$], 13.6 (3 C, $\mathrm{CCH_3}$), 17.6 ($^{3}J(\mathrm{C,Sn}) = 8.4$ Hz; $\mathrm{SiCH_2S}$), 27.3 [3 C, $^{1}J(\mathrm{C},^{119/117}\mathrm{Sn}) = 60.9/58.1$ Hz; $\mathrm{C}C\mathrm{H_2CH_3}$], 29.0 [3 C, $^{2}J(\mathrm{C,Sn}) = 19.5$ Hz; $\mathrm{SnCH_2}C\mathrm{H_2C}$], 124.6 (C-4 of $\mathrm{SC_6H_5}$), 126.0 (2 C, C-2,6 or C-3,5 of $\mathrm{SC_6H_5}$), 127.9 (2 C, C-2,6 or C-3,5 of $\mathrm{SiC_6H_5}$), 128.6 (2 C, C-2,6 or C-3,5 of $\mathrm{SC_6H_5}$), 129.5 (2 C, C-4 of $\mathrm{SiC_6H_5}$), 134.6 (4 C, C-2,6 or C-3,5 of $\mathrm{SiC_6H_5}$), 136.7 [2 C, $^{3}J(\mathrm{C,Sn}) = 11.2$ Hz; C-1 of $\mathrm{SiC_6H_5}$], 140.3 (C-1 of $\mathrm{SC_6H_5}$). – ^{29}Si NMR: $\delta = -6.7$

[^2J(Si,Sn) = 20.6 Hz]. – ^{119}Sn NMR: δ = −1.5. – EI-MS, *m/z* (%): 610 (0.3) [M$^+$], 553 (100) [M$^+$ − C_4H_9], 197 (27) [$(C_6H_5)_2SiCH_3^+$], 110 (25) [C_6H_5SH]. – $C_{32}H_{46}SSiSn$ (609.6): calcd. C 63.05, H 7.61; found C 62.6, H 8.0.

Diphenyl[(phenylthio)methyl][(trimethylsilyl)methyl]silane (**14**): At −60 °C 7.7 g (18 mmol) of **6c** was added to a freshly prepared solution of 36 mmol of $LiC_{10}H_8$ in 60 ml of THF, and the solution was stirred for 5 min at −60 °C. 3.9 g (36 mmol) of Me_3SiCl was added to the reaction mixture at −78 °C. The reaction mixture was warmed to room temp.; 50 ml of Et_2O and 15 ml of water were added, and the mixture was extracted 3 times with Et_2O. The combined organic solutions were washed 3 times with H_2O and dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation to give **14**. Yield 63%; b.p. 165 °C/10^{-3} Torr. – ^{1}H NMR: δ = −0.14 [s, 9H, ^2J(H,Si) = 6.6 Hz; $SiCH_3$], 0.45 [s, 2H, ^2J(H,Si) = 8.9 Hz; $SiCH_2Si$], 2.65 [s, 2H, ^2J(H,Si) = 6.7 Hz; $SiCH_2S$], 7.0–7.65 (m, 20H; SiC_6H_5 and SC_6H_5). – ^{13}C NMR: δ = −0.3 ($SiCH_2Si$), 1.3 [3 C, $Si(CH_3)_3$], 17.3 ($SiCH_2S$), 124.8 (C-4 of SC_6H_5), 126.2 (2 C, C-4 of SiC_6H_5), 127.9 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 128.7 (2 C, C-2,6 or C-3,5 of SC_6H_5), 129.7 (2 C, C-2,6 or C-3,5 of SC_6H_5), 134.9 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 135.8 (2 C, C-1 of SiC_6H_5), 140.2 (C-1 of SC_6H_5). – ^{29}Si NMR: δ = −8.9 [$C_2Si(C_6H_5)_2$], 0.8 [$CSi(CH_3)_3$]. – EI-MS, *m/z* (%): 392 (24) [M$^+$], 377 (8) [M$^+$ − CH_3], 320 (4) [M$^+$ − $Si(CH_3)_3$ + H], 271 (31) [M$^+$ − $CH_2SC_6H_5$ + 2H], 269 (100) [M$^+$ − $CH_2SC_6H_5$], 253 (8) [M$^+$ − $CH_2SC_6H_5$ − CH_3 − H], 197 (14) [$(C_6H_5)_2SiCH_3^+$], 191 (41) [M$^+$ − $CH_2SC_6H_5$ − C_6H_5 − H]. – $C_{23}H_{28}SSi_2$ (392.7): calcd. C 70.35, H 7.19; found C 70.4, H 7.2.

