Head-to-Head versus Head-to-Tail Dimerizations of Transient Silenes – The Solvent-Dependent Regiospecifity of the Dimerization of 2-(2-Methoxyphenyl)-1,1-bis(trimethylsilyl)silene

Kathleen Schmohl[a], Matthias Blach[a], Helmut Reinke[a], Rhett Kempe[b], and Hartmut Oehme*[a]

Fachbereich Chemie der Universität Rostock[a],
D-18051 Rostock, Germany
Fax: (internat.) +49(0)381/498-1763

Institut für Organische Katalyseforschung an der Universität Rostock e.V.[b],
D-18055 Rostock, Germany

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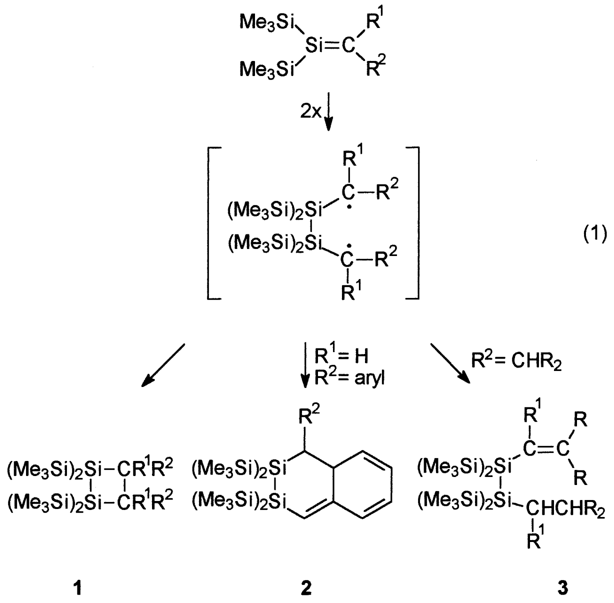
The regiospecifity of the dimerization of the transient 2-(2-methoxyphenyl)-1,1-bis(trimethylsilyl)silene (**6**), synthesized by base-initiated trimethylsilanolate elimination from (2-methoxyphenyl)[tris(trimethylsilyl)silyl]methanol (**5**) according to a modified Peterson mechanism, decisively depends on the donating ability of the solvent in which the silene is generated. In ether, **6** undergoes a formal [2 + 2] dimerization to afford 3,4-bis(2-methoxyphenyl)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**12**), whereas in toluene the head-to-tail [2 + 2] cyclodimer, 2,4-bis-(2-methoxyphenyl)-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**13**) was obtained. 1,1-Bis(trimethylsilyl)-2-(2,4,6-trimethoxyphenyl)silene (**18**), similarly made by a modified Peterson reaction, under the same conditions reacted with the eliminated trimethylsilanolate with readdition at the polar Si=C bond to give, after hydrolysis,2-(2,4,6-trimethoxybenzyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsiloxy)trisilane (**19**). A possible mechanism explaining the solvent-dependent regiospecificity of the dimerization of **6** is discussed. The structures of **12** and **13** were determined on the basis of NMR and MS data as well as X-ray structural analyses.

In the absence of trapping agents, sterically congested transient silenes undergo rapid dimerizations, in which head-to-head as well as head-to-tail reactions are observed[1]. The factors influencing the mode of dimerization are not clear, but, obviously, increasing polarity of the Si=C bond favors a head-to-tail coupling. Transient 1,1-bis(trimethylsilyl)silenes, made by the photolysis of acyl-tris(trimethylsilyl)silanes[2] or by a modified Peterson reaction[2][3][4], generally dimerize in a head-to-head mode. The reaction is supposed to proceed through radical intermediates[5]. After Si−Si bond formation the resulting diradicals stabilize with the formation of products, the structures of which depend on the nature of the substituents at the silene carbon atom (Eq. 1). 1,2-disilacyclobutanes **1** are usually obtained as the formal head-to-head [2 + 2] cyclodimers of the transient 1,1-bis(trimethylsilyl)silenes. When at least one of the silene C substituents is an aryl group, moderately stable tetrahydro-2,3-disilanaphthalenes **2**[6] are in some cases isolated as the kinetically preferred formal [2 + 4] silene dimers, which on thermal treatment gradually isomerize to give **1**. Silenes containing α hydrogen in the substituent at the silene C atom ("allylic" hydrogen) stabilize preferentially under hydrogen transfer to give linear dimers **3**[2][3a][5][7].

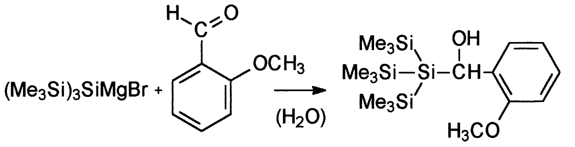


(1)

Recently we found that 2-(2-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene (**4**) dimerizes exclusively in a head-to-tail reaction affording the respective 1,3-disilacyclobutane[4]. This unusual regiospecificity was discussed as being effected by the 2-dimethylamino group of the aromatic substituent, causing an intermolecular interaction with the electrophilic silene silicon atom of a neighboring silaethene molecule. This donor−acceptor interaction finally leads to a head-to-tail dimerization following a mechanism, which is discussed later in this text. In this paper we describe the synthesis and dimerization behavior of 2-(2-methoxyphenyl)-1,1-bis(trimethylsilyl)silene, i.e. the dimethylamino donor group in the above-mentioned silaethene is replaced by a methoxy group, to examine the proposed cyclodimerization mechanism.

