2-(2,4-Di-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)silene and 2-(2,4,6-Tri-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)silene – Two New Sterically Protected but Still Unstable Silaethenes

Frank Luderer, Helmut Reinke, and Hartmut Oehme*

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

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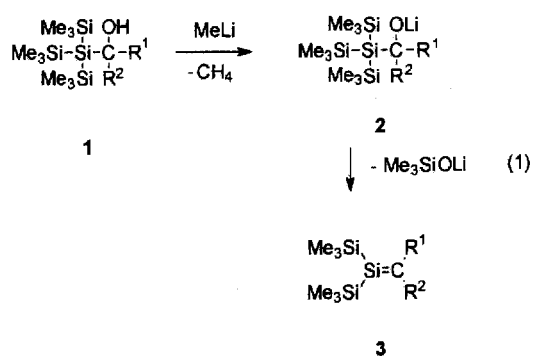
(2,4-Di-*tert*-butylphenyl)tris(trimethylsilyl)silylmethanol (**1a**), prepared by the reaction of tris(trimethylsilyl)silylmagnesium bromide with 2,4-di-*tert*-butylbenzaldehyde, was deprotonated by treatment with methyllithium in ether at −78 °C to give the transient 2-(2,4-di-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)silene (**3a**), which dimerizes in a head-to-head fashion with the formation of (*E*)-/(*Z*)-3,4-bis(2,4-di-*tert*-butylphenyl)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**5**). Besides **5** an unstable compound **4** was obtained, which was preliminarly assigned as 5,7-di-*tert*-butyl-1-(2,4-di-*tert*-butylphenyl)-1,2,3,8a-tetrahydro-2,2,3,3-tetrakis(trimethylsilyl)-1,2-disilanaphthalene (**4**), the formal [2 + 4] cyclodimer of **3a**. Compound **4** gradually decomposes to give (*E*)-/(*Z*)-**5**, and is considered to be the kinetically preferred dimer of **3a**, which is converted into the thermodynamically stable **5**. 2,4,6-Tri-*tert*-butylbenzaldehyde reacts with tris(trimethylsilyl)silyllithium resulting in the formation of 6,8-di-*tert*-butyl-1,2,3,4-tetrahydro-4,4-dimethyl-2,2-bis(trimethylsilyl)-2-silanaphthalene (**6**). Compound **6** is the product of the insertion of the Si=C bond into the C–H bond of an *o*-*tert*-butyl group of the intermediate 2-(2,4,6-tri-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)silene (**3b**), which despite extreme steric shielding proved to be still unstable. For compounds (*Z*)-**5** and **6** the results of the X-ray analyses are given.

The treatment of 1-(hydroxyalkyl)tris(trimethylsilyl)silanes (**1**) with organometallic bases leads to a clean elimination of trimethylsilanolate and the formation of Si=C bond systems (eq. 1). The silenes generated till now according to this modified Peterson mechanism proved to be unstable and undergoes various dimerization reactions in the absence of scavenger agents[1]. Thus, as the typical stabilization process a formal [2 + 2] head-to-head cyclodimerization was observed, leading to 1,2-disilacyclobutanes. In the case of silenes possessing "allylic" hydrogens also linear dimers were obtained. Both reactions were described also by other authors and appear to be typical of sterically congested silenes bearing trimethylsilyl groups at the silene silicon atom[2–4]. 2-Mesityl-1,1-bis(trimethylsilyl)silene dimerizes in a formal [2 + 4] process to give a tetrahydro-2,3-disilanaphthalene as the kinetically preferred product which on thermal treatment is gradually converted into the thermodynamically stable [2 + 2] cyclodimer, the 1,2-disilacyclobutane[1b].

An increase of the steric bulk of the substituents R^1 and R^2 in the silene **3** was expected to enhance the kinetic stability of the silaethene system, and we actually observed considerable differences in the reaction behavior going from 2-mesityl-1,1-bis(trimethylsilyl)silene to 2-(2,4,6-triisopropylphenyl)-1,1-bis(trimethylsilyl)silene. Whereas the mesityl derivative **3** (R^1 = H, R^2 = Mes) is rapidly converted into the mentioned dimers, in the case of the generation of the triisopropylphenyl analogue (**3**: R^1 = H, R^2 = 2,4,6-iPr$_3$C$_6$H$_2$) according to eq. (1), due to the steric congestion by the aromatic substituent and the two trimethylsilyl groups, the silene dimerization becomes a comparatively slow reaction, making the readdition of the just eliminated lithium trimethylsilanolate to the polar Si=C bond the dominating process. Furthermore, the steric congestion leads to a weakening of the central silicon–carbon bond in the alkoxide **2**. Thus, under special conditions products resulting from an Si–C bond cleavage were obtained[5].



