Synthesis of Transient Silenes by a Modified Peterson Reaction

Clemens Krempner, Helmut Reinke, and Hartmut Oehme*

Fachbereich Chemie der Universität Rostock,
D-18051 Rostock, Germany

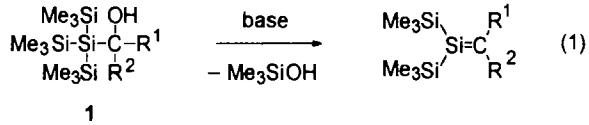
Received July 4, 1994

Key Words: Silenes / Silene dimerization / 1,2-Disilacyclobutanes / 2,3-Disilanaphthalene, tetrahydro-

Tris(trimethylsilyl)silylmagnesium bromide, obtained in situ from tris(trimethylsilyl)silyllithium and magnesium bromide, reacts with acetone, pivalaldehyde, or 2,4,6-trimethylbenzaldehyde to give the (1-hydroxyalkyl)tris(trimethylsilyl)silanes $(Me_3Si)_3SiC(OH)Me_2$ (**1a**), $(Me_3Si)_3CH(OH)tBu$ (**1b**), and $(Me_3Si)_3SiCH(OH)Mes$ (**1c**), resp. After deprotonation with methyllithium in ether at −78°C **1a−c** eliminate trimethylsilanolate according to a modified Peterson mechanism to form transient silenes $(Me_3Si)_2Si{=}CR^1R^2$ (**6a**: $R^1 = R^2 = Me$; **6b**: $R^1 = H$, $R^2 = tBu$; **6c**: $R^1 = H$, $R^2 = Mes$). In the absence of trapping agents these silenes dimerize, **6a** leading to the linear dimer 1-isopropenyl-2-isopropyl-1,1,2,2-tetrakis(trimethylsilyl)disilane (**7**) and **6b** giving the head-to-head cyclodimerization product (*E*)-3,4-di-*tert*-butyl-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**8**), whereas **6c** in a very unusual cyclodimerization step affords (*E*)-1,2,3,8a-tetrahydro-1-mesityl-5,7,8a-trimethyl-2,2,3,3-tetrakis(trimethylsilyl)-2,3-disilanaphthalene (**9**). Compound **9** is the result of an unexpected [2 + 4] reaction, in which the silene formally acts as the monoene and − involving the aromatic substituent − simultaneously also as the diene. The reaction of **1a−c** with methyllithium in THF at low temperature initiates 1,3-*Si,O*-trimethylsilyl migrations leading to (trimethylsiloxy)[bis(trimethylsilyl)silyl]alkanes $(Me_3Si)_2SiH{-}CR^1R^2OSiMe_3$ **3a−c**. Reaction of **1a−c** with an excess of methyllithium, *tert*-butyllithium, or phenyllithium, leads to trisilanes $(Me_3Si)_2SiR^3{-}CHR^1R^2$ **11a−e**, formed by the addition of the organolithium reagent to the Si=C bond of the transient silenes **6a−c**. Deprotonation of **1b** and **1c** in the presence of 2,3-dimethyl-1,3-butadiene gives the [2 + 4] cycloadducts 6-*tert*-butyl-3,4-dimethyl-1,1-bis(trimethylsilyl)-1-sila-3-cyclohexene (**12a**) and 6-mesityl-3,4-dimethyl-1,1-bis(trimethylsilyl)-1-sila-3-cyclohexene (**12b**). For **8** and **9** the results of the X-ray analyses are given.

The modification of the Peterson reaction in such a way that by elimination of trimethylsilanolate from deprotonated (1-hydroxyalkyl)tris(trimethylsilyl)silanes (**1**) Si=C systems, i.e. silenes, are formed is a promising route to this interesting class of unsaturated organosilicon compounds (eq. 1). In 1988 we found that lithiated **1**, obtained in situ by the reaction of tris(trimethylsilyl)silyllithium (**2**) with aliphatic ketones, is converted to give, depending on the reaction conditions, either (trimethylsiloxy)[bis(trimethylsilyl)silyl]alkanes **3** or the polysilanes **4**. Compounds **3** are formed by a 1,3-trimethylsilyl migration and protonation of the silanide by the enolizable ketone, and the products **4** are proposed to be the result of an addition of excess **2** to the double bond of transient silenes (obtained according to eq. 1) followed by a 1,3-*Si,C*-trimethylsilyl shift and protonation during hydrolytic workup[1]. The disadvantage of this in situ method, with respect to the synthesis of silenes, is the enolizability of the ketones applied (only aliphatic ketones can be used, aromatic aldehydes and ketones do not undergo lithium silanide carbonyl addition) and the fact that under the conditions of an effective excess of **2** (i.e., when the ketone is dropped to the solution of **2**) the reactive silene is trapped by the lithium silanide **2**.

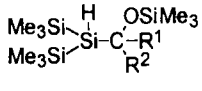
Related concepts were followed by Apeloig et al., who elegantly excluded the problem of the enolizability of the ketone by using adamantanone[2] and by Ishikawa et al., who studied the reaction of acyltris(trimethylsilyl)silanes with organolithium reagents[3].



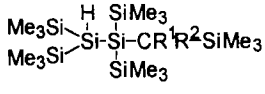
(1)

1

$(Me_3Si)_3SiLi$ **2**



3



4

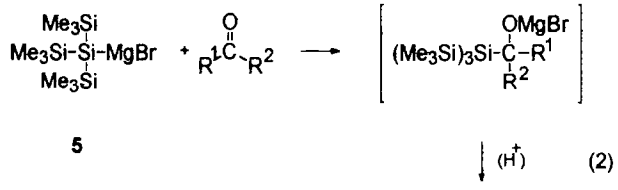
In this paper we describe a method leading to isolated (1-hydroxyalkyl)tris(trimethylsilyl)silanes (**1**). In the presence of a base these alcohols are easily converted into transient silenes, which are characterized by various dimerization and addition reactions. The availability of pure, isolated hydroxyalkyl polysilanes **1** in the synthesis of silenes according to the Peterson concept offers the possibility of a free choice of the reaction medium and the base used to initiate the silanolate elimination. With respect to the significance of the solvent for the silene generation and its subsequent reactions, this is of particular importance.

  0009−2940/95/0202−0143 $ 10.00+.25/0

Synthesis of the (1-Hydroxyalkyl)tris(trimethylsilyl)silanes 1a–c

The Peterson Reaction in its original form, i.e. the reaction of 1-silylalkyllithium derivatives with aldehydes or ketones, gives olefins directly, whereas the use of 1-silylalkyl-Grignard reagents in the reaction with carbonyl compounds gives 2-hydroxy-alkylsilanes as stable intermediates[4]. Similarly, hydroxyalkyl polysilanes **1** are obtained, when tris(trimethylsilyl)silylmagnesium bromide (**5**) is allowed to react with carbonyl derivatives instead of the lithium silanide **2**. Furthermore, **5** also reacts with aromatic aldehydes and ketones in a Grignard-like carbonyl addition, so that the scope of the reaction – compared with the application of **2** – can be extended considerably. Compound **5** is obtained by reaction of $(Me_3Si)_3SiLi \cdot 3\ THF$[5] with anhydrous magnesium bromide in diethyl ether and is used in situ.

