

Synthesis, structure and spectroscopic properties of branched oligosilanes

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Abstract

A number of various branched heptasilanes [(Me₃Si)₂MeSi]₂MeSiX (**2**: X = Ph; **3**: X = Me; **6**: X = Br; **7**: X = I; **8**: X = Cl; **9**: X = F; **10**: X = OH) bearing two (Me₃Si)₂MeSi groups as well as branched decasilanes [(Me₃Si)₂MeSi]₃Si–X (**12**: X = H; **13**: X = Br; **14**: X = Cl; **15**: X = F; **16**: X = OH) bearing three (Me₃Si)₂MeSi groups at one silicon centre were synthesized. The structures of the compounds prepared were elucidated on the basis of comprehensive NMR and MS studies. Additionally, the molecular structures of the decasilanes **12** and **14–16** were obtained from X-ray diffraction data, which verify a ca. spherical shape with the core silicon atom at the centre of the sphere. The spatial demand of three (Me₃Si)₂MeSi groups forces a widening of the Si–Si–Si angles of the XSiSi₃ tetrahedra toward the group X (X = H, Cl, F, OH) and a remarkable elongation of the central Si–X bonds. The analysis of the Si–Si–Si–Si dihedral angles of the tetrasilane subunits in the decasilanes **12** and **14–16** indicates the existence of three conformations denoted as *anti*, *ortho* and *gauche* and four different arrangements of pentasilane subunits, denoted as *anti-gauche*, *anti-ortho*, *ortho-gauche* and *ortho-ortho*. The absorption spectra of the heptasilanes **2–10** exhibit broadened absorption maxima, shifted strongly to the red relative to those of the decasilanes **11–16**. As a result of strongly limited conformational flexibility due to steric overcrowding, the singlet excitation in **11–16** is at much higher energy than in linear pentasilanes. A comparison of NMR chemical shifts of **2–16** with those of branched silanes of the type (Me₃Si)₃SiX and (Me₃Si)₂MeSiX reveals that the replacement of methyl groups by additional SiMe₃ groups in the β-position leads to a strong low-field shift of the signal of the central nucleus. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Silanes; Branched oligosilanes; Structure elucidation; UV–vis-spectroscopy

1. Introduction

Compounds containing branched oligosilyl substituents of type (Me₃Si)₂RSi — (R = oligosilyl, trimethylsilyl, aryl, alkyl, hydrogen) have been shown to display unusual chemical behaviour as well as novel electronic properties [1]. For example, Bock et al. demonstrated that radical anions as well as radical cations of tris(trimethylsilyl)silyl derivatives are stabilized by delocalizing the negative or positive charge, respectively, into the oligosilyl groups [2]. The ability of branched oligosilyl substituents to act as a π-acceptor was discussed by Pitt [3] in the course of studies of the

electronic spectra of heptamethyltrisil-2-yl derivatives substituted by electronegative donor groups and by West et al. [4] in the course of ESR studies of the phenyl-tris(trimethylsilyl)silane radical anion. Furthermore, the remarkable steric requirements of branched oligosilyl groups, especially of the space-filling (Me₃Si)₃Si group, made these substituents versatile ligands in main group [5] and in transition metal chemistry [6].

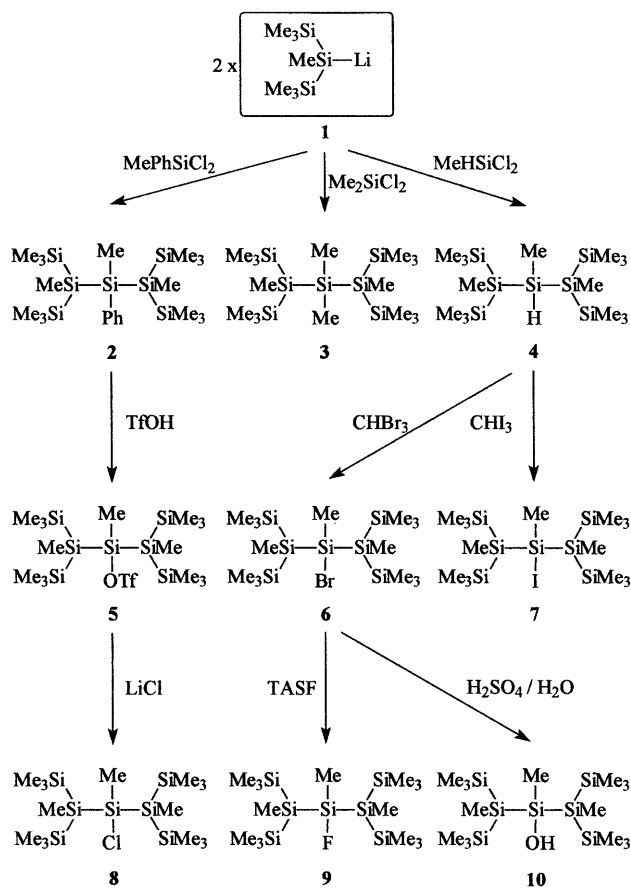
Of special interest in the search for sterically more demanding ligands for the kinetic stabilization of low-valent intermediates are compounds in which two or three bulky (Me₃Si)₂RSi substituents are fixed at the same central atom. Some of those derivatives, mainly of heavier main Group IV elements, have been prepared and for a few of those compounds the X-ray crystal structures were reported [7]. Recently, Apeloig, [8]

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Marschner [9] and Oehme [10] succeeded in synthesizing compounds containing two hypersilyl [11] groups at carbon or silicon atoms, respectively, starting with $(\text{Me}_3\text{Si})_3\text{SiLi} \times 3\text{THF}$ [12]. Moreover, Klinkhammer [13] reported the preparation and X-ray structure of a tris(hypersilyl)stannyl anion, whereas the silicon and carbon analogues of the compound had not been synthesized before. Reducing the bulkiness of the oligosilyl substituents by going from the $(\text{Me}_3\text{Si})_3\text{Si}$ group to the $(\text{Me}_3\text{Si})_2\text{MeSi}$ group, Lambert succeeded in the fixation of three of those units at one central silicon atom in synthesizing a highly branched decasilane [14].

These recent developments prompted us to design branched oligosilane structures by Si–Si linkage of methyl-bis(trimethylsilyl)silylmetal-derivatives [15] with substituted dichlorosilanes and trichlorosilanes via salt elimination reactions. This way it should be possible to get stable, hemispherical and space-filling molecules that might be used as ligands with exceptional steric properties [16]. In this paper, we report the synthesis of various halosilanes and hydroxysilanes substituted on the central silicon atom by two or three $(\text{Me}_3\text{Si})_2\text{MeSi}$ groups. In addition, we discuss the results of the X-ray structure analysis of some selected compounds and report the spectroscopic properties of the synthesized oligosilanes.



Scheme 1. Synthesis of heptasilanes 2–10.