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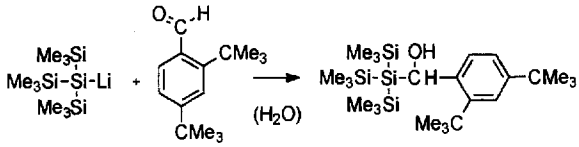
Following our intention of a further increase of the steric protection of the labile Si=C system, we introduced the 2,4,6-tri-*tert*-butylphenyl group, the supermesityl substituent. This substituent, due to the two *o*-*tert*-butyl groups offers an extreme steric shielding and proved to be very suitable in stabilizing unusual bonding systems particularly of the elements of the groups 15 and 16. The precursor of the generation of 2-(2,4,6-tri-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)silene (**3b**) according to the Peterson mechanism should be the respective alcohol **1b**, which was intended to be synthesized by the reaction of tris(trimethylsilyl)silylmagnesium bromide with 2,4,6-tri-*tert*-butylbenzaldehyde. When we tried to prepare this aldehyde by the reaction of 1,3,5-tri-*tert*-butylbenzene with dichloromethyl methyl ether in the presence of titanium tetrachloride using the method of Wayland[6], we noticed that the reaction is accompanied by the loss of one *o*-*tert*-butyl group and we obtained the 2,4-di-*tert*-butylbenzaldehyde instead of the supermesityl compound. So we decided to extend our studies to the 2,4-di-*tert*-butylphenyl derivatives, and we describe in this paper the generation of the two title silaethens and their conversion into a dimer and the product of an unexpected insertion reaction, resp.

Synthesis of (2,4-Di-*tert*-butylphenyl)tris(trimethylsilyl)-silylmethanol (1a) and Its Conversion into the Transient 2-(2,4-Di-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)silene (3a)

(2,4-Di-*tert*-butylphenyl)tris(trimethylsilyl)silylmethanol (**1a**) was prepared by the reaction of tris(trimethylsilyl)silylmagnesium bromide with 2,4-di-*tert*-butylbenzaldehyde [eq. (2)] in 50% yield as a stable, colorless crystalline compound. The formulated structure is in full agreement with the ^{1}H-, ^{13}C-, and ^{29}Si-NMR and MS data (see Experimental).



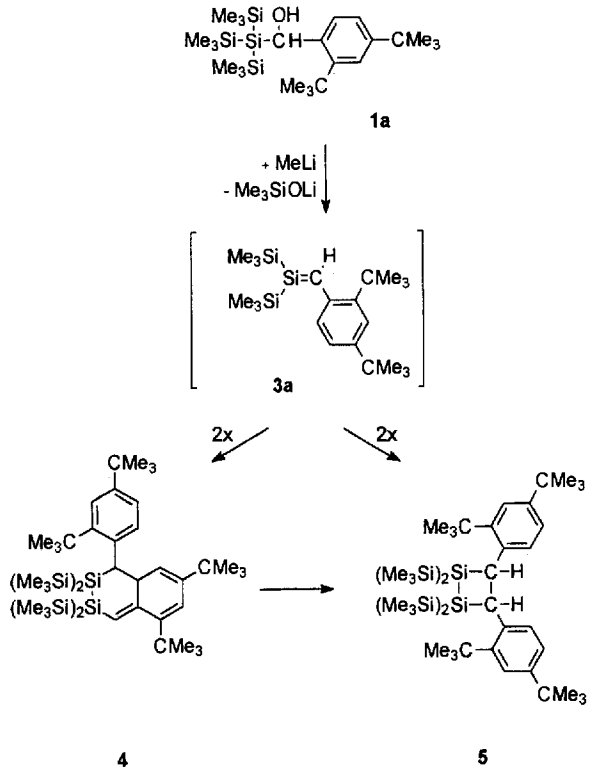
(2)

1a

The deprotonation of **1a** with MeLi in ether at −78 °C initiates the elimination of lithium trimethylsilanolate and the generation of the transient silene **3a**. Hydrolytic work-up of the reaction mixture gave two products, which were identified as (*E*)-/(*Z*)-3,4-bis(2,4-di-*tert*-butylphenyl)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**5**) (73%) and 5,7-di-*tert*-butyl-1-(2,4-di-*tert*-butylphenyl)-1,2,3,8a-tetrahydro-2,2,3,3-tetrakis(trimethylsilyl)-2,3-disilanaphthalene (**4**) (10%) (Scheme 1). Compound **4** was obtained as the mixture of the (*E*)/(*Z*) isomers. Interestingly, the (*Z*) isomer, which could cleanly be separated, predominates in the mixture [(*E*)/(*Z*) = 1:6].