The reaction of **5** with acetone, pivalaldehyde, and 2,4,6-trimethylbenzaldehyde at −78°C in ether results in the formation of **1a–c** (eq. 2). Compounds **1a–c** are colorless, stable and waxy solids. Their structures are proven on the basis of IR-, ^{1}H-, ^{13}C-, ^{29}Si-NMR and MS data (see Experimental).



(2)

1	R^1	R^2
a	Me	Me
b	H	tBu
c	H	Mes

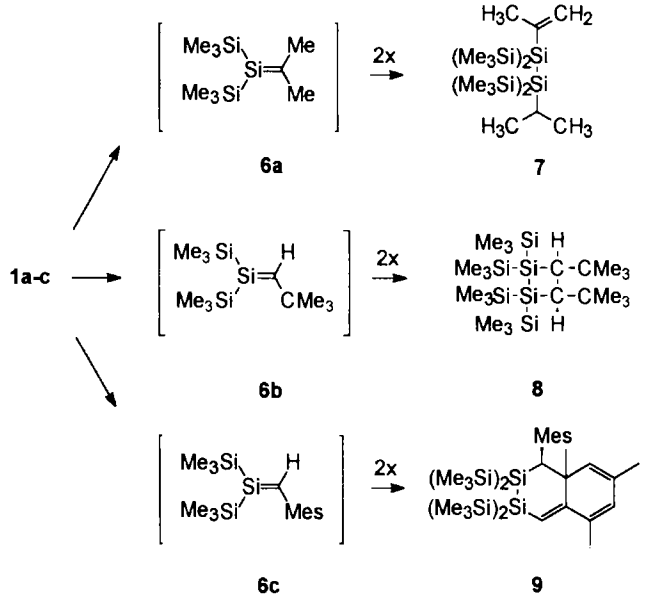
Compound **1c** exhibits an interesting dynamic effect in its ^{1}H-NMR spectrum, characterizing the compound as an extremely crowded silane. Below 300 K the two *o*-methyl groups of the mesityl substituent show two separated sharp signals; their coalescence is observed at 340 K, and above 388 K only one sharp signal appears (solvent [D_5]pyridine). A similar pattern is observed for the signals of the *m* protons of the mesityl group. These results are interpreted as being due to a hindered rotation around the aryl–COH bond (Ar-CH_3: T_c 340 K, $\Delta\nu$ = 159 Hz; Ar-H: T_c 322 K, $\Delta\nu$ = 39.8 Hz; calcd. rotation barrier $\Delta G^{\neq}$ = 67 kJ/mol).

Generation and Conversion of the Transient Silenes 6a–c in the Absence of Trapping Agents

After deprotonation with strong bases **1a–c** are spontaneously converted into products, the structures of which are determined by the substituents R^1 and R^2 as well as by the nature of the base used and the solvent, in which the reaction is carried out.

So treatment of 2-[tris(trimethylsilyl)silyl]-2-propanol (**1a**) with methyllithium in ether at −78°C gives 1-isopropenyl-2-isopropyl-1,1,2,2-tetrakis(trimethylsilyl)disilane (**7**) in 78% yield (Scheme 1). Compound **7** has already been prepared by Ishikawa and coworkers[4a] by reaction of acetyltris(trimethylsilyl)silane with methyllithium. This reaction proceeds via an intermediate obviously identical with lithiated **1a**. The mechanisms of both reactions involve the elimination of lithium trimethylsilanolate and the formation of 2,2-dimethyl-1,1-bis(trimethylsilyl)silene (**6a**), which dimerizes in a head-to-head fashion to give after hydrogen transfer the polysilane **7**. This type of linear dimerization is not uncommon; it has also been observed for some 2-alkyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silenes by Brook et al.[6] and also by Apeloig et al.[2] and appears to be typical of sterically crowded reactive silenes bearing "allylic" protons..

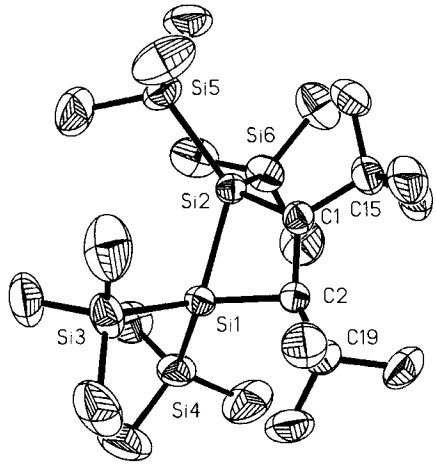
Scheme 1. Reactions of the hydroxyalkyl polysilanes **1a–c** with equimolar quantities of methyllithium in ether at −78°C



Deprotonation of 2,2-dimethyl-1-[tris(trimethylsilyl)silyl]-1-propanol (**1b**) with methyllithium under the same conditions gives (*E*)-3,4-di-*tert*-butyl-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**8**) in 72% yield[7]. After elimination of lithium trimethylsilanolate from deprotonated **1b** according to a Peterson-type mechanism the transient silene **6b** is formed, which dimerizes in a head-to-head [2+2] cycloaddition reaction to give **8** (Scheme 1). Its structural elucidation is based on NMR and MS data as well as on an X-ray analysis. The fact that in both the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra two signals for magnetically nonequivalent trimethylsilyl groups are observed agrees with the proposed 1,2-disilacyclobutane structure. Also the chemical shifts of the distinct nuclei are comparable with those reported in the literature for similarly structured 1,2-disilacyclobutanes[8a] and trisilacyclobutanes[8b], and the relative high-field shift of δ = −66.34 for the ring silicon atoms in the ^{29}Si-NMR spectrum of **8** – compared with δ = −37 up to −48 observed for related compounds[2,3a,6b] – is ob-

viously due to the substitution pattern of the ring carbon atoms. Particularly interesting is also the high intensity of the fragment ion m/z = 348 in the mass spectrum of **8**, corresponding to a $[(Me_3Si)_2SiSi(SiMe_3)_2]^+$ structure, which is again indicative of a Si–Si linkage in the cyclodimer of the silene **6b**.

