Structurally and conformationally defined small methyl polysilanes

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Possessing the property of σ-bond electron delocalisation, polysilanes are a class of compounds with unique properties. In recent years major progress has been achieved in the theoretical understanding and the synthesis of polysilanes. Much insight into the connection between conformation and electronic properties has been gained from studies of defined small polysilane molecules. The transition from Wurtz type coupling reactions to the stepwise construction of polysilane molecules employing silyl anions as key intermediates has permitted access to defined compounds with a higher degree of structural complexity. Besides this, several methods have been developed to control the conformational properties and thus gain control over the electronic properties of polysilanes.

1 Introduction

Over the last few decades polysilanes have emerged as an important class of inorganic polymers.[1,2] Catenated silicon atoms can be regarded as one-dimensional sub-structures of the silicon crystal lattice. As silicon is the single most important element for the microelectronic technology, the question if the properties of polysilanes resemble those of bulk silicon was raised early. The fact that polysilane electrical conductivity could be enhanced by orders of magnitude by doping with certain oxidants seemed to provide support for this assumption.[3] The last few years have seen several advances both in the theoretical understanding and the synthesis of polysilanes.

While hexaethyldisilane, the first known compound containing a silicon–silicon bond, was prepared as early as 1869,[4] the systematic investigation of the chemistry of polysilanes was only started after WWII.[5,6] The research groups of Gilman and Kumada and later West and Hengge have carried out much of the fundamental synthetic research on polysilanes. During the 1960s the UV absorption of polysilanes *via* the catenated silicon framework was discovered.[6,7] This effect was later assigned to σ–σ* transitions of the polysilane chain. As a bathochromic shift of absorption was observed on elongation of the chain, a delocalisation of σ-bond electrons, similar to the extended delocalisation in the π-systems of polyenes, was presumed. This assumption was consistent with compiled data from oligo- and polysilanes, indicating that different conformations of polysilanes contribute differently to the absorption characteristics. Theoretical considerations suggested that *trans*-segments in the chain (with a dihedral angle around 180°) would promote extended delocalisation, while *gauche*-conformations were attributed to disrupture of the conjugation.[8]

As Si–Si bond distances in polysilanes are relatively long, rotational processes are comparatively facile. Therefore, several energetically similar but different conformations are usually present at ambient temperature and contribute to the UV absorption spectrum, resulting in broad bands. Conformations containing longer segments of all-*trans* type arrangements are favored at lower temperatures and thermochromic properties with bathochromic shifts with decreasing temperature were observed.[9]

Recently, the matter of conformational dependence of σ-bond conjugation was studied both theoretically and experimentally with new efforts. Theoretical results, especially from Michl's group, indicated that the conformational behaviour of polymers consisting of saturated chains in general may not necessarily resemble that of alkanes.[10] The fact that the substituents in polysilanes usually are large compared to hydrogen atoms in *n*-alkanes introduces steric interactions between these substituents, which are not present in *n*-alkanes. Repulsive interactions between substituents on silicon atoms in 1,3-position cause the alkane-like *trans*-conformation (which would be described as *anti*-conformation in the improved terminology) to become a transition state in polysilanes and to split into two conformational minima at approximate dihedral angles of ±165° (termed *transoid*). Similar interactions between substituents in 1,4-position split the alkane *gauche*-conformations into four minima at ±55° (*gauche*) and ±90° (*ortho*). By theoretical and experimental methods it was shown that decamethyltetrasilane nicely conforms to this model and exhibits conformational minima at 53° (*gauche*), 91° (*ortho*) and 162° (*transoid*).[11] By introduction of larger substituents than methyl, additional interactions may occur and new minima around ±150° (*deviant*) and ±40° (*cisoid*) can arise (Fig. 1).[12,13] The requirement for a better description of conformational behaviour caused Michl and West to propose a general new systematic nomenclature for the conformation of linear chains (Fig. 1).[14]

One of the consequences of the different conformational behaviour of polysilanes and alkanes is that it casually explains the fact that polymeric polysilanes tend to adopt helical superstructures. This was already known from the excellent studies by Fujiki and others.[15] The introduction of chiral side chains even allowed to influence the sign of helicity of these structures.