Its structure was elucidated on the basis of NMR and MS data, which are very similar to those obtained for other 1,2-disilacyclobutanes in previous studies[1]. As expected, two signals of the magnetically nonequivalent trimethylsilyl groups are observed in the ^{1}H-, ^{13}C- as well as the ^{29}Si-NMR spectra. Also the results of the MS studies were indicative. Finally, the configuration of **5** was revealed by an X-ray investigation. As can be seen in Figure 1, the two aromatic substituents are in a (*Z*) position. The four-membered ring is rather bent. The two planes through the atoms C1−Si1−Si2 and Si2−C2−C1 intersect at an angle of 26.9°. Thus, the two bulky aromatic groups can be placed in a diequatorial position. Due to the steric demands of these substituents the Si1−C1 (1.953 Å), Si2−C2 (1.962 Å) and particularly the C1−C2 (1.606 Å) bond lengths are elongated, but agree with the values obtained for similarly congested 1,2-disilacyclobutane systems[1,5,7].

Scheme 1. Generation of the silene **3a** by deprotonation and lithium trimethylsiloxide elimination from **1a** by treatment with MeLi in ether at −78 °C and its dimerization to the tetrahydro-2,3-disilanaphthalene **4** and the 1,2-disilacyclobutane **5**

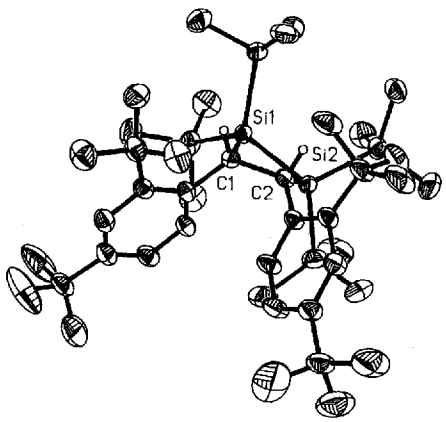


4 **5**

The 1,2-disilacyclobutane **5** is the product of a formal [2 + 2] cyclodimerization, the expected result of the stabilization of the transient silene **3a**. The tetrahydro-2,3-disilanaphthalene **4** is easily recognized as the result of a formal [2 + 4] cycloaddition reaction of **3a**, in which the silene both acts as the monoene and − involving the aromatic substituent − as the diene. A similar behavior was observed already for 2-mesityl-1,1-bis(trimethylsilyl)silene[1a,b] and 2-(2,5-diisopropylphenyl)-1,1-bis(trimethylsilyl)silene[1d]. Both [2 + 4] products proved to be unstable and are gradually converted into the respective 1,2-disilacyclobutanes. The same applies to compound **4**, which could not be obtained in a pure form, since it gradually decomposes to give **5** and particularly when we tried to purify the compound by recrystallization we always obtained only mixture of the (*E*)/(*Z*) isomers of **5**. The preliminary structural proof is

based on ^{1}H-NMR spectra only, which show a signal pattern very similar to the corresponding mesityl derivative. Thus, we again found four distinct signals of the four trimethylsilyl groups, one of them significantly shifted to higher field. This is understood as being due to the influence of the shielding cone of the neighboring aromatic substituent. Thus, **4** is considered to be the kinetically preferred product of the dimerization of the silene **3a**, which is gradually converted into the thermodynamically stable dimer **5**. Another mode of stabilization of **4**, the migration of a proton from C-8a → C-4, resulting in a rearomatization of the system could not be detected.

Figure 1. Molecular structure of (*Z*)-**5**; for simplicity the hydrogen atoms are omitted and the probability of the thermal ellipsoids is reduced to 30%[a]

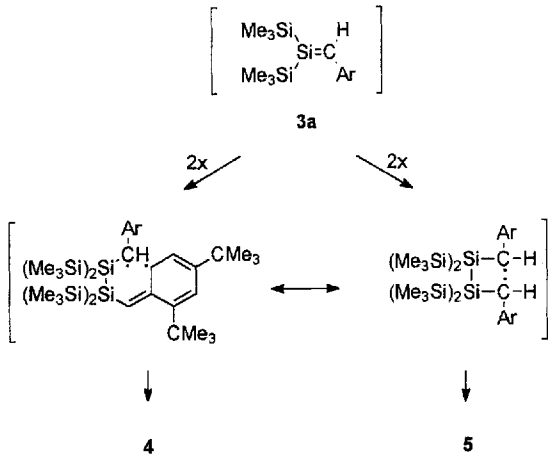


[a] Selected bond lengths [Å] and angles [°]: C1–C2 1.605(7), C1–Si1 1.952(5), C2–Si2 1.961(6), Si1–Si2 2.358(2); C1–Si1–Si2 79.9(2), C2–Si2–Si1 76.3(2), C2–C1–Si1 97.6(3), C1–C2–Si2 100.9(3).