Figure 1. Molecular structure of the 1,2-disilacyclobutane compound **8**. There are one and a half molecules within the asymmetric unit. The structure of one molecule is shown neglecting the hydrogen atom positions (ORTEP, 50% probability level). Selected distances [Å] and angles [°]: Si1–Si2 2.353(1), Si1–C2 1.947(3), Si2–C1 1.964(3), C1–C2 1.577(4), C1–C15 1.555(4), C2–C19 1.570(4); Si1–Si2–C1 76.16(9), C2–Si1–Si2 76.33(8), Si1–C2–C1 98.43(16), Si2–C1–C2 97.58(17), C2–Si1–C1 –20.66(12)



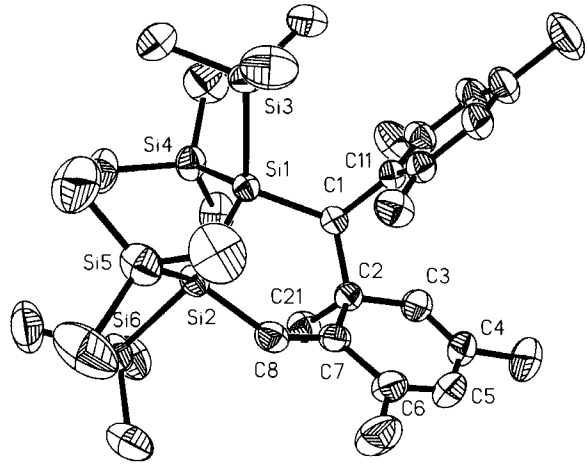
The result of the X-ray analysis is illustrated in Figure 1. The four-membered ring is slightly folded. The planes through the atoms Si2–Si1–C2 and Si2–C1–C2 meet at an angle of 35.9°. The ring C–C bond distance of 1.58 Å is significantly longer than a usual C–C single bond. Thus, in agreement with the results obtained for sterically congested 1,2-disilacyclobutanes by other authors[2,6a], the C–C bond in **8** is characterized as a comparatively weak bond. From a crystallographic point of view it is of interest that there are one and a half molecules within the asymmetric unit. Hence the monoclinic cell is made up of 6 molecules.

In conclusion, **6b** shows the typical behavior of silenes bearing space-demanding substituents, which preferably undergo head-to-head dimerizations to give 1,2-disilacyclobutanes, whereas sterically less crowded silenes usually dimerize in a head-to-tail fashion[9].

A completely different dimerization behavior is observed for 2-mesityl-1,1-bis(trimethylsilyl)silene (**6c**), obtained as transient intermediate by deprotonation of **1c**. The reaction of methyllithium with **1c** in diethyl ether at low temperature affords a colorless, air-stable, crystalline product. Based on NMR and MS studies and particularly as a result of an X-ray analysis the structure of the compound has been established as (*E*)-1,2,3,8a-tetrahydro-1-mesityl-5,7,8a-trimethyl-2,2,3,3-tetrakis(trimethylsilyl)-2,3-disilanaphthalene (**9**)[10] (Scheme 1). The yield is 70%.

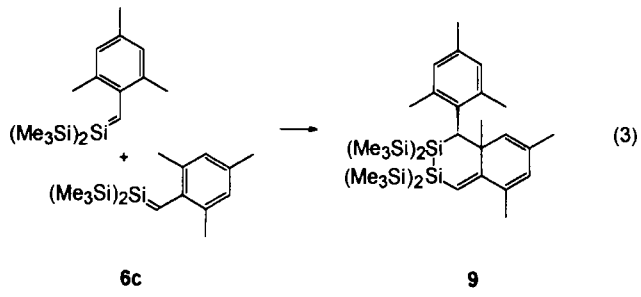
Four distinct signals for the four trimethylsilyl groups are found both in the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra of **9**. One ^{1}H-Me_3Si signal is shifted significantly to higher field, which is certainly due to the influence of the shielding cone of the neighboring mesityl substituent (see also Figure 2). All NMR signals are in full agreement with the proposed structure, but the final elucidation results from the X-ray analysis. For the disilacyclohexene substructure a boat form is found, the intersection angle of the plane Si1–Si2–C8 being 16.8° and that of the plane C1–C2–C7 43.6° with respect to the plane Si1–C1–C7–C8. Interestingly, the bond distance C1–C2 (1.59 Å) is rather long.

Figure 2. Molecular structure of compound **9**. Hydrogen atom positions are not shown because of clearness (ORTEP, 50% probability level). Selected distances [Å] and angles [°]: Si1–Si2 2.369(1), Si1–C1 1.956(2), Si2–C8 1.873(2), C1–C2 1.590(2), C1–C11 1.527(2), C2–C7 1.546(3), C2–C21 1.549(2), C7–C8 1.348(3); Si2–Si1–C1 104.01(6), Si1–Si2–C8 101.18(7), Si1–C1–C2 118.52(12), C1–C2–C7 118.84(14), C2–C7–C8 122.46(16), C7–C8–Si2 131.82(15)



We interprete the formation of this unexpected structure as the result of a head-to-head dimerization of the transient silene **6c**, which in an unusual [2 + 4] cycloaddition reaction formally acts as the monoene and – involving the aromatic substituent – also as the diene [eq. (3)]. This is surprising insofar as sterically congested transient silenes in the absence of trapping agents usually undergo head-to-head reactions to form 1,2-disilacyclobutanes[9]. The behavior of **6c** is also remarkably different from that of 2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene, which is moderately stable in solution and decomposes under photolysis conditions to give a substituted dihydro-benzocyclobutane[11]. A formal [2 + 4] cycloaddition reaction similar to the formation of **9** is reported by Fink et al. for the dimerization of 2,3,4-tri-*tert*-butyl-1-mesityl-1-silacyclobutadiene[12a].

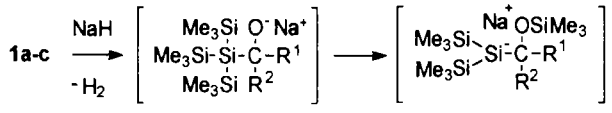
Transient silenes with structures similar to those described in this paper have been proven to dimerize via radical intermediates[3a,6,13]. After Si–Si bond formation the resulting 1,4-diradicals stabilize to give either 1,2-disilacyclobutanes or (in the presence of allylic protons) linear dimers of type **7**. The mesityl substituent in **6c** allows an extension of the conjugation system of the diradical inter-



(3)

6c **9**

mediate, and the observed [2 + 4] reaction can easily be understood as the straightforeward stabilization of a transient 1,6-diradical. In the case of the mentioned dimerization of the silacyclobutadiene such an uncomplicated reaction path is excluded, and the observed transient diradical stabilizes primarily by intramolecular hydrogen atom abstraction[12b]. This unusual behavior of **6c** may also be due to the bulkiness of the mesityl substituent and the expected weakness of the C–C bond in a hypothetic 1,2-disilacyclobutane, the [2 + 2] dimer of **6c**. Thus, the observed formal [2 + 4] cycloaddition to **9** may be interpreted as the preferred way for **6c** to evade the 1,2-disilacyclobutane ring closure. On the other hand, an alternative mechanism consisting of an addition of the lithium silanide **10c** to the Si=C bond of the silene **6c** followed by a nucleophilic substitution of the trimethylsiloxy group cannot be excluded.