2. Results and discussion

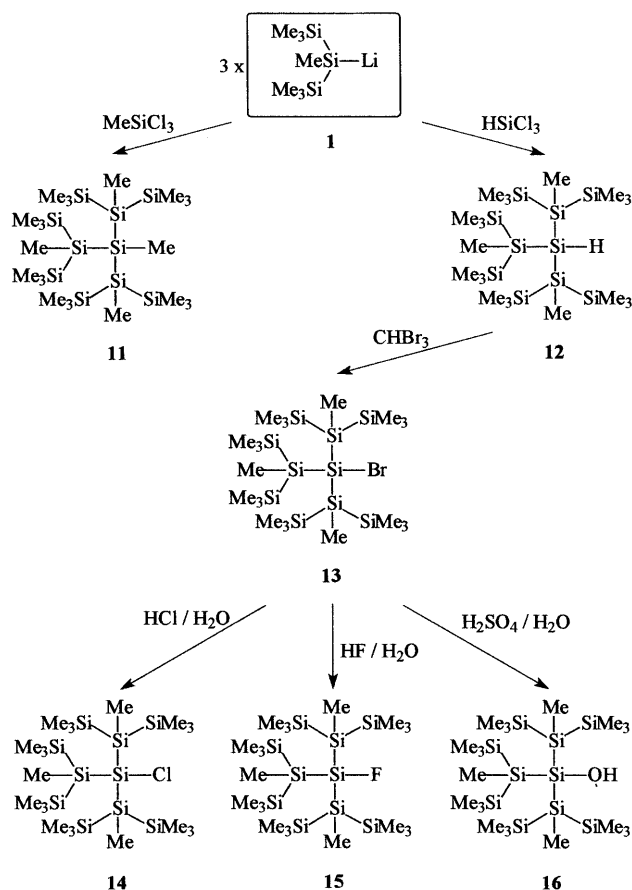
2.1. Synthesis of heptasilanes 2–10

As mentioned above, our strategy for preparing branched oligosilanes involved the selective formation of Si–Si bonds by salt elimination reactions of methyl-bis(trimethylsilyl)silyllithium (**1**) with easily available dichlorosilanes and trichlorosilanes. Normally, the required starting material **1** can be prepared by a cleavage of methyl-tris(trimethylsilyl)silane with methyllithium in tetrahydrofuran and can be used in situ for coupling reactions as described previously [16]. But the outcome of those coupling reactions strongly depends on the temperature and the solvent applied. Particularly, the metal–halogen exchange and the Si–Si bond cleavage were observed in the case of polar solvents such as tetrahydrofuran. Therefore, after changing the solvent from tetrahydrofuran to pentane, the silanide **1** was allowed to react with the appropriate chlorosilanes at low temperatures. In fact, the reaction of two equivalents of **1** with dichloromethylphenylsilane, dichlorodimethylsilane and dichloromethylsilane at -78°C gave the heptasilanes **2**, **3** and **4**, respectively, in excellent yields (Scheme 1).

Starting with the hydrosilane **4** [17], bromosilane **6** and iodosilane **7** were easily prepared by reaction with tribromomethane or triiodomethane at 120°C , whereas the chlorosilane **8** could not be synthesized in this way. Nevertheless, compound **8** was obtained by selective cleavage of the Si–Ph bond of phenylsilane **2** with trifluoromethanesulfonic acid giving the silyl triflate **5**. Without isolation of **5**, the triflate group was replaced by chloride in the presence of LiCl in THF to give pure **8**. The corresponding fluorosilane **9** was synthesized by fluorination of the bromosilane **6** with TASF [18] in toluene. On the other hand, hydrolysis of **6** led to the formation of hydroxysilane **10**. It should be emphasised that the isolated heptasilanes **2**, **3** and **6–10** are easily available, air-stable compounds, which could be purified by Kugelrohr distillation in vacuum and were obtained in high yields. The structures proposed for compounds **2**, **3** and **6–10** are in full agreement with the straightforward NMR spectra and the MS data.

2.2. Synthesis of decasilanes 12–16

As mentioned above, Lambert [14] showed that the treatment of three equivalents of **1** with methyl-trichlorosilane led to the formation of the highly branched decasilane **11** (Scheme 2). In view of the relative bulkiness of the three $(\text{Me}_3\text{Si})_2\text{MeSi}$ groups bonded at one silicon centre, the ease of formation of **11** is really surprising. Therefore, it should be possible to synthesize comparable structures, substituted by groups such as hydrido, chloro or phenyl at the central silicon atom.



Scheme 2. Synthesis of decasilanes 11–16.

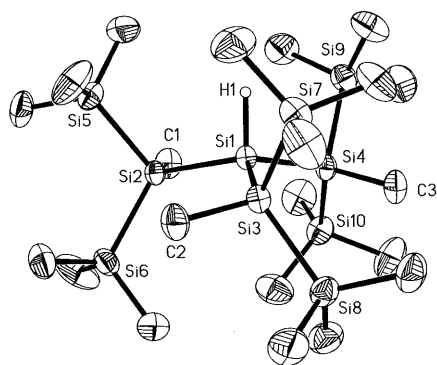


Fig. 1. Molecular structure of **12** in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–H1, 1.48(2); Si1–Si, 2 2.365(2); Si1–Si3, 2.3660(13); Si1–Si, 4 2.3654(13); Si2–Si, 5 2.3458(14); Si2–Si6, 2.3516(13); Si2–C1, 1.901(3); Si2–Si1–H1, 102.3(10); Si2–Si1–Si3, 115.51(5); Si2–Si1–Si4, 116.03(5); Si3–Si1–Si4, 115.84(5); Si1–Si2–Si5, 108.68(5); Si1–Si2–Si6, 119.55(5); Si5–Si2–Si6, 109.24(5).

With the intention to confirm the concept, the procedure used successfully for the generation of the heptasilanes **2** and **4** was modified by treatment of a threefold molar excess of **1** with phenyltrichlorosilane

and tetrachlorosilane, respectively. Unfortunately, neither the desired phenylsilane nor chlorosilane, bearing three $(\text{Me}_3\text{Si})_2\text{MeSi}$ substituents, could be detected. In contrast, the reaction of **1** with trichloromethylsilane and trichlorosilane at -78°C afforded the decasilanes **11** (yield 76%) and **12** (yield 67%), respectively, as colourless solids. The proposed structure of **12** was confirmed by NMR, MS and IR data and was in full agreement with the results of an X-ray crystal structure analysis [19]. The NMR spectra of **12** are rather straightforward. In the ^1H -NMR spectra as well as in the ^{13}C -NMR spectra only one signal was found for the SiMe_3 groups, and also the ^{29}Si -NMR spectra showed only one signal for the SiMe_3 silicon atoms. The results of the X-ray analysis of **12** (Fig. 1) confirm the expected extensive shielding of the hydrogen atom by the three $(\text{Me}_3\text{Si})_2\text{MeSi}$ substituents.

The extreme steric congestion gives rise to a chemical inertness of **12**. Thus, it is not unexpected that attempts to replace the hydrogen atom by a chlorine atom under the formation of the chlorosilane **14** by heating a solution of **12** in trichloromethane and tetrachloroethene, respectively, failed. Even after 3 weeks under reflux no exchange had occurred. In order to replace the hydrogen atom with an iodine atom we used triiodomethane, *N*-iodosuccinimide and iodine, respectively, in the reaction with **12** instead of trichloromethane and tetrachloroethene. However, although the chromatographic control of the progress of the reactions indicated that **12** was completely consumed, no iodasilane could be detected. Only fragmentation and decomposition of the starting material were observed. Nevertheless, by analogy with the preparation of **6**, the hydridosilane **12** was treated with an excess of tribromomethane at 80°C for 10 days. Crystallization of the crude product from dry acetone gave the bromosilane **13** in a yield of 30%. In comparison with **12**, bromosilane **13**, which contains a good leaving group, should be the ideal starting material for substitution reactions at the central silicon atom. In fact, **13** could be substituted very easily by hydrolysis in a mixture of THF and 10% sulfuric acid, yielding the hydroxysilane **16** almost quantitatively.

The treatment of **13** with concentrated hydrochloric acid in ether led to full exchange of the halogen groups under formation of the chlorosilane **14**. The reaction behaviour of **13** is unusual insofar as sterically less congested bromosilanes hydrolyse to silanols or siloxanes. Nevertheless, besides **14** only traces of the corresponding hydroxysilane **16** were observed. In a similar manner, **13** could be converted into the fluorosilane **15** almost quantitatively by the reaction with 40% hydrofluoric acid.

2.3. Molecular structures and conformations of the decasilanes **12** and **14–16**

The synthesized branched decasilanes **12–16** (Scheme 2) are all solid, air-stable compounds, which were purified by crystallization and characterized on the basis of NMR, MS and IR data (see Section 3). In addition, the molecular structures of the decasilanes **12** [19] and **14–16** have been derived from X-ray diffraction data. The results of the X-ray analyses give a good idea of the steric congestion in the molecules. As we see in Figs. 1–4 the presented molecules have a threefold axis along the central Si–X bond (X = H, Cl, F, OH) and adopt a ca. spherical shape, with the core silicon atom at the centre of the sphere. The functional group X is fully enclosed by the three (Me₃Si)₂MeSi substituents, filling the hole between these groups.