The Generation and Cyclodimerization Behavior of the Transient 2-(2-Methoxyphenyl)-1,1-bis(trimethylsilyl)silene (6)

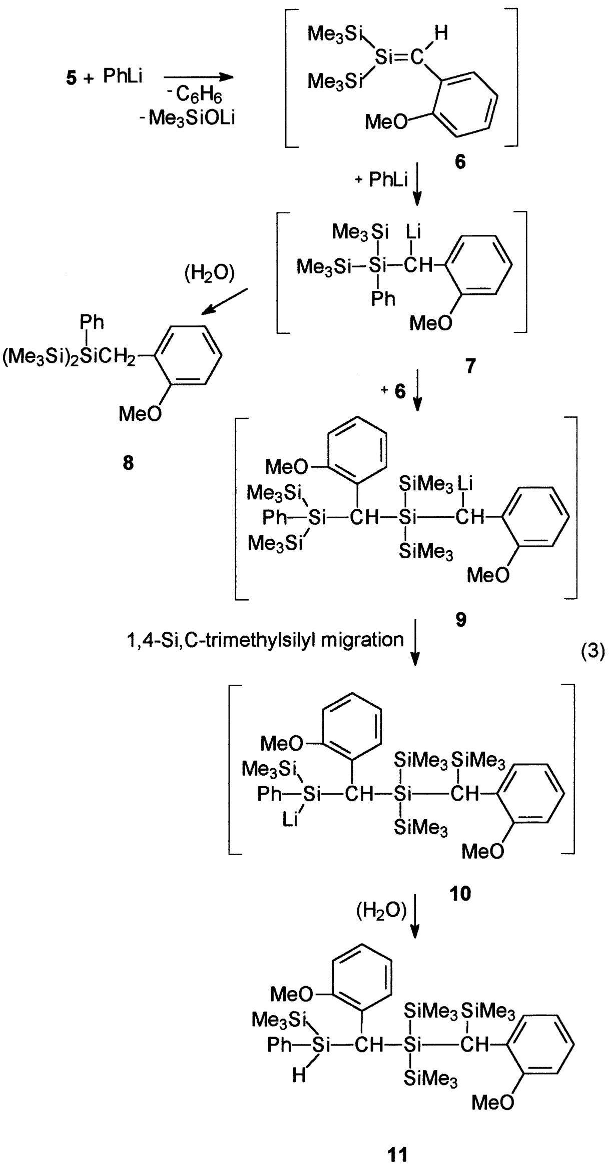
2-(2-Methoxyphenyl)-1,1-bis(trimethylsilyl)silene (**6**) was generated by the base-induced elimination of trimethylsilanol from (2-methoxyphenyl)-[tris(trimethylsilyl)silyl]-methanol (**5**) according to a modified Peterson mechanism. The alcohol **5** was obtained by the standard method[7] from tris(trimethylsilyl)silylmagnesium bromide and 2-methoxybenzaldehyde (Eq. 2).



(2)

5

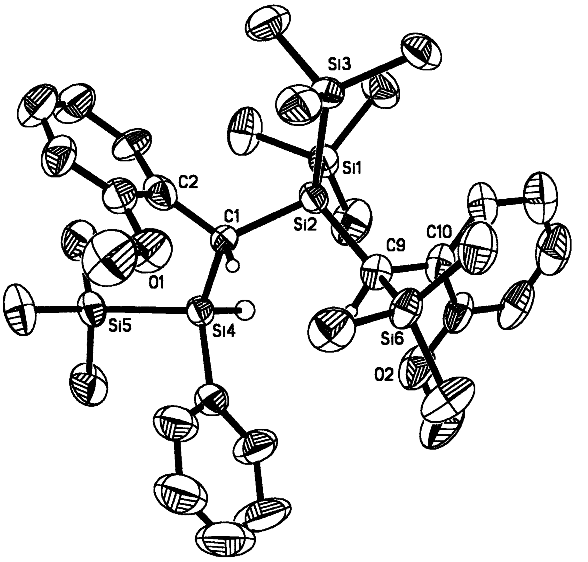
Interestingly, the outcome of the deprotonation reaction of **5** with organolithium reagents markedly depended on the solvent in which the reaction was carried out, and on the reaction conditions applied. Thus, the reaction of **5** with excess phenyllithium in ether led to the trisilane **8** (Eq. 3). This experiment is generally our standard method to check the clean trimethylsilanolate elimination from the starting 1-hydroxyalkyl-tris(trimethylsilyl)silane and the formation of the respective silene[7]. **8** was formed by immediate addition of excess phenyllithium to the Si=C bond of generated **6**, affording after hydrolysis the trisilane **8** . The high yield, in which **8** was obtained (84%), indicates a straightforward silene formation according to the modified Peterson mechanism.