As discovered by Brook et al.[2a,7], the head-to-head dimerization of reactive silenes having a structur similar to those described in this paper, proceeds via radical intermediates. After the Si–Si bond formation the resulting 1,4-diradical stabilizes to give a 1,2-disilacyclobutane or (in the presence of allylic protons) a linear dimer. Applying this mechanism to the dimerization of the silene **3a**, we obtain a very straightforward picture (Scheme 2). The 1,4-diradical may stabilize by ring closure affording **5**. But the structure of the radical intermediate allows an extension of the conjugation system and the reaction may proceed via a 1,6-diradical intermediate giving **4**.

In conclusion, it should be stated that the steric protection by the 2,4-di-*tert*-butylphenyl substituent is less pronounced than that of the 2,4,6-triisopropylphenyl group. Products arising from silanolate readditions to the silene typical of the behavior of 2-(2,4,6-triisopropylphenyl)-1,1-bis(trimethylislyl)silene, generated under the conditions of the modified Peterson mechanism, and Si–C bond cleavages, as described at the beginning of the paper, could not be detected. Insofar, **3a** shows the expected behavior of a sterically congested, but reactive silene.

Scheme 2. Proposed mechanism for the dimerization of the silene **3a** (Ar = 2,4-di-*tert*-butylphenyl)



Generation of 2-(2,4,6-Tri-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)silene (3b) and Intramolecular Insertion of the Si=C Bond into the C–H Bond of An *o*-*tert*-Butyl Methyl Group Giving the Tetrahydro-2-silanaphthalene (6)

Attempts to prepare (2,4,6-tri-*tert*-butylphenyl)tris(trimethylsilyl)silylmethanol (**1b**) failed. Tris(trimethylsilyl)silylmagnesium bromide did not react with 2,4,6-tri-*tert*-butylbenzaldehyde in ether. Even after three weaks at room temperature – finally at slightly elevated temperature – no reaction occurred. Obviously, the carbonyl group of the aldehyde is extremely shielded by the two *o*-*tert*-butyl groups, so that the approach of the silicon nucleophile is completely hindered.

To increase the nucleophilic properties of the silanide we used tris(trimethylsilyl)silyllithium in the reaction with 2,4,6-tri-*tert*-butylbenzaldehyde instead of the magnesium derivative. After a reaction time of about one week at room temperature, chromatographic control of the progress of the reaction indicated that the aldehyde was completely consumed. Hydrolytic work-up gave 6,8-di-*tert*-butyl-1,2,3,4-tetrahydro-4,4-dimethyl-2,2-bis(trimethylsilyl)-2-silanaphthalene (**6**) (26%) besides approx. 10% of 2,2′,4,4′,6,6′-hexa-*tert*-butylstilbene (**7**).

Even under these conditions the alcohol **1b** could not be detected. This is in agreement with our general experience that lithium 1-tris(trimethylsilyl)silylalkoxides **2** spontaneously eliminate trimethylsiloxide to give silenes. Thus, the formation of **6** is interpreted as the result of an in situ reaction of the lithium alkoxide **2b**, which immediately eliminates Me_3SiOLi producing the silene **3b**. However, although the Si=C group in **3b** is extremely sterically shielded, the silene is not stable under the conditions applied. The sterical congestion of the molecule obviously prevents a dimerization but the highly reactive silene group is inserted into a C–H bond of an *o*-*tert*-butyl group of the supermesityl substituent (Scheme 3).