10a-c

(4)

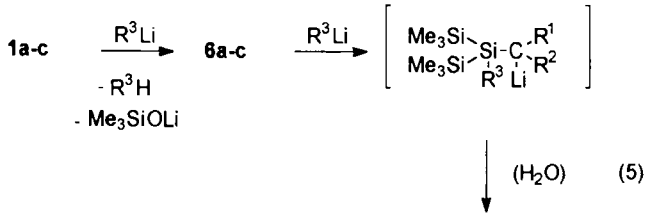
3	R^1	R^2
a	Me	Me
b	H	tBu
c	H	Mes

3a-c

When the deprotonation of **1a–c** is carried out with methyllithium at low temperature in THF instead of diethyl ether, only a 1,3-*Si,O*-trimethylsilyl migration is observed leading to (trimethylsiloxy)[bis(trimethylsilyl)silyl]alkanes **3a–c**. The same products are obtained when sodium hydride is used as the base in THF as well as in diethyl ether [eq. (4)]. Under these conditions no **7**, **8**, or **9**, resp., are found. Compounds **3a–c** are colorless, stable, distillable liquids. Compound **3a** has already been described to be formed by the in situ reaction of **2** with acetone in THF[1a]. The rearrangement **1a–c** → **3a–c** is an example of a general oxyanion-silanion interconversion, observed for the first time by Brook and coworkers, when [tris(trimethylsilyl)silyl]methanol is treated with sodium/potassium alloy[14].

Trapping Reactions of the Transient Silenes 6a–c with Organolithium Reagents and 2,3-Dimethyl-1,3-butadiene

When the hydroxyalkyl polysilanes **1a–c** are treated with two or more equivalents of methyllithium, phenyllithium, or *tert*-butyllithium, after deprotonation of the alcohol and elimination of trimethylsilanolate, excess organolithium reagent is added to the Si=C bond of the transient silenes resulting in the formation of the appropriate trisilanes **11a–e** [eq. (5)]. Compounds **11a–d** are colorless liquids or semisolids, **11e** is crystalline. They are fully characterized by NMR and MS data (see Experimental). Compound **11b** has already been described as the final product of the reaction of *tert*-butyllithium with pivaloyltris(trimethylsilyl)silane[15].



(5)

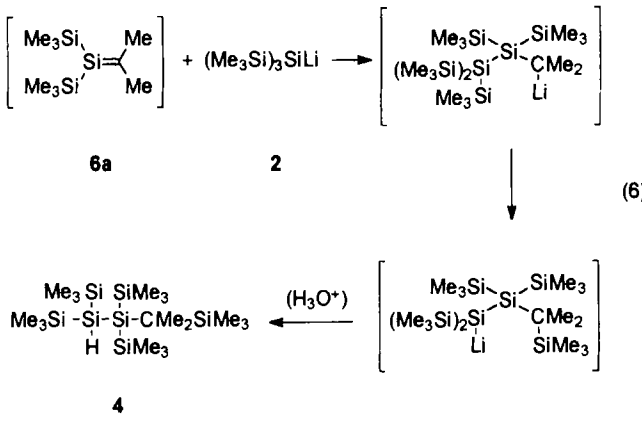
11	R^1	R^2	R^3
a	Me	Me	Me
b	H	tBu	tBu
c	H	tBu	Ph
d	H	Mes	Me
e	H	Mes	Ph

11a-e

The formation of **11a–e** is the outcome of an expected attack of the nucleophilic organolithium reagent at the polar Si=C bond. But at the same time this result is a valuable proof of the intermediate existence of the silenes **6a–c** also in the course of the formation of the dimers **7**, **8**, and **9**. To the best of our knowledge, the Peterson reaction, modified in the way described in this paper, is the only method of a thermal 1,2-elimination leading to Si=C systems, in which the silicon atom is the anionic centre and the neighboring carbon atom bears the electronegative leaving group. This is a completely reversed situation compared with the 1,2 salt elimination processes studied by Wiberg et al.[16]. Whereas the addition of organolithium compounds to the polar Si=C bond with the observed regiospecifity is obvious, the formation of **11a–e** by reaction of the nucleophilic organolithium derivatives with any precursor of the silenes **6a–c** is hardly conceivable.

The formation of the already mentioned polysilane **4** as the result of the in situ reaction of excess tris(trimethylsilyl)-silyllithium (**2**) with acetone follows the same mechanism. The lithium silanide **2** is added to the polar Si=C double bond of the transient silene **6a**. The resulting adduct undergoes a 1,3-trimethylsilyl migration from silicon to carbon forming the obviously best stabilized anion, and the

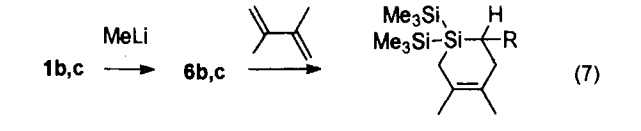
silanide is protonated during the hydrolytic workup to give **4**[1b] [eq. (6)].



6a **2** (6)

4

Deprotonation of e.g. **1b** and **1c** in the presence of 2,3-dimethyl-1,3-butadiene gives the [2 + 4] cycloaddition products of the respective silenes **6b** and **6c**: 6-*tert*-butyl-3,4-dimethyl-1,1-bis(trimethylsilyl)-1-sila-3-cyclohexene (**12a**) and the 6-(2,4,6-trimethylphenyl) analogue **12b** [eq. (7)]. The intended conversion of **1a** under the same conditions into the 6,6-dimethyl-1-silacyclohexene has failed. The spectral data of **12a** and **12b** are in full agreement with the formulated structures (see Experimental). This result again agrees with the expected behavior of reactive silenes.



(7)

12	R
a	tBu
b	Mes

12a,b

In conclusion, we have shown that the elimination of trimethylsilanolate from deprotonated (1-hydroxyalky)tris(trimethylsilyl)silanes according to a modified Peterson mechanism is a suitable method for the synthesis of silenes. The application of tris(trimethylsilyl)silylmagnesium bromide and its reaction with carbonyl compounds offers an easy and versatile access to pure, isolated 1-hydroxyalkyl polysilanes. Further variations of the method and studies concerning the scope of the reaction are the subject of current investigations.

We gratefully acknowledge the support of our research by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We thank Dr. *M. Michalik* and Prof. *N. Stoll* for recording the NMR and MS spectra, resp.

Experimental

All reactions involving organometallic reagents were carried out under purified argon. – NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane 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 is prepared as reported in the literature[5].

Preparation of Ethereal or THF Solutions of Tris(trimethylsilyl)-silylmagnesium Bromide (**5**): A solution of tris(trimethylsilyl)silyllithium–tetrahydrofuran (7.3 g, 0.016 mol), dissolved in 80 ml of diethyl ether or THF, was dropped at room temp. to an ethereal solution of magnesium bromide (2.9 g, 0.016 mol). The suspension was stirred for 1 h and used immediately.

Preparation of the Hydroxyalkyl Polysilanes **1a–c**. – *General Procedure:* To the solution of **5** (0.016 mol), prepared as described above, 0.016 mol of the appropriate aldehyde or ketone was dropped at −78°C within 30 min with vigorous stirring. Stirring was continued for an additional 3 h. Afterwards an aqueous ammonium chloride solution was added, the organic layer was separated and the aqueous solution extracted several times with ether. After drying of the combined extracts with magnesium sulfate, the volatile products were removed in vacuo and the residue purified as described below.

