Controlled Conversion of the Transient 2-Mesityl-1,1-bis(trimethylsilyl)silene into a Tetrahydro-2,3-disilanaphthalene, a 1,2-Disilacyclobutane, or a 1,3-Disilacyclobutane

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Mesityl[tris(trimethylsilyl)silyl]methanol (**1**) reacts with strong bases with elimination of trimethylsilanolate according to a Peterson-type mechanism, the outcome of the reaction being dependent on solvent, temperature, and nature of the organometallic base applied. Thus, **1** was converted by treatment with MeLi in ether at −78 °C to (*E*)-1,2,3,8a-tetrahydro-1-mesityl-5,7,8a-trimethyl-2,2,3,3-tetrakis(trimethylsilyl)-2,3-disilanaphthalene (**3**), formally a [2 + 4] cyclodimer of the transient silene $(Me_3Si)_2Si{=}CHMes$ (**2**). The reaction of **1** with PhMgBr in THF after some days resulted in the formation of (*Z*)-3,4-dimesityl-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**6**) as the main product besides small quantities of **3**, the polysilane $(Me_3Si)_3SiSi(SiMe_3)_2CH_2Mes$ (**10**), and the alkoxysilane $(Me_3Si)_3SiCH(Mes)OSi(SiMe_3)_2CH_2Mes$ (**7**). Compound **6**, the formal [2 + 2] cycloadduct of **2**, can also be obtained by thermal treatment of **3** and is considered to be the thermodynamically more stable silene dimer whereas **3** is the kinetically preferred product. At high LiBr concentrations in the reaction mixture **1** was converted by PhMgBr in THF to (*E*)-2,4-dimesityl-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**13**) besides **6** and [bis(trimethylsilyl)silyl]mesityl(trimethylsiloxy)methane (**11**). The unforeseen formation of **13** is discussed as proceeding via the silene−lithium bromide adduct $(Me_3Si)_2Si(Br)CH(Li)Mes$ (**12**). In the absence of LiBr **1** was converted by MeLi in THF at −78 °C to **11** and the trisilane $(Me_3Si)_2Si(Me)CH_2Mes$ (**4b**). Probable pathways of the formation of all new compounds are discussed. For **6** and **13** the results of the X-ray structural analyses are given.

Elimination of trimethylsilanolate from deprotonated (1-hydroxyalkyl)-tris(trimethylsilyl)silanes according to a modified Peterson mechanism has proven to be a suitable method for the synthesis of silenes. This could be demonstrated by in situ reactions of tris(trimethylsilyl)silyllithium with ketones[1] or by the reaction of acyltris(trimethylsilyl)silanes with organolithium reagents[2]. A substantial improvement of the method was achieved because the (hydroxyalkyl)-tris(trimethylsilyl)silanes became easily accessable as pure compounds by the reaction of tris(trimethylsilyl)silylmagnesium bromide with aldehydes or ketones, and meanwhile we succeeded in converting some of these alcohols $(Me_3Si)_3Si{-}C(OH)R^1R^2$ to transient silenes, which were characterized by various dimerization and addition reactions[3].

The generation and conversion of silenes are generally strongly influenced by the reaction conditions[4]. Moreover, the outcome of the base-initiated elimination of trimethylsilanolate from (hydroxyalkyl)polysilanes in the modified Peterson reaction depends on the solvent, the temperature and the base applied. This is the result of our investigations, which are described in this paper. We have chosen mesityl-[tris(trimethylsilyl)silyl]methanol (**1**) and studied its behavior towards organolithium and Grignard compounds in ether or tetrahydrofuran, varying also the reaction temperature and the molar ratio of the components.

The conversion of the alcohol **1** by deprotonation with methyllithium in ether at −78 °C was already described in a previous paper[3c]. Under these conditions lithium trimethylsilanolate is eliminated to give the transient 2-mesityl-1,1-bis(trimethylsilyl)silene (**2**), which rapidly dimerizes to the tetrahydro-2,3-disilanaphthalene **3** in >70% yield (Scheme 1). This result is surprising insofaras sterically congested transient silenes − particularly those bearing trimethylsilyl groups at the silene silicon atom − in the absence of a scavenger usually undergo head-to-head dimerizations to 1,2-disilacyclobutanes[1b,2a,5] or (in the presence of "allylic" hydrogens) linear dimers[1b,2a,6]. Compound **3** is considered to be the result of an unexpected [2 + 4] cycloaddition reaction in which the silene **2** formally acts as a monoene and − involving the aromatic substituent − also as a diene. When **1** was treated with two or more equivalents of methyllithium or phenyllithium in ether at low temperatures, the intermediate silene **2** was trapped by excess organolithium reagent leading after hydrolytic workup to the trisilanes **4**. The reaction of the (hydroxyalkyl)polysilane **1** with methyllithium in the presence of 2,3-dimethylbutadiene under identical conditions gave the silacyclohexane **5**, the [2