2 Polysilane chains

In order to study the influence of conformation on the UV absorption experimentally Tsuji and Tamao have recently prepared peralkyloligosilanes with exclusive *syn*- and *anti*-conformations.[16]

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Christoph Marschner, a native of Linz, Austria, was born in 1963. He studied technical chemistry at the Technical University Graz, Austria (1983–1988), where he also carried out his PhD work (1989–1992) in synthetic organic chemistry. He was subsequently awarded a Schrödinger Post-Doctoral Research Fellowship for his work with Professor Barry M. Trost at Stanford University. After his return to the Technical University Graz he became assistant professor at the Institute of Inorganic Chemistry and started independent research on organosilicon chemistry. As an APART scholar of the Austrian Academy of Science he spent a year (1998) at the University of California, Berkeley, in the group of Professor T. Don Tilley. In 1999 he was awarded the START-prize of the Austrian government for his work on polysilanes. He finished his habilitation in 2000 and was promoted to tenured associate professor in 2001. His research interests include main group (especially Group 14) and transition metal organometallic chemistry. The main emphasis of his research over the last decade was put on silyl anion and polysilane chemistry. The discovery that polysilyl anions can be prepared under preservation of the polysilane scaffold has stimulated the study and development of polysilyl anion- and especially polysilyl dianion chemistry. The exploitation of this methodology has permitted straightforward access to many cyclic and cage-like polysilane molecules.

Judith Baumgartner studied technical chemistry at the Technical University Graz, Austria and was the first PhD student of Prof. Alois Fürstner, working on the use of activated metals for organic synthesis. She continued to work on organometallic chemistry in Graz and in 1998 spent a year as Schrödinger Post-Doctoral Research Fellow in the laboratory of Prof. Peter Vollhardt at the University of California, Berkeley, working on C–H activation employing novel organoiridium chemistry. After the birth of her third daughter in 2000 she accepted an offer to set up the single-crystal diffraction facility at the Institute of Inorganic Chemistry. Her chemical interests are currently centred on polysilanes and Group 14 derivatives of late transition metal carbonyl compounds.

Andreas Wallner was born in 1976 in the Tyrol, Austria. He studied chemistry at the Karl-Franzens University in Graz from 1996 to 2002 and graduated with a thesis on the chemo-enzymatic synthesis of natural products. Soon after he started to work on his PhD thesis with Prof. Marschner, on synthetic and spectroscopic studies of the conformations of novel oligosilanes, which he has recently finished.

Christoph Marschner

Judith Baumgartner

Andreas Wallner

This was achieved by connecting polysilanyl units with fixed conformations (Fig. 2). By such compounds with up to 22 silicon atoms in the chain, consisting of *syn*-conformational subunits, were obtained.[16b,d] The corresponding UV spectra confirmed that σ-bond conjugation is indeed interrupted by *syn*-conformational turns. Thus, absorption bands of all compounds composed of *syn*-turn units resembled those of alkylated tetrasilanes.[16b,d] In contrast to this, compounds with locked all-*anti*-conformation subunits (Fig. 2) exhibited sharp and strong absorption bands, corresponding to the low-temperature measurements of

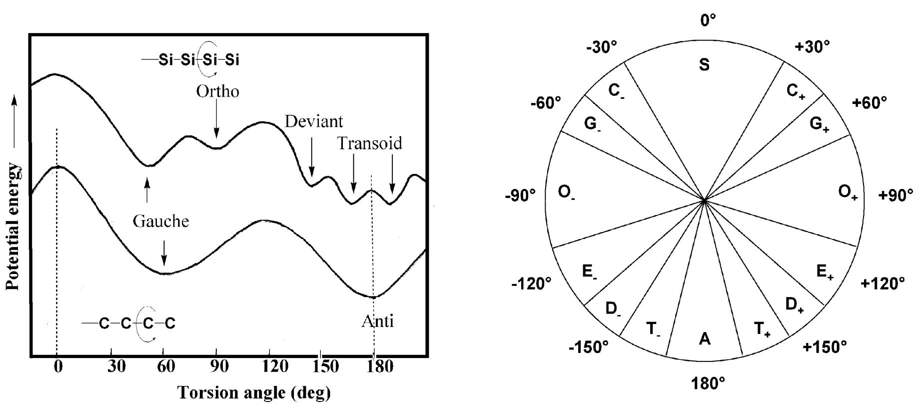


Fig. 1 Qualitative description of potential energy *vs.* dihedral angle for hydrocarbons and polysilanes (taken with permission from ref. 1*d*. Copyright John Wiley & Sons).