Diphenylbis[(trimethylsilyl)methyl]silane (**15**): Preparation analogous to **8c** by reaction of **7c** with Me_3SiCl. Yield 65%; b.p. 165 °C/10^{-3} Torr. – ^{1}H NMR: δ = −0.11 (s, 18H; CH_3), 0.42 (s, 4H; CH_2Si), 7.3–7.4, 7.5–7.6 (m, 10H; SiC_6H_5). – ^{13}C NMR: δ = 1.3 (6 C; CH_3), 1.9 (2 C; CH_2Si), 127.5 (4 C), 134.8 (4 C) (C-2,6 and C-3,5 of SiC_6H_5), 128.9 (2 C, C-4 of SiC_6H_5), 139.5 (2 C, C-1 of SiC_6H_5). – ^{29}Si NMR: δ = −7.9 [$C_2Si(C_6H_5)_2$], 0.7 (2 Si) [$CSi(CH_3)_3$]. – EI-MS, *m/z* (%): 356 (4) [M$^+$], 341 (31) [M$^+$ − CH_3], 269 (100) [M$^+$ − $Si(CH_3)_3$ − CH_3], 191 (88) [M$^+$ − C_6H_5 − $CH_2Si(CH_3)_3$]. – $C_{20}H_{32}Si_3$ (356.7): calcd. C 67.34, H 9.04; found C 67.5, H 8.9.

Diphenyl[(tributylstannyl)methyl][(trimethylsilyl)methyl]silane (**17**): Preparation analogous to **14** by reaction of **16** with Bu_3SnCl. Yield 69%; b.p. 175 °C/10^{-3} Torr. – ^{1}H NMR: δ = −0.22 [s, ^2J(H,Si) = 6.5 Hz, 9H; $SiCH_3$], 0.22 [s, ^2J(H,Sn) = 63.8 Hz, 2H; $SiCH_2Sn$], 0.25 [s, ^2J(H,Si) = 8.8 Hz, 2H; $SiCH_2Si$], 0.50–1.30 (m, 27H; $SnCH_2C$, CCH_2C, CCH_2CH_3, CCH_3), 7.20–7.50 (m, 10H; SiC_6H_5). – ^{13}C NMR: δ = −9.1 [^1J(C,$^{119/117}$Sn) = 189.2/180.1 Hz; $SiCH_2Sn$], 1.3 [3 C, ^1J(C,Si) = 51.1 Hz; $SiCH_3$], 2.5 ($SiCH_2Si$), 10.3 [3 C, ^1J(C,$^{119/117}$Sn) = 328.8/314.1 Hz; $SnCH_2C$], 13.7 (3 C, CCH_3), 27.4 [3 C, ^3J(C,$^{119/117}$Sn) = 60.4/58.0 Hz; CCH_2CH_3], 29.0 [3 C, ^2J(C,Sn) = 19.5 Hz; $SnCH_2CH_2C$], 127.5 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 128.8 (2 C, C-4 of SiC_6H_5), 134.6 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 140.3 (2 C, C-1 of SiC_6H_5). – ^{29}Si NMR: δ = −5.6 [^2J(Si,Sn) = 19.2 Hz; C_3SiCH_2Sn], 0.7 [$CSi(CH_3)_3$]. – ^{119}Sn NMR: δ = −1.7. – EI-MS, *m/z* (%): 517 (18) [M$^+$], 445 (3) [M$^+$ − $Si(CH_3)_3$ + H], 275 (100) [M$^+$ − 2 C_6H_5 − $CH_2Si(CH_3)_3$ − H]. – $C_{29}H_{50}Si_2Sn$ (573.6): calcd. C 60.73, H 8.79; found C 60.8, H 9.3.