1a: The reaction was carried out in THF by starting with 0.93 g of acetone. The yield after chromatographic purification (silica gel/hexane) and sublimation at 70°C/0.01 Torr was 3.2 g (65%), m.p. 167°C (with partial sublimation). – IR (nujol): $\tilde{\nu}$ = 3555 and 3610 cm^{-1} (OH), 3451 (OH ass.). – ^1H NMR ([D$_6$]benzene): δ = 0.28 (s, $SiCH_3$, 27 H), 0.58 (br. s, OH, 1 H), 1.30 (s, CCH_3, 6 H). – ^{13}C NMR ([D$_6$]benzene): δ = 2.0 ($SiCH_3$), 34.2 (CCH_3), 68.4 (CCH_3). – ^{29}Si NMR ([D$_6$]benzene): δ = −63.6 ($SiSiMe_3$), −13.8 ($SiMe_3$). – MS, *m/z* (%): 305 (30) [M^+ − H], 289 (98) [M^+ − OH], 247 (13) [M^+ − Me_2COH], 215 (100) [M^+ − Me_3SiOH − H]. – $C_{12}H_{34}OSi_4$ (306.7): calcd. C 46.99, H 11.17; found C 46.86, H 11.12.

1b: 1.38 g of pivalaldehyde in ether. Purification by chromatography (silica gel/hexane) and sublimation (80°C/0.01 Torr). Yield 4.0 g (75%); m.p. 170°C. – IR (nujol): $\tilde{\nu}$ = 3615 and 3596 cm^{-1} (OH), 3476 (OH ass.). – ^1H NMR ([D$_6$]benzene): δ = 0.32 (s, $SiCH_3$, 27H), 0.91 (s, CCH_3, 9H), 1.04 (d, ^3J = 6.1 Hz, OH, 1H), 3.65 (d, ^3J = 6.1 Hz, OCH, 1H). – ^{13}C NMR ($CDCl_3$, DEPT): δ = 2.29 ($SiMe_3$), 27.86 (CCH_3), 36.17 (CCH_3), 77.82 (OCH). – ^{29}Si NMR ($CDCl_3$): δ = −12.47 ($SiMe_3$), −77.17 ($SiSiMe_3$). – MS, *m/z* (%): 333 (0.8) [M^+ − H], 319 (100) [M^+ − CH_3], 317 (65) [M^+ − OH], 261 (8) [M^+ − $SiMe_3$], 244 (53) [$(Me_3Si)_2SiCHC_4H_9^+$]. – $C_{14}H_{38}OSi_4$ (334.8): calcd. C 50.23, H 11.44; found C 50.54, H 11.46.

1c: 2.37 g of 2,4,6-trimethylbenzaldehyde in ether. Impurities were separated by sublimation (70°C/0.01 Torr), and the residue was recrystallized twice from acetonitrile, yield 4.2 g (66%). – IR (nujol): $\tilde{\nu}$ = 3507 cm^{-1} (OH). – ^1H NMR ([D$_6$]acetone): δ = 0.12 (s, $SiCH_3$, 27H), 2.17 (s, Ar-*p*-CH_3, 3H), at room temp. one broad signal 2.35, at −20°C 2.21 and 2.50 (2 s, Ar-*o*-CH_3, 6H), 3.72 (d, ^3J = 4.1 Hz, OCH, 1H), 5.64 (d, ^3J = 4.4 Hz, COH, 1H), at room temp. one broad signal 6.75, at −20°C 6.72 and 6.77 (2 s, ArH, 2H). – ^{13}C NMR ([D$_6$]acetone): δ = 2.13 ($SiCH_3$), 20.76 (Ar-*p*-CH_3), 21.53 and 23.44 (Ar-*o*-CH_3), 62.75 (COH), 129.34, 131.02, 133.45, 135.61, 137.89 and 140.99 (aromat. C). – ^{29}Si NMR ($CDCl_3$): δ = −11.94 ($SiCH_3$), −71.26 [$Si(SiMe_3)_3$]. – MS, *m/z* (%): 397 (1.5) [M^+ + 1], 379 (100) [M^+ − OH], 307 (7) [M^+ − Me_3SiOH − H], 149 (25) [M^+ − $Si(SiMe_3)_3$]. – $C_{19}H_{40}OSi_4$ (396.9): calcd. C 57.50, H 10.16; found C 57.52, H 10.81.

3b: 0.05 g (2.5 mmol) of NaH was added to the solution of 0.5 g (1.5 mmol) of **1b** in 25 ml of THF at room temp. After stirring for 1 h and hydrolytic workup an oil was obtained, which was purified by chromatography (silica gel, hexane). Yield 0.25 g (50%). – IR (capillary): $\tilde{\nu}$ = 2065 cm^{-1} (SiH). – ^1H NMR ([D$_6$]benzene): δ = 0.17, 0.27 and 0.30 (3 s, $SiCH_3$, 3 × 9H), 1.00 (s, CCH_3, 9H), 3.46 (d, ^3J = 2.1 Hz, SiH, 1H), 3.84 (d, ^3J = 2.1 Hz, OCH, 1H). – ^{13}C NMR ([D$_6$]benzene): δ = 1.67, 1.88 and 1.94 ($SiCH_3$), 28.75

(CCH_3), 36.77 (CCH_3), 76.84 (OCH). – ^{29}Si NMR ([D$_6$]benzene): δ = −61.75 (J_{SiH} = 154 Hz, SiH), −15.06 and −14.67 (Si*Si*Me$_3$), 14.79 (OSiMe$_3$). – MS (70 eV), *m/z* (%): 319 (2) [M$^+$ − CH_3], 245 (22) [M$^+$ − OSiMe$_3$], 175 (50) [M$^+$ − CH(OSiMe$_3$)*t*Bu], 159 (100) [Me$_3$SiOCH*t*Bu$^+$]. – $C_{14}H_{38}OSi_4$ (334.8): calcd. C 50.23, H 11.44; found C 50.12, H 11.36.

3c: As described for the synthesis of **3b**, 0.06 g (2.5 mmol) of NaH was allowed to react with 0.5 g (1.26 mmol) of **1c**. Kugelrohr distillation (140°C/10^{-1} Torr) gave 0.47 g (93%) of **9c**. – IR (capillary): $\tilde{\nu}$ = 2043.4 and 2088.4 cm^{-1} (SiH). – ^{1}H NMR ([D$_6$]benzene): δ = 0.01, 0.11 and 0.26 (3 s, $SiCH_3$, 3 × 9H), 2.10 (s, Ar-*p*-CH_3, 3H), 2.25 (s, Ar-*o*-CH_3, 3H), 2.69 (s, Ar-*o*-CH_3, 3H), 3.97 (d, ^3J = 5.43 Hz, SiH, 1H), 5.55 (d, ^3J = 5.9 Hz, CH, 1H), 6.67 and 6.78 (2 s, aromat. H, 2H). – ^{13}C NMR ([D$_6$]benzene, DEPT): δ = 0.94, 1.22 and 1.33 ($SiCH_3$), 21.54, 21.76 and 22.85 (Ar-CH_3), 63.83 (CHOSi), 129.80 and 132.03 (aromat. CH), 132.75, 136.26, 138.90 and 139.60 (aromat. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −58.4 (SiH, J_{SiH} = 162.8 Hz), −14.61 and −15.33 (Si*Si*Me$_3$), 17.09 (OSiMe$_3$). – MS (70 eV), *m/z* (%): 395 (0.2) [M$^+$ − 1], 381 (0.6) [M$^+$ − CH_3], 307 (4) [M$^+$ − OSiMe$_3$], 221 (100) [Me$_3$SiOCHMes$^+$]. – $C_{19}H_{40}OSi_4$ (396.9): calcd. C 57.50, H 10.16; found C 57.42, H 10.09.