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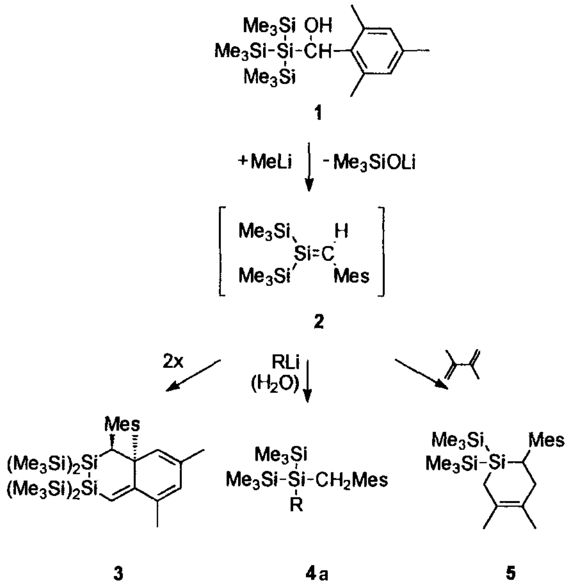
+ 4] cycloaddition product of the silene **2** and the diene (Scheme 1)[3c]. All these results demonstrate that **1** eliminates trimethylsilanolate according to the Peterson mechanism producing the silene **2**, which undergoes the conversions described.

Scheme 1. Reaction of the polysilanyl alcohol **1** with MeLi in ether at −78 °C, [2 + 4] cyclodimerization of the silene **2** and trapping reactions of **2** with organolithium reagents or 2,3-dimethylbutadiene



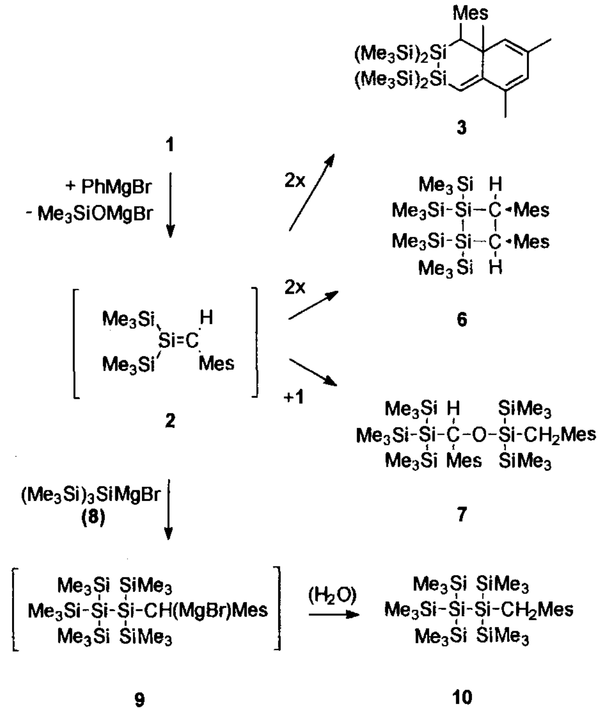
Deprotonation of the (Hydroxyalkyl)polysilane 1 by Treatment with Phenylmagnesium Bromide in Ether or Tetrahydrofuran

Considerable differences in the result of the degradation reaction of the polysilanyl alcohol can be expected by changing the organometallic base. The counter cation of the deprotonated alcohol **1** influences the nucelophilicity of the alkoxide oxygen atom and its interaction with the neighboring trimethylsilyl group. The significance of the solvent with respect to the solvation of the metal ion and any reaction intermediate is obvious.