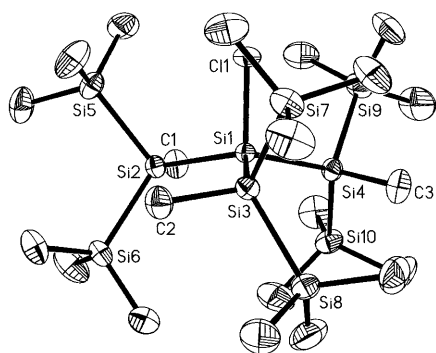


Fig. 2. Molecular structure of **14** in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–Cl1, 2.1370(11); Si1–Si2, 2.3799(12); Si1–Si3, 2.3771(12); Si1–Si4, 2.3829(12); Si2–Si5, 2.3663(13); Si2–Si6, 2.3705(13); Si2–C1, 1.900(3); Cl1–Si1–Si2, 101.59(5); Si2–Si1–Si3, 115.24(4); Si2–Si1–Si4, 117.35(4); Si3–Si1–Si4, 115.55(4); Si1–Si2–Si5, 110.43(5); Si1–Si2–Si6, 118.78(5); Si5–Si2–Si6, 108.43(5).

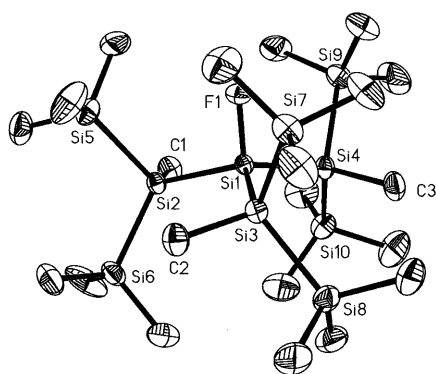


Fig. 3. Molecular structure of **15** in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–F1, 1.637(2); Si1–Si2, 2.375(2); Si1–Si3, 2.377(2); Si1–Si4, 2.368(2); Si2–Si5, 2.357(2); Si2–Si6, 2.361(2); Si2–C1, 1.890(4); F1–Si1–Si2, 102.39(10); Si2–Si1–Si3, 115.04(6); Si2–Si1–Si4, 115.70(6); Si3–Si1–Si4, 115.52(6); Si1–Si2–Si5, 107.97(6); Si1–Si2–Si6, 119.58(7); Si5–Si2–Si6, 109.21(7).

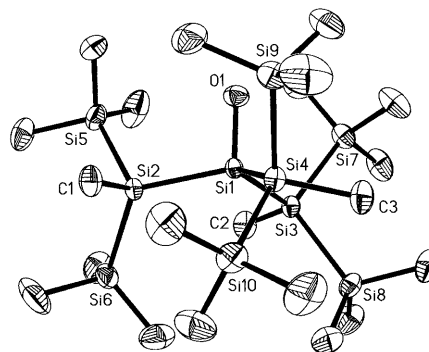


Fig. 4. Molecular structure of **16** in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–O1, 1.689(4); Si1–Si2, 2.3773(15); Si1–Si3, 2.3814(11); Si1–Si4, 2.3770(11); Si2–Si5, 2.3603(13); Si2–Si6, 2.3569(14); Si2–C1, 1.905(3); O1–Si1–Si2, 102.84(14); Si2–Si1–Si3, 114.40(4); Si2–Si1–Si4, 114.88(4); Si3–Si1–Si4, 114.76(4); Si1–Si2–Si5, 108.11(5); Si1–Si2–Si6, 120.65(5); Si5–Si2–Si6, 108.59(5).

The intramolecular distances between the group X (F, Cl, OH) and the three next neighbouring Me₃Si carbon atoms are relatively short. For example, the average C–X distances of **15** (C–F1, 3.45 Å) and **16** (C–O1, 3.50 Å) correspond ca. with the sum of the van der Waals radii [20] of a methyl group (2.0 Å) and a fluorine (1.47 Å) or a hydroxy group (1.52 Å), respectively. Only the average distance C–Cl1 (3.58 Å) in **14** is slightly smaller than the sum of the van der Waals radii of a methyl group and chlorine atom amounting to about 3.76 Å. The central Si–X bonds are remarkably elongated (Si1–H1 1.482; Si1–F1 1.637; Si1–Cl1 2.137; Si1–O1 1.689 Å). The spatial demand of the three (Me₃Si)₂MeSi groups forces a widening of the Si–Si–Si angles of the XSiSi₃ tetrahedra toward the group X within the range of 115–117°. The sum of the three Si–Si–Si bond angles around the central silicon atoms are 347.55 (**12**), 346.26 (**14**), 348.14 (**15**) and 344.04° (**16**). Most of the Si–Si bond lengths lie unremarkably within the range of 2.360–2.370 Å. Only the three bonds emanating from the central silicon are slightly elongated within the range 2.375–2.385 Å. At the positions where the trimethylsilyl groups of the three (Me₃Si)₂Me Si substituents contact each other, the angles Si1–Si2–Si6 are significantly widened within the range 118.8–120.7°, reducing the steric interactions. Thus, the average distances of neighboring methyl groups are 4.0 (**12**, **14**, **16**) and 3.9 Å (**15**) and are comparable with the sum of the van der Waals radii of two methyl groups amounting to about 4.0 Å. These results are in good agreement with the structural data obtained for the corresponding decasilane **11** reported by Lambert et al. [14].

Very instructive is a view along the Si2–Si1 axis of the molecules, shown for the decasilane **14** (Fig. 5), which reveals that the conformation is predominantly determined by the steric repulsion of the three

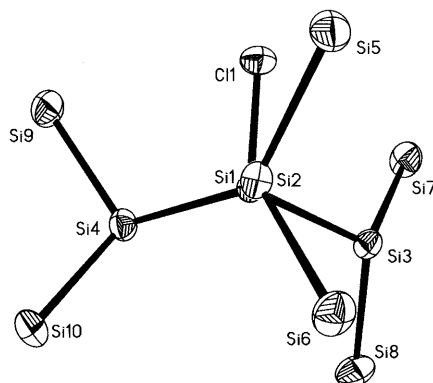


Fig. 5. Molecular structure of **14** in the crystal (ORTEP, 30% probability level, H-atoms and C-atoms omitted for clarity). Selected dihedral angles ($^{\circ}$): Cl1–Si1–Si2–Si5, 21.71(6); Cl1–Si1–Si2–Si6, 147.84(5); Si3–Si1–Si2–Si5, 87.65(6); Si4–Si1–Si2–Si5, 131.03(5); Si3–Si1–Si2–Si6, 38.48(7); Si4–Si1–Si2–Si6, 102.84(6).

(Me_3Si) $_2\text{MeSi}$ groups, while the Si–Cl1 group is playing a minor role. For example, neither is the trimethylsilyl group (Si5) in a *gauche* conformation nor is the trimethylsilyl group (Si6) in an *anti* conformation with Cl1, since this would lead to an extreme approach of the neighbouring SiMe_3 groups. Therefore, both trimethylsilyl groups evade the steric strain by rotating the (Me_3Si) $_2\text{MeSi}$ group around the Si2–Si1 axis, decreasing the dihedral angles Si5–Si2–Si1–Cl1 (21.71) and Si6–Si2–Si1–Cl1 (147.84 $^{\circ}$). Obviously due to the steric stress in the molecule the conformation of the tetrasilane subunits also differ strongly from the usual *gauche* or *anti* conformation of linear permethyloligosilanes. Thus, the dihedral angles in **14** were found to be 38.48 (Si6–Si2–Si1–Si3), 102.84 (Si6–Si2–Si1–Si4), 87.65 (Si5–Si2–Si1–Si3) and 131.03 $^{\circ}$ (Si5–Si2–Si1–Si4).