The deprotonation of **5** with stoichiometric quantities of phenyllithium in ether at low temperature (starting at −78 °C and allowing the solution to warm up to room temperature) led to a complex mixture of components, from which only small quantities of a resultant silene product **11** could be separated in a pure form. On the basis of IR, NMR, and MS data, and particularly by means of an X-ray structural analysis it was identified as the silane **11** (Eq. 3). Its formation is interpreted as the result of the addition of phenyllithium at the polar Si=C bond of **6** giving an organolithium derivative **7** which attacks a further silene molecule. The resulting organolithium intermediate **9** undergoes a rapid rearrangement, a 1,4-Si,C-trimethylsilyl migration, with formation of the lithium silanide **10**, which is hydrolyzed during the aqueous workup affording **11**. Such trimethylsilyl migrations are not unusual; some years ago we observed a similar 1,3-Si,C shift[9], and the isomerization **9**→**10** is easily understood in terms of the particular stabilization of the silaanion by the phenyl and trimethylsilyl substituents. As we noticed, the deprotonation step of **5** proceeds comparatively slowly. Assuming that the elimination of lithium trimethylsilanolate is a fast process, the generated silene will always meet an effective excess of phenyllithium, which initiates this side reaction. The molecular structure of **11** is illustrated in Figure 1. The significant deviations from standard values of the bond distances and angles given characterize **11** as a considerably congested compound.

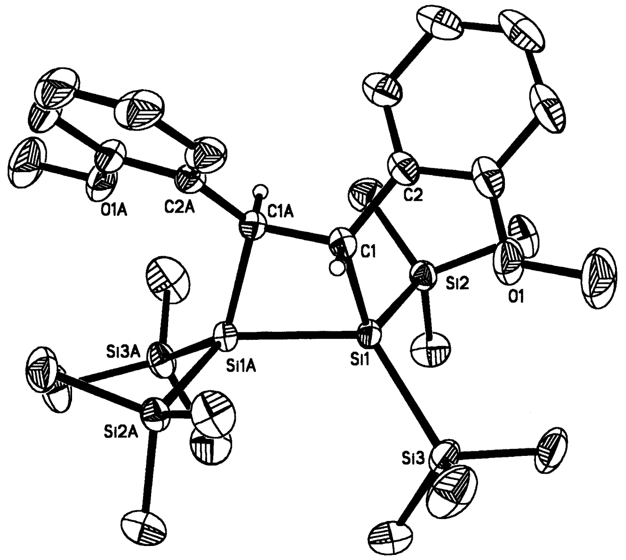
The clean generation of **6** by deprotonation of **5** with PhLi, indicated by the formation of **8** in high yield, led to the assumption that the mixture of unidentified compounds obtained by the reaction of **5** with stoichiometric quantities of PhLi in ether may probably consist of the various isomers of the formal [2 + 4] head-to-head cycloadducts **2** of the silene **6** (see Eq. 1). These products are known to undergo an isomerization on thermal treatment to give the thermodynamically stable 1,2-disilacyclobutane. This was the reason for changing the procedure of the reaction of **5** with equimolar quantities of PhLi in ether in such a way that after warming-up of the mixture to room temperature and subsequent removal of the solvent the residue was dis-

Figure 1. Molecular structure of **11** in the crystal [H atoms (except Si4-H and C1-H) omitted, ORTEP, 30% probability level][a]



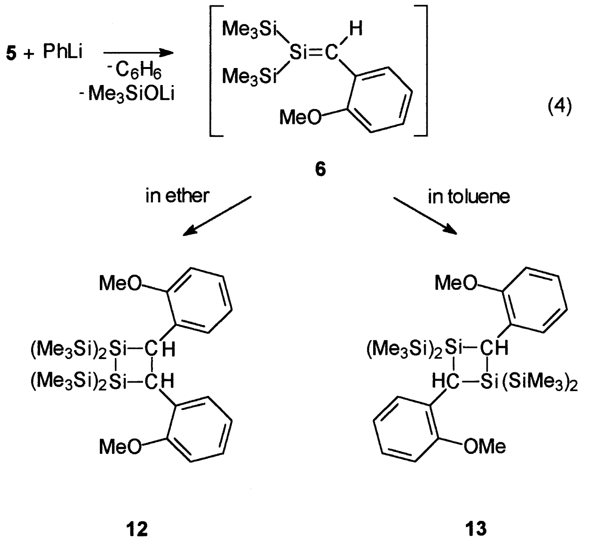
[a] Selected bond lengths [Å] and angles [°]: C1−Si2 1.912(5), C1−Si4 1.891(5), Si1−Si2 2.491(3), Si2−Si3 2.379(2), Si4−Si5 2.351(2), Si2−C9 1.873(6), C9−Si6 1.885(6); C1−Si2−C9 103.6(7), C9−Si2−Si3 118.7(2), C1−Si2−Si3 107.7(2), C1−Si2−Si1 113.3(2), Si1−Si2−Si3 107.02(9), C1−Si4−Si5 117.1(2).

