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Cyclic and Bicyclic Methylpolysilanes and Some Oligosilanylene-Bridged Derivatives

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A number of novel cyclo- and bicyclosilanes connected by linear silanylene chains have been prepared and characterized by X-ray crystallography and NMR spectroscopy. The UV absorption properties of all compounds were studied and found to show low-energy absorption maxima red-shifted compared to acyclic compounds with comparable chain lengths. Synthesis of the new polysilanes was accomplished using silyl anions as key intermediates, which allow a stepwise controlled setup.

Introduction

The chemistry of cyclopolysilanes started with Kipping's work on phenylated rings in the early 1920s,[1] but it took almost another thirty years before the first permethylated cyclohexasilane was described.[2] Even today, the initial synthetic approach used for cyclosilane preparation, the Wurtz-type coupling of dihalosilanes with alkali metals, is still often the preferred method. Wurtz-type conditions were also investigated with respect to their potential for the cross coupling of diorganodichlorosilanes and organotrichlorosilanes to obtain bicyclic oligosilanes. Nevertheless, this preparative method suffers from some serious drawbacks such as the harsh conditions, which permit only starting materials with very robust substituents (usually alkyl and aryl groups), the sometimes disappointingly low yields,[3] and the limitation to certain ring sizes, depending on the steric properties of the substituents. We and Kira's group have recently reported on the syntheses of cyclic and also bicyclic polysilanes[4] by a stepwise construction approach, using dianionic polysilanes.[5] Not only does this method permit an easy and direct entry to cyclopolysilanes of different ring sizes in excellent yields, it also facilitates straightforward, further derivatization of the molecules.

The main interest in polysilanes stems from their unique properties due to electron delocalization in their σ-bond scaffold, which is not confined to acyclic polysilanes.[6] The UV absorption properties of polysilanes via the catenated silicon framework were discovered in the 1960s.[7] The phenomenon of a bathochromic shift behavior with increasing chain length was explained as $\sigma{-}\sigma^*$ transitions of the polysilane chain and was found to be strongly dependent on the Si−Si backbone conformation.[8] Thus, the thermochromic behavior of the UV absorption bands in polysilanes[9] can be explained as change of conformation in the backbone. It is the common understanding today that *anti*-conformational

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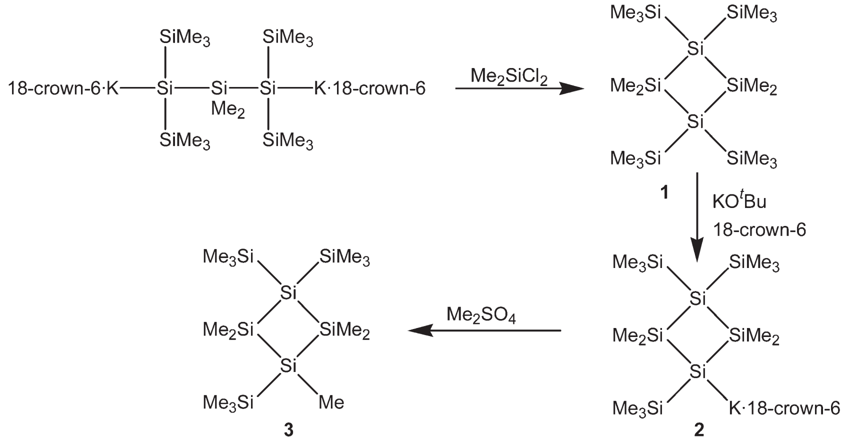
Scheme 1. Synthesis of Cyclotetrasilane Compounds 1, 2, and 3



units of polysilanes extend the σ-conjugated system and afford the first absorption maximum at longer wavelengths, while *syn*-conformational units lead to rupture of the conjugation and afford the first absorption maximum at shorter wavelengths.[10] Theoretical studies, especially from Michl's group, pointed out that the conformational behavior of linear alkanes is different from saturated chain polymers in general.[11] For an improved description of conformational behavior Michl and West proposed a new systematic nomenclature.[12]

In more recent times several attempts were made to control the conformational properties of polysilanes. The applied strategies range from the introduction of chiral side-chains[13] to the incorporation of the polysilane into a rigid framework,[14,15] and from the inclusion of alkylated polysilanes into cyclodextrines[16] to the use of pentacoordination of silicon atoms.[17] Work from our group[18,19] and others[20] featured the use of bulky end-groups such as the tris(trimethylsilyl)silyl unit in order to align methylated polysilane chains.

A recently published study showed that the UV absorption behavior of partially trimethylsilyl substituted methylcyclosilanes is considerably different from that of the permethylated cyclosilanes of the same ring size. To some extent it seems as if the permethylated silanylene segments between the trimethylsilyl attachment points behave like acyclic *transoid*-oriented chains.[4c] The current study is therefore concerned with the intention to study molecules containing cyclic or even bicyclic oligosilane units but also polysilanylene chains of different length, which can serve as connections between the cyclosilanes.