Interestingly, calculations by Michl and coworkers [21] have shown that the relatively unstrained linear decamethyltetrasilane has three conformational minima, whose energies lie within 1 kcal mol $^{-1}$ of each other, and whose dihedral angles are near 53 (*gauche*)

91 (*ortho*) and 162 $^{\circ}$ (*anti*). Furthermore, Michl pointed out that these values are nearly the same as in the conformers of linear dodecamethylpentasilane and that the all-*anti* forms seem to be the most stable of all conformers, as it was shown in $n\text{-Si}_4\text{Me}_{10}$ [21]. The results of our conformational analyses of the decasilanes **12** and **14–16** reveal four tetrasilane subunits with different dihedral angles (Fig. 5) and 12 possible pentasilane subunits, each defined by two dihedral angles. Following the denomination of conformers by Michl et al. [21], we termed the dihedral angles obtained for **12** and **14–16** as *gauche* (30–38), *ortho* (88–107) and *anti* (127–134 $^{\circ}$). In addition, Table 1 lists the dihedral angles for the 12 pentasilane subunits in the decasilanes **12** and **14–16**. We found a total of 12 *ortho*, six *anti* and six *gauche* arrangements of the tetrasilane subunits and four combinations of pentasilane subunits, denoted as *anti–gauche*, *anti–ortho*, *ortho–gauche* and *ortho–ortho* [14].

In conclusion, it should be stated that the arrangement of the tetrasilane as well as of the pentasilane chains is strongly determined by the space filling (Me_3Si) $_2\text{MeSi}$ groups. Thus, it is not unexpected that in the pentasilane subunits of the compounds **12** and **14–16** no all-*anti* conformers were observed, which has been noted to be optimal for delocalization or σ -conjugation [22]. Moreover, the conformational parameters of **14** as well as of **11** reported by Lambert et al. [14] are comparable to those for **12**, **15** and **16**, indicating that in these classes of compounds the space demand of the central group X (X = H, Me, Cl, F, OH) is ca. the same.

2.4. UV spectra — conformational effects

The absorption spectra of typical linear permethyloligosilanes strongly depend on the degree of catenation as well as on the conformation of the silicon-backbone [22]. Thus, the absorption maxima of oligosilane chains move to longer wavelengths as the number

Table 1
Tetrasilane dihedral angles ($^{\circ}$) for compounds **12** and **14–16**

Pentasilane subunits	12	14	15	16	Conformers
Si5–Si2–Si1–Si3–Si7	88–127	88–128	89–128	90–129	<i>ortho–anti</i>
Si5–Si2–Si1–Si3–Si8	88–108	88–106	89–107	90–106	<i>ortho–ortho</i>
Si5–Si2–Si1–Si4–Si9	132–93	131–90	133–94	134–95	<i>anti–ortho</i>
Si5–Si2–Si1–Si4–Si10	132–33	131–36	133–32	134–31	<i>anti–gauche</i>
Si6–Si2–Si1–Si3–Si7	39–127	38–128	37–128	35–129	<i>gauche–anti</i>
Si6–Si2–Si1–Si3–Si8	39–108	38–106	37–107	35–106	<i>gauche–ortho</i>
Si6–Si2–Si1–Si4–Si9	102–93	103–90	102–94	101–95	<i>ortho–ortho</i>
Si6–Si2–Si1–Si4–Si10	102–33	103–36	102–32	101–31	<i>ortho–gauche</i>
Si7–Si3–Si1–Si4–Si9	93–127	90–129	93–128	95–129	<i>ortho–anti</i>
Si7–Si3–Si1–Si4–Si10	93–107	90–105	93–107	95–105	<i>ortho–ortho</i>
Si8–Si3–Si1–Si4–Si9	33–127	36–129	31–128	30–129	<i>gauche–anti</i>
Si8–Si3–Si1–Si4–Si10	33–107	36–105	31–107	30–105	<i>gauche–ortho</i>

Table 2

UV absorption spectral data for compounds **3**, **4**, **6** and **8–16**

Heptasilanes	$\lambda_{\max}$ (nm)	ϵ	Decasilanes	$\lambda_{\max}$ (nm)	ϵ
3	254.8	2.27×10^4	11	239.5	3.40×10^4
4	253.4	1.72×10^4	12	238.5 ^a	3.42×10^4
8	247.5	2.10×10^4	14	230.6	5.70×10^4
6	245.5	2.40×10^4	13	233.8	4.08×10^4
9	259.0	1.55×10^4	15	219.5	5.38×10^4
10	262.2	1.49×10^4	16	~ 225 ^a	4.25×10^4

^a Shoulder.

of silicon atoms increases, with a limiting wavelength near 300 nm. Oligosilanes with more than three silicon atoms exhibit broad absorption maxima with multiple peaks attributable to the presence of conformational isomers [23]. Consequently, the degree of σ -conjugation in the oligosilane chain is a very sensitive function of the chain conformation.

In order to examine the conformational dependence of electronic properties of highly branched oligosilanes more closely, near-UV spectra of the silanes **2–16** were measured in heptane as solvent. Absorption spectral data of the compounds **3**, **4**, **6** and **8–16** at 293 K are summarized in Table 2. UV spectra of the decasilanes **11–16** are shown in Fig. 6. The UV spectra of the heptasilanes **3**, **4**, **6** and **8–10** are shown in Fig. 7.

The absorption curves of the decasilanes **11–16** show multiple peaks, however they exhibit very broad absorption maxima within the range of 210–240 nm. Interestingly, although the conformational parameters

of these class of compounds are quite similar, the positions of their first intense peaks in the UV spectra are markedly different. Especially the absorption maxima of the methyl substituted silane **11** ($\lambda_{\max} = 239.5$ nm) are definitely at longer wavelengths than those of silanes **13–16**. Moreover, the absorption of **11** is clearly at a shorter wavelength than those of the linear dodecamethylpentasilane ($\lambda_{\max} = 250$ nm) [24]. These remarkable differences in excitation energies between **11** and the linear dodecamethylpentasilane should also apply to the functionalized silanes **12–16** compared to their linear analogues, which however had not yet been synthesized.

In contrast to these results, the absorption curves of the heptasilanes **3**, **4**, **6** and **8–10** show a more homogeneous picture (Fig. 7). They exhibit broad absorption maxima with a significant shift to the red relative to those of the former compounds, within the range of 245–262 nm. Especially the observed value of the absorption maximum of **3** ($\lambda_{\max} = 254.8$ nm) is slightly longer than that of the linear dodecamethylpentasilane ($\lambda_{\max} = 250$ nm) [24].

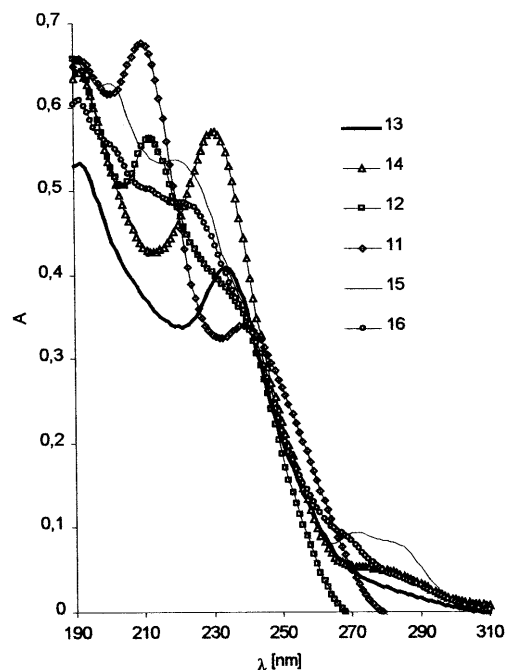


Fig. 6. UV absorption spectra of the decasilanes **11–16** (1×10^{-5} M) in heptane.

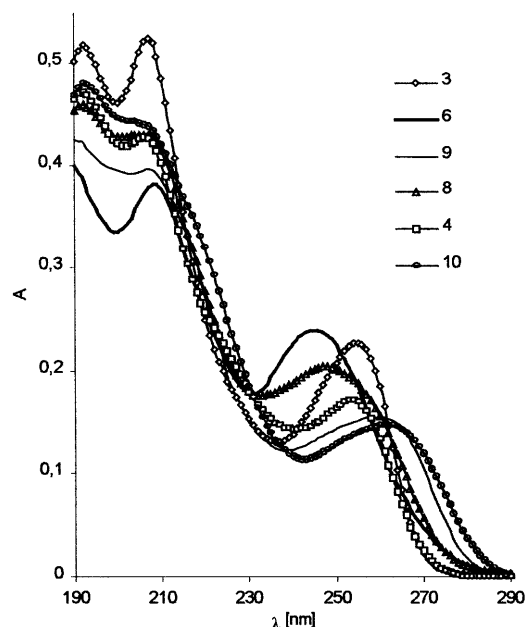


Fig. 7. UV absorption spectra of the heptasilanes **3**, **4**, **6** and **8–10** (1×10^{-5} M) in heptane.

