

# Generation and conversion of the transient 1,1-bis(trimethylsilyl)-2-(2,4,6-triisopropylphenyl)-silene

Frank Luderer, Helmut Reinke, Hartmut Oehme \*

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

Received 10 July 1995

## Abstract

Treatment of 2,4,6-triisopropylbenzaldehyde with tris(trimethylsilyl)silylmagnesium bromide (**2**) gives 2,4,6-triisopropylphenyl-tris(trimethylsilyl)silyl-methanol (**3**) in approximately 70% yield and E-3,4-bis(2,4,6-triisopropylphenyl)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**5**) (15%). **5** is the [2 + 2] head-to-head cyclodimer of the transient 1,1-bis(trimethylsilyl)-2-(2,4,6-triisopropylphenyl)-silene (**4**), formed by trimethylsilylanolate elimination according to a Peterson mechanism from the magnesium alkoxide, derived from the alcohol **3**. Deprotonation of **3** with MeLi at low temperature in ether produces a complex mixture of products, the main constituents being the silene dimer **5** (10%) and bis(trimethylsilyl)-2,4,6-triisopropylbenzyl-trimethylsiloxysilane (**10**) (60%), which is formed by readdition of the eliminated lithiumtrimethylsilylanolate at the Si=C bond of **4**. The deprotonation of **3** with MeMgBr or PhMgBr (activated by LiBr) in THF at room temperature results in the formation of the polysilane  $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{SiMe}_3)_2\text{CH}_2(2,4,6\text{-C}_6\text{H}_2\text{iPr}_3)$  (**13**). Its generation indicates that there exists an equilibrium between the magnesium alkoxide derived from the alcohol **3** on one side, and the magnesium silanide **2** and 2,4,6-triisopropylbenzaldehyde on the other side. Possible pathways of the formation of the compounds mentioned, as well as of further by-products, are discussed. The 1,2-disilacyclobutane **5** is characterized by an X-ray crystal structure analysis.

*Keywords:* Silenes; Silene dimerization; 1,2-Disilacyclobutanes; Polysilanes; Peterson reaction

## 1. Introduction

1-Hydroxyalkyl-tris(trimethylsilyl)silanes proved to be suitable precursors for the synthesis of transient silenes. A series of these alcohols  $(\text{Me}_3\text{Si})_3\text{SiC}(\text{OH})\text{R}^1\text{R}^2$  was prepared by interaction of tris(trimethylsilyl)silylmagnesium bromide (**2**) with appropriate carbonyl derivatives; it could be demonstrated that treatment of them with strong bases in a clean reaction causes the elimination of trimethylsilylanolate and formation of silaalkenes, which were characterized by various dimerization and addition reactions [1]. The method is an improvement of the formerly practiced in situ process, in which tris(trimethylsilyl)silyllithium (**1**) and ketones were directly converted into silenes [2,3,4] or when acyl-tris(trimethylsilyl)silanes gave silenes after the nucleophilic addition of organolithium derivatives [5].

The increase of the steric bulk of the substituents  $\text{R}^1$  and  $\text{R}^2$  in the alcohol is expected to enhance the kinetic stability of the silene made from it by base-initiated

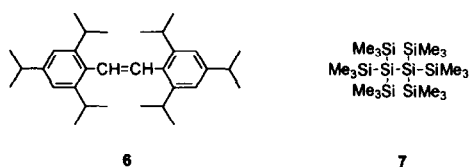
trimethylsilylanolate elimination. This led us to prepare 2,4,6-triisopropylphenyl-tris(trimethylsilyl)silyl-methanol (**3**) and to study its conversion into 1,1-bis(trimethylsilyl)-2-(2,4,6-triisopropylphenyl)-silene (**4**) under the conditions of a modified Peterson reaction.

## 2. Results and discussion

### 2.1. Synthesis of 2,4,6-triisopropylphenyl-tris(trimethylsilyl)silyl-methanol (**3**)

Tris(trimethylsilyl)silylmagnesium bromide (**2**), made by interaction of  $(\text{Me}_3\text{Si})_3\text{SiLi} \cdot 3\text{THF}$  [6] with anhydrous magnesium bromide in ether, reacts with 2,4,6-triisopropylbenzaldehyde at room temperature within 24 h to give the alcohol **3** in approximately 70% yield besides E-3,4-bis(2,4,6-triisopropylphenyl)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**5**) (15%), small quantities of the stilbene **6**, and traces of hexakis(trimethylsilyl)disilane **7** (Scheme 1). The alcohol **3**, the expected product of the reaction, is obtained

\* Corresponding author.



as a colorless gradually crystallizing oil. It can be stored indefinitely in the cold, but at room temperature the compound slowly decomposes to an oily mixture of unidentified products containing 2,4,6-triisopropylbenzaldehyde as one component. This instability may be due to a severe steric strain in the molecule weakening the central Si–C bond and causing an easy bond splitting reproducing the aldehyde. This tendency is also confirmed by the results of experiments described below, when we were treating the alcohol **3** with base under conditions of a modified Peterson reaction. Unfortunately, the quality of the crystals of **3** was insufficient for an X-ray crystal structure analysis and attempts to recrystallize **3** always lead to partially decomposed material.

The structure of the polysilanylalcohol **3** is elucidated on the basis of its IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR and MS spectra. Interestingly, the *o*-isopropylphenyl groups give four methyl signals in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3**, indicating that owing to the steric congestion the internal mobility in the molecule is seriously restricted.