The structure proposed for compound **6** is in full agreement with the straightforward NMR spectra and the MS data and was also confirmed by an X-ray structural analysis (Figure 2). The silacyclohexene subunit adopts a boat con-

Scheme 3. Reaction of tris(trimethylsilyl)silyllithium with 2,4,6-tri-*tert*-butylbenzaldehyde and the formation of the tetrahydro-2-silanaphthalene **6**

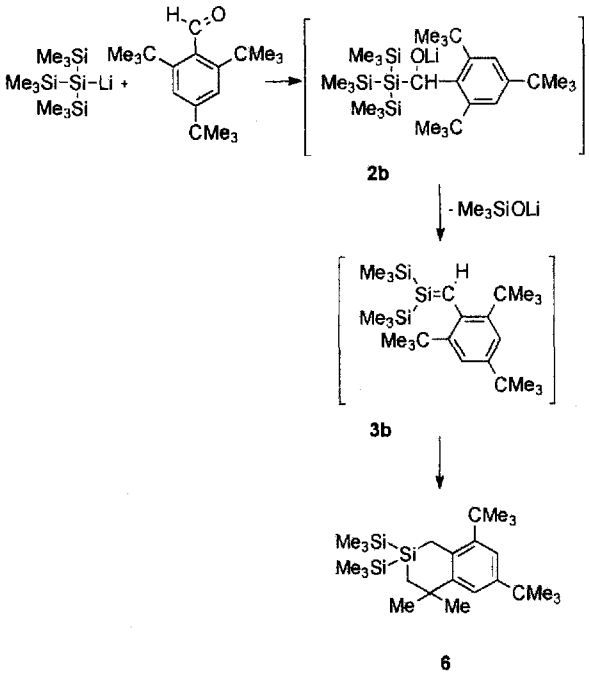
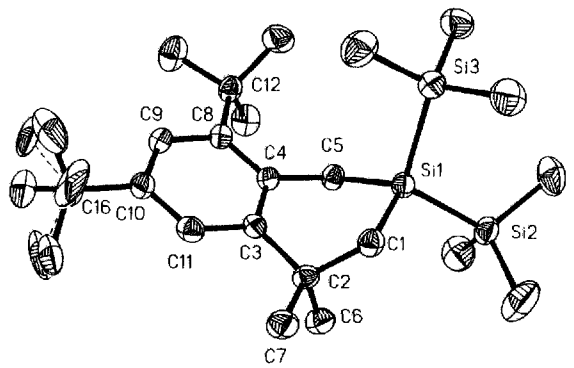


Figure 2. Molecular structure of **6**; for simplicity the hydrogen atoms are omitted and the probability of the thermal ellipsoids is reduced to 30%[a]



[a] Selected bond lengths [Å] and angles [°]: C1–C2 1.547(5), C1–Si1 1.892(4), Si1–C5 1.898(4), C2–C3 1.544(5), C3–C4 1.412(5), C4–C5 1.533(5); C1–Si1–C5 102.2(2), C2–C1–Si1 113.9(3), C3–C2–C1 109.5(3), C4–C3–C2 123.0(3), C3–C4–C5 118.5(3), C4–C5–Si1 113.3(2).

formation, the puckering parameters being $Q = 0.698(4)$ Å, $\Theta = 94.0(3)°$ and $\phi = 293.8(3)°$[8].

Insertion reactions of highly reactive double-bond systems of the heavier main-group elements into C–H bonds were observed occasionally. In a very similar reaction 2,4,6-tri-*tert*-butylselenobenzaldehyde, when heated in benzene solution, isomerizes quantitatively to give the respective benzoselenanne[9]. Also the intramolecular insertion of a silaphosphene into the C–H bond of the adjacent isopropyl group of the (2,4,6-triisopropylphenyl)silyl substituent was described[10]. Interestingly, 2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene, which is moderately stable in solution, isomerizes during extended photolysis with insertion of the silene double bond into the C–H bond of one *o*-methyl group of the mesityl substituent – but in a reverse form – giving a dihydrobenzocyclobutene[11].

The formation of the stilbene **7**, found as a byproduct in the reaction of tris(trimethylsilyl)silyllithium with 2,4,6-tri-*tert*-butylbenzaldehyde, is not yet really clear. But, as described previously, a substituted stilbene was also found when (2,4,6-triisopropylphenyl)tris(trimethylsilyl)silylmethanol was synthesized by the interaction of tris(trimethylsilyl)silyllithium with 2,4,6-triisopropylbenzaldehyde[5]. We suppose that the alkoxide **2b** undergoes a Brook rearrangement to a tris(trimethylsilyl)siloxy carbanion which – supported by the steric strain of the molecule – is easily split into lithium tris(trimethylsilyl)siloxide and supermesitylcarbene, which dimerizes to give **7**. These suggestions, of course, need further experimental support.