As mentioned above the space demand of the $(\text{Me}_3\text{Si})_2\text{MeSi}$ group in the branched decasilanes **11–16** leads to strong limitations in the conformational flexibility in the silicon backbones, i.e. interconversion of conformers through rotations around Si–Si single bonds are restricted. As a result, only four combinations of conformers *anti-gauche*, *anti-ortho*, *ortho-gauche* and *ortho-ortho*, but no *anti-anti* conformers were observed in the pentasilane subunits, for which it is commonly believed that the *anti-anti*-form has the lowest singlet excitation energy of all conformers [23]. Furthermore, it is well known, that the excitation energy rapidly increases upon twisting from *trans* to *ortho* or *gauche* conformation. Thus, the obtained broadened absorption maxima of **11–16** shifted strongly to the blue, can be explained as a statistical distribution of various conformers and, hence, absorb at a higher energy that depends on twisting in the pentasilane chains. In contrast, the corresponding broadened absorption maxima of the heptasilanes **3, 4, 6** and **8–10** are significantly shifted to the red. This suggests, due to the minor steric stress in the molecules, a considerably higher conformational flexibility in the silicon backbones. Consequently, it is reasonable to assume that in the four possible pentasilane pathways of **3, 4, 6** and **8–10** besides a statistical distribution of other conformers also *anti-anti* conformers exist, causing a noticeably lower singlet excitation energy.

Interestingly, we found that the fluorosilane **9** and hydroxysilane **10** show a significant bathochromic shift of the absorption, coupled with some reduction in the intensity relative to the methyl substituted silane **3**. This can be attributed to a weak interaction of the nonbonding electrons with the heptasilane skeleton [3]. These results are completely different from those obtained for the bulkier analogues **12–16**, in which such a significant interaction is not evident. Although sharp maxima of absorptions could not be determined in all cases, the

maximum moves clearly to shorter wavelengths relative to the methyl substituted silane **11**, suggesting that the elongated Si–X bonds render the non-bonding electron interactions with the silicon backbone negligible.

2.5. IR and NMR spectra — trends of chemical shifts

The ^{29}Si -NMR chemical shift data for the central silicon atom of the oligosilanes **2–16** are summarised in Table 3 together with the data for selected silanes, trisilanes and tetrasilanes reported in the literature. As already reported by Radeaglia et al. [25] in the case of substituted siloxanes and phenylsilanes, it can be seen, that the low-field shift value of the central silicon atom increases with the electronegativity of the group X. Furthermore, the replacement of methyl groups in Me_3SiX by one or more trimethylsilyl groups in the α -position leads to a strong high-field shift, which can be attributed mainly to the electronegativity difference between these groups. For example, the observed value for the central silicon nucleus of tetrakis(trimethylsilyl)silane ($\delta = -135.9$), a compound in which four trimethylsilyl groups are fixed at the same silicon atom, is the lowest so far described for comparable oligosilanes. Contrary, the additional replacement of methyl groups of compounds $(\text{Me}_3\text{Si})_2\text{MeSiX}$ and $(\text{Me}_3\text{Si})_3\text{SiX}$ by trimethylsilyl groups in the β -position leads to a low-field shift of the signal for the central silicon nucleus. The observed influences on the chemical shift are in full agreement with the data for a series of branched as well as linear permethylated oligosilanes, reported by Ishikawa and West [26]. ^1H -, ^{13}C - and ^{19}F -NMR chemical shifts (Table 4) observed for the central group X indicate the same effect, a strong high-field shift by trimethylsilyl substitution in the α -position and a strong low-field shift as a result of β -substitution of additional SiMe_3 groups.

Table 3

Comparison of ^{29}Si -NMR shift values (ppm) of the heptasilanes and decasilanes **2–16** with the corresponding trisilanes and tetrasilanes measured in benzene- d_6

	$\delta_{\text{Si}^*\text{X}=\text{CH}_3}$	$\delta_{\text{Si}^*\text{X}=\text{H}}$	$\delta_{\text{Si}^*\text{X}=\text{F}}$	$\delta_{\text{Si}^*\text{X}=\text{Cl}}$	$\delta_{\text{Si}^*\text{X}=\text{Br}}$	$\delta_{\text{Si}^*\text{X}=\text{I}}$	$\delta_{\text{Si}^*\text{X}=\text{OH}}$	$\delta_{\text{Si}^*\text{X}=\text{Ph}}$
$\text{Me}_3\text{Si}^*\text{X}$	0.0	–17.5 ^a	32.0	30.2 ^b	26.4 ^b	8.7 ^b	16.0 ^{c, d}	–4.6
$(\text{Me}_3\text{Si})_2\text{MeSi}^*\text{X}$	–48.5 ^e	–72.7 ^f	36.3 ^f	9.9 ^f	2.4 ^f	–22.8 ^f	8.8	–46.2 ^f
$(\text{Me}_3\text{Si})_3\text{Si}^*\text{X}$	–88.3	–115.6	34.2	–12.6	–24.8 ^g	–56.8 ^g	–9.7	–77.0
$[(\text{Me}_3\text{Si})_2\text{MeSi}]_2\text{MeSi}^*\text{X}$	–33.0	–67.1	54.3	26.7	17.2	–14.2	26.1	–34.4
$[(\text{Me}_3\text{Si})_2\text{MeSi}]_3\text{Si}^*\text{X}$	–55.4	–111.4	74.8	27.9	12.3		37.6	

^a Ref. [27].

^b Ref. [28].

^c Ref. [29].

^d Measured in CDCl_3 .

^e Ref. [26a].

^f Ref. [30].

^g Ref. [31].

Table 4

Selected spectroscopic data of the silanes **4**, **9**, **11**, **12** and **15** compared with those reported in the literature

Compounds	δ_{H} (ppm) X = H	δ_{F} (ppm) X = F	δ_{C} (ppm) X = CH ₃	$^1J_{\text{Si-H}}$ (Hz)	$\tilde{\nu}_{\text{Si-H}}$ (cm ⁻¹)
Me ₃ SiX	4.04 ^a	–158.0 ^b	0.0	182 ^c	2121 ^d
(Me ₃ Si) ₂ MeSiX	3.37 ^e	–208.9	–6.9 ^f	163 ^g	2075 ^g
[(Me ₃ Si) ₂ MeSi] ₂ MeSiX	3.95	–182.2	0.5	160	2058
(Me ₃ Si) ₃ SiX	2.52	–255.1	–13.3	154 ^h	2051
[(Me ₃ Si) ₂ MeSi] ₃ SiX	3.53	–204.4	0.4 ⁱ	147	2017

^a Ref. [34].^b Ref. [35].^c Ref. [36].^d Ref. [37].^e Ref. [38].^f Ref. [26b].^g Ref. [39].^h Ref. [33].ⁱ Ref. [14].

Interestingly, the values of coupling constants $^1J(\text{Si-H})$ of the selected hydridosilanes (Table 4) increase as substituents on the central silicon atoms become bulkier. It is well known that in substituted hydridosilanes the s-character of the Si hybrid orbital is correlated with spin–spin coupling constants [32]. The trend of $^1J(\text{Si-H})$ indicates that the s-character of the Si–H orbitals becomes smaller as the substituents become bulkier. Especially the value of $^1J(\text{Si-H})$ of [(*i*-Pr)₃Si]₃SiH [33], a molecule with a nearly planar structure of the central SiSi₃ skeleton, is the lowest among those of hydridosilanes so far reported.