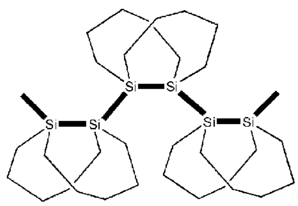
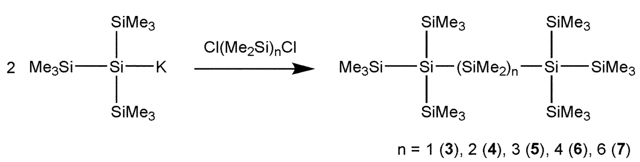


Fig. 2 Examples of polysilane chains constructed from *syn* or *anti* substructural units with locked conformations.[16]

conformationally unrestricted oligosilanes of the same chain lengths.[16a,c,e]

Another way to control the conformation of short polysilane chains was reported recently by Kira and co-workers. Previous work had shown that poly(dimethylsilane) can be used to form inclusion complexes with cyclodextrins.[17] Inclusion of *n*-permethyldecasilane was accomplished into three molecules of γ-cyclodextrin.[18] Based on the very narrow UV absorption bands of the polysilane, an all-*trans* rod-like conformation of the chain was postulated. The absorption maximum of the inclusion product was found to be 5 nm red shifted from a solution of the free chain at a temperature of 77 K. This was explained by an expected all-*anti*-conformation in the cyclodextrin compared to a mainly *transoid*-conformation at low temperature in solution.

A recent study from our laboratory showed that the use of tris(trimethylsilyl)silyl groups attached to permethylated oligosilanes (**3–7**) (Scheme 1) also exerts some conformational constraints on the chain.



Scheme 1 Synthesis of tris(trimethylsilyl)silyl terminated polymethylsilanes.

Single-crystal X-ray diffraction analyses of compounds **3–7** (Fig. 3) showed all to exhibit mainly *transoid*- and *anti*-type conformations (with dihedral angles ranging from 155 to 180°) along the main-chain in the solid state (Table 1).[19]

Compound **7** with a longest linear chain of ten silicon atoms can be seen as a small molecular model for poly(dimethylsilane). The space-filling plot depicted in Fig. 4 shows the helical arrangement along the chain.

As the conformations of the chains in the solid state are frequently dominated by packing forces, it was important to compare the conformations of crystalline samples and solutions.

Table 1 Dihedral angles along the main chain derived from the crystal structures of compounds **2–7**

Compound	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	Conformation
2	163	—	—	—	—	—	—	*T*
3	167	167	—	—	—	—	—	*TT*
4	159	180	159	—	—	—	—	*TAT*
5	161	160	167	164	—	—	—	*TTTT*
6	162	159	180	159	162	—	—	*TTATT*
7	161	168	161	155	167	164	164	*TTTTTTT*

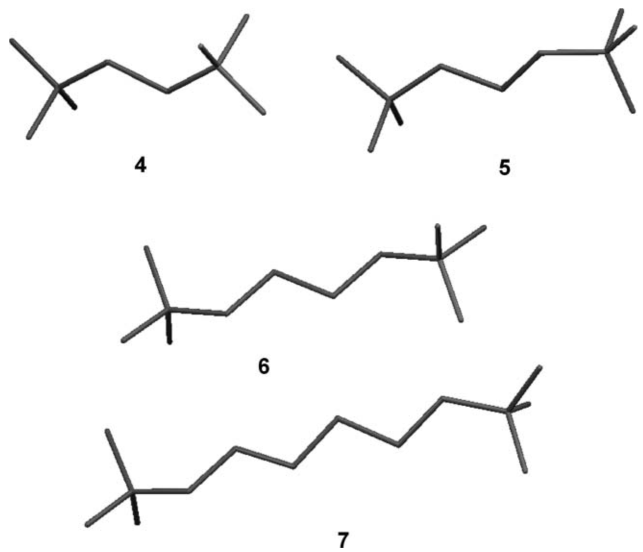


Fig. 3 Solid-state structures of the polysilane backbone of compounds **4–7**.

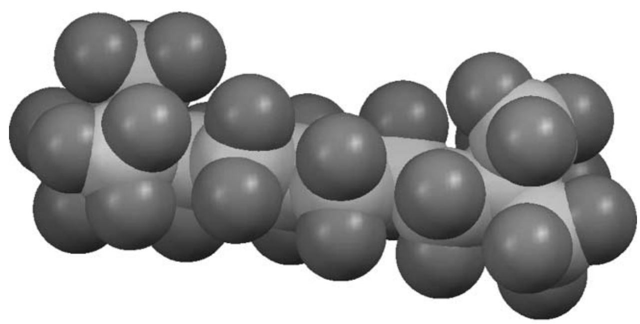


Fig. 4 Space-filling plot of the crystal structure of compound **7**, which gives an impression of the molecule's helical character (hydrogen atoms omitted for clarity).