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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 ref.[12] 2,4-Di-*tert*-butylbenzaldehyde was synthesized according to the method of Wayland[6] by starting with 1,3,5-tri-*tert*-butylbenzene (yield 60%). 2,4,6-Tri-*tert*-butylbenzaldehyde was obtained by a modification of the method described by Okazaki et al. for the synthesis of 2,4,6-tri-*tert*-butylthiobenzaldehyde[13]. The reaction of 2,4,6-tri-*tert*-butylphenyllithium, prepared either by sonication from 2,4,6-tri-*tert*-butylbromobenzene and lithium in ether in the presence of tetramethylethylendiamine or by metal/halogen exchange from 2,4,6-tri-*tert*-butylbromobenzene and *n*-butyllithium in THF, with methyl formate gave 2,4,6-tri-*tert*-butylbenzaldehyde in 50% yield. Since for both aldehydes no full spectral characterization was found in the literature, the ^{1}H- and ^{13}C-NMR data are given:

2,4-Di-tert-butylbenzaldehyde: ^{1}H NMR ($CDCl_3$): $\delta = 1.34$ (s, *p*-*t*Bu, 9H), 1.53 (s, *o*-*t*Bu, 9H), 7.34 (dd, $^3J = 7.0$ Hz, $^4J = 1.8$ Hz, 5-CH, 1H), 7.50 (d, $^4J = 1.8$ Hz, 3-CH, 1H), 7.88 (d, $^3J = 7.0$ Hz, 6-CH, 1H), 10.78 (s, CHO, 1H). – ^{13}C NMR ($CDCl_3$): $\delta = 31.47$ and 31.60 (CH_3), 32.98 and 34.80 (CCH_3), 119.44, 122.20 and 122.34 (arom. CH), 127.60, 149.95 and 150.63 (arom. quat. C), 192.42 (CHO).

2,4,6-Tri-tert-butylbenzaldehyde: ^{1}H NMR ([D$_6$]benzene): $\delta =$ 1.40 (s, *p*-*t*Bu, 9H), 1.44 (s, *o*-*t*Bu, 18H), 7.57 (s, arom. CH, 2H), 11.20 (s, CHO, 1H). – ^{13}C NMR ([D$_6$]benzene): $\delta = 31.41$ (p-CCH_3), 32.47 (*o*-CCH_3), 32.60 (*o*-CCH_3), 36.76 (p-CCH_3), 121.66 (arom. CH), 138.00, 147.92 and 150.92 (arom. quat. C), 202.29 (CHO).

(2,4-Di-tert-butylphenyl)tris(trimethylsilyl)silylmethanol (**1a**): To an ethereal solution of 3.52 g (0.01 mol) of tris(trimethylsilyl)silylmagnesium bromide[14a] was added 2.18 g (0.01 mol) of 2,4-di-*tert*-butylbenzaldehyde at –40 °C. The mixture was stirred at this temperature for 4 h and subsequently allowed to warm up to room temp., and stirring was continued overnight. After the addition of

diluted HCl the organic layer was separated and the aqueous phase extracted several times with ether. The combined extracts were dried with $MgSO_4$, the solvent was evaporated and the residue was recrystallized from acetonitrile. Yield of **1a** 2.34 g (50%), m.p. 94°C. – IR (nujol): $\tilde{\nu}$ = 3520.0 cm^{-1} (OH, free). – ^1H NMR ([D$_6$]benzene): δ = 0.43 (s, $SiCH_3$, 27H), 1.31 (d, ^3J = 4.58 Hz, OH, 1H), 1.40 and 1.51 (2 s, CCH_3, 2 × 9H), 5.80 (d, ^3J = 4.58 Hz, OCH, 1H), 7.40 (dd, ^3J = 7.93 Hz, ^4J = 2.13 Hz, 5-CH, 1H), 7.55 (d, ^4J = 2.13, 3-CH, 1H), 7.77 (d, ^3J = 7.93 Hz, 6-CH). – ^{13}C NMR ([D$_6$]benzene, DEPT): δ = 1.83 ($SiCH_3$), 31.54 and 32.72 (CCH_3), 34.78 and 35.96 (CCH_3), 65.45 (OCH), 122.78, 123.56 and 133.76 (arom. CH), 140.51, 145.83 and 149.68 (arom. quat. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −13.1 (Si*Si*Me$_3$), −68.1 (*Si*SiMe$_3$). – MS; *m/z* (%): 466 (10) [M$^+$], 451 (1) [M$^+$ − CH_3], 376 (30) [M$^+$ − Me_3SiOH], 319 (80) [M$^+$ − $(SiMe_3)_2$ − H], 219 (100) [M$^+$ − $Si(SiMe_3)_3$]. – $C_{24}H_{50}OSi_4$ (467.00): calcd. C 61.73, H 10.79; found C 61.09, H 10.70.