Moreover, the values of the Si–H stretching frequencies, obtained for the hydridosilanes summarised in Table 4, indicate that the Si–H bonds are dramatically weakened by successive substitution of trimethylsilyl groups in the α -position and the β -positions. Thus, the observed value for the hydridosilane **12** (2017 cm⁻¹) is the lowest so far described for comparable oligosilanes. Although the origin of the effect is unclear, the assumption of steric repulsion alone leading to a flattening of the central SiSi₃ skeleton of **12** and making the Si–H bond quite weak is not valid, since the stretching frequency of [(*i*-Pr)₃Si]₃SiH was found to be 2050 cm⁻¹ [33]. However, it is expected that mainly σ -conjugation into the pentasilane chains together with inductive effects of the trimethylsilyl groups decrease the Si–H bond strength.

2.6. Conclusions

We have prepared various branched halosilanes and hydroxysilanes substituted at the central silicon atom by two or three (Me₃Si)₂MeSi groups. X-ray analyses revealed the branched decasilanes **12** and **14–16** to be hemispherical and space-filling molecules, in which the group X (X = H, Cl, F, OH) is strongly shielded and the Si–Si–Si–Si dihedral angles are remarkably twisted.

Absorption spectra of the heptasilanes **2–10** exhibit broadened absorption maxima, shifted strongly to the red relative to those of the highly branched decasilanes **11–16**. These results support the suggestion that if the conformational flexibility is strongly limited by steric overcrowding, the singlet excitation in higher oligosilane dendrimers tends to be localized at a relatively small number of silicon atoms in a way dictated by chain conformation. Finally, spectroscopic investigations have shown that the properties of the Si–X function are strongly influenced by electronic effects of the pentasilanes chains as well as by the space demand of two or three (Me₃Si)₂MeSi groups. Despite the extensive shielding of the Si–X function, the oligosilanes **2–15** are proven to be reactive, and their chemical behaviour is the subject of current studies.

3. Experimental

3.1. General procedures and material

All reactions involving organometallic reagents were carried out under an atmosphere of argon using standard Schlenk techniques. Methyl-tris(trimethylsilyl)silane [31], methyl-bis(trimethylsilyl)silyllithium (**1**) [15] and 1,1,1,2,3,4,5,5,5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (**4**) [17] were prepared as previously described. NMR: Bruker AC 250, Bruker ARX 300, Bruker ARX 400 (250 MHz, 62.9 MHz, 79.5 MHz and 235.3 MHz, for ¹H, ¹³C, ²⁹Si and ¹⁹F, respectively). For ¹H-, ¹³C- and ²⁹Si-NMR, benzene-*d*₆ as solvent, TMS as internal standard; for ¹⁹F-NMR, benzene-*d*₆ as solvent, CFC₃ as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas. UV–vis: Perkin–Elmer Lambda 2, quartz cells of 1.0 cm path length and spectral grade *n*-heptane.

3.2. 1,1,1,2,3,4,5,5,5-Nonamethyl-3-phenyl-2,4-bis(trimethylsilyl)pentasilane (**2**)

Dichloromethylphenylsilane (2.44 ml, 15 mmol) was added at -78°C to a solution of methyl-bis(trimethylsilyl)silyllithium (30 mmol) in pentane (100 ml). Stirring was continued for 1 h and the mixture was allowed to warm to room temperature (r.t.) within 2 h. After filtration and removal of the solvent under reduced pressure the residue was distilled (170°C , 0.03 mbar) to give **2** (5.99 g, 80%). M.p. 50°C . $^1\text{H-NMR}$: δ 7.49–7.53, 7.06–7.2 (2m, phenyl, 5H), 0.71 (s, SiMePh, 3H), 0.39 (s, SiMe, 6H), 0.11, 0.18 (2s, SiMe₃, $2 \times 18\text{H}$). $^{13}\text{C-NMR}$: δ 140.2, 135.0, 128.3, 128.1 (C-aromat.), -2.9 (SiMePh), -10.1 (SiMe), 0.8, 1.1 (SiMe₃). $^{29}\text{Si-NMR}$: δ -34.4 (SiMePh), -80.5 (SiMe), -11.6 , -11.8 (SiMe₃). MS: (70 eV) m/z (%) = 498 (5) [M^+], 483 (3) [$\text{M}^+ - \text{Me}$], 309 (100) [$\text{M}^+ - \text{SiMe}(\text{SiMe}_3)_2$]. HRMS: Calc. for $\text{C}_{21}\text{H}_{50}\text{Si}_7$ 498.22387. Found: 498.22974. Anal. Calc. for $\text{C}_{21}\text{H}_{50}\text{Si}_7$ (499.235): C, 50.52; H, 10.10. Found: C, 48.56; H, 9.99%.

3.3. 1,1,1,2,3,3,4,5,5,5-Decamethyl-2,4-bis(trimethylsilyl)pentasilane (**3**)

Dichlorodimethylsilane (1.82 ml, 15 mmol) was added at -78°C to a solution of methyl-bis(trimethylsilyl)silyllithium (30 mmol) in pentane (100 ml). Stirring was continued for 1 h and the mixture was allowed to warm to r.t. within 2 h. After filtration and removal of the solvent under reduced pressure the residue was distilled (120°C , 0.01 mbar) to give **3** (5.82 g, 87%). M.p. 41°C . $^1\text{H-NMR}$: δ 0.44 (s, SiMe₂, 6H), 0.28 (s, SiMe, 6H), 0.25 (s, SiMe₃, 36H). $^{13}\text{C-NMR}$: δ 0.5 (SiMe₂), -10.7 (SiMe), 1.1 (SiMe₃). $^{29}\text{Si-NMR}$: δ -33.0 (SiMe₂), -81.6 (SiMe), -12.0 (SiMe₃). MS: (70 eV) m/z (%) = 436 (14) [M^+], 421 (6) [$\text{M}^+ - \text{Me}$]. Anal. Calc. for $\text{C}_{16}\text{H}_{48}\text{Si}_7$ (437.162): C, 43.96; H, 11.07. Found: C, 43.97; H, 10.92%.

3.4. 3-Bromo-1,1,1,2,3,4,5,5,5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (**6**)

A mixture of 1.1.1.2.3.4.5.5.5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (**4**) (5.3 g, 12 mmol) and CHBr_3 (2.1 ml, 23 mmol) was heated to 120°C for 15 h. After removal of the volatiles, the residue was distilled (145°C , 0.005 mbar) to give **6** (5.76 g, 92%). M.p. 62°C . $^1\text{H-NMR}$: δ 0.99 (s, SiMeBr, 3H), 0.31 (s, SiMe, 6H), 0.33, 0.24 (2s, SiMe₃, $2 \times 18\text{H}$). $^{13}\text{C-NMR}$: δ 5.2 (SiMeBr), -10.4 (SiMe), 0.9, 0.87 (SiMe₃). $^{29}\text{Si-NMR}$: δ 17.2 (SiMeBr), -75.0 (SiMe), -12.0 , -10.9 (SiMe₃). MS: (70 eV) m/z (%) = 502 (0.4) [M^+], 487 (9) [$\text{M}^+ - \text{Me}$], 429 (15) [$\text{M}^+ - \text{SiMe}_3$], 348 (65) [$\text{M}^+ - \text{SiMe}_3 - \text{HBr}$]. HRMS: Calc. for $\text{C}_{15}\text{H}_{43}\text{BrSi}_7$ 500.10923. Found: 500.10895. Anal. Calc. for

$\text{C}_{15}\text{H}_{45}\text{BrSi}_7$ (502.03): C, 35.89; H, 9.04; Br, 15.92. Found: C, 34.30; H, 8.85; Br, 13.56%.

3.5. 3-Iodo-1,1,1,2,3,4,5,5,5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (**7**)

A mixture of 1.1.1.2.3.4.5.5.5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (**4**) (1.6 g, 3.8 mmol), CHI_3 (1.6 g, 4 mmol) and toluene (20 ml) was heated to 110°C for 20 h. After removal of the volatiles, the residue was distilled (175°C , 0.03 mbar) to give **7** (1.41 g, 68%). $^1\text{H-NMR}$: δ 1.20 (s, SiMeI, 3H), 0.30 (s, SiMe, 6H), 0.33, 0.26 (2s, SiMe₃, $2 \times 18\text{H}$). $^{13}\text{C-NMR}$: δ 2.9 (SiMeI), -9.2 (SiMe), 1.0, 1.1 (SiMe₃). $^{29}\text{Si-NMR}$: δ -14.2 (SiMeI), -75.0 (SiMe), -11.5 , -10.6 (SiMe₃). MS: (70 eV) m/z (%) = 548 (1) [M^+], 475 (51) [$\text{M}^+ - \text{SiMe}_3$]. Anal. Calc. for $\text{C}_{15}\text{H}_{45}\text{I}_7$ (549.03): C, 32.82; H, 8.26. Found: C, 32.50; H, 8.17%.