The formation of the 1,2-disilacyclobutane **5**, the formal [2 + 2] cyclodimer of the silene **4**, is a somewhat unexpected result of the reaction, since the interaction of **2** with carbonyl compounds usually comes to an end after the addition step of the silanide at the carbonyl group. This is the main advantage of the application of

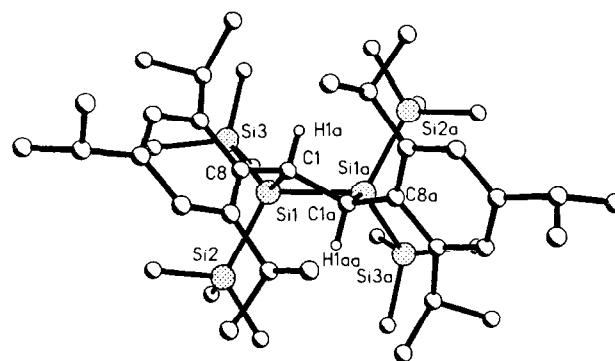
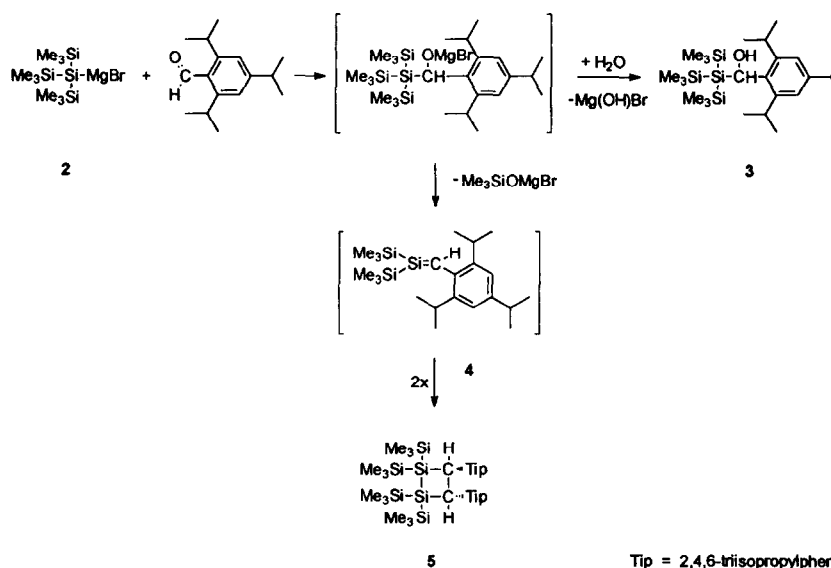


Fig. 1. Molecular structure of **5**. The asymmetric unit is made up of half the molecule. Therefore the symmetry equivalent atoms are labelled as 'a'. Consequently the orthorhombic unit cell contains four complete molecules. Selected bond distances (pm) and angles (deg): Si1–Si1a 233.4(2), Si1–C1 197.3(4), C1–C1a 158.3(8), C1–Si1–Si1a 76.10(12), C1a–C1–Si1 96.7(2), the torsional angle of the four-membered ring C1a–C1–Si1–Si1a is 28.52°.

the magnesium silanide **2** over the lithium analogue in the reaction with aldehydes or ketones, which allows the preparation and isolation of pure 1-hydroxyalkyl-tris(trimethylsilyl)silanes [**1a**]. However, owing to the necessary higher temperature and the prolonged reaction time, the magnesium alkoxide formed primarily by the interaction of **2** with triisopropylbenzaldehyde under the applied conditions partly eliminates trimethylsilanolate to give the reactive silene **4**, which dimerizes under formation of **5**. Formal [2 + 2]-head-to-head cyclodimerizations of this type are not uncommon [7] and appear to be typical for sterically congested silenes bearing trimethylsilyl groups at the silene silicon atom [1,4,5,8].

The structure of **5** is revealed by NMR and MS data as well as by an X-ray crystal structure analysis (Fig. 1).



Scheme 1. The reaction of tris(trimethylsilyl)silylmagnesium bromide (**2**) with 2,4,6-triisopropylbenzaldehyde.

Again, the two *o*-isopropyl groups of the aromatic substituents show four distinct methyl signals in the  $^1\text{H}$  NMR spectrum, with one of them being significantly shifted to higher field. Provided, the structure in solution is similar to that in the solid state, this can easily be understood as being due to the influence of the shielding cones of the two aromatic rings on the respective isopropyl methyl groups placed above them. This fixation of the *o*-isopropyl groups shown in Fig. 1 is obviously also preserved in solution at elevated temperatures. Dynamic NMR studies of **5** in  $\text{CDBr}_3$  up to  $80^\circ\text{C}$  gave no change of the  $^1\text{H}$  NMR *o*-isopropyl signal pattern.

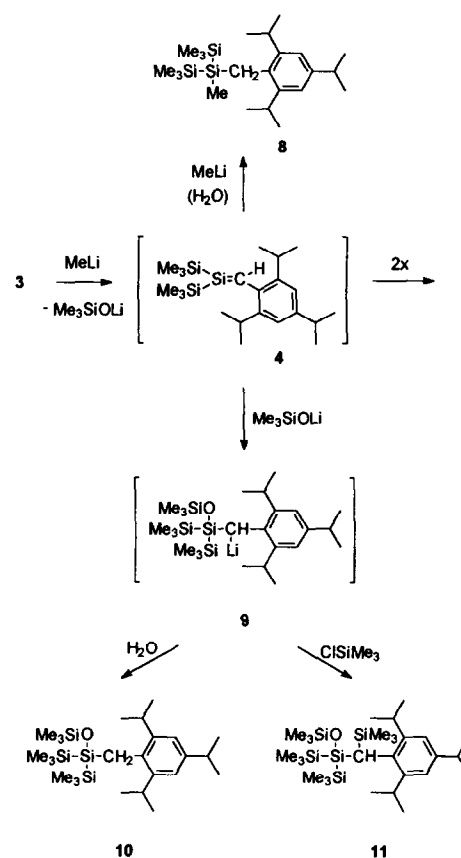
The X-ray crystal structure analysis of **5** revealed that the molecule has a  $\text{C}_2$  axis crossing the C–C and Si–Si bonds of the 1,2-disilacyclobutane ring. The four membered ring of **5** is rather bent. The two planes through the atoms C1–Si1–Si1a and C1–C1a–Si1a intersect at an angle of  $40.18^\circ$ . Thus, the two bulky triisopropylphenyl substituents can be placed in a diequatorial position, whereas the two ring CH atoms adopt a diaxial orientation. The C–C (158.4 pm) and Si–C (197.3 pm) bond distances in the ring are slightly lengthened, but agree with the values obtained for similar 1,2-disilacyclobutane systems [1,4,9]. In contrast, owing to the steric stress of the two triisopropylphenyl substituents, the ring Si–Si bond distance (233.4 pm) is comparatively short and, interestingly, almost identical with the value found by Apeloig and co-workers for the dimer of bis(trimethylsilyl)-adamantylidene-silene [4].