Bis[(dimethylsilyl)methyl]diphenylsilane (**18**): Preparation analogous to **8c** by reaction of **7c** with $Me_2Si(H)Cl$. Yield 65%; b.p. 120 °C/10^{-3} Torr. – ^{1}H NMR: δ = −0.12 [d, 12H, ^3J(H,H) = 3.7, ^2J(H,Si) = 10.7 Hz; $SiCHC_2$], 0.38 [d, 4H, ^3J(H,H) = 3.7, ^2J(H,Si) = 12.4 Hz; $SiCH_2Si$], 3.94 [heptett, 1H, ^3J(H,H) = 3.6 Hz; SiH], 7.20–7.55 (m, 10H; SiC_6H_5). – ^{13}C NMR: δ = −1.7 (4 C, $SiCH_3$), −1.4 (2 C, $SiCH_2Si$), 127.6 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 129.0 (2 C, C-4 of SiC_6H_5), 134.6 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 138.6 (2 C, C-1 of SiC_6H_5). – ^{29}Si NMR: δ = −16.1 [$CH_2SiH(CH_3)_2$], −7.3 [$(CH_2)_2Si(C_6H_5)_2$]. – EI-MS, *m/z* (%): 328 (5) [M$^+$], 313 (14) [M$^+$ − CH_3], 255 (68) [M$^+$ − $CH_2Si(CH_3)_2H$], 250 (83) [M$^+$ − C_6H_5 − H], 235 (94) [M$^+$ − C_6H_5 − CH_3 − H], 197 (46) [$(C_6H_5)_2SiCH_3^+$], 177 (100) [M$^+$ − C_6H_5 − $CH_2Si(CH_3)_2H^+$ − H]. – $C_{18}H_{28}Si_3$ (328.7): calcd. C 65.78, H 8.59; found C 66.2, H 8.3.

1,1-Dimethyl-3,3-diphenyl-1,3-disilacyclobutane (**19**)[14,15]: At −40 °C 7.7 g (18 mmol) of **6c** was added to a freshly prepared solution of 72 mmol $LiC_{10}H_8$, and the solution was stirred for 1 h at −20 °C. 2.3 g (18 mmol) of Me_2SiCl_2 was added to the reaction mixture at −78 °C and after warming to 0 °C over a period of 20 min 4.0 g (37 mmol) of Me_3SiCl was added. The reaction mixture was warmed to room temp., 50 ml of Et_2O and 15 ml of water were added, and the mixture was extracted 3 times with Et_2O. The combined organic solutions were washed 3 times with H_2O and dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation to give **19**. Yield 46%; b.p. 105 °C/10^{-3} Torr. – ^{1}H NMR: δ = 0.30 [s, 6H, ^2J(H,Si) = 6.9 Hz; $SiCH_3$], 0.60 [s, 4H, ^2J(H,Si) = 6.2 Hz; $SiCH_2Si$], 7.3–7.4, 7.6–7.7 (m, 10H; SiC_6H_5). – ^{13}C NMR: δ = 2.1 (2 C, $SiCH_2Si$), 2.3 (2 C, $SiCH_3$), 127.9 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 129.2 (2 C, C-4 of SiC_6H_5), 134.1 (4 C, C-2,6 or C-3,5 of SiC_6H_5), 138.4 (2 C, C-1 of SiC_6H_5). – ^{29}Si NMR: δ = −7.1 [$C_2Si(C_6H_5)_2$], 4.9 [$C_2Si(CH_3)_2$]. – EI-MS, *m/z* (%): 268 (14) [M$^+$], 253 (85) [M$^+$ − CH_3], 197 (100) [$(C_6H_5)_2SiCH_3^+$], 190 (50) [M$^+$ − C_6H_5 − H].

1-Methyl-1,3,3-triphenyl-1,3-disilacyclobutan (**20**)[15]: Preparation analogous to that of **19**. Yield 42%; b.p. 150 °C/10^{-3} Torr. – ^{1}H NMR: δ = −0.50 [s, 3H, ^2J(H,Si) = 6.9 Hz; CH_3], 0.7–1.0 (m, 4H; $SiCH_2Si$), 7.2–7.75 (m, 15H; SiC_6H_5). – ^{13}C NMR: δ = 0.9 ($SiCH_3$), 1.5 (2 C, $SiCH_2C$), 127.89 (2 C), 127.90 (2 C), 128.0 (2 C) (C-2,6 or C-3,5 of SiC_6H_5), 129.26, 129.36, 129.43 (C-4 of SiC_6H_5), 133.3 (2 C), 134.25 (2 C), 134.29 (2 C) (C-2,6 or C-3,5 of SiC_6H_5), 137.81, 137.85, 139.4 (C-1 of SiC_6H_5). ^{29}Si NMR: δ = −6.5 [$C_2Si(C_6H_5)_2$], −0.9 [$C_2Si(C_6H_5)CH_3$]. – EI-MS, *m/z* (%): 330 (4) [M$^+$], 315 (14) [M$^+$ − CH_3], 218 (100), 197 (30) [$(C_6H_5)_2SiCH_3^+$].

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