3.6. 3-Chloro-1,1,1,2,3,4,5,5,5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (**8**)

Trifluoromethanesulfonic acid (0.1 ml, 1.1 mmol) was added at r.t. to a stirred solution of compound **2** (0.5 g, 1.0 mmol) in CH_2Cl_2 . After removal of the solvent under reduced pressure, the solid residue was dissolved in 10 ml THF and 50 mg (1.2 mmol) of anhydrous LiCl were added. Stirring was continued for 1 day. After filtration and removal of the solvent under reduced pressure, the residue was distilled (165°C , 0.02 mbar) to give **8** (0.41 g, 90%). M.p. $47\text{--}48^{\circ}\text{C}$. $^1\text{H-NMR}$: δ 0.84 (s, SiMeCl, 3H), 0.30 (s, SiMe, 6H), 0.32, 0.23 (2s, SiMe₃, $2 \times 18\text{H}$). $^{13}\text{C-NMR}$: δ 6.3 (SiMeCl), -11.0 (SiMe), 0.8, 0.83 (SiMe₃). $^{29}\text{Si-NMR}$: δ 26.7 (SiMeCl), -75.4 (SiMe), -11.3 , -11.2 (SiMe₃). MS: (CI) m/z (%) = 457 (4) [$\text{M}^+ + \text{H}$], 441 (30) [$\text{M}^+ - \text{Me}$], 421 (40) [$\text{M}^+ - \text{Cl}$], 348 (100) [$\text{M}^+ - \text{ClSiMe}_3$]. Anal. Calc. for $\text{C}_{15}\text{H}_{45}\text{ClSi}_7$ (457.57): C, 39.37; H, 9.91; Cl, 7.75. Found: C, 39.30; H, 9.83; Cl, 7.54%.

3.7. 3-Fluoro-1,1,1,2,3,4,5,5,5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (**9**)

A mixture of compound **6** (0.3 g, 0.6 mmol), tris(dimethylamino)-sulfonium-difluorotrimethylsilicate (TASF) (0.181 g, 0.65 mmol) and toluene (10 ml) was stirred at r.t. for 1 day. After filtration and removal of the volatiles, the residue was distilled (115°C , 0.02 mbar) to give **9** (0.195 g, 74%). $^1\text{H-NMR}$: δ 0.75 (d, $^3J = 9.5$ Hz, SiMeF, 3H), 0.31 (s, SiMe, 6H), 0.31, 0.22 (2s, SiMe₃, $2 \times 18\text{H}$). $^{13}\text{C-NMR}$: δ 5.8 (d, $^2J = 12.4$ Hz, SiMeF), -11.9 (SiMe), 0.7, 0.5 (SiMe₃). $^{29}\text{Si-NMR}$: δ 54.3 (d, $^1J = 331.5$ Hz, SiMeF), -80.9 (SiMe), -11.5 , -12.8 (SiMe₃). $^{19}\text{F-NMR}$: δ -182.2 (SiMeF). MS: (CI) m/z (%) = 441 (10) [$\text{M}^+ + 1$], 425 (50) [$\text{M}^+ - \text{Me}$]. HRMS: Calc. for $\text{C}_{15}\text{H}_{45}\text{FSi}_7$ 440.18428. Found:

440.18903. Anal. Calc. for $C_{15}H_{45}FSi_7$ (441.120): C, 40.84; H, 10.28. Found: C, 40.26; H, 10.39%.

3.8. 3-Hydroxy-1,1,1,2,3,4,5,5,5-nonamethyl-2,4-bis(trimethylsilyl)pentasilane (10)

Sulfuric acid (15 ml of 10%) was added to a solution of compound **6** (0.3 g, 0.6 mmol) in tetrahydrofuran (30 ml) and the mixture was vigorously stirred for 1 day at r.t. After addition of diethylether the organic phase was separated, dried with $MgSO_4$, and evaporated. The oily residue was distilled (120°C, 0.005 mbar) to give **10** (0.241 g, 92%). IR (Nujol) $\tilde{\nu}$ = 3672 cm^{-1} (OH). 1H -NMR: δ 0.65 (s, SiMeOH, 3H), 0.53 (s, OH, 1H), 0.28 (s, SiMe, 6H), 0.29, 0.24 (2s, SiMe₃, 2 × 18H). ^{13}C -NMR: δ 6.7 (SiMeOH), –11.6 (SiMe), 0.9 (SiMe₃). ^{29}Si -NMR: δ 26.1 (SiMeOH), –81.5 (SiMe), –11.9, –12.8 (SiMe₃). MS: (70 eV) m/z (%) = 438 (2) [M^+], 365 (10) [M^+ – SiMe₃], 348 (100) [M^+ – HOSiMe₃]. Anal. Calc. for $C_{15}H_{46}OSi_7$ (439.134): C, 41.03; H, 10.56. Found: C, 40.73; H, 10.38%.

3.9. 1,1,1,2,3,4,5,5,5-Nonamethyl-3-[1',2',2',2'-tetramethyl-1'-(trimethylsilyl)disilanyl]-2,4-bis(trimethylsilyl)pentasilane (11)

Trichloromethylsilane (1.18 ml, 10 mmol) was added at –78°C to a solution of methyl-bis(trimethylsilyl)silyllithium (33 mmol) in pentane (100 ml). Stirring was continued for 1 h, and the mixture was allowed to warm to r.t. within 2 h. After filtration and removal of the solvent under reduced pressure, the solid residue was recrystallized from acetone to give **11** (4.64 g, 76%). The spectroscopic data obtained were in full agreement with those reported [14].

3.10. 1,1,1,2,4,5,5,5-Octamethyl-3-[1',2',2',2'-tetramethyl-1'-(trimethylsilyl)disilanyl]-2,4-bis(trimethylsilyl)pentasilane (12)

Trichlorosilane (1.01 ml, 10 mmol) was added at –78°C to a solution of methyl-bis(trimethylsilyl)silyllithium (33 mmol) in pentane (100 ml). Stirring was continued for 1 h, and the mixture was allowed to warm to r.t. within 2 h. After filtration and removal of the solvent under reduced pressure at 20°C, the solid residue was suspended with cold acetone and filtered off, yield 4.01 g (67%). M.p. 165–167°C. IR (Nujol) $\tilde{\nu}$ = 2016.7 cm^{-1} (SiH). 1H -NMR: δ 3.53 (s, SiH, 1H), 0.39 (s, SiMe, 9H), 0.31 (s, SiMe₃, 54H). ^{13}C -NMR: δ –6.1 (SiMe), –0.7 (SiMe₃). ^{29}Si -NMR: δ –11.7 (SiMe₃), –80.8 (SiMe), –111.4 (d, 1J = 147 Hz, SiH). MS: (CI) m/z (%) = 597 (15) [M^+ + 1], 523 (30) [M^+ – SiMe₃], 507 (55) [M^+ – Me – HSiMe₃], 406 (100) [M^+ – HMeSi(SiMe₃)₂]. Anal. Calc. for $C_{21}H_{64}Si_{10}$ (597.60): C, 42.21; H, 10.79. Found: C, 41.89; H, 10.59%.