Deprotonation of **1a–c** *with Methyllithium in the Absence of Trapping Agents*

7: To a solution of **1a** (0.5 g, 1.63 mmol) in 30 ml of ether an equimolar quantity of methyllithium is added at −78°C, and the mixture is stirred for 3 h. After usual workup a solid was obtained which was purified by chromatography (silica gel/hexane) to give 0.28 g (78%) of pure **7**. The spectroscopic data obtained were in full agreement with those reported[3a].

8: An equimolar quantity of methyllithium was added to a solution of **1b** (0.5 g, 1.5 mmol) in 20 ml of ether at −78°C. After stirring of the solution for 1 h it was allowed to warm up, and stirring was continued for further 2 h. After usual workup a solid product was obtained which was purified by two recrystallizations from acetone to give 0.28 g (76%) of **8**. It began to sublimate at 270°C. – ^{1}H NMR ($CDCl_3$): δ = 0.21 and 0.33 (2 s, $SiCH_3$, 36H), 1.01 (s, CCH_3, 18H), 2.15 (s, ring CH, 2H). – ^{13}C NMR ($CDCl_3$, DEPT): δ = 2.20 and 3.24 ($SiCH_3$), 31.85 ($CCCH_3$), 34.25 (CCH_3), 50.37 [*C*−*t*Bu]. – ^{29}Si ($CDCl_3$): δ = −13.11 and −14.32 ($SiMe_3$), −66.34 (ring Si). – MS, *m/z* (%): 487 (1.8) [M$^+$ − H], 473 (4.5) [M$^+$ − CH_3], 431 (4) [M$^+$ − CMe_3], 348 (100) [(Me$_3$Si)$_2$SiSi(SiMe$_3$)$_2^+$], 333 (52) [{(Me$_3$Si)$_2$Si}$_2^+$ − CH_3]. – $C_{22}H_{56}Si_6$ (489.2): calcd. C 54.01, H 11.54; found C 52.84, H 12.11.

9: To a solution of 0.5 g (1.26 mmol) of **1c** in 20 ml of ether an equimolar quantity of MeLi was added with stirring at −78°C. Stirring was continued for 1 h, and the mixture was allowed to warm up to room temp. within 2 h. After hydrolytic workup and removal of the solvent the solid residue was recrystallized twice from acetone. Yield 0.27 g (70%); m.p. 152–154°C. – ^{1}H NMR ([D$_6$]benzene): δ = 0.07 (s, $SiCH_3$, 9H), 0.520, 0.523 and 0.55 (3 s, $SiCH_3$, 27H), 1.49, 1.56, 2.06, 2.16, 2.34 and 2.47 (6 s, CH_3, 6 × 3H), 3.87 (s, SiC*H*Mes, 1H), 5.14, 5.65 and 6.37 (3 s, olef. H, 3 × 1H), 6.76 and 6.82 (2 s, aromat. H, 2 × 1H). – ^{13}C NMR ([D$_6$]benzene, DEPT, C,H-COSY): δ = 1.93, 2.33, 2.56 and 3.04 ($SiCH_3$), 20.67, 21.09, 21.14, 23.14, 26.02 and 37.94 (CCH_3), 37.53 (Si*C*HMes), 45.21 (C-8a), 119.61, 125.31 and 136.15 (olefin. CH), 129.36 and 130.92 (aromat. CH), 125.46, 133.14, 134.18, 135.51, 137.43, 141.63 and 160.93 (quart. olefin. and aromat. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −94.70 and −87.10 (*Si*SiMe$_3$), −12.44, −11.83, −11.26 and −10.22 ($SiMe_3$). – MS (70 eV), *m/z* (%): 612 (7) [M$^+$], 597 (4) [M$^+$ − CH_3], 539 (14) [M$^+$ − $SiMe_3$], 348 (100) [(Me$_3$Si)$_2$SiSi(SiMe$_3$)$_2^+$]. – $C_{32}H_{60}Si_6$ (613.3): calcd. C 62.67, H 9.86; found C 61.57, H 9.81.

Synthesis of the Trisilanes **11a–e**. – *General Procedure:* A solution of 0.5 g of **1a–c** in 30 ml of ether was added at room temp. to a fivefold molar excess of the appropriate organolithium reagent in 10 ml of ether. The reaction of **1b** with *tert*-butyllithium was carried out at −20°C. After stirring for 3 h an aqueous ammonium chloride solution was added, and the mixture was worked up as usual.

11a: Prepared from **1a** (0.5 g, 1.63 mmol) and methyllithium. Purification of the product by kugelrohr distillation (100°C/10^{-2} Torr), yield 0.44 g (91%). – ^{1}H NMR ($CDCl_3$): δ = 0.22 (s, $SiCH_3$, 18H), 1.20 (d, ^3J = 7.3 Hz, CCH_3, 6H), 1.62 (hept, ^3J = 7.3 Hz, $CHMe_3$, 1H), 7.32 and 7.48 (2 broad m, ArH, 5H). – ^{13}C NMR ($CDCl_3$): δ = 0.52 ($SiMe_3$), 12.76 (CMe_2), 20.78 ($CHCH_3$), 127.69, 127.73, 135.44 and 136.95 (aromat. C). – ^{29}Si NMR ($CDCl_3$): δ = −16.47 ($SiMe_3$), −34.11 (*Si*SiMe$_3$). – MS, *m/z* (%): 294 (24) [M$^+$], 279 (16) [M$^+$ − CH_3], 251 (10) [M$^+$ − $CHMe_2$], 217 (68) [M$^+$ − C_6H_5], 105 (100) [PhSi$^+$]. – $C_{15}H_{30}Si_3$ (294.7): calcd. C 61.14, H 10.26; found C 60.98, H 10.45.

11b: Prepared from **1b** (0.5 g, 1.5 mmol) and *tert*-butyllithium. Sublimation at 40°C/10^{-2} Torr yield 0.30 g (67%). The spectral data were identical with those reported in the literature[15].

11c: Prepared from **1b** (0.5 g, 1.5 mmol) and phenyllithium. Separation by kugelrohr distillation (110°C/10^{-2} Torr), yield 0.46 g (96%). – ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, $SiCH_3$, 18H), 0.94 (s, CCH_3, 9H), 1.24 (s, CH_2, 2H), 7.23–7.52 (m, ArH, 5H). – ^{13}C NMR ($CDCl_3$, DEPT): δ = 0.22 ($SiCH_3$), 28.83 (CH_2), 31.56 (CMe_3), 33.36 (CCH_3), 127.25, 127.46, 135.44 and 138.18 (aromat. C). – ^{29}Si NMR ($CDCl_3$): δ = −45.25 (*Si*SiMe$_3$), −15.95 ($SiMe_3$). – MS, *m/z* (%): 322 (27) [M$^+$], 307 (100) [M$^+$ − CH_3]. – $C_{17}H_{34}Si_3$ (322.7): calcd. C 63.27, H 10.62; found C 63.25, H 10.63.