In the case of the reaction of the alcohol **1** with phenylmagnesium bromide in ether the progress of the reaction is extremely slow also at room temperature, so that from a synthetic point of view the method is impracticable. In THF the reaction is faster, but nevertheless some days are necessary to complete the conversion at room temperature. Thus, the reaction of **1** with an excess of PhMgBr in THF gave after hydrolytic workup the trisilane **4a** (R = Ph) almost quantitatively. In the presence of 2,3-dimethylbutadiene the reaction of **1** with an equimolar amount of PhMgBr under the same conditions furnished the silacyclohexene **5**. These results indicate that the deprotonation of **1** with PhMgBr in THF at room temperature in a clean reaction primarily led to the silene **2**, which was trapped either by the excess Grignard reagent or by the diene.

The outcome of the reaction of the alcohol **1** with PhMgBr in THF in the absence of a scavenger is much more complex. Four products could be separated and identified. The main product was (*Z*)-3,4-dimesityl-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**6**), obtained in 47% yield, besides the 2,3-disilanaphthalene **3** (10%); furthermore, two compounds were identified as the polysilane **10** (6%) and the alkoxysilane **7** (5%) (Scheme 2).

Scheme 2. Reaction of **1** with phenylmagnesium bromide at room temperature in THF

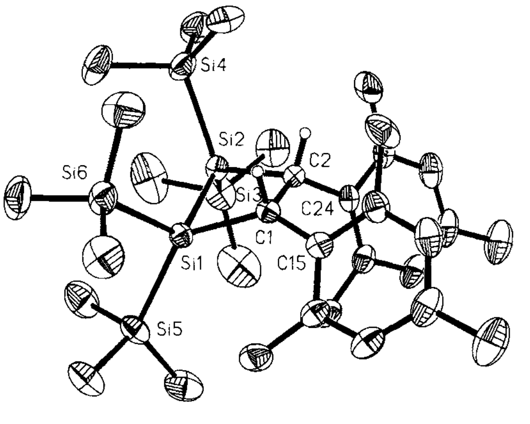


The disilacyclobutane **6** is the formal [2 + 2] head-to-head cyclodimer of the silene **2**. Its formation is rather surprising, since the conversion of **1** by treatment with MeLi in ether at low temperature afforded exclusively **3**, the [2 + 4] cyclodimer of **2**[3c]. Isolated solid **3** proved to be indefinitely stable at room temperature. But preliminary studies of the thermal behavior of **3** showed that in solution the compound is gradually converted to **6**. In the ^{1}H-NMR spectra of a solution of **3** in [D$_6$]benzene which had been kept for some days at room temperature the intensity of the signals of the 1,2-disilacyclobutane **6** slowly increased (besides the signals of traces of some unidentified material) at the expense of those of the disilanaphthalene **3**. After 24 days about 50% of **3** had been converted to **6**. We thus conclude that the disilanaphthalene **3**, prepared from **1** and MeLi at −78 °C in ether, is the kinetically preferred product of the silene dimerization whereas the 1,2-disilacyclobutane **6** is the thermodynamically more stable one. Thus, the higher temperature in the reaction of **1** with PhMgBr and the longer reaction time easily explain the formation of the obviously thermodynamically favored silene dimer **6**.

The discussed 1,2-disilacyclobutane structure is in agreement with the spectral data of **6** and was also confirmed by an X-ray crystal structural analysis (Figure 1). The four-membered ring is considerably bent, the intersection angle of the two planes through the atoms Si1−C1−C2 and

Si1−Si2−C2 being 171.3°. Whereas the ring Si−Si bond length (2.36 Å) is in the expected range, the average ring Si-C bond lengths (1.96 Å) and the C1−C2 distance (1.61 Å) are signifcantly elongated due to the high steric congestion of the *C* substituents and are thus characterized as weak bonds. But as the most surprising and interesting result the structural analysis revealed that the two mesityl substituents adopt a *Z* position. This fact is not really understood and may be connected with the reaction path to **6**, probably proceeding via intermediate **3**. Despite serious efforts the corresponding *E* form of **6** could not be detected in the reaction mixture.