The generation of the stilbene **6** will be discussed further below. The small quantity of hexakis(trimethylsilyl)-disilane **7** [10], found in the reaction mixture, is considered to be the result of an electron transfer process taking place between the silanide **2** and the aromatic aldehyde, indicated by a deep orange colour of the solution appearing when the two components are mixed in ether. In conclusion, **2** is partly oxidized by the aromatic aldehyde to give the polysilane **7**.

A similar product composition is obtained when tris(trimethylsilyl)silyllithium (**1**) is used in the reaction with triisopropylbenzaldehyde. After mixing the components in ether at  $-78^\circ\text{C}$  and allowing them to interact for 2 h, the reaction is stopped by addition of water to the cold solution. This way, **3** is obtained in a yield of approximately 50%, besides 10% of the stilbene **6**. Longer reaction times and higher temperatures lead to a decrease of the yield of the alcohol **3**.

## 2.2. The base initiated conversion of the alcohol **3** and the products arising from the transient silene **4**

The deprotonation of **3** with methyllithium in ether at low temperature leads in a clean reaction to the elimination of lithiumtrimethylsilylanolate and the formation of the transient silene **4**. This is indicated by the interac-



Scheme 2. The generation of the silene **4** by deprotonation of the alcohol **3** with methyllithium in ether and the conversion of **4** by excess MeLi or readdition of Me<sub>3</sub>SiOLi.

tion of **3** with excess methyllithium, which produces the trisilane **8** besides traces of **6** (Scheme 2). After deprotonation of the alcohol **3** by the organometallic base and subsequent lithium trimethylsilylanolate elimination, the excess of the nucleophilic organolithium reagent adds at the just generated Si=C double bond to give, after hydrolytic work up, the trisilane **8**. The formation of trisilanes of that type by reaction of 1-hydroxyalkyl-tris(trimethylsilyl)silanes with excess methyllithium or phenyllithium is considered as a general proof for the generation of intermediate silenes along the Peterson type mechanism [1].

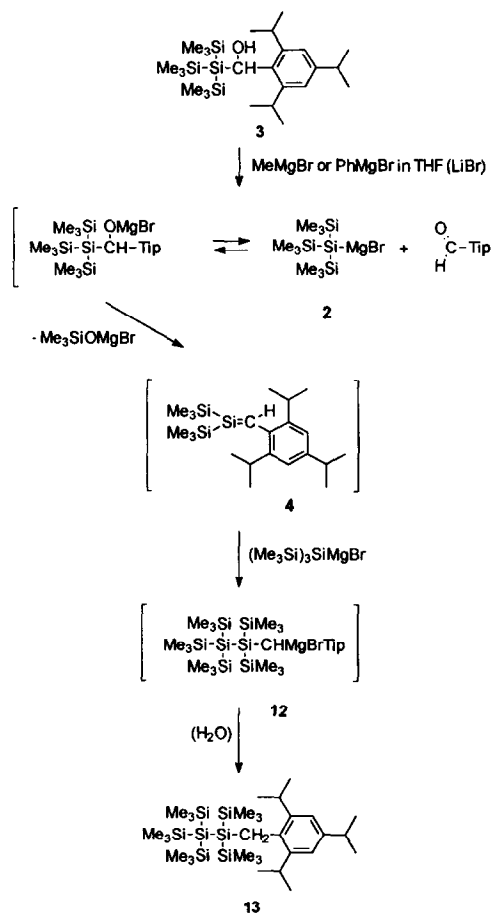
The reaction of the alcohol **3** with stoichiometric quantities of MeLi in ether at  $-70^\circ\text{C}$  produces a complex mixture of products. Chromatographic work up and subsequent careful distillation of the main fraction gives two compounds, which were identified on the basis of IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR and mass spectra as the 1,2-disilacyclobutane **5** (10%) and bis(trimethylsilyl)-(2,4,6-triisopropylbenzyl)-trimethylsilyloxysilane (**10**) (60%) (Scheme 2). **5** is described above as the cyclo-dimer of **4**. Its detection indicates that the silene **4** — despite a considerable steric congestion — is still reactive and dimerizes in the well known [2 + 2] head-to-head fashion.

The formation of the siloxane **10** is easily understood as the result of the addition of the lithium trimethylsilylanolate, eliminated in the course of the Peterson reaction, at the silene Si=C double bond, to give the organolithium intermediate **9**, which is hydrolysed during the aqueous work up. Such silanolate readditions have already been described in the literature [5b,11] and always have to be taken into account as a self-evident side reaction in the course of the silene generation according to the modified Peterson mechanism. However, until now, in our investigations we never observed this rearrangement. In all cases studied, the liberated silenes were highly reactive intermediates, which in absence of scavenger reagents immediately underwent different types of dimerizations. Obviously, owing to the considerable kinetic stabilization of the silene **4** by the bulky aromatic substituent and the two trimethylsilyl groups, the silene dimerization becomes a comparatively slow reaction making the silanolate addition the dominating process.