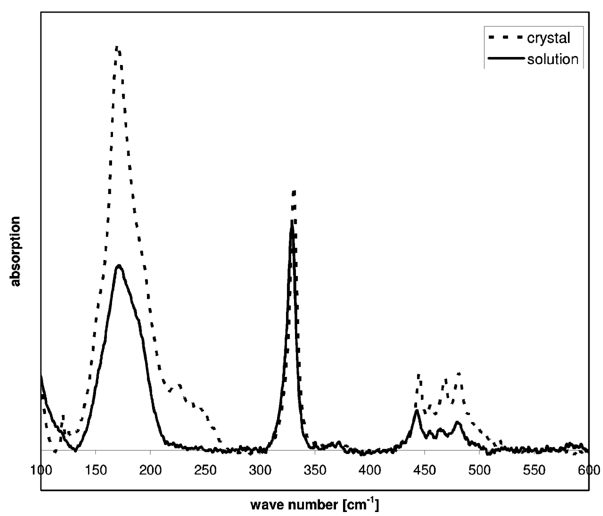


Fig. 5 Raman spectra of samples of compound **5** in solid state and in solution.

Employing Raman spectroscopy (a typical comparison of spectra in solution and the solid state is shown in Fig. 5) it was possible to confirm the same conformations in both states for compounds **3–6**.

The UV absorption spectra of compounds **3–7** also confirmed the assumption of conjugated chains. As can be seen in Fig. 6, which shows the UV spectra of compounds **1–7**, all compounds show an absorption band around 210 nm, which can be attributed to the trisilane units in the tris(trimethylsilyl)silyl group. Compounds **3–6** exhibit a second band which displays a bathochromic shift on increasing chain length. The second band is relatively narrow indicating one predominant conformation. Interestingly, for compounds **4** and **6**, larger extinction coefficients and narrower bands for the lower energy transition could be observed. While the reason for this behaviour is not completely clear yet, we assume that it is connected to the fact that compounds **4** and **6** have centres of inversion and therefore one *anti*-dihedral angle (180°).

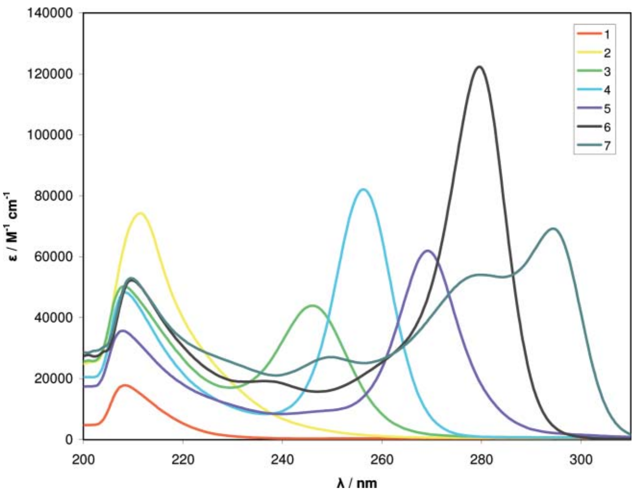


Fig. 6 UV absorption spectra of samples of **1–7** in pentane solution [$(Me_3Si)_4Si$ (**1**) and $[(Me_3Si)_3Si]_2$ (**2**)].

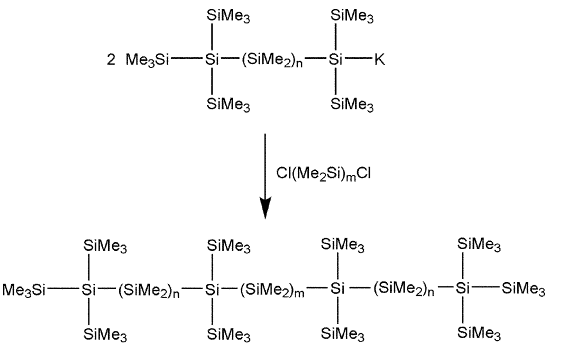
Compound **7** shows the limits of conformation control *via* bulky terminal groups. While **7** exhibits one absorption maximum at 294 nm (Fig. 6), which is further red shifted compared to **6**, it also displays additional maxima at 280 and 250 nm, which indicate the presence of other conformers with shorter conjugated segments in solution. This situation is also reflected in the different Raman spectra of **7** in solution and the solid state.