Figure 1. Molecular structure of the 1,2-disilacyclobutane **6**. Basically there are two molecules within the asymmetric unit. Bonds and angles between comparable atoms of the independent molecules are very similar. For the sake of clarity only one molecule is shown with the essential hydrogen atoms at C1 and C2 (ORTEP, 30% probability level). Selected bond lengths [Å] and angles [°]: Si1−Si2 2.358(2), Si1−C1 1.963(5), Si2−C2 1.949(5), C1−C2 1.613(7); C1−Si1−Si2 77.6(29, C2−Si2−Si1 79.6(2), C2−C1−Si1 101.4(3), C1−C2−Si2 99.4(3), torsional angle of the four-membered ring C1−Si1−Si2−C2 8.7(2)

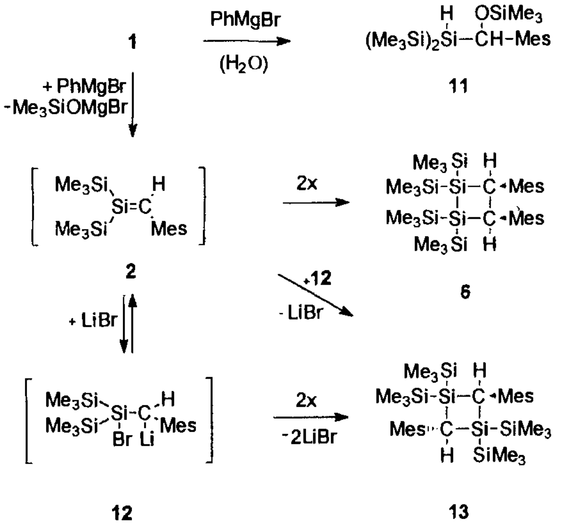


Compound **7** is the adduct of the alcohol **1** or its conjugate base with the silene **2**, and the formation of the polysilane **10** is interpreted as the result of the addition of tris(trimethylsilyl)silylmagnesium bromide (**8**) to the polar Si=C bond of **2**. The organomagnesium intermediate **9**, thus obtained, was hydrolyzed during the workup to **10**.

The presence of **8** in the reaction mixture results from an equilibrium between the magnesium alkoxide derived from the alcohol **1**, the magnesium silanide **8** and 2,4,6-trimethylbenzaldehyde, resp. The reverse process was used for the synthesis of **1**[3c]. With increasing steric demand of the organic substituent of the deprotonated polysilanyl alcohol, the equilibrium is shifted to the silanide and the aldehyde, so that e. g. in the reaction of (2,4,6-triisopropylphenyl)[tris(trimethylsilyl)silyl]methanol with PhMgBr the formation of the polysilane structured similar to **10** becomes the dominating process[7a]. A similar addition of a silanide to an Si=C bond occurred in the reaction of tris(trimethylsilyl)silyllithium with the transient silene $(Me_3Si)_2Si{=}CMe_2$ followed in this particular case by an additional 1,3-Si,C-trimethylsilyl migration to give $(Me_3Si)_2SiH{-}Si(SiMe_3)_2C{-}Me_2SiMe_3$ after hydrolysis[7b].

The conversion of **1** by deprotonation with Grignard reagents was considerably accelerated in the presence of lithium bromide in the reaction mixture. In the case of high LiBr concentrations the reaction was complete already after few hours. However, not only the reaction rate was influenced, but also the products obtained under these conditions were different, indicating that also the reaction mechanism had changed. When phenylmagnesium bromide was added at 0°C to a solution of **1** in THF containing a large excess of LiBr, chromatographic control of the progress of the reaction indicated that the alcohol had been consumed already after 4 h. Usual workup and chromatographic separation of the complex reaction mixture furnished three main products: the 1,2-disilacyclobutane **6** (5%), (*E*)-2,4-dimesityl-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**13**) (28%) and [bis(trimethylsilyl)silyl]mesityl(trimethylsiloxy)methane (**11**) (8%) (Scheme 3).

Scheme 3. Reaction of **1** with PhMgBr at 0°C in THF in the presence of lithium bromide



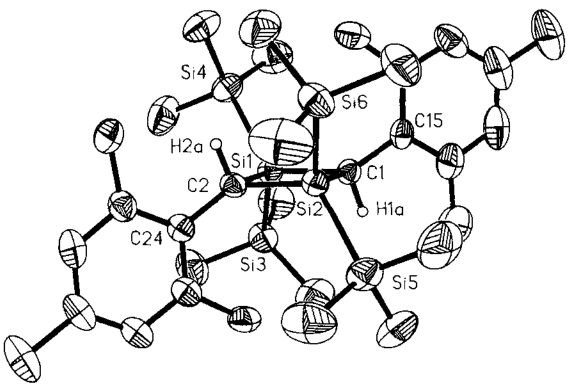
Alkoxysilane **11** was already described as the product obtained, when **1** was treated with sodium hydride in ether or THF. Under these conditions the deprotonated alcohol **1** only undergoes a 1,3-Si,O-trimethylsilyl migration leading to a sodium silanide which was protonated by unreacted **1** or during the workup to give **11**.