11d: Prepared from **1c** (0.5 g, 1.26 mmol) and methyllithium. Kugelrohr distillation at 140°C/0.1 Torr, yield 0.35 g (86%). – ^{1}H NMR ($CDCl_3$): δ = 0.00 [s, Si(CH_3)$_3$, 18H], 0.19 (s, $SiCH_3$, 3H), 2.19 (s, *o*-CH_3, 6H), 2.209 and 2.212 (2 s, *p*-CH_3 and $SiCH_2$, 5H). – ^{13}C NMR ($CDCl_3$, DEPT): δ = −5.47 and −0.85 ($SiMe_3$), 13.92 (CH_2), 20.70 (*p*-CH_3), 21.40 (*o*-CH_3), 128.65 (aromat-CH), 132.92, 134.19 and 136.32 (aromat. C). – ^{29}Si NMR ($CDCl_3$): δ = −15.20 ($SiMe_3$), −43.55 (*Si*SiMe$_3$). – MS, *m/z* (%): 322 (20) [M$^+$], 307 (100) [M$^+$ − CH_3], 249 (35) [M$^+$ − $SiMe_3$]. – $C_{17}H_{34}Si_3$ (322.7): calcd. C 63.27, H 10.62; found C 62.89, H 10.81.

11e: Prepared from **1c** (0.5 g, 1.26 mmol) and phenyllithium. Kugelrohr distillation at 175°C/0.1 Torr, yield 0.45 g (92%), m.p. 76°C. – ^{1}H NMR ($CDCl_3$): δ = 0.02 (s, $SiCH_3$, 18H), 2.02 (s, *o*-CH_3, 6H), 2.18 (s, *p*-CH_3, 3H), 2.49 (s, $SiCH_2$, 2H), 6.70 (s, Mes ring CH, 2H), 7.20–7.24 and 7.37–7.41 (2 m, Ph, 5H). – ^{13}C NMR ($CDCl_3$, DEPT): δ = −0.18 ($SiCH_3$), 13.75 (CH_2), 20.70 (*p*-CH_3), 21.56 (*o*-CH_3), 127.72, 127.80, 128.63 and 135.04 (aromat. CH), 133.24, 134.78, 135.88 and 138.58 (aromat. C). – ^{29}Si NMR ($CDCl_3$): δ = −15.38 ($SiMe_3$), −42.56 (*Si*SiMe$_3$). – MS, *m/z* (%): 383 (8) [M$^+$ − H], 369 (10) [M$^+$ − CH_3], 307 (100) [M$^+$ − Ph], 265 (20) [M$^+$ − Mes], 251 (5) [M$^+$ − CH_2Mes], 234 (25) [M$^+$ − Ph, − $SiMe_3$]. – $C_{22}H_{36}Si_3$ (384.8): calcd. C 68.67, H 9.43; found C 68.71, H 9.68.

Deprotonation of **1b** *and* **1c** *with Methyllithium in the Presence of 2,3-Dimethyl-1,3-butadiene. Preparation of* **12a** *and* **12b**: To a solution containing **1b** or **1c** and a fourfold molar excess of 2,3-dimethyl-1,3-butadiene in 30 ml of ether was added at −40°C an equimolar quantity of methyllithium. Stirring was continued for further 4 h, and the mixture was worked up as usual.

12a: Prepared from 0.5 g (1.5 mmol) of **1b**, 0.5 g (6.0 mmol) of 2,3-dimethylbutadiene and 1.5 mmol of MeLi. Compound **12a** is

separated by kugelrohr distillation (75°C/10^{-2} Torr) and purified by chromatography (silica gel, hexane). Yield 0.29 g (60%). – ^{1}H NMR ([D$_6$]benzene, C,H- and H,H-COSY): δ = 0.26 and 0.31 (2 s, SiCH$_3$, 2 × 9H), 1.08 [s, C(CH$_3$)$_3$, 9H], 1.26, 1.28, 1.31 and 1.32 (dd, ^3J = 4.46, ^3J = 12.23 Hz, SiCH, 1H), 1.46, 1.51, 1.59 and 1.64 (2 d, ^2J = 16.07 Hz, SiCH$_2$, 2H), 1.77 (s, C=CCH$_3$, 3H), 1.86 (s, C=CCH$_3$, 3H); 2.03, 2.07 and 2.12 (pseudo-t, J = 14.75 Hz) and 2.21, 2.22, 2.26, 2.27 (dd, ^3J = 4.45, ^2J = 14.75 Hz, *t*BuCC*H*$_2$, 2H). – ^{13}C NMR ([D$_6$]benzene): δ = 0.04 and 0.95 (SiCH$_3$), 16.74 (SiCH$_2$), 20.50 and 22.40 (H$_3$*C*C=C*C*H$_3$), 30.69 (*C*CH$_3$), 32.65 (*C*CH$_3$), 35.31 (*t*BuC*C*H$_2$), 39.05 (SiCH), 126.20 and 129.11 (Me*C*=*C*Me). – ^{29}Si NMR (CDCl$_3$): δ = –49.36 (*Si*SiMe$_3$), –15.35 and –15.16 (SiMe$_3$). – MS, *m/z* (%): 327 (55) [M$^+$ + H], 311 (95) [M$^+$ – CH$_3$], 253 (80) [M$^+$ – SiMe$_3$]. – C$_{17}$H$_{38}$Si$_3$ (326.7): calcd. C 62.49, H 11.72; found C 60.68, H 11.42.

12b: 0.5 g (1.26 mmol) of **1c** was allowed to react with 0.5 g (6.0 mmol) of 2,3-dimethylbutadiene and 1.3 mmol of MeLi at –78°C. Compound **12b** was recrystallized from acetonitrile, m.p. 52°C, yield 0.21 g (43%). – ^{1}H NMR ([D$_6$]benzene, C,H- and H,H-COSY): δ = 0.11 and 0.28 (2 s, SiCH$_3$, 2 × 9H), 1.61 (d, ^2J = 14.7 Hz, SiCH$_2$, 1H), 1.80 (d, ^2J not determined, since the second signal was overlapped by one C=CCH$_3$ signal, 1H), 1.77 and 1.91 (2 s, C=CCH$_3$, 2 × 3H), 2.26 (s, *p*-CH$_3$, 3H), 2.39 and 2.47 (2 s, *o*-CH$_3$, 2 × 3H), 2.29 (dd, ^2J = 14.35, ^3J = 5.8 Hz, Mes-CCH$_2$, 1H), 2.87 (pseudo-t, J = 13.5 Hz, Mes-CCH$_2$, 1H), 3.28 (dd, ^2J = 11.6, ^3J = 5.8 Hz, Mes-CH, 1H), 6.87 (s, aromat. CH, 2H). – ^{13}C NMR ([D$_6$]benzene): δ = 0.06 and 0.39 (SiCH$_3$), 17.76 (SiCH$_2$), 20.70 and 22.81 (C=C*C*H$_3$), 20.70 (*p*-CH$_3$), 22.23 and 24.27 (*o*-CH$_3$), 24.31 (Mes*C*H), 37.69 (MesCH*C*H$_2$), 129.56 and 130.80 (aromat. CH), 127.17, 129.30, 133.70, 135.25, 135.45 and 139.77 (aromat. and olefin. C). – ^{29}Si NMR ([D$_6$]benzene): δ = –42.48 (*Si*SiMe$_3$), –16.40 and –15.70 (Si*Si*Me$_3$). – MS, *m/z* (%): 388 (30) [M$^+$], 373 (50) [M$^+$ – CH$_3$], 269 (100) [M$^+$ – Mes]. – C$_{21}$H$_{40}$Si$_3$ (388.8): calcd. C 67.96, H 10.36; found C 67.79, H 10.30.