Figure 2. Molecular structure of *E*-**12** in the crystal [H atoms (except the ring-CH) omitted, ORTEP, 30% probability level][a]



[a] Selected bond lengths [Å] and angles [°]: C1−C1A 1.549(5), C1−Si1 1.953(2), Si1−Si1A 1.3477(13), C1−C2 1.507(3), Si1−Si2 2.3589(10), Si1−Si3 2.3585(10); C1−Si1−Si1A 76.05(7), C1−C1A−Si1A 98.57(9), C1−Si1−Si2 107.52(8), C1−Si1−Si3 124.79(8), Si2−Si1−Si3 109.51(4).

solved in toluene and heated under reflux for 4 h. Aqueous workup actually afforded 42% of (*E*/*Z*)-3,4-di(2-methoxyphenyl)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**12**). Repeated recrystallization from acetone gave pure (*E*)-**12**.



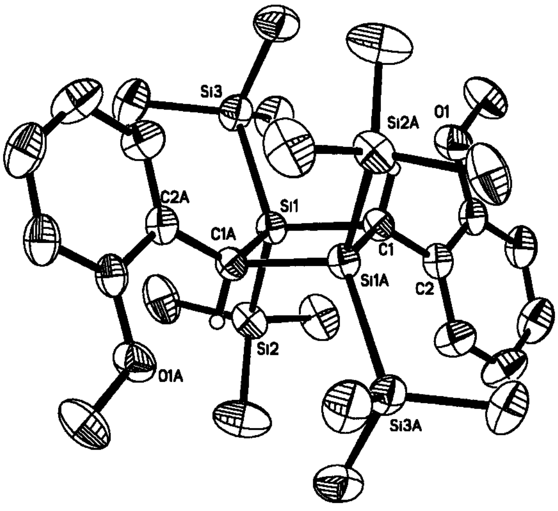
Compound **12** is the expected formal head-to-head [2 + 2] cyclodimer of the silene **6**. Its structure was elucidated by a full spectral analysis and an X-ray structural analysis characterizing the compound investigated as the C_2 symmetrical (*E*)-isomer (Figure 2). The four-membered ring is folded, the torsional angle Si1−Si1−C1−C1 being 24.7°. The C1−Si1 distances are slightly elongated, but most structural parameters are within the expected range.

As mentioned above, the outcome of the reaction of **5** with organolithium reagents decisively depends on the solvent used. A number of products were identified when **5** was deprotonated with equimolar quantities of methyllithium or *n*-butyllithium in toluene at low temperature and the mixture stirred after warming up to room temperature for 4 days. Besides unreacted **5**, traces of **16** and large quantities of a polymeric material a solid compound was isolated, which was unambiguously identified as the 1,3-disilacyclobutane **13**, the formal head-to-tail cyclodimer of the silene **6**. The structure elucidation of **13** was performed by NMR and MS investigations as well as by an X-ray structural analysis. As seen in Figure 3, the compound isolated in a yield of 27% is the (*E*)-isomer of the 1,3-disilacyclobutane **13**. The ring is planar. Apart from slightly elongated ring Si−C distances, which are considered as being due to steric congestion, the bond parameters are in the expected range. The reaction of **5** with organolithium reagents in pentane under the same conditions afforded (*E*)-**13** in 16% yield.

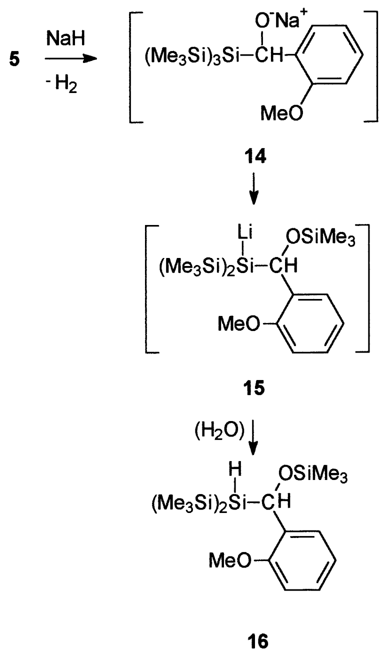
The byproduct **16** is the result of a 1,3-migration of one trimethylsilyl group from the central silicon atom to the alkoxid oxygen atom of deprotonated **5**, followed by hydrolysis of the silanide formed (Eq. 5). The same H-silane **16** is obtained in high yield by treatment of **5** with sodium hydride in ether. Such Si,O migrations were observed for the first time by Brook et al.[8] and appear to be typical of the behavior of 1-hydroxyalkylpolysilanes towards base[7].