Reaction of (2,4-Di-tert-butylphenyl)tris(trimethylsilyl)silylmethanol (**1a**) *with Methyllithium in Ether:* To a solution of 0.47 g (1 · 10^{-3} mol) of **1a** in ether was added at −78°C an equimolar amount of MeLi in ether. The mixture was allowed to warm up to room temp. and was stirred overnight. After the addition of a saturated aqueous NH_4Cl solution the organic layer was separated, the aqueous solution was extracted several times with ether, the collected extracts were dried and the solvent was evaporated. Chromatographic separation of the residue gave **4** as a crystalline but labile compound and **5**, which was further separated by repeated chromatography (silica gel/heptane) into (*Z*)-**5** and an impure residue preliminarily assigned as (*E*)-**5** (0.4 g, 10%).

4: Yield 0.04 g (10%). – ^1H NMR ($CDCl_3$): δ = −0.20, 0.24, 0.28 and 0.34 (4 s, $SiCH_3$, 4 × 9H), 0.74, 1.18, 1.38 and 1.50 (4 s, CCH_3, 4 × 9H), 3.24 (m, 8a-CH, 1H), 3.74 (d, ^3J = 4.28, 1-CH, 1H), 5.60 (dd, ^3J = 4.88, ^4J = 1.21, 8-CH, 1H), 5.64 (s, 4-CH, 1H), 6.55 (br. s, 6-CH), 1H), 6.66 (dd, ^3J = 8.23 Hz, ^4J = 2.13 Hz, arom. 5-CH, 1H), 7.05 (d, ^3J = 2.13 Hz, arom. 3-CH, 1H), 7.70 (d, ^3J = 8.23 Hz, arom. 6-CH, 1H).

(*Z*)-**5**: Yield 0.24 g (63%), m.p. 165°C. – ^1H NMR ([D$_6$]benzene): δ = 0.43 and 0.60 (2 s, $SiCH_3$, 2 × 18H), 1.35 and 1.47 (2 s, CCH_3, 2 × 18H), 4.80 (s, ring CH, 2H), 7.24 (dd, ^3J = 8.23, ^4J = 2.13, arom. 5-CH, 2H), 7.44 (d, ^4J = 2.13 Hz, arom. 3-CH, 2H), 8.19 (d, ^3J = 8.23 Hz, arom. 6-CH). – ^{13}C NMR ([D$_6$]benzene, DEPT): 2.42 and 2.53 ($SiCH_3$), 31.51 and 32.68 (CCH_3), 34.51 and 35.93 (CCH_3), 39.67 (ring C), 121.34, 122.57 and 134.69 (arom. CH), 140.62, 145.88 and 147.23 (arom. quat. C). – ^{29}Si NMR: ([D$_6$]benzene): δ = −11.5 and −12.5 (Si*Si*Me$_3$), −37.4 (*Si*SiMe$_3$). – MS; *m/z* (%): 753 (1.5) [M$^+$], 680 (2) [M$^+$ − $SiMe_3$], 348 (100) [$(Me_3Si)_2Si_2^+$]. – $C_{42}H_{80}Si_6$ (753.61): calcd. C 66.94, H 10.70; found C 66.71, H 10.50.

Reaction of Tris(trimethylsilyl)silyllithium with 2,4,6-Tri-tert-butylbenzaldehyde: An ethereal solution containing 1.82 g (4 · 10^{-3} mol) of tris(trimethylsilyl)silyllithium and 1.10 g (4 · 10^{-3} mol) of 2,4,6-tri-*tert*-butylbenzaldehyde was stirred at room temp. for one weak. Aqueous work-up as described above and chromatographic separation of the raw product mixture gave 0.45 g (26%) of **6** and 0.10 g of the stilbene **7**. Compound **6** was recrystallized from alcohol, m.p. 68°C. – ^1H NMR ([D$_6$]benzene): δ = 0.20 (s, $SiCH_3$, 18H), 1.23 (s, 3-CH_2, 2H), 1.50 and 1.67 [2 s, $C(CH_3)_3$, 2 × 9H], 1.63 [s, $C(CH_3)_2$, 6H], 2.82 (s, 1-CH_2, 2H), 7.65 (br. s, arom. CH, 2H). – ^{13}C NMR ([D$_6$]benzene, DEPT): δ = −0.90 ($SiCH_3$), 12.69 (3-CH_2), 21.14 (1-CH_2), 31.79 and 32.31 [$C(CH_3)_3$], 33.64 ([$C(CH_3)_2$], 34.95 [$C(CH_3)_2$], 36.44 and 33.77 [$C(CH_3)_3$], 120.69 and 121.54 (arom. CH), 134.87, 146.39, 147.06 and 148.10 (arom. quat. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −16.4 (Si*Si*Me$_3$), −51.1 (*Si*SiMe$_3$). – MS; *m/z* (%): 432 (85) [M$^+$], 359 (75) [M$^+$ − $SiMe_3$], 303 (100) [M$^+$ − $SiMe_3$ − C_4H_8]. – $C_{25}H_{48}Si_3$ (432.91): calcd. C 69.36, H 11.16; found C 68.87, H 11.00.