In recent studies we have established the chemistry of generating silyl anions from compounds containing tris(trimethylsilyl)silyl units.[20] This method allows also the generation of longer organosilicon chains from compounds such as **1–7** in a way similar to the synthesis of **3–7** (Scheme 2).[21]

The conformational and optical properties of these compounds are currently under investigation. As the polysilyl anion chemistry allows facile derivatisation, such compounds may be interesting building blocks for the synthesis of materials with NLO properties.

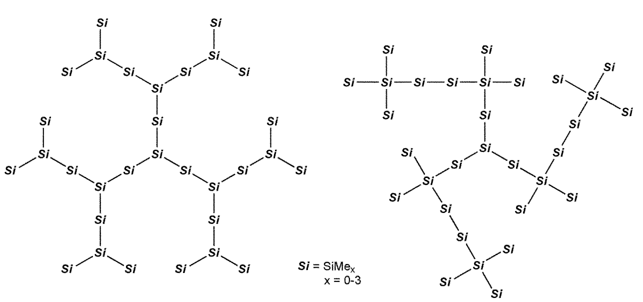
3 Polysilane dendrimers

While polysilanes are interesting materials, the silicon–silicon bonds are relatively weak and therefore prone to cleavage under a number of conceivable conditions. As the optical properties are closely connected to the chain length, cleavage of the chain is associated with a profound change of these properties. Some



Scheme 2 Synthesis of longer and partially silylated tris(trimethylsilyl)silyl terminated polymethylsilanes.

degree of structural redundancy would be able to avoid this degradation. Dendrimeric structures should provide exactly this feature. Not only would a certain chain length be present several times in the molecule, the spherical shape of dendrimers would provide additional steric protection for the inner bonds. In 1995 the groups of Lambert,[22] Sekiguchi,[23] and Suzuki[24] were the first to accomplish the syntheses of such compounds in a stepwise fashion (Scheme 3). Although the very nature of the dendrimeric structures does not allow all-*transoid*-conformers the absorption properties of these compounds are quite remarkable.[25] While the positions of the UV absorption maxima resemble those of the longest polysilane chains present in the molecule, the extinction coefficients are much higher as a function of the high redundancy. More recent synthetic approaches have concentrated on different dendrimer architectures such as double cored-structures[26] and the functionalization of the polysilane shell.[27]



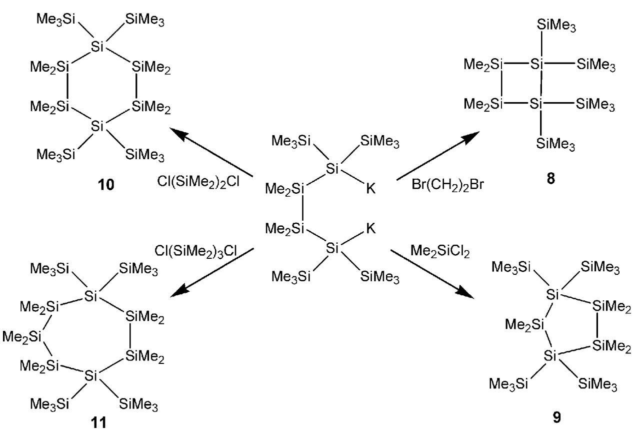
Scheme 3 Examples of dendrimeric methylpolysilanes.[22,23]

4 Cyclopolysilanes

The property of UV absorption is not confined to acyclic polysilanes. Also cyclosilanes[28] exhibit this feature. Interestingly, the smaller alkylated rings [$(R_2Si)_n$, $n = 3$–7] exhibit hypsochromic shifts with increasing ring size. With further increasing the ring size the absorption behaviour is reversed and starts to resemble that of linear compounds.[29] The properties of the smaller rings resemble those of aromatic hydrocarbons to a certain degree. They can be reduced and oxidised to form electron delocalised anion- and cation-radicals and can also form charge-transfer complexes with π-acceptors. The easier reduction of four- and five-membered rings, compared to six- and seven-membered rings, correlates with their bathochromic absorption behaviour.[29]

The most common synthetic route to cyclosilanes is again Wurtz type coupling, usually in the presence of an equilibrating catalyst. Further derivatisation, for example of dodecamethylcyclohexasilane, can be achieved under forcing chlorinating conditions to give mixtures of di- and trichlorinated products.[30] After laborious separation procedures subsequent substitution reactions provide access to derivatives with different substitution patterns.