Expectedly, the trimethylsilylanolate addition reaction can be suppressed and the yield of the silene dimer increased by trapping the eliminated trimethylsilylanolate with chlorotrimethylsilane. Actually, addition of chlorotrimethylsilane to the cold reaction mixture shortly after the deprotonation of the alcohol **3** leads to an increase of the yield of **5** to 49% and at the same time, the organolithium intermediate **9**, formed primarily by addition of Me<sub>3</sub>SiOLi at the Si=C bond of **4**, is trapped to give the siloxane **11** (Scheme 2).

The outcome of the reaction of the polysilynyl alcohol **3** with the Grignard reagents MeMgBr or PhMgBr as organometallic bases is rather different from the deprotonation experiments of **3** with methyl lithium described above. This indicates the high significance of the counter cation of the alkoxide resulting from the deprotonation of **3**. The interaction of **3** with MeMgBr or PhMgBr and the conversion of the corresponding magnesium alkoxide proceeds extremely slowly in ether as well as in THF. However, the reaction is considerably accelerated when lithium bromide is present in the reaction mixture. This is always the case when the applied Grignard compound is made from the commercial organolithium reagent and magnesium bromide, but the same effect is achieved when LiBr is given additionally to the reaction mixture. Although the influence of various salts on the reactivity of, for example, Grignard reagents is well documented in the literature [12], the function of the lithium bromide in increasing the reactivity of the intermediate organomagnesium compounds is not fully understood, but was also observed similarly in the reaction of mesityl-tris(trimethylsilyl)silyl-methanol with MeMgBr [1b].

In the presence of LiBr the conversion of the alcohol **3** with MeMgBr or PhMgBr at room temperature in THF is complete after a few hours and results in the



Scheme 3. The deprotonation of the alcohol **3** with MeMgBr or PhMgBr in THF and the addition of tris(trimethylsilyl)silylmagnesium bromide at the silene Si=C bond.

formation of a complex mixture of products. Chromatographic separation leads to a new crystalline compound, which unfortunately decomposed when we were trying to perform an X-ray structure analysis. However, <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR and MS studies unambiguously revealed the structure as the polysilane **13** (Scheme 3). Besides **13** (36%) the stilbene **7** was obtained in form of a mixture of the *E/Z*-isomers (10%) and also reproduced 2,4,6-triisopropylbenzaldehyde could be identified. The silene dimer **5** and the siloxane **10** could not be detected.

**13** is easily recognized as the addition product of the silanide **2** at the Si=C double bond of the silene **4** producing the organometallic intermediate **12**, which is hydrolysed to give **13**. The same type of silanide silene addition has already been observed as the result of the in situ interaction of **1** with acetone. In that particular case the addition step is followed by a 1,3-Si,C-trimethylsilyl migration to give, after hydrolysis of the intermediate lithium silanide, the hydridopolysilane (Me<sub>3</sub>Si)<sub>2</sub>-SiH-Si(SiMe<sub>3</sub>)<sub>2</sub>-CMe<sub>2</sub>SiMe<sub>3</sub> [3]. Whereas for the formation of this compound the silanide **1** is available as one of the starting materials, in case of the formation of

**13** by interaction of **3** with MeMgBr, the appearance of the silanide **2** in the reaction mixture is interpreted as the result of an equilibrium attaining between the magnesium alkoxide derived from **3** on one side, and **2** and triisopropylbenzaldehyde on the other side. When **3** is deprotonated with Grignard reagents, the elimination of magnesiumtrimethylsilanolate from the magnesium alkoxide proceeds comparatively slowly, so that there is sufficient time for the attainment of the equilibrium. In case of the reaction of **3** with organolithium compounds, the lithiumalkoxide decomposes much faster leading to the silene **4**, which is trapped by the silanolate to give the readdition product **10**. With increasing steric bulk of the organic substituent at the polysilyl alcohol, the equilibrium attaining after deprotonation is shifted to the silanide and the aldehyde. Thus, in case of the interaction of **3** with MeMgBr, **13** is the main product, whereas the deprotonation of mesityl-tris(trimethylsilyl)silyl-methanol with the same Grignard reagent produces only traces of the similarly structured polysilane besides the respective silene dimer [1b].

An open problem is the origin of the stilbene **6** obtained in varying quantities in the reaction of tris(trimethylsilyl)silylmagnesium bromide with triisopropylbenzaldehyde, as well as in the reactions of the alcohol **3** with organometallic bases. Interestingly, the 1,2-disilacyclobutane **5**, dissolved in CHCl<sub>3</sub>, decomposes within 2 weeks at room temperature to give E-2,4,6,2',4',6'-hexaisopropylstilbene (**6**) quantitatively. This may suggest the idea that **6** is generally formed by an asymmetric ring scission of **5**. However, this ring cleavage could not be reproduced in other solvents under conditions comparable with those applied in the reactions described. Another possible way to **6** may consist in the dimerization of 2,4,6-triisopropylbenzylcarbene. It is well known that  $\alpha$ -silylalkylether at elevated temperatures undergo a degradation reaction under formation of alkoxysilanes and carbenes [13]. Similarly, a Brook-rearrangement of the lithium or magnesium alkoxide derived from the alcohol **3** and subsequent C–O bond cleavage resulting in the formation of the siloxide anion (Me<sub>3</sub>Si)<sub>3</sub>SiO<sup>−</sup> and the triisopropylbenzylcarbene appears to be not unlikely. In addition the C–O bond scission will be supported by the steric congestion of the intermediate alkoxysilane anion. The significance of these steric factors is also obvious with respect to the formation of the polysilane **13**. Of course, these suggestions need further experimental support.

### 3. Experimental section

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<sub>3</sub>Si)<sub>3</sub>SiLi · 3THF is prepared as reported in the literature [6]; 2,4,6-triisopropylbenzaldehyde is made according to the method of Wayland et al. [14].