Crystal Structure Determinations: Crystals of compounds **8** and **9** were investigated with a Siemens P4 diffractometer after taking rotation photographs and performing a photo search to find a suitable reduced cell. The structures were solved by direct methods (XS program for crystal structure solution, version 4.2 for MSDOS, Copyright 1990 Siemens Analytical Xray Inst. Inc.) and refined by the full-matrix least-squares method of SHELXL-93[17]. The silicon and carbon atoms were refined anisotropically. Almost all hydrogen atom positions could be elucidated from the difference maps, the remaining hydrogens were placed into theoretical positions. All hydrogen positions were refined by using the riding model. The weighting scheme was calculated according to $w = 1/[\sigma^2(F_o^2) + (0.0745 \cdot P)^2 + 1.58 \cdot P]$ for **8** and $w = 1/[\sigma^2(F_o^2) + (0.0634 \cdot P)^2 + 0.59 \cdot P]$ for **9**, where $P = [\mathrm{Max}(F_o^2 \text{ or } 0) + 2 \cdot F_c^2]/3$ in both cases. For **8** the Flack x parameter was found to be $x = 0.1815$ with esd = 0.1215. The most important details can be seen from Table 1.

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 number CSD-58715 (for **8**; for **9** please refer to ref.[10j]), the names of the authors, and the journal citation.

Table 1. Crystal and structure solution data of **8** and **9**

	8	**9**
Formula	$C_{22}H_{56}Si_6$	$C_{32}H_{60}Si_6$
M [g·mol^{-1}]	489.21	613.34
a [Å]	16.382(3)	10.275(2)
b [Å]	10.559(6)	10.934(2)
c [Å]	28.933(3)	20.072(4)
α [°]	90	97.84(3)
β [°]	95.91	98.66(3)
γ [°]	90	114.36(3)
V [Å^3]	4978.16	1980.89
$\rho_{calcd.}$ [g·cm^{-3}]	0.979	1.028
Z	6	2
Crystal system	monoclinic	triclinic
Space group	C2 [5]	P$\bar{1}$ [2]
F(000) [e]	1632	672
my (Mo-K$_\alpha$) [cm^{-1}]	2.6	2.29
Radiation	λ = 0.71089 Å (Mo-K$_\alpha$), graphite monochromator	
Diffractometer	Siemens P4	
Crystal size [mm]	0.12 x 0.3 x 1.0	0.3 x 0.38 x 1.4
Temperature [°C]	25	25
Data collecting mode	omega-scan	
Scan range (θ) [°]	4.5 - 50	4.5 - 52
hkl range	± 19, ± 12, ± 34	- 1/12, -13/12, ± 24
Measured refl.	9307	7683
Unique refl.	8637	7683
Observed refl.	8039	6670
$F_o \geq$	2σ (I)	
Refined param.	379	361
*R*1 for $F_o > 4\cdot\sigma(F_o)$	0.0481	0.0444
*R*1 for all	0.0522	0.0509
*wR*2 for all	0.1383	0.1325
GoF	1.054	1.061
Δρ (max/min) [e/Å^{-3}]	+0.39/-0.21	+0.47/-0.24

[1] [1a] R. Wustrack, H. Oehme, *J. Organomet. Chem.* **1988**, *352*, 95. – [1b] H. Oehme, R. Wustrack, A. Heine, G. M. Sheldrick, D. Stalke, *J. Organomet. Chem.* **1993**, 452, 33.

[2] D. Bravo-Zhivotovskii, V. Brande, A. Stanger, M. Kapon, Y. Apeloig, *Organometallics* **1992**, *11*, 2326.

[3] [3a] J. Ohshita, Y. Masaoka, M. Ishikawa, *Organometallics* **1991**, *10*, 3775. – [3b] J. Ohshita, Y. Masaoka, M. Ishikawa, T. Takeuchi, *Organometallics* **1993**, *12*, 876.

[4] I. Fleming in *Comprehensive Organic Chemistry* (Eds.: D. Barton, W. D. Ollis), Pergamon, Oxford – New York, **1979**, vol. 3, p. 643.

[5] G. Gutekunst, A. G. Brook, *J. Organomet. Chem.* **1982**, *225*, 1.

[6] [6a] A. G. Brook, J. W. Harris, J. Lennon, M. El Sheikh, *J. Am. Chem. Soc.* **1979**, *101*, 83. – [6b] K. Baines, A. G. Brook, *Organometallics* **1987**, *6*, 692.

[7] C. Krempner, H. Oehme, *J. Organomet. Chem.* **1994**, *464*, C7.

[8] [8a] A. G. Brook, S. N. Nyburg, W. F. Reynolds, J.-M. Chang, J.-S. Lee, J.-P. Picard, *J. Am. Chem. Soc.* **1979**, *101*, 6750; A. G. Brook, R. K. M. R. Kallury, Y. C. Poon, *Organometallics* **1982**, *1*, 987. – [8b] D. Bravo-Zhivotovskii, Y. Apeloig, J. Ovchinnikov, V. Igonin, Y. T. Struchkov, *J. Organomet. Chem.* **1993**, *446*, 123.

[9] G. Raabe, J. Michl in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New-York, **1989**, part 2, chapter 17, p. 1100.

[10] C. Krempner, H. Reinke, H. Oehme, *Angew. Chem.* **1994**, *106*, 1709; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1615.

[11] A. G. Brook, H.-J. Wessely, *Organometallics* **1985**, *4*, 1487.

[12] [12a] D. B. Puranik, M. P. Johnson, M. J. Fink, *J. Chem. Soc., Chem. Commun.* **1989**, 706. – [12b] J. R. Gee, W. A. Howard, G. L. McPherson, M. J. Fink, *J. Am. Chem. Soc.* **1991**, *113*, 5461.

[13] A. G. Brook, K. M. Baines, *Adv. Organomet. Chem.* **1986**, *25*, 26.

[14] A. G. Brook, J. J. Crusciel, *Organometallics* **1984**, *3*, 1317.

[15] A. G. Brook, P. Chiu, J. McClenaghnan, A. J. Lough, *Organometallics* **1991**, *10*, 3292.

[16] N. Wiberg, *J. Organomet. Chem.* **1984**, *273*, 141.

[17] G. M. Sheldrick, *SHELXL-93*, Universität Göttingen, **1993**.

[249/94]