As an alternative to the Wurtz type synthesis of cyclosilanes we have recently developed a systematic synthetic approach employing α,ω-oligosilyl dianions.[31] By the reaction of dianionic silanes containing different silanylene spacers with α,ω-dichlorosilanes the ring size of the product can be controlled conveniently. Scheme 4 shows examples of this concept starting from the readily available 1,4-dipotassiopolysilane[31a,b] derived from compound **4**. Four- to seven-membered rings (**8–11**) were synthesised this way.



Scheme 4 Synthesis of cyclopolysilanes with different ring size.

The UV spectra of these rings show a subsequent red shift of the absorption maxima with increasing ring size (Fig. 7). Compounds **10** and **11** exhibit two absorptions in addition to the strong bands around 210 nm, which are typical for trisilane units. It is interesting to note that the seven membered-ring **11**, which due to its cyclic nature should not be able to adopt an all-*transoid*-

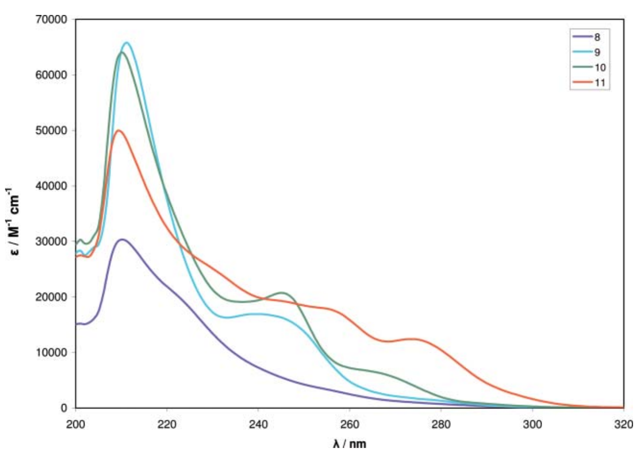


Fig. 7 UV absorption spectra of samples of cyclosilanes **8–11** in pentane solution.

conformation, nevertheless absorbs in the same region as does the linear heptasilane **5**. This behaviour is somewhat similar to what was observed for polysilane dendrimers.

The trimethylsilyl groups attached to the cyclosilanes can again be used for further functionalisation by intermediate conversion to a silyl anion and subsequent derivatisation (see below). However, these silyl groups also serve as to enforce specific conformations. 1,1,4,4-Tetrakis(trimethylsilyl)octamethylcyclohexasilane (**10**) is a good example for this. While most cyclohexasilanes studied so far feature a *chair*-conformation,[32] as in cyclohexane, this particular compound exhibits a *twist*-conformation (Fig. 8). For cyclohexasilanes this conformation is more easily accessible than for cyclohexanes.[33] Interestingly, the *twist*-conformation is not only present in the solid state as indicated by the crystal structure analysis but also in solution as shown by Raman spectroscopic investigation.[34] Nevertheless, the preference for a specific conformation is subtle. The change of two trimethylsilyl groups in 1,4-*trans*-position for *tert*-butyldimethylsilyl groups re-establishes the *chair*-conformation, while after the change of one trimethylsilyl group for a methyl group the *twist*-conformation is still maintained.[21a] Changing the positions of the trimethylsilyl substituents in the cyclohexasilane also changes the conformation. 1,1,3,3-Tetrakis(trimethylsilyl)octamethylcyclohexasilane now exhibits an example of a *twisted*-*boat*-conformation in the solid state.[34]