Whereas the silene **6**, generated in ether, dimerizes to give the "normal" head-to-head product, a change of the solvent causes a complete reversal of the dimerization regiospecificity. Actually, the yield of **13** was not very high, but it should be emphasized that in the product mixture of the reaction

Figure 3. Molecular structure of *E*-**13** in the crystal [H atoms (except the ring-CH) omitted, ORTEP, 30% probability level][a]



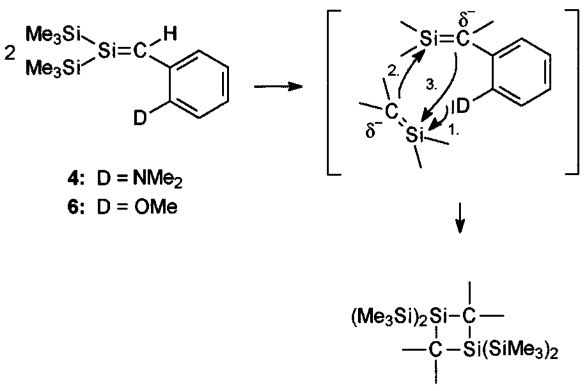
[a] Selected bond lengths [Å] and angles [°]: C1–Si1 1.923(2), Si1–Si2 2.3682(11), Si1–Si3 2.3668(11); C1–Si1–C1A 91.14(10), Si1–C1–Si1A 88.86(10).



(5)

of **5** with methyllithium in toluene no silene head-to-head dimer **12** could be detected. Similarly, no trace of the head-to-tail dimer **13** was observed after the reaction of **5** with MeLi in ether.

This solvent-dependent behavior of the silene **6** is fully consistent with the model proposed for the dimerization of 2-(2-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene (**4**), affording (in this case also in ether) exclusively the head-to-tail dimer. The deviation of **4** from the usual dimerization pattern of 1,1-bis(trimethylsilyl)silenes was discussed as a consequence of a strong donor–acceptor interaction of the dialkylamino group with the electrophilic silene silicon atom[4]. An effective intramolecular donor–acceptor interaction, which actually is expected to lead to an increase in the polarity of the silene double bond, thus facilitating a head-to-tail dimerization, is rather unlikely for steric reasons. We assume that the head-to-tail dimerization of **4** is achieved by an intermolecular donor–acceptor interaction, the *ortho*-dimethylamino group acting as some kind of anchor. Its interaction with the electrophilic silene silicon atom of a neighboring molecule and the attack of the activated nucleophilic silene carbon atom at the Si=C group of the first silene molecule possibly initiate a head-to-tail dimerization through a cyclic seven-membered transition state. This picture, outlined in eq. 6, can directly be transferred to the dimerization of **6** in toluene.



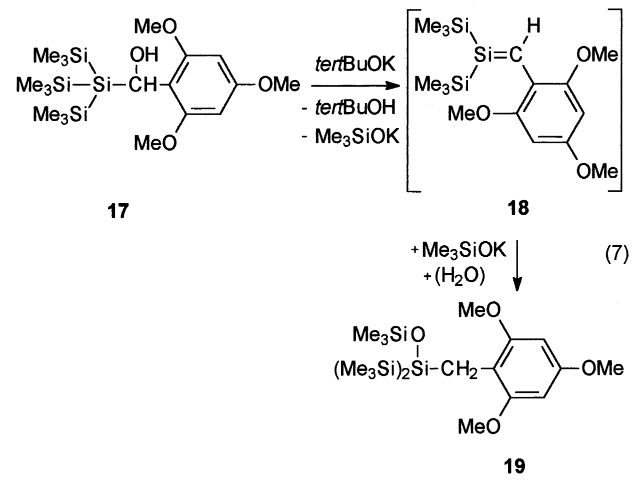
(6)

Of course, the donating ability of the dialkylamino group of **4** is much stronger than that of the methoxy group in **6**. Therefore the dimerization mode of **4** is solvent independent. On the other hand, in case of the generation of the silene **6** in ether, the donor solvent competes successfully with the weakly donating *o*-methoxy group, interrupting the intermolecular interaction. Thus, when ether is used as the solvent, the dimerization of **6** follows the usual reaction pattern providing the head-to-head product **12**.

The Reaction of (2,4,6-Trimethoxyphenyl)[tris(trimethylsilyl)silyl]methanol (17) with Potassium *tert*-Butoxide

1,1-Bis(trimethylsilyl)-2-(2,4,6-trimethoxyphenyl)silene (**18**), generated through the modified Peterson mechanism from (2,4,6-trimethoxyphenyl)[tris(trimethylsilyl)silyl]methanol (**17**) offers the same structural requirements for following a dimerization pattern comparable to that of **6** and was therefore included in our studies. Unexpectedly, the reaction of **17** with MeLi or PhLi in ether as well as in toluene proceeded very slowly. Better results were obtained when potassium *tert*-butoxide was used as the deprotonating base. However, the reaction of **17** with *t*BuOK in both solvents gave no silene dimer, and we obtained a colorless oil, which was identified as 2-(2,4,6-trimethoxyphenyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsiloxy)trisilane (**19**) (Eq. 7).

The siloxane **19** is formed by readdition of the silanolate, just eliminated from **17**, at the Si=C bond of the silene **18**. This behavior is typical for highly congested silenes generated by the Peterson process[3b][10]. Obviously, the increase



of the bulkiness of the substituent at the silene carbon atom diminishes the dimerization tendency making the silanolate addition the dominating process.

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Experimental Section

General: 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[11] and **17**[12] were prepared as reported in the literature.