#### 3.1. The reaction of tris(trimethylsilyl)silylmagnesium bromide (**2**) with 2,4,6-triisopropylbenzaldehyde

To a stirred solution of 3.52 g (0.01 mol) of **2** in ether 2.32 g (0.01 mol) of 2,4,6-triisopropylbenzaldehyde are given at −40°C. After stirring for 4 h at this temperature, the mixture is allowed to warm up to room temperature and stirring is continued for about 1 day. Aqueous work up with diluted HCl, extraction of the organic material with ether, drying and evaporation of the extracts gives an oil, from which **3** is best separated by kugelrohr distillation (160–170°C, 10<sup>−2</sup> Torr). In a separate run, **5** and **6** are separated from the crude oil by chromatography (silica gel–heptane).

**3**: Yield 3.34 g (70%), m.p. 77°C. IR (nujol):  $\tilde{\nu}$  = 3442.3 cm<sup>−1</sup> (ass.) and 3534.3 cm<sup>−1</sup> (free) (OH). <sup>1</sup>H NMR (benzene-d<sub>6</sub>):  $\delta$  = 0.40 (s, SiCH<sub>3</sub>, 27H), 1.31 (d, <sup>3</sup>J = 7.0 Hz), 1.47 (d, <sup>3</sup>J = 6.7 Hz), 1.51 (d, <sup>3</sup>J = 7.0 Hz) and 1.56 (d, <sup>3</sup>J = 6.7 Hz) (*o*-<sup>1</sup>Pr–CH<sub>3</sub>, each 3H), 1.35 (d, <sup>3</sup>J = 7.0 Hz, *p*-<sup>1</sup>Pr–CH<sub>3</sub>, 6H), 1.21 (d, <sup>3</sup>J = 3.7 Hz, OH, 1H), 2.92 (spt, <sup>3</sup>J = 7.0 Hz, *p*-<sup>1</sup>Pr–CH, 1H), 3.23 (br.spt, *o*-<sup>1</sup>Pr–CH, <sup>3</sup>J = 6.7 Hz, 1H), 3.76 (br.spt, *o*-<sup>1</sup>Pr–CH, <sup>3</sup>J approx. 7.0 Hz, 1H); 5.9 (d, <sup>3</sup>J = 3.7 Hz, CH, 1H), 7.14 and 7.28 (2s, arom. CH, 2H). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, DEPT):  $\delta$  = 1.94 (SiMe<sub>3</sub>), 22.23, 24.31, 24.34, 25.01, 26.17, 28.23, 29.80, 30.56 and 34.52 (<sup>1</sup>Pr), 63.06 (HCOH), 120.20 and 121.12 (arom. CH), 121.68, 122.84, 138.37 and 147.31 (arom. C). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>):  $\delta$  = −72.0 (SiSiMe<sub>3</sub>), −12.1 (SiSiMe<sub>3</sub>). MS, *m/z* (%): 481 (5) [M<sup>+</sup> + H], 463 (100), [M<sup>+</sup> − OH], 233 (70) [M<sup>+</sup> − Si(SiMe<sub>3</sub>)<sub>3</sub>]. C<sub>25</sub>H<sub>52</sub>OSi<sub>4</sub> (481.02). Calc.: C 62.42, H 10.90; Found: C 62.33, H 10.74.

**5**: Yield 0.6 g (15%); m.p. 205°C (dec.). <sup>1</sup>H NMR (benzene-d<sub>6</sub>):  $\delta$  = 0.50 (s, SiCH<sub>3</sub>, 18H), 0.54 (s, SiCH<sub>3</sub>, 18H), 1.29 (d, <sup>3</sup>J = 6.70 Hz, *p*-<sup>1</sup>Pr–CH<sub>3</sub>, 12H), 0.61, 1.39, 1.47 and 1.49 (4d, <sup>3</sup>J = 6.73 Hz, *o*-<sup>1</sup>Pr–CH<sub>3</sub>, 4 × 6H) 2.85 (spt, <sup>3</sup>J = 6.70 Hz, *p*-<sup>1</sup>Pr–CH, 2H), 3.77 and 3.95 (2spt, <sup>3</sup>J = 6.73 Hz, *o*-<sup>1</sup>Pr–CH, 2 × 2H), 4.91 (s, ring-CH, 2H), 7.08 and 7.16 (2d, <sup>4</sup>J = 2.15 Hz, arom. CH, 2 × 2H). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, DEPT):  $\delta$  = 2.97 and 3.37 (SiMe<sub>3</sub>), 24.03, 24.20, 24.72, 24.85, 26.87, 27.81, 28.72, 29.25 and 34.01 (<sup>1</sup>Pr), 43.23 (ring C), 122.36 and 123.67 (arom. CH), 135.90, 145.10, 146.44 and 147.15 (arom. C). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>):  $\delta$  = −46.0 (SiSiMe<sub>3</sub>), −12.9 and −11.7 (SiMe<sub>3</sub>). MS, *m/z* (%): 780 (0.7) [M<sup>+</sup>], 765 (1) [M<sup>+</sup> − CH<sub>3</sub>], 348 (100) [(Me<sub>3</sub>Si)<sub>2</sub>SiSi(SiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. C<sub>44</sub>H<sub>84</sub>Si<sub>6</sub> (781.66). calc.: C 67.61, H 10.83; found: C 66.98, H 10.94.