The most fascinating result of these experiments is the formation of the 1,3-disilacyclobutane **13**. Its structure is in full agreement with the straightforward ^1H-, ^{13}C-, and ^{29}Si-NMR spectra, with the MS data, and was also proven by an X-ray crystal structural analysis (Figure 2). The four-membered ring is almost planar. The two planes each containing the Si atoms and one C atom intersect at an angle of 177°. The four-membered ring structure leads to a relatively short distance between Si1 and Si2 of 2.74 Å.

Compound **13** is the formal [2 + 2] head-to-tail cyclodimer of the silene **2**. During our studies of the generation of silenes using the modified Peterson concept we never observed that type of dimerization and it seems rather unlikely that **13** is formed by a straightforward silene dimerization. We know that **2**, generated by deprotonation of **1** with

MeLi in ether at low temperature, gives the dimer **3**, and the reaction of **1** with PhMgBr in THF at room temperature results in the formation of **6**. Furthermore, the formation of **13** is not the result of a simple Mg/Li exchange leading to conditions comparable with a reaction of **1** with organolithium reagents in THF, which will be described in the following.

Figure 2. Structure of **13** in the crystal (H atoms are omitted for clarity, ORTEP, 50% probability level). Selected bond lengths [Å] and angles [°]: Si1–C2 1.943(4), Si1–C2 1.943(4), Si1–Si3 2.392(2), Si1–Si4 2.377(2), Si2–C1 1.941(3), Si2–C2 1.945(4), Si2–Si5 2.383(2), Si2–Si6 2.381(2), C1–C11 1.516(5), C2–C21 1.511(5); C2–Si1–C1 90.11(15), C2–Si2–C1 90.10(15), Si1–C1–Si2 89.91(15), Si1–C2–Si2 89.79(15)

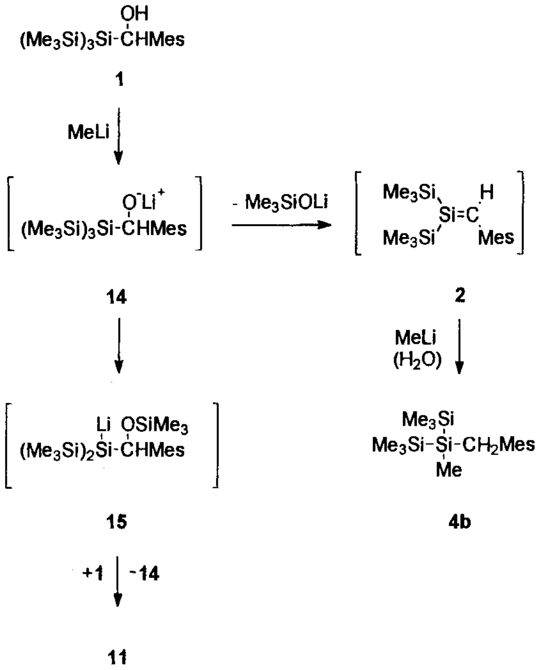


Obviously, the formation of the 1,3-disilacyclobutane **13** is connected with the presence of lithium bromide in the reaction mixture. This is also in agreement with the methods previously applied to the synthesis of **13**[3b], since in these cases we prepared the magnesium silanide **8** as well as MeMgBr by exchange reactions of the corresponding lithium derivatives with anhydrous magnesium bromide. When **1** was treated with either Grignard reagents or organolithium compounds in THF with the exclusion of LiBr, **13** could not be detected. This led us to assume that the formation of the 1,3-disilacyclobutane proceeds via an intermediate **12**, formed by addition of LiBr to the Si=C bond of the silene **2** (Scheme 3). The 1,3-disilacyclobutane **13** is then formed either by intermolecular LiBr elimination from the bifunctional **12** or intramolecular salt elimination after addition of the nucleophilic organolithium derivative **12** to the silene double bond of **2**. The two pathways may be distinguished by kinetic measurements[8], but due to the complex composition of the reaction mixture we had to give up such attempts. Equilibria existing between silenes, lithium salts LiX and the silene-salt addition products $R_2Si(X)-C(Li)R'_2$ and the two mentioned alternative pathways to 1,3-disilacyclobutanes were observed and discussed by Wiberg et al. for similar reactions[8]. On the other hand, it is a well-known phenomenon that the reactivity of e. g. Grignard reagents is considerably influenced by the presence of various salts[9]. So also an intermolecular trimethylsilanolate elimination by a nucleophilic reaction of the magnesium analoge of **15**, acitvated by the present lithium bromide, cannot be excluded.