3.11. 3-Bromo-1,1,1,2,4,5,5,5-octamethyl-3-[1',2',2',2'-tetramethyl-1'-(trimethylsilyl)disilanyl]-2,4-bis(trimethylsilyl)pentasilane (13)

A mixture of compound **12** (3 g, 5.02 mmol) and $CHBr_3$ (20 ml) was heated to 80°C for 10 days. After removal of the volatiles, the solid residue was recrystallized twice from acetone to give **13** (1.02 g, 30%). M.p. 164°C. 1H -NMR: δ 0.51 (s, SiMe, 9H), 0.36 (s, SiMe₃, 54H). ^{13}C -NMR: δ 1.9 (SiMe₃), –5.9 (SiMe). ^{29}Si -NMR: δ 12.3 (SiBr), –9.8 (SiMe₃), –68.7 (SiMe). MS: (CI) m/z (%) = 660 (30) [M^+ – Me], 595 (100) [M^+ – Br], 406 (95) [M^+ – BrMeSi(SiMe₃)₂]. HRMS: Calc. for $C_{20}H_{60}BrSi_{10}$ 659.1466. 659.1571. Anal. Calc. for $C_{21}H_{63}BrSi_{10}$ (676.49): C, 37.29; H, 9.38. Found: C, 35.64; H, 9.05%.

3.12. 3-Chloro-1,1,1,2,4,5,5,5-octamethyl-3-[1',2',2',2'-tetramethyl-1'-(trimethylsilyl)disilanyl]-2,4-bis(trimethylsilyl)pentasilane (14)

Concentrated HCl (20 ml) was added to a solution of compound **13** (0.1 g, 0.16 mmol) in diethylether (30 ml). The mixture was vigorously stirred for 7 days at r.t. The organic phase was separated, dried with $MgSO_4$, and evaporated. The solid residue was recrystallized from acetone to give **14** (0.085 g, 90%). M.p. 189°C. 1H -NMR: δ 0.5 (s, SiMe, 9H), 0.35 (s, SiMe₃, 54H). ^{13}C -NMR: δ 1.6 (SiMe₃), –6.6 (SiMe). ^{29}Si -NMR: δ 27.9 (SiCl), –10.6 (SiMe₃), –67.1 (SiMe). MS: (CI) m/z (%) = 629 (5) [M^+ – H], 615 (30) [M^+ – Me], 595 (54) [M^+ – Cl], 406 (100) [M^+ – ClMeSi(SiMe₃)₂]. HRMS: Calc. for $C_{20}H_{60}ClSi_{10}$ 615.1972. Found: 615.20764. Anal. Calc. for $C_{21}H_{63}ClSi_{10}$ (632.04): C, 39.91; H, 10.05. Found: C, 37.13; H, 9.85%.

3.13. 3-Fluoro-1,1,1,2,4,5,5,5-octamethyl-3-[1',2',2',2'-tetramethyl-1'-(trimethylsilyl)disilanyl]-2,4-bis(trimethylsilyl)pentasilane (15)

HF (20 ml of 40%) was added to a solution of compound **13** (0.1 g, 0.16 mmol) in ether (30 ml). The mixture was vigorously stirred for 4 days at r.t. After addition of 100 ml of water the organic phase was separated, dried with $MgSO_4$, and evaporated. The solid residue was recrystallized from acetone to give **14** (0.082, g 90%). M.p. 184–185°C. 1H -NMR: δ 0.50 (s, SiMe, 9H), 0.32 (s, SiMe₃, 54H). ^{13}C -NMR: δ 1.2 (SiMe₃), –7.3 (SiMe). ^{29}Si -NMR: δ 74.8 (d, 1J = 339.4 Hz, SiF), –11.4 (SiMe₃), –73.2 (SiMe). ^{19}F -NMR: δ –204.4 (SiMeF). MS: (CI) m/z (%) = 613 (4) [M^+ – H], 599 (55) [M^+ – Me], 425 (100) [M^+ – MeSi(SiMe₃)₂], 406 (40) [M^+ – MeFSi(SiMe₃)₂]. HRMS: Calc. for $C_{20}H_{60}FSi_{10}$ 599.24451. Found: 599.23718. Anal. Calc. for $C_{21}H_{63}FSi_{10}$ (615.59): C, 40.97; H, 10.32. Found: C, 37.76; H, 10.14%.

3.14. 3-Hydroxy-1,1,1,2,4,5,5,5-octamethyl-3-[1',2',2',2'-tetramethyl-1'-(trimethylsilyl)disilanyl]-2,4-bis(trimethylsilyl)pentasilane (16)

Sulfuric acid (15 ml of 10%) was added to a solution of compound **13** (0.1 g, 0.15 mmol) in tetrahydrofuran (30 ml) and the mixture was vigorously stirred for 1 day at r.t. After the usual workup, the solid residue was recrystallized from acetone to give **16** (0.083 g, 92%). M.p. 180°C. IR (Nujol) $\tilde{\nu}$ = 3654 cm^{-1} (OH). $^1\text{H-NMR}$: δ 0.49 (s, SiMe, 9H), 0.33 (s, SiMe₃, 54H). $^{13}\text{C-NMR}$: δ 1.5 (SiMe₃), –7.1 (SiMe). $^{29}\text{Si-NMR}$: δ 37.6 (SiOH), –11.7 (SiMe₃), –73.2 (SiMe), MS: (CI) m/z (%) = 612 (6) [M^+], 595 (99) [$\text{M}^+ - \text{OH}$], 423 (100) [$\text{M}^+ - \text{MeSi}(\text{SiMe}_3)_2$]. HRMS: Calc. for $\text{C}_{21}\text{H}_{64}\text{OSi}_{10}$ 612.2666. Found: 612.26501. Anal. Calc. for $\text{C}_{21}\text{H}_{64}\text{OSi}_{10}$ (613.60): C, 41.11; H, 10.51. Found: C, 39.47; H, 10.38%.

3.15. Crystal structure determination of 12, 14, 15 and 16

The crystal structure determinations were performed on a STOE-IPDS diffractometer with graphite monochromated Mo–K α radiation. The structures were solved by direct methods (SHELXS-86) [40] and refined by full matrix least-squares techniques against F^2 (SHELXL-93) [41]. The position of the central hydrogen atom (H1) in compound **12** could be elucidated from

the difference map. XP (Siemens Analytical X-ray Instruments) was used for structure representations (for full crystallographic data see Table 5).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134653 for compound **12**, no. 134651 for compound **14**, no. 134650 for compound **15** and no. 134652 for **16**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 5
Summary of crystal and structure solution data of **12**, **14**, **15** and **16**

	12	14	15	16
Formula	$\text{C}_{21}\text{H}_{64}\text{Si}_{10}$	$\text{C}_{21}\text{H}_{63}\text{ClSi}_{10}$	$\text{C}_{21}\text{H}_{63}\text{FSi}_{10}$	$\text{C}_{21}\text{H}_{64}\text{OSi}_{10}$
Formula weight (g mol^{-1})	597.62	632.065	615.61	613.62
<i>a</i> (Å)	20.236(4)	18.154(4)	20.283(4)	20.339(4)
<i>b</i> (Å)	12.012(2)	12.101(2)	12.015(2)	12.053(2)
<i>c</i> (Å)	19.174(4)	19.061(4)	19.139(4)	19.064(4)
α (°)	90.00	90.00	90.00	90.00
β (°)	117.43(3)	90.42(3)	117.32(3)	117.31(3)
γ (°)	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	4136.7(14)	4187.2(14)	4143.9(14)	4152.5(14)
<i>D</i> (g cm^{-3})	0.960	1.003	0.987	0.982
<i>Z</i>	4	4	4	4
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
μ (Mo–K α) (mm^{-1})	0.327	0.388	0.331	0.329
Crystal size (mm)	$0.5 \times 0.3 \times 0.2$	$0.3 \times 0.3 \times 0.2$	$0.2 \times 0.3 \times 0.4$	$0.3 \times 0.3 \times 0.2$
Temperature (°C)	293(2)	293(2)	293(2)	293(2)
Scan range (2θ) (°)	2.04–24.38	1.99–21.99	2.20–20.00	2.03–24.26
<i>hkl</i> Range	–23/0, –13/13, –19/21	–20/20, –13/13, 0/21	0/23, –13/13, –22/19	–23/0, –13/13, –18/20
Measured reflections	12167	9504	11964	12078
Unique reflections	6555	5131	6567	6253
Observed reflections	3556	3568	2352	3595
Refined parameters	284	289	289	293
R_1 [$I > 2\sigma(I)$]	0.044	0.036	0.043	0.039
R_2 for all	0.105	0.060	0.155	0.079
Goodness-of-fit	0.855/1.024	0.859/0.983	0.601/0.864	0.794/0.985

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