**6**: The stilbene is obtained as a mixture of the E/Z-isomers, which were separated chromatographi-

cally and by recrystallization from alcohol but were not structurally assigned. Yield 0.1 g (5%). *Isomer a*: m.p. 147°C (lit. 147–148°C [15]). <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ = 1.41 (d, <sup>3</sup>J = 7.03 Hz, *o*-<sup>i</sup>Pr-CH<sub>3</sub>, 24H), 1.43 (d, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH<sub>3</sub>, 12H), 3.00 (spt, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH, 2H), 3.74 (spt, <sup>3</sup>J = 7.03 Hz, *o*-<sup>i</sup>Pr-CH, 4H), 6.83 (s, olef. CH, 2H), 7.31 (s, arom. CH, 4H). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, DEPT): δ = 24.36 (*o*-<sup>i</sup>Pr-CH<sub>3</sub>), 24.41 (*p*-<sup>i</sup>Pr-CH<sub>3</sub>), 30.57 (*o*-<sup>i</sup>Pr-CH), 34.83 (*p*-<sup>i</sup>Pr-CH), 120.93 and 132.65 (olef. and arom. CH), 133.82, 147.10 and 148.07 (arom. C). *Isomer b*: m.p. 105°C. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ = 1.15 (d, <sup>3</sup>J = 7.03 Hz, *o*-<sup>i</sup>Pr-CH<sub>3</sub>, 24H), 1.32 (d, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH<sub>3</sub>, 12H), 2.88 (spt, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH, 2H), 3.29 (spt, <sup>3</sup>J = 7.03 Hz, *o*-<sup>i</sup>Pr-CH, 4H), 6.89 (s, olef. CH, 2H), 7.14 (s, arom. CH, 4H). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, DEPT): δ = 23.81 (*o*-<sup>i</sup>Pr-CH<sub>3</sub>), 24.26 (*p*-<sup>i</sup>Pr-CH<sub>3</sub>), 30.40 (*o*-<sup>i</sup>Pr-CH), 34.69 (*p*-<sup>i</sup>Pr-CH), 121.13 and 129.96 (olef. and arom. CH), 131.54, 146.76 and 148.41 (arom. C).

### 3.2. Reaction of the polysilanylalcohol **3** with excess methylolithium in ether

To an ethereal solution of 0.48 g (0.001 mol) of **3** is added at -78°C a fourfold molar excess of methylolithium. The mixture is allowed to warm up to room temperature and stirring is continued for 5 h. After addition of diluted aqueous hydrochloric acid, extraction with ether and evaporation of the dried extracts, an oil is obtained from which 0.25 g (62%) of pure **8** are separated (besides a small quantity of **6**) by chromatography (silica gel–heptane).

**8**: Colourless oil. <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ = 0.24 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 18H), 0.34 (s, SiCH<sub>3</sub>, 3H), 1.38 (d, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH<sub>3</sub>, 6H), 1.43 (d, <sup>3</sup>J = 6.70 Hz, *o*-<sup>i</sup>Pr-CH<sub>3</sub>, 12H), 2.61 (s, SiCH<sub>2</sub>, 2H), 2.96 (spt, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH, 1H), 3.27 (spt, <sup>3</sup>J = 6.70 Hz, *o*-<sup>i</sup>Pr-CH, 2H), 7.20 (s, arom. CH, 2H). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, DEPT): δ = -6.46 (SiCH<sub>3</sub>), 0.68 (Si(CH<sub>3</sub>)<sub>3</sub>), 11.72 (SiCH<sub>2</sub>), 23.95 (*o*-<sup>i</sup>Pr-CH<sub>3</sub>), 24.48 (*p*-<sup>i</sup>Pr-CH<sub>3</sub>), 30.39 (*o*-<sup>i</sup>Pr-CH), 34.61 (*p*-<sup>i</sup>Pr-CH), 120.55 (arom. CH), 133.66, 145.17 and 145.19 (arom. C). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): δ = -44.9 (SiSiMe<sub>3</sub>), -15.6 (SiSiMe<sub>3</sub>). MS, *m/z* (%): 406 (35) [M<sup>+</sup>], 333 (100) [M<sup>+</sup>-SiMe<sub>3</sub>], 189 (72) [M<sup>+</sup>-CH<sub>2</sub>Aryl]. C<sub>23</sub>H<sub>46</sub>Si<sub>3</sub> (406.84). Calc.: C 67.90, H 11.39; Found: C 67.89, H 11.09.

### 3.3. Reaction of **3** with stoichiometric quantities of methylolithium in ether

(a) An equimolar quantity of MeLi is given at -78°C to an ethereal solution of 0.48 g (0.001 mol) of **3**. The mixture is stirred for 5 h and worked up as described above. Chromatography (silica gel–heptane) of the resulting oil gives a main fraction which is further sepa-

rated by distillation giving 0.29 g (60%) of **10** and 0.04 g (10%) of **5**.

**10**: Colourless oil, b.p. 175°C (10<sup>-2</sup> Torr). IR (nujol):  $\tilde{\nu}$  = 1051.4 cm<sup>-1</sup> (SiOSi). <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ = 0.25 (s, SiSiCH<sub>3</sub>, 18H), 0.28 (s, OSiCH<sub>3</sub>, 9H), 1.40 (d, <sup>3</sup>J = 6.70 Hz, *p*-<sup>i</sup>Pr-CH<sub>3</sub>, 6H), 1.44 (d, <sup>3</sup>J = 6.70 Hz, *o*-<sup>i</sup>Pr-CH<sub>3</sub>, 12H), 2.85 (s, CH<sub>2</sub>, 2H), 2.96 (spt, <sup>3</sup>J = 6.70 Hz, *p*-<sup>i</sup>Pr-CH, 1H), 3.33 (spt, <sup>3</sup>J = 6.70, *o*-<sup>i</sup>Pr-CH, 2H), 7.20 (s, arom. CH, 2H). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, DEPT): δ = -1.06 (SiSiCH<sub>3</sub>), 2.27 (OSiCH<sub>3</sub>), 19.61 (CH<sub>2</sub>), 23.79 (*o*-<sup>i</sup>Pr-CH<sub>3</sub>), 25.52 (*p*-<sup>i</sup>Pr-CH<sub>3</sub>), 30.49 (*o*-<sup>i</sup>Pr-CH), 34.67 (*p*-<sup>i</sup>Pr-CH), 120.51 (arom. CH), 133.76, 145.08 and 145.26 (arom. C). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): δ = -19.5 (SiSiMe<sub>3</sub>), 2.2 and 6.9 (SiMe<sub>3</sub>). MS, *m/z* (%): 480 (10) [M<sup>+</sup>], 465 (15) [M<sup>+</sup>-CH<sub>3</sub>], 407 (33) [M<sup>+</sup>-SiMe<sub>3</sub>], 318 (47) [M<sup>+</sup>-(Me<sub>3</sub>Si)<sub>2</sub>O], 277 (100) [M<sup>+</sup>-Aryl]. C<sub>25</sub>H<sub>52</sub>OSi<sub>4</sub> (481.02). Calc.: C 62.42, H 10.90; Found: C 62.66, H 10.85.