Reaction of Mesityl[tris(trimethylsilyl)silyl]methanol (1) with Methyllithium in THF

In the absence of LiBr the polysilanyl alcohol **1** was converted by equimolar amounts of MeLi in THF at low temperature to the alkoxysilane **11** (65%) besides the trisilane **4b** (6%) (Scheme 4).

Scheme 4. Reaction of **1** with MeLi at −78 °C in THF



Compound **4b** was already described as the product formed by addition of methyllithium to the Si=C bond of the silene **2** and subsequent hydrolysis[3c]. Its formation indicates an effective excess of methyllithium in the reaction mixture, which is obviously caused by partial deprotonation of the alcohol **1** by the intermediate lithium silanide **15** producing **11** and the lithium alkoxide **14**. This side reaction can widely be excluded by applying an excess of methyllithium for the deprotonation of **1**. Under these conditions the reaction of **1** with an excess of MeLi in THF at −78 °C led almost quantitatively to the trisilane **4b**.

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Experimental

All reactions involving organometallic reagents were carried out under purified argon. – NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane as internal standard. – IR: Nicolet 205 FT-IR. – MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas. – $(Me_3Si)_3SiLi \cdot 3$ THF was prepared as reported in the literature[10]. – All yields given refer to amounts obtained after chromatographic separation and purification. – The syntheses and the spectral data characterizing the structures of **1**, **3**, **4a**, **4b**, **5**, **8**, and **11** were described previously[3c].

Reaction of **1** *with Phenylmagnesium Bromide in THF:* To a solution of 0.5 g ($1.26 \cdot 10^{-3}$ mol) of **1** in 4 ml of THF a solution of an equimolar amount of PhMgBr in THF was added, and the mixture was stirred at room temp. for one week. After addition of aqueous NH_4Cl solution the organic material was extracted several times with ether, the combined extracts were dried, and the solvent was evaporated. Chromatographic separation (silica gel KG 60, heptane) of the solid residue gave 0.04 g of **3** (10%), 0.18 g of **6** (47%), 0.025 g of **7** (5%), and 0.02 g of **10** (6%). Compounds **6**, **7** and **10** were recrystallized from acetonitrile, **3** was further purified by recrystallization from acetone.

(Z)-3,4-Dimesityl-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**6**): Colorless crystals, m. p. 156–157°C. – ^1H NMR ([D$_6$]benzene): δ = 0.25 and 0.44 (2 s, $SiCH_3$, 2 × 18H), 1.96 (s, *p*-CH_3, 6H), 2.28 and 2.66 (2 broad s, *o*-CH_3, 2 × 6H), 4.75 (s, CH, 2H), 6.55 (s, aromat. CH, 4H). – ^{13}C NMR ([D$_6$]benzene, DEPT): δ = 2.4 ($SiCH_3$), 20.5 (*p*-CH_3), 22.6 and 24.6 (*o*-CH_3), 39.8 (CH), 130.0 (aromat. CH), 135.6 and 136.0 (aromat. C-2,5), 133.8 and 138.6 (aromat. C-1,4). – ^{29}Si NMR ([D$_6$]benzene): δ = −41.4 (*Si*-$SiMe_3$), −12.6 and −10.8 ($SiMe_3$). – MS, *m/z* (%): 612 (4.5) [M$^+$], 597 (6) [M$^+$ – CH_3], 539 (5) [M$^+$ – $SiMe_3$], 493 (50) [M$^+$ – Mes], 348 (100) [$(Me_3Si)_4Si_2^+$]. – $C_{32}H_{60}Si_6$ (613.3): calcd. C 62.67, H 9.86; found C 62.50, H 9.90.