(2-Methoxyphenyl)[tris(trimethylsilyl)silyl]methanol (**5**): As described previously[7], 14.7 g (0.03 mol) of $(Me_3Si)_3SiLi \cdot 3$ THF were converted in ether with an equimolar quantity of $MgBr_2$ into $(Me_3Si)_3SiMgBr$ and to this suspension 4.1 g (0.03 mol) of 2-methoxybenzaldehyde were added at −78°C. After stirring for 2 h the mixture was allowed to warm up to room temperature, diluted HCl was added, the organic layer was separated, dried with $MgSO_4$, and evaporated. The residue was purified by Kugelrohr distillation (150°C / 0.03 Torr). Yield 8.7 g (75%) pale yellow crystals, m.p. 48°C. **5** is rather unstable and should be kept in the cold. At room temperature the solid gradually decomposes to an oily product of unidentified structure. Attempts to recrystallize **5** were therefore also unsuccessful. – IR (cap.): $\tilde{\nu} = 3523\ cm^{-1}$ (OH free), 3439 (OH ass.). – ^1H NMR ($[D_6]$benzene): $\delta = 0.28$ (s, $SiCH_3$, 27 H), 1.30 (d, $^3J = 4.0$ Hz, OH, 1 H), 3.27 (s, OCH_3, 3 H), 5.38 (d, $^3J = 4.0$ Hz, CH, 1 H), 6.42–7.49 (m, ArH, 4 H). – ^{13}C NMR ($[D_6]$benzene): $\delta = 1.8$ ($SiCH_3$), 54.2 (OCH_3), 62.6 (COH), 109.8, 121.0, 126.8, 127.2 (arom. CH), 136.3, 154.5 (arom. quart. C). – ^{29}Si NMR ($[D_6]$benzene): $\delta = -12.8$ $(SiMe_3)_3$, − 68.8 (*Si*$SiMe_3$). – MS: *m/z* (%): 383 (6) $[M^+ - H]$, 367 (100) $[M^+ - OH]$. – $C_{17}H_{36}O_2Si_4$ (384.82): calcd. C 53.06, H 9.43; found C 52.58, H 8.85).

(2-Methoxybenzyl)-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane (**8**): To a solution of 0.5 g (1.3 mmol) of **5** in 20 ml of ether a fivefold molar excess of PhLi was added at room temperature. After stirring for 2 h diluted HCl was added, the ethereal phase separated and dried with $MgSO_4$. The oily product obtained after evaporation was purified by chromatography (silica gel, heptane/ethyl acetate, 20:1) to give 0.4 g (84%) **8**. – ^1H NMR ($[D_6]$benzene): $\delta = 0.16$ (s, $SiCH_3$, 18 H), 2.75 (s, CH_2, 2 H), 3.27 (s, OCH_3, 3 H), 6.49–7.61 (m, ArH, 9 H). – ^{13}C NMR ($[D_6]$benzene): $\delta = -0.2$ ($SiCH_3$), 13.9 (CH_2), 54.3 (OCH_3), 110.2, 120.7, 125.9, 128.0, 128.2, 130.3, 135.6 (aromat. CH), 130.0, 137.9, 156.7 (aromat. quart. C). – MS: *m/z* (%) = 357 (8.5) $[M^+ - CH_3]$, 299 (100) $[M^+ - CSiMe_3]$. – $C_{20}H_{32}OSi_3$ (372.73): calcd. C 64.45, H 8.65; found C 64.56, H 8.74.

2,4-Bis(2-methoxyphenyl)-1-phenyl-1,3,3,4-tetrakis(trimethylsilyl)-1,3-disilabutane (**11**): An equimolar quantity of phenyllithium was added to a solution of 0.5 g (1.3 mmol) of **5** in ether at −78°C and stirred for 2 h. After warming of the mixture to room temperature, diluted HCl was added, the organic layer separated, dried with $MgSO_4$, and evaporated. Chromatographic separation of the residue (silica gel, heptane) and recrystallization of the product from acetone gave 0.04 g (9.2%) of **11**. Colorless crystals, m.p. 255°C. – IR (KBr): $\tilde{\nu} = 2094\ cm^{-1}$ (SiH). – ^1H NMR ($[D_6]$benzene): $\delta = -0.18$, 0.13, 0.20, 0.28 (4s, $SiCH_3$, 4 × 9 H), 2.87 (s, CH, 1H), 3.28 and 3.58 (2s, OCH_3, 2 × 3 H), 3.44 and 5.06 (2d, $^3J = 5.4$ Hz for both, SiH and PhSiCH, 3 × 1 H), 6.48–7.92 (m, ArH, 13 H). – ^{13}C NMR ($[D_6]$benzene): $\delta = -1.5$, 0.5, 2.8, 3.4 ($SiCH_3$), 9.4, 15.6 (CH), 54.2, 54.4 (OCH_3), 110.0, 110.3, 119.8, 120.9, 121.9, 125.4, 125.6, 125.7, 128.8, 132.3, 132.4, 133.3, 135.9, 138.3, 138.4, 155.7 (aromat.C). – ^{29}Si NMR ($[D_6]$benzene): $\delta = -22.3$ *Si*$(SiMe_3)_2$, −16.7, −16.3, −15.2 (Si*Si*Me_3, SiH), 1.6 ($CSiMe_3$). – MS: *m/z* (%) 622 (2) $[M^+]$, 651 (7) $[M^+ - CCH_3]$, 593 (100) $[M^+ - CSiMe_3]$. – $C_{34}H_{58}O_2Si_6$ (667.34): calcd. C 61.19, H 8.76; found C 61.33, H 8.72.