Results and Discussion

Synthesis of New Cyclosilanes. Some years ago we prepared four-membered heterocyclosilanes starting from 1,1,3,3-tetrakis(trimethylsilyl)-1,3-dipotassiodimethyltrisilane.[5b] With the same 1,3-dianion also the formation of cyclotetrasilane **1** was possible by treatment with dichlorodimethylsilane (Scheme 1). The treatment of **1** with 1 equiv of potassium *tert*-butoxide provided the respective anionic compound **2** in a clean reaction.[5b] Further derivatization to compounds such as **3** is thus easily possible (Scheme 1). Attempts to convert **1** to the respective dianionic compound by reaction with 2 equiv of potassium *tert*-butoxide in the presence of crown ether were not successful. Also the reaction of **3** with 1 equiv of potassium *tert*-butoxide failed. In both cases mixtures of acyclic compounds together with traces of the expected materials were observed. Related ring-opening behavior was observed before in the reaction of 1,1,2,2-tetrakis(trimethylsilyl)tetramethylcyclotetrasilane with potassium *tert*-butoxide.[5b]

Recently, we synthesized a series of octamethylcyclohexasilanes containing two bis(trimethylsilyl)silylene units in either 1,2,[21] 1,3,[21] or 1,4[4a] orientation. The synthesis of a cyclohexasilane with three bis(trimethylsilyl)silylenes in 1,3,5 orientation was another goal. This compound was already reported by Blinka and West as the product of Al(Fe)Cl$_3$-catalyzed rearrangement of permethylated cyclododecasilane.[22] Our own attempts to obtain the compound by a related reaction from an isomeric starting material revealed that this process exclusively leads to cyclopentasilanes.[23] We therefore decided to obtain

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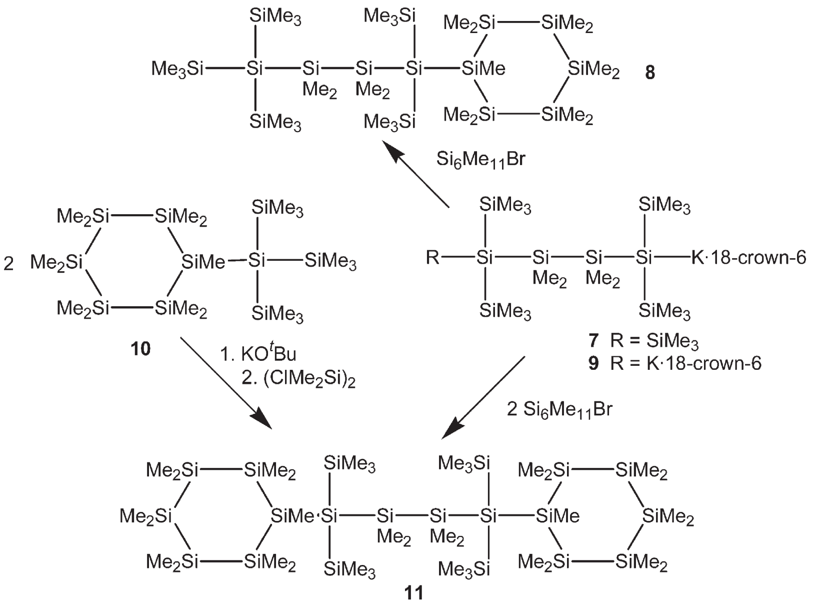
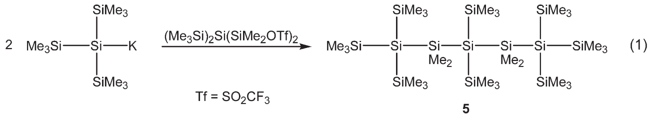
Scheme 2. Synthesis of Undecamethylcyclohexasilanyl-Containing Compounds 8 and 11

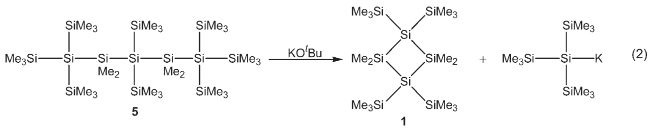


the compound utilizing oligosilanyl dianion chemistry. The initial idea was to obtain the compound by reaction of a suitable 1,5-dianionic precursor with dichlorodimethylsilane. The thus required synthesis of 1,1,1,3,3,5,5,5-octakis(trimethylsilyl)tetramethylpentasilane (**5**) was achieved by reaction of 2 equiv of tris(trimethylsilyl)silylpotassium with bis(trifluoromethylsulfonyloxydimethylsilyl)bis(trimethylsilyl)silane (eq 1). The latter was obtained from the reaction of bis(trimethylsilyl)bis(phenyldimethylsilyl)silane (**4**) with 2 equiv of triflic acid.