{Mesityl[tris(trimethylsilyl)silyl]methoxy}(2,4,6-trimethylbenzyl)bis(trimethylsilyl)silane (**7**): Colorless crystals, m. p. 121°C. – ^1H NMR ([D$_6$]benzene): δ = −0.12 and 0.29 (2 s, $SiCH_3$, 2 × 9H), 0.295 (s, $SiCH_3$, 27H), 2.09 and 2.14 (2 s, *p*-CH_3 2 × 3H), 2.37 (s, *o*-CH_3, 6H), 2.39 and 2.69 (2 s, *o*-CH_3, 2 × 3H), 2.80 (s, CH_2, 2H), 5.89 (s, CH, 1H), 6.67 and 6.77 (2 s, aromat. CH, 2 × 1H), 6.74 (s, aromat. CH, 2H). – ^{13}C NMR ([D$_6$]benzene, DEPT): δ = 0.8, 1.3 and 2.7 (3 × $SiCH_3$), 19.2 (CH_2), 20.70, 20.76, 21.7, 22.8 and 24.4 (aryl-CH_3), 67.5 (CH), 129.3, 129.8 and 131.5 (aromat. CH), 132.9, 133.6, 134.8, 136.0, 137.4, 140.3, 148.4 (quart. aromat. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −68.8 [*Si*($SiMe_3$)$_3$], −19.6 and −18.9 [OSi(*Si*Me_3)$_2$], −12.3 [Si(*Si*Me_3)$_3$], 10.5 [O*Si*($SiMe_3$)$_2$]. – MS, *m/z* (%): 703 (40) [M$^+$ + H], 687 (25) [M$^+$ – CH_3], 569 (75) [M$^+$ – CH_2Mes], 455 (100) [M$^+$ – Si($SiMe_3$)$_3$]. – $C_{35}H_{70}OSi_7$ (702.4): calcd. C 59.80, H 10.04; found C 59.05, H 9.85.

(2,4,6-Trimethylbenzyl)bis(trimethylsilyl)[tris(trimethylsilyl)silyl]silane (**10**): Colorless crystals, m. p. 128–129°C. – ^1H NMR ([D$_6$]benzene): δ = 0.28 (s, $SiCH_3$, 18H), 0.42 (s, $SiCH_3$, 27H), 2.15 (s, *p*-CH_3, 3H), 2.36 (s, *o*-CH_3, 6H), 2.66 (s, CH_2, 2H), 6.75 (s, aromat. CH, 2H). – ^{13}C NMR ([D$_6$]benzene, DEPT): δ = 3.8 and 4.6 ($SiCH_3$), 17.1, 20.9 and 23.1 (*C*H_2Mes, *o*- and *p*-CH_3), 129.3 (aromat. CH), 133.9, 135.0 and 136.1 (quart. aromat C). – ^{29}Si NMR ([D$_6$]benzene): δ = −89.7 [*Si*($SiMe_3$)$_3$], −68.9 [*Si*($SiMe_3$)$_2$], −12.3 [Si(*Si*Me_3)$_2$], −9.6 [Si(*Si*Me_3)$_3$]. – MS, *m/z* (%): 554 (2) [M$^+$], 539 (20) [M$^+$ – CH_3], 481 (25) [M$^+$ – $SiMe_3$], 421 (65) [M$^+$ – CH_2Mes], 307 (100) [M$^+$ – 2 $SiMe_3$ – H]. – $C_{25}H_{58}Si_7$ (555.3): calcd. C 54.12, H 10.55; found C 53.06, H 10.51.

Reaction of **1** *with Phenylmagnesium Bromide in THF in the Presence of Lithium Bromide:* To a solution of 0.5 g (1.26 · 10^{-3} mol) of **1** and 0.77 g (8.87 · 10^{-3} mol) of LiBr in 3 ml of THF a solution of 1.26 · 10^{-3} mol of PhMgBr in THF was added, and the mixture was stirred for 4 h. The reaction was quenched by addition of an aqueous NH_4Cl solution, the mixture was extracted several times with ether and the solvent evaporated from the combined extracts. The residue was separated and purified by column chromatography (silica gel KG 60, heptane) to afford products: 0.02 g of **6** (5%), 0.11 g of **13** (28%), and 0.04 g of **11** (8%). Compound **13** was recrystallized from acetone.