(E)-3,4-Bis(2-methoxyphenyl)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**12**): An equimolar quantity of PhLi was given to a stirred solution of 0.5 g (1.3 mmol) of **5** in 25 ml of ether. After warming up to room temperature, the solvent was removed in vacuo, 20 ml of toluene were added and the solution was refluxed for 4 h. After addition of diluted HCl the organic phase was separated, dried with $MgSO_4$, and evaporated. The oily residue crystallized after addition of a few ml of *n*-heptane to give 0.16 g (42%) of (*E*/*Z*)-**12**, repeated recrystallization from acetone afforded pure (*E*)-**12**, m.p. 175°C. – ^1H NMR ($[D_6]$benzene): $\delta = 0.17$, 0.44 (2s, $SiCH_3$, 2 × 18 H), 3.45 (s, OCH_3, 6 H), 4.18 (s, ring CH, 2 H), 6.51–7.12 (m, ArH, 8 H). – ^{13}C NMR ($[D_6]$benzene): $\delta = 1.9$, 2.0 ($SiCH_3$), 29.8 (ring C), 54.7 (OCH_3), 109.4, 120.8, 125.0, 126.5 (arom. CH), 133.4, 156.2 (arom. quart. C). – ^{29}Si NMR ($[D_6]$benzene): $\delta = -49.9$ (ring Si), −14.0, −11.3 ($SiMe_3$). – MS: *m/z* (%): 589 (22) $[M^+ + H]$, 573 (12) $[M^+ - CCH_3]$, 515 (19) $[M^+ - CSiMe_3]$, 348 (100) $[M^+ - C(Me_3Si)_2SiSi(SiMe_3)_2]$. – $C_{28}H_{52}O_2Si_6$ (589.24): calcd. C 57.08, H 8.90; found C 57.30, H 8.79.

(E)-2,4-Bis(2-methoxyphenyl)-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**13**): To 0.6 g (1.6 mmol) of **5**, dissolved in 25 ml of toluene, an equimolar quantity of *n*BuLi was added under stirring at −78°C. The solution was allowed to warm up to room temperature within 2 h and afterwards it was refluxed for 4 h. After hydrolysis the organic layer was separated, dried with $MgSO_4$ and evaporated to give an oily residue which crystallized on addition of some heptane. Repeated recrystallization from heptane afforded 0.06 g (13%) of colorless crystals of (*E*)-**13**, m.p. 235°C. – ^1H NMR ($[D_6]$benzene): $\delta = 0.28$ (s, $SiCH_3$, 36 H), 3.37 (s, OCH_3, 6 H), 3.87 (s, ring CH, 2 H), 6.47–7.67 (m, ArH, 8 H). – ^{13}C NMR ($[D_6]$benzene): $\delta = 0.6$ ($SiCH_3$), 7.6 (ring C), 54.9 (OCH_3), 110.2, 120.3, 124.4, 130.5 (arom. CH), 133.5, 156.6 (arom. quart. C). – ^{29}Si NMR ($[D_6]$benzene): $\delta = -13.4$ (ring Si), −13.9 ($SiMe_3$). – MS: *m/z* (%): 589 (3) $[M^+ + H]$, 573 (6) $[M^+ - CCH_3]$, 515 (100)

Table 1. Crystal and structure solution data of **11**, **12**, and **13**

	11	**12**	**13**
Formula	$C_{34}H_{58}O_2Si_6$	$C_{28}H_{52}O_2Si_6$	$C_{28}H_{52}O_2Si_6$
M [g·mol^{-1}]	667.34	589.24	589.24
a [Å]	17.429(2)	17.138(3)	21.324(4)
b [Å]	12.104(2)	10.323(2)	10.130(2)
c [A]	19.984(2)	21.022(3)	17.056(3)
β [°]	94.630(10)	105.59(4)	99.06(3)
V [Å^3]	4202.1(9)	3582.2(11)	3638.3(12)
$\rho_{calcd.}$ [g·cm^{-3}]	1.055	1.093	1.076
Z	4	4	4
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c	C2/c
F(000) [e]	1448	1280	1280
μ (Mo-K_α) [mm^{-1}]	0.224	0.255	0.251
Radiation λ [A]	0.71073	0.71073	0.71073
Diffractometer	Siemens P4	Siemens P4	Stoe-IPDS
Crystal size	0.94 × 0.62 × 0.56	0.88 × 0.60 × 0.38	0.6 × 0.5 × 0.4
Temperature [°C]	293	293	293
Data collection Mode	omega scan	omega scan	laser-scanned imaging plate
Scan range (2θ) [°]	3.94−42.00	4.02−44.00	3.86−48.62
hkl range	−1/18 −1/13 −1/18	−1/18 −11/1 −1/18	−24/24 −11/11 −24/24
Measured refl.	5703	2806	9445
Unique refl.	4519	2198	2914
Observed refl.	3573	1984	2139
$I \geq 2\sigma(I)$	$2\sigma(I)$	$2\sigma(I)$	$2\sigma(I)$
Refined param.	380	163	189
*R*1	0.0768	0.0444	0.038
*wR*2 for all	0.2158	0.1238	0.109
GoF for all	1.027	1.088	1.047