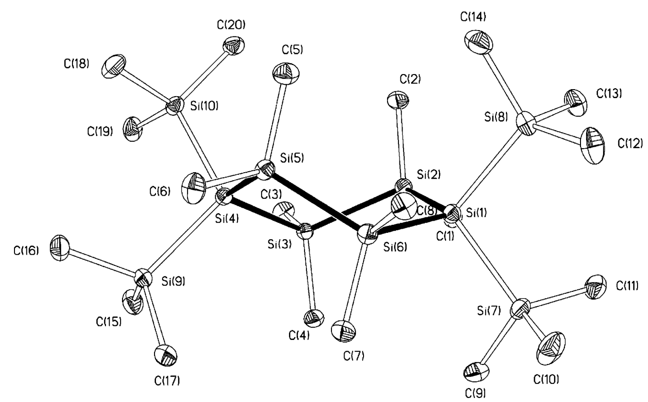


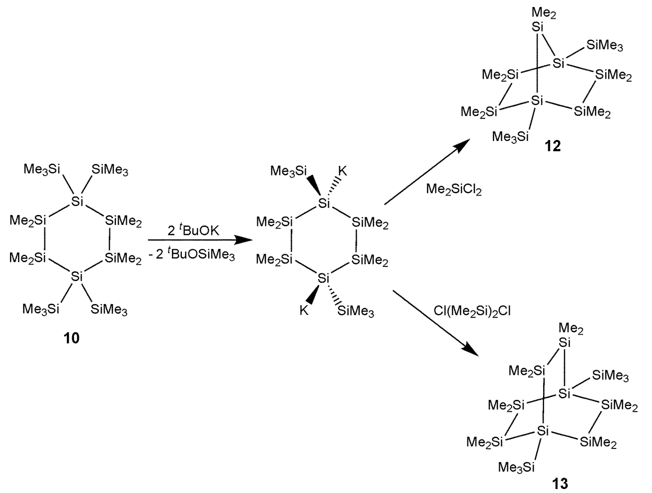
Fig. 8 Crystal structure of **10** exhibiting the cyclohexasilane in a *twist*-conformation.

5 Cage and cluster polysilanes

Bi- and polycyclic polysilanes are also of considerable interest.[35] However, also for this class of compounds examples consisting of only one structural element are most abundant: for compounds of the type: $(RSi)_n$ examples of tetrahedranes ($n = 4$),[36] prismanes ($n = 6$)[37] and cubanes ($n = 8$)[38] are known. These compounds were obtained in one-pot or stepwise Wurtz type reactions.

While the syntheses of cyclosilanes with mixtures of different disubstituted silyl dihalides (R_2SiX_2) work at least reasonably well to give cyclic compounds of the type $(R_2Si)_nSiR'_2$, attempts to obtain bicyclic compounds from Wurtz-type reaction of mixtures of Me_2SiCl_2 and $MeSiCl_3$ gave the expected bicyclic polysilanes as isomeric mixtures in disappointingly low yields, accompanied by large amounts of homocyclic compounds.[39,40] In order to reduce the number of bonds which have to be formed in such a reaction Kira *et al.* have coupled two equivalents of tris(chlorodimethylsilyl)methylsilane with alkali metal and obtained the [2.2.2]bicyclooctasilane in 19% yield.[41]

In a more general approach to bicyclic polysilanes we could employ trimethylsilyl substituted cyclosilanes such as **10**. The same procedure as described above for the synthesis of **8–11** allows to convert the cyclosilanes into cyclic dianions. Reaction with α,ω-dichlorosilanes affords the selective formation of bicyclosilanes (Scheme 5) in very good yields.[21,42]

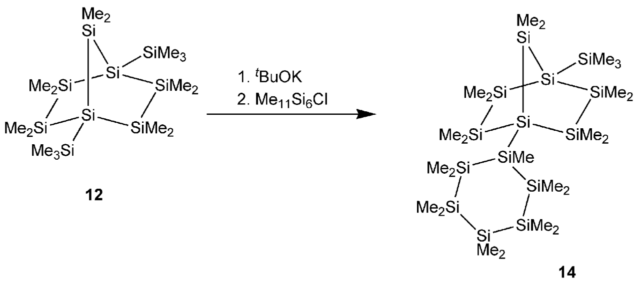


Scheme 5 Synthesis of bicyclic methylpolysilanes from a cyclopolysilanyl dianion.