2,4-Dimesityl-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**13**): Colorless crystals, m. p. 240–241°C. – ^1H NMR ($CDCl_3$): δ = 0.07 (s, $SiCH_3$, 36H), 2.18 (s, *p*-CH_3, 6H), 2.45 (s, *o*-CH_3, 12H), 3.87 (s, ring-CH, 2H), 6.70 (s, aryl-CH, 4H). – ^{13}C NMR ($CDCl_3$, DEPT): δ = 0.68 ($SiCH_3$), 14.91 (*p*-CH_3), 20.59 (ring-C), 24.25 (*o*-CH_3), 128.74 (aryl-*m*-C), 132.29, 134.46, 136.09 (aryl-*ipso*-C, aryl-*o*-C, aryl-*p*-C). – ^{29}Si NMR ($CDCl_3$): δ = −12.25 (*Si*$SiMe_3$), −6.10 (Si*Si*Me_3). – MS, *m/z* (%): 613 (60) [M$^+$ + H], 612 (28) [M$^+$], 597 (8) [M$^+$ – CH_3], 539 (72) [M$^+$ – $SiMe_3$], 493 (100) [M$^+$ – Mes]. – $C_{32}H_{60}Si_6$ (613.3): calcd. C 62.67, H 9.86; found C 61.97, H 9.93.

Reaction of **1** *with Methyllithium in THF:* To a solution of 0.5 g (1.26 · 10^{-3} mol) of **1** in 4 ml THF at −78°C an equimolar amount of MeLi was added, and the mixture was stirred for 1.5 h. Then an aqueous NH_4Cl solution was added to the cold solution and the mixture was extracted several times with ether. The combined ethereal extracts were dried, the solvent was evaporated and the residue separated by column chromatography (silica gel KG 60, heptane) to furnish **11** in 65% yield (0.33 g) and **4b** in a 6% yield (0.025 g).

Crystal Structure Determinations: A crystal of compounds **6** was investigated with a Siemens P4 diffractometer after taking a rotational photograph. The structure was solved by direct methods (Siemens SHELXTL, 1990, Siemens Analytical X-ray Inst. Inc.) and refined by the full-matrix least-squares method of SHELXL-93[11]. Both the carbon and silicon atoms were refined anisotropically. The hydrogen atoms were placed into their theoretical positions and refined by means of the riding model. The weighting scheme was calculated according to $w = 1/[\sigma^2(F_o^2) + (0.0881\,P)^2 + 8.3029\,P]$, where $P = (F_o^2 + 2\,F_c^2)/3$. The most important data are compiled in Table 1. Additional information concerning the crystal structure of compound **13** may be obtained from the Fachinformationszentrum Karlsruhe (CSD-58237)[3b].

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-

Table 1. Crystal and structure solution data of **6** and **13**

	6	**13**
Formula	$C_{32}H_{60}Si_6$	$C_{32}H_{60}Si_6$
M [g·mol^{-1}]	613.34	613.34
a [Å]	13.8020(10)	10.266(2)
b [Å]	17.304(2)	20.557(4)
c [Å]	34.002(3)	18.367(4)
β [°]	99.62	97.14(3)
V [Å^3]	8006.5(13)	3846.1(14)
$\rho_{calcd.}$ [g·cm^{-3}]	1.018	1.059
Z	8	4
Crystal system	Monoclinic	Monoclinic
Space group (No. I. T.)	$P2_1/c$ (14)	$P2_1/c$ (14)
F(000) [e]	2688	1344
μ (Mo-K$_\alpha$) [cm^{-1}]	2.3	2.4
Radiation	λ = 0.71089 A (Mo-K$_\alpha$), graphite monochromator	
Diffractometer	Siemens P4	
Crystal size [mm]	0.8 x 0.7 x 0.4	0.8 x 0.3 x 0.2
Temperature [°C]	25	25
Data collecting mode	omega-scan	
Scan range (2θ) [°]	3.5 - 45	4.5 - 52
hkl range	0/14, 0/20, -40/39	-1/12, -1/25, -22/22
Measured refl.	11462	9360
Unique refl.	10928	7558
Observed refl.	6641	4246
$F_o \geq$	2σ (I)	
Refined param.	685	343
*R*1 for $F_o > 4\cdot\sigma(F_o)$	0.0735	0.0672
*R*1 for all	0.1279	0.1347
w*R*2 for all	0.2191	0.1903
GoF	1.078	1.040
$\Delta\rho$ (max/min) [e/Å^{-3}]	+0.461/-0.318	+0.266/-0.248

76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401911 (for compound **6**), the names of the authors, and the journal citation.

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