[M^+ − $CSiMe_3$]. − $C_{28}H_{52}O_2Si_6$ (589.24): calc. C 57.08, H 8.90; found C 57.14, H 8.91.

(2-Methoxyphenyl)bis(trimethylsilyl)silyltrimethylsiloxymethane (**16**): To a stirred solution of 0.6 g (1.6 mmol) of **5** in 35 ml of ether a catalytic amount of sodium hydride was added at −78°C. After warming up to room temperature water was added, the organic layer separated and dried with $MgSO_4$. Evaporation gave a colorless oil, which was purified by chromatography (silica gel, heptane/ethyl acetate, 30:1). − IR (cap.): $\tilde{\nu}$ = 2074 cm^{-1} (SiH). − ^1H NMR ([D$_6$]benzene): δ = 0.09 (s, $OSiCH_3$, 9 H), 0.25 (s, $SiSiCH_3$, 18 H), 3.37 (s, OCH_3, 3 H), 3.68 (d, ^3J = 2.45 Hz, SiH, 1 H), 5.67 (d, ^3J = 2.52 Hz, CH, 1 H), 6.50−7.67 (m, ArH, 4 H). − ^{13}C NMR ([D$_6$]benzene): δ = 0.3, 0.6, 0.8 ($SiCH_3$), 54.6 (OCH_3), 61.2 (CH), 109.9, 120.9, 126.7, 127.2 (arom. CH), 135.6, 154.2 (arom. quart. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −52.9 (*Si*$SiMe_3$), −15.0, −15.3 (Si*Si*Me_3), 17.7 ($OSiMe_3$). − MS: *m/z* (%): 384 (3) [M^+], 311 (90) [M^+ − $CSiMe_3$], 209 (100) [M^+ − $CHSi(SiMe_3)_2$]. − $C_{17}H_{36}O_2Si_4$ (384.82): calcd. C 53.06, H 9.43; found C 52.88, H 9.39.

2-(2,4,6-Trimethoxbenzyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsiloxy)trisilane (**19**): To a solution of 0.55 g (1.2 mmol) of **17** in 30 ml of toluene the equimolar quantity of *t*BuOK was added at −78°C. The mixture was allowed to warm up gradually to room temperature and was then heated under reflux for 4 h. Hydrolysis, separation and drying of the organic phase and evaporation gave a colorless oil, which was purified by chromatography (silica gel, heptane/ethyl acetate, 20:1), yield 0.23 g (59%). − IR (cap.): $\tilde{\nu}$ = 1062 cm^{-1} (SiOSi). − ^1H NMR ([D$_6$]benzene): δ = 0.18 (s, OSiCH$_3$, 9 H), 0.21 (s, $SiSiCH_3$, 18 H), 2.72 (s, CH_2, 2 H), 3.39 (s, OCH_3, 6 H), 3.42 (s, OCH_3, 3 H), 6.12 (s, ArH, 2 H). − ^{13}C NMR ([D$_6$]benzene): δ = −1.3 ($SiSiCH_3$), 2.3 ($OSiCH_3$), 12.9 (CH_2), 54.8 (*o*-OCH_3), 54.9 (*p*-OCH_3), 90.6 (arom. CH), 109.1, 157.9, 158.7 (arom. quart. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −19.6 (Si*Si*-*i*Me_3), 0.9 (*Si*$SiMe_3$), 6.3 ($OSiMe_3$). − MS: *m/z* (%): 445 (1) [M^++H], 429 (10) [M^+ − CCH_3], 371 (100) [M^+ − $CSiMe_3$], 355 (12) [M^+ − $COSiMe_3$]. − $C_{19}H_{40}O_4Si_4$ (444.87): calcd. C 51.30, H 9.06; found C 51.23, H 9.03.

Crystal-Structure Determination of **11**, **12**, *and* **13**: The crystal-structure determinations were performed on a SIEMENS P4 four-circle diffractometer with graphite monochromator in the case of compounds **11** and **12** and on a STOE IPDS system with graphite monochromator for **13**. The structures were solved by direct methods (Siemens SHELXTL, 1990, Siemens Analytical X-ray Inst. Inc. for **11** and **12** and SHELXS-86[13] for **13**) and refined by the full-matrix least-squares method of Siemens SHELXTL, Ver. 5.03 (**11**, **12**) and SHELXL-93[14] (**13**). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into theoretical positions and refined using the riding model.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102330 (**11**), CCDC-102331 (**12**), and CCDC-102332 (**13**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk].

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