(b) An equimolar quantity of MeLi is added to a solution of 0.48 g (0.001 mol) of **3** in ether at -78°C. The procedure is continued in two variations. When chlorotrimethylsilane (0.11 g, 0.001 mol) is added to the cold solution after 2 h and the mixture is stirred for further 24 h at room temperature, usual work up gives 0.19 g (49%) of **5** and traces of **10**. Addition of chlorotrimethylsilane to the reaction mixture after at least 5 h, stirring at room temperature for 24 h and usual work up leads to 0.20 g **11** (36%).

**11**: Colourless crystals, m.p. 151°C. IR (nujol):  $\tilde{\nu}$  = 1035.8 cm<sup>-1</sup> (SiOSi). <sup>1</sup>H NMR (benzene-d<sub>6</sub>): δ = 0.02, 0.35, 0.36 and 0.51 (4s, SiCH<sub>3</sub>, 4 × 9H), 1.33, 1.47, 1.50 and 1.51 (4d, <sup>3</sup>J = 6.7 Hz, *o*-<sup>i</sup>Pr-CH<sub>3</sub>, 4 × 3H), 1.38 (d, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH<sub>3</sub>), 2.60 (s, CHSiMe<sub>3</sub>, 1H), 2.95 (spt, <sup>3</sup>J = 7.03 Hz, *p*-<sup>i</sup>Pr-CH, 1H), 3.31 and 3.62 (2spt, <sup>3</sup>J = 6.70 Hz, *o*-<sup>i</sup>Pr-CH, 2 × 1H), 7.15 and 7.25 (2d, <sup>4</sup>J = 2.13 Hz, arom. CH, 2 × 1H). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, DEPT): δ = 0.40, 0.91, 2.69 and 3.34 (SiCH<sub>3</sub>), 23.81, 24.01, 24.37, 24.98, 25.43, 28.30, 29.83, 30.76 and 34.36 (<sup>i</sup>Pr and CHSi), 121.30 and 122.68 (arom. CH), 138.31, 144.53, 144.76 and 146.65 (arom. C). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>): δ = -21.5, -20.6, -2.7, 1.4 and 6.6 (not assigned). MS, *m/z* (%): 537 (1) [M<sup>+</sup>-CH<sub>3</sub>], 479 (18) [M<sup>+</sup>-SiMe<sub>3</sub>], 405 (80) [M<sup>+</sup>-SiMe<sub>3</sub>-HSiMe<sub>3</sub>], 73 (100) [SiMe<sub>3</sub><sup>+</sup>]. C<sub>28</sub>H<sub>60</sub>Si<sub>5</sub> (553.21). Calc.: C 60.79, H 10.93; Found: C 60.58, H 10.85.

### 3.4. Reaction of **3** with methylmagnesium bromide

0.48 g (0.001 mol) of **3**, dissolved in THF, are added at -78°C to a stirred solution of 0.18 g (0.001 mol) of PhMgBr in THF containing 0.44 g (0.005 mol) of LiBr. The reaction mixture is allowed to warm up to room temperature and stirring is continued overnight. Work up as described above and chromatographic separation

and purification (silica gel–heptane) delivers **13** in the form of colourless crystals besides **6** (0.02 g, 10%) and some 2,4,6-triisopropylbenzaldehyde.

**13**: Yield 0.12 g (36%), m.p. 105°C.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  = 0.11 (s, SiCH<sub>3</sub>, 18H), 0.33 (s, SiCH<sub>3</sub>, 27H), 1.20 (d,  $^3J$  = 7.0 Hz,  $p$ -<sup>i</sup>Pr-CH<sub>3</sub>, 6H), 1.5 (br.m,  $o$ -<sup>i</sup>Pr-CH<sub>3</sub>, 12H), 2.62 (s, SiCH<sub>2</sub>, 2H), 2.81 (spt,  $^3J$  = 7.00 Hz,  $p$ -<sup>i</sup>Pr-CH, 1H), 3.16 (spt,  $^3J$  = 6.70 Hz,  $o$ -<sup>i</sup>Pr-CH, 2H), 6.87 (s, arom. CH, 2H).  $^{13}\text{C}$  NMR (benzene- $d_6$ , DEPT):  $\delta$  = 3.82 and 4.34 (SiCH<sub>3</sub>), 15.25 (SiCH<sub>2</sub>), 24.42 ( $o$ -<sup>i</sup>Pr-CH<sub>3</sub>), 21.90 and 26.55 (br.,  $o$ -<sup>i</sup>Pr-CH), 30.40 ( $p$ -<sup>i</sup>Pr-CH<sub>3</sub>), 34.53 ( $p$ -<sup>i</sup>Pr-CH), 120.23 (arom. CH), 133.75 and 145.80 (arom. C).  $^{29}\text{Si}$  NMR (benzene- $d_6$ ): -89.9 [Si(SiMe<sub>3</sub>)<sub>3</sub>], -67.7 [Si(SiMe<sub>3</sub>)<sub>2</sub>], -13.0 and -9.6 (SiSiMe<sub>3</sub>). MS,  $m/z$  (%): 638 (2) [M<sup>+</sup>], 623 (20) [M<sup>+</sup>-CH<sub>3</sub>], 435 (10) [M<sup>+</sup>-Aryl], 421 (55) [M<sup>+</sup>-CH<sub>2</sub>Aryl], 391 (100) [M<sup>+</sup>-Si(SiMe<sub>3</sub>)<sub>3</sub>]. C<sub>31</sub>H<sub>70</sub>Si<sub>7</sub> (639.49). calc.: C 58.22, H 11.03; found: C 58.20, H 11.03.