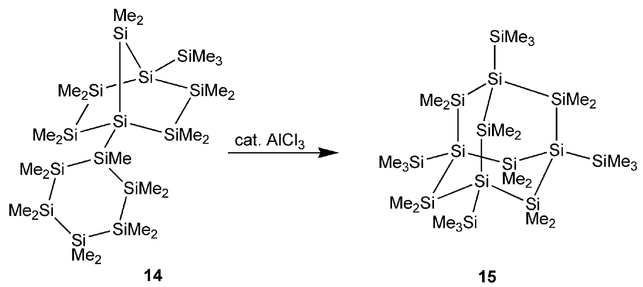
A particularly interesting polycyclic polysilane structure would be a molecule with the adamantane structure. The reason for this is the fact that elemental silicon itself crystallises in the diamond structure. A sila-adamantane molecule would therefore be a substructure of elemental silicon. A number of silicon containing adamantanes have already been prepared,[27,43,44] but the all-silicon skeleton molecule remained elusive for some while. Our initial attempts to obtain such a compound employing a trianionic cyclohexasilane in the reaction with a trichloroisotetrasilane failed due to the problems to obtain the required 1,3,5-trianionic cyclohexasilane. Eventually the problem was solved in a way which is surprisingly similar to von Schleyer's original adamantane synthesis.[45] As the Lewis-acid catalysed rearrangement of acyclic and cyclic polysilanes has been discovered by Ishikawa and Kumada[46] almost 40 years ago, we thought about the synthesis of an isomer of a sila-adamantane. One of the driving forces for the rearrangement of polysilanes is the formation of highly silylated silicon atoms.[47] We therefore expected that a sila-adamantane which is silylated at the bridgehead atoms would have a higher tendency to form. The primary task to test our hypothesis was to synthesise as tricyclic molecule containing 14 silicon atoms. Employing once again polysilyl potassium chemistry this was accomplished by the bridgehead metalation of [2.2.1]bicycloheptasilane **12** and subsequent reaction with undecamethylcyclohexasilanyl chloride (Scheme 6).

The obtained compound **14** eventually underwent the aluminium trichloride catalysed rearrangement to the expected molecule with sila-adamantane scaffold (**15**) (Scheme 7).[48]

The crystal structure analysis of **15** (Fig. 9) confirmed the expected rhombohedral structure. It should be noted that the



Scheme 6 Synthesis of sila-adamantane isomer (**14**).



Scheme 7 Lewis acid catalysed isomerisation to sila-adamantane (**15**).

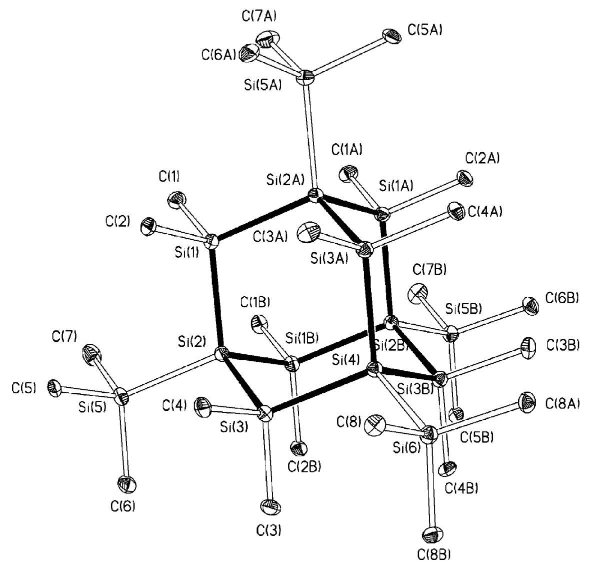


Fig. 9 Crystal structure of sila-adamantane **15**.

compound comprises exactly the structural elements which are required to convert it to a silyl anion, which can be used for the synthesis of derivatives of **15**. The construction of higher clusters in a way as outlined above is currently under way.

6 Conclusions and outlook

While research on polysilane polymers has flourished over recent decades the interest in small molecule polysilane chemistry has grown again only in recent years after some time of stagnation. Both, the theoretical understanding of the phenomenon of σ-bond electron delocalisation and the synthetic accessibility have been improved considerably.

The thorough analysis of the conformational properties of polysilanes has helped to better understand the behaviour of polymers in general. The simplistic picture of conformation, derived from the analysis of alkanes has therefore been amended.

With the many attempts to develop molecular electronic devices, the synthesis of tailor-made polysilane (and also polygermane and polystannane) structures and especially cluster molecules has become an attractive field of research. The development of polysilyl[20,31] (and polygermyl[49] and polystannyl[50]) anion chemistry allows to overcome many of the problems associated with the Wurtz type coupling synthetic methods. This way extended polysilane structures with well defined conformational properties and with the possibility of easy functionalisation have become accessible. Investigations concerning the use of these compounds as molecular wires or rectifiers are currently in progress.

Using a combination of crystal structure analysis and Raman spectroscopy it was found that conformations of small methylated polysilanes with bulky terminal groups are frequently the same in the solid state and in solution. This seems to be in part a consequence of the fact that these molecules can be considered as polysilane backbones with alkyl shells. The low polarity of the compounds therefore does not allow for much intermolecular interaction (even in the solid state) besides van der Waals forces. This behaviour leads to the conclusion that compounds such as the ones described may be used as model substances for the study of interactions of alkanes of different shapes in the solid state.

Acknowledgements

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