Crystal-Structure Determinations: Crystals of (*Z*)-**5** and **6** (recrystallized from a mixture of ethanol and acetone) were investigated by using a Siemens P4 diffractometer after taking rotational photographs. The structures were solved by direct methods (Siemens SHELXTL, Copyright 1990, Siemens Analytical X-ray Inst. Inc.) and refined by the full-matrix least-squares method of SHELXL-93[14]. Carbon and silicon atoms were refined anisotropically. The hydrogen atoms were placed into their theoretical positions and refined by using the riding model. The weighting scheme was calculated according to $w = 1/[\sigma^2(F_o^2) + (0.1641\ P)^2 + 2.2882\ P]$ for (*E*)-**5** and $w = 1/[\sigma^2(F_o^2) + (0.688\ P)^2 + 1.433\ P]$ for **6**, where $P = (F_o^2 + 2F_c^2)/3$. – The most important data can be taken from Table 1. The fairly high values of the regression coefficients for the refinement of the data set (*Z*)-**5** are due to problems that remain unsolved. The residual electron density and space-filling considerations suggest that there could be some solvent in the crystal lattice. In this case however, the content does not seem to be stoichiometric and the difference map shows one peak in a definite position. Further calculations showed that the peak distances are neither in agreement with bond lengths in acetone nor with those in ethanol. – Another problem is the high mobility of some atoms or groups of atoms. There were several hints concerning split positions during the SHELXL-93 calculations but attempts to make use of those positions failed to give better results. – In the crystal

Table 1. Crystal and structure solution data of compounds (*Z*)-**5** and **6**

	(*Z*)-**5**	**6**
Formula	$C_{42}H_{80}Si_6$	$C_{25}H_{48}Si_3$
M [g·mol^{-1}]	753.60	432.90
a [Å]	11.4020(10)	9.916(2)
b [Å]	11.554(2)	31.744(2)
c [Å]	21.129(2)	10.2710(10)
α [°]	81.180(10)	90
β [°]	86.690(10)	114.93
γ [°]	74.760(10)	90
V [Å^3]	2653.4(6)	2931.8(7)
$\rho_{calcd.}$ [g·cm^{-3}]	0.943	0.981
Z	2	4
Crystal system	triclinic	monoclinic
Space group (No. I. T.)	$P\bar{1}$ (2)	$P2_1/n$ (14)
F(000) [e]	832	960
μ (Mo-K_α) [cm^{-1}]	0.180	0.170
Radiation	λ = 0.71089 Å (Mo-K_α), graphite monochromator	
Diffractometer	Siemens P4	
Crystal size [mm]	0.8 × 0.7 × 0.2	0.8 × 0.7 × 0.3
Temperature [°C]	25	25
Data collecting mode	ω scan	
Scan range (2θ) [°]	3.70 – 44.0	4.56 – 45.0
hkl range	0/12, −12/12, −23/23	0/10, 0/34, −11/10
Measured refl.	6901	4085
Unique refl.	6497	3833
Observed refl.	4680	2822
$F_o \geq$	2σ(*I*)	2σ(*I*)
Refined param.	434	281
*R*1 for $F_o > 4\cdot\sigma(F_o)$	0.0907	0.0599
*R*1 for all	0.1214	0.0857
w*R*2 for all	0.3026	0.1736
GoF	1.072	1.060
Δρ (max/min) [e/Å^{-3}]	1.420/−0.294	0.302/−0.235

structure of **6** there is a disorder problem regarding the *tert*-butyl group at C-10. Although the SHELXL-93 calculations gave better results when the split positions were taken into consideration and restraints were used, some problems still remain, e.g. disagreeable restraints or a number of larger correlation matrix elements. – A PLATON calculation yielded the following puckering parameters for the silacyclohexene unit in **6**: Q = 69.8(4) pm (puckering amplitude), Θ = 94.0(3)° and ϕ = 293.8(3)°[8]. – Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404135 [(*Z*)-**5**] or -404136 (**6**), the names of the authors, and the journal citation.

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