### 3.5. Crystal structure determination of 5

For the data collection a Siemens P4 diffractometer was used. After taking a rotational photo of a crystal

Table 1  
Crystal and structure solution data for compound 5

Formula	C <sub>44</sub> H <sub>84</sub> Si <sub>6</sub>
M (g mol <sup>-1</sup> )	781.65
<i>a</i> (Å)	10.534
<i>b</i> (Å)	21.847
<i>c</i> (Å)	22.717
$\alpha$ (deg)	90
$\beta$ (deg)	90
$\gamma$ (deg)	90
<i>V</i> (Å <sup>3</sup> )	5234.47
$\rho_{\text{calcd.}}$ (g cm <sup>-3</sup> )	0.992
<i>Z</i>	4
Crystal system	orthorhombic
Space group (No. I.T.)	<i>Pbcn</i> (60)
<i>F</i> (000) (e)	1782
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	1.8
Radiation	$\lambda$ = 0.71089 Å (Mo K $\alpha$ ), graphite monochromator
Diffractometer	Siemens P4
Crystal size (mm)	0.62 × 0.44 × 0.28
Temperature (°C)	25
Data collecting mode	omega-scan
Scan range (2 $\theta$ ) (deg)	3.72–45
<i>hkl</i> range	-11/0, -23/0, -24/0
Measured reflections	3382
Unique reflections	3382
Observed reflections	2193
<i>F</i> <sub>0</sub>	≥ 2 $\sigma$ ( <i>I</i> )
Refined parameter	237
<i>R</i> 1 for <i>F</i> <sub>0</sub> > 4 $\sigma$ ( <i>F</i> <sub>0</sub> )	0.0673
<i>R</i> 1 for all	0.1050
<i>wR</i> 2 for all	0.2004
GoF	1.064
$\Delta\rho$ (max/min) (e/Å <sup>-3</sup> )	+0.353/-0.321

with the dimensions 0.28 × 0.44 × 0.62 mm<sup>3</sup> a photo search was started to find a suitable reduced cell. The data collection was performed in routine  $\omega$ -scan. The structure was solved by direct methods (Siemens SHELXTL, copyright 1990, Siemens Analytical Xray Inst. Inc.) and refined by the full-matrix least squares method of SHELXL-93 [16]. Both the carbon and silicon atoms were refined anisotropically. The hydrogens were put into their theoretical positions and refined using the riding model. The weighting scheme was calculated according to  $w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 2.9607P]$  where  $P = (F_o^2 + F_c^2)/3$ . Other important data 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 401989, the names of the authors, and the journal citation.

### Acknowledgement

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

### References

- [1] (a) C. Krempner, H. Reinke and H. Oehme, *Chem. Ber.*, 128 (1995) 143; (b) C. Krempner, H. Reinke and H. Oehme, *Chem. Ber.*, in press.
- [2] R. Wustrack and H. Oehme, *J. Organomet. Chem.*, 352 (1988), 95.
- [3] H. Oehme, R. Wustrack, A. Heine, G.M. Sheldrick and D. Stalke, *J. Organomet. Chem.*, 452 (1993) 33.
- [4] D. Bravo-Zhivotovskii, V. Brande, A. Stanger, M. Kapon and Y. Apeloig, *Organometallics*, 11 (1992) 2326.
- [5] (a) J. Ohshita, Y. Masaoka and M. Ishikawa, *Organometallics*, 10 (1991) 3775; (b) J. Ohshita, Y. Masaoka, M. Ishikawa and T. Takeuchi, *Organometallics*, 12 (1993) 876.
- [6] G. Gutekunst and A.G. Brook, *J. Organomet. Chem.*, 225 (1982) 1.
- [7] G. Raabe and J. Michl, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds* Wiley, New York, 1989, Part 2, Chapter 17, p. 1100.
- [8] A.G. Brook and K.M. Baines, *Adv. Organomet. Chem.*, 25 (1986) 24.
- [9] A.G. Brook, S.C. Nyburg, W.F. Reynolds, Y.C. Poon, Y.-M. Chang, J.-S. Lee and J.-P. Picard, *J. Am. Chem. Soc.*, 101 (1979) 6752.
- [10] S.P. Mallela, J. Bernal and R.A. Geanangel, *Inorg. Chem.*, 31 (1992) 1626; H. Bock, J. Meuret and K. Ruppert, *J. Organomet. Chem.*, 445 (1993) 19; A. Heine, R. Herbst Irmer, G.M. Sheldrick and D. Stalke, *Inorg. Chem.*, 32 (1993) 2694.

- [11] A.G. Brook, P. Chiu, J. McClenaghan and A.J. Lough, *Organometallics*, *10* (1991) 3292.
- [12] A. Loupy and B. Tchoubar, *Salt Effects in Organic and Organometallic Chemistry*, VCH, Weinheim, 1992, p. 252.
- [13] A.G. Brook, *Acc. Chem. Res.*, *7* (1974) 77; A.G. Brook and P.J. Dillon, *Can. J. Chem.*, *47* (1969) 4347.
- [14] B. Wayland, A. Sherry, G. Poszmik and A. Bunn, *J. Am. Chem. Soc.*, *114* (1992) 1673.
- [15] R.C. Fuson, E.C. Horning, M.L. Ward, S.P. Rowland and J.L. Marsh, *J. Am. Chem. Soc.*, *64* (1942) 32.
- [16] G.M. Sheldrick, SHELXL-93, Universität Göttingen, 1993.