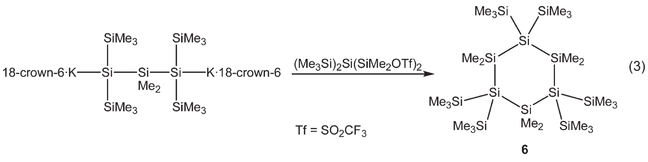
(1)

While it was possible to obtain a 1,5-dipotassium compound starting from 1,1,1,5,5,5-hexakis(trimethylsilyl)hexamethylpentasilane,[5a] the reaction of **5** with even 1 equiv of potassium *tert*-butoxide led to the formation of **1** and tris(trimethylsilyl)silylpotassium (eq 2). A similar back-biting process was observed before in the reaction of 1,1,1,6,6,6-hexakis(trimethylsilyl)octamethylhexasilane with potassium *tert*-butoxide, which led to the formation of 1,1-bis(trimethylsilyl)octamethylcyclopentasilane.[24]



(2)

A change of strategy, employing the ditriflate-neopentasilane building block that was used for the synthesis of **5**, allowed the synthesis of **6** utilizing 1,1,3,3-tetrakis(trimethylsilyl)-1,3-dipotassiodimethyltrisilane (eq 3). While the identity of **6** was confirmed unambiguously by single-crystal structure analysis, its ^1H and ^{29}Si NMR spectroscopic properties are not in agreement with reported data.[22] This provided final proof that **6** was not formed by Al(Fe)Cl_3-catalyzed rearrangement of permethylated cyclododecasilane.[22]



(3)

Attempts to convert **6** to the respective oligosilyl anions by reaction with potassium *tert*-butoxide revealed that these reactions are not clean. It was possible to obtain the monoanion, which slowly undergoes a back-biting process. Attempts to achieve formation of a dianion by addition of 2 equiv of potassium *tert*-butoxide and 18-crown-6 failed. This failure is somewhat surprising considering the fact that the formation of dianions was easily possible with 1,1,3,3- and 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilanes.[4a,c]

Synthesis of Connected Ring Systems. With a number of cyclo- and bicyclosilane building blocks in hand we set out to prepare a number of oligosilane compounds containing both cyclic and acyclic structure elements. The selective formation of polysilanyl mono- and dianions enabled the stepwise synthesis of well-defined oligosilanes.[25]

Reaction of the monopotassium compound **7**, which was obtained from 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane (**16**), with undecamethylcyclohexasilanyl bromide led to the formation of 1,1,4,4,4-pentakis(trimethylsilyl)-1-undecamethylcyclohexasilanyltetramethyltetrasilane (**8**) (Scheme 2). In a similar way the reaction of the 1,4-dipotassium compound **9** with 2 equiv of undecamethylcyclohexasilanyl bromide gave 1,1,4,4-tetrakis(trimethylsilyl)-1,4-bis(undecamethylcyclohexasilanyl)-2,2,3,3-tetramethyltetrasilane (**11**) (Scheme 2). An alternative (slightly lower yielding) route to **11** arose from the coupling of 2 equiv of the monopotassium compound derived from **10**[4a] with dichlorotetramethyldisilane (Scheme 2).

Reactions of 2 equiv of the monopotassium derivative of **12** with 1,2-, 1,4-, or 1,6-dichloropermethylsilanes gave the di-,

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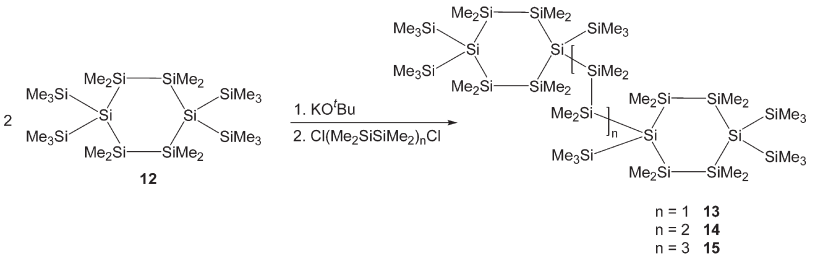
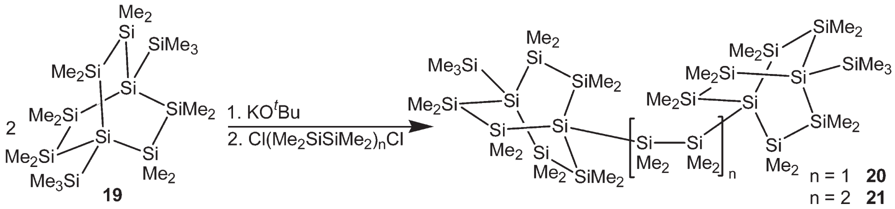
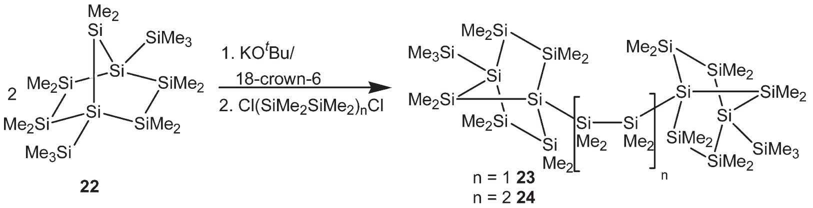
Scheme 3. Synthesis of Di-, Tetra-, and Hexasilanylene-Linked Bis[1,4,4-tris(trimethylsilyl)octamethylcyclohexasilanyl] Compounds 13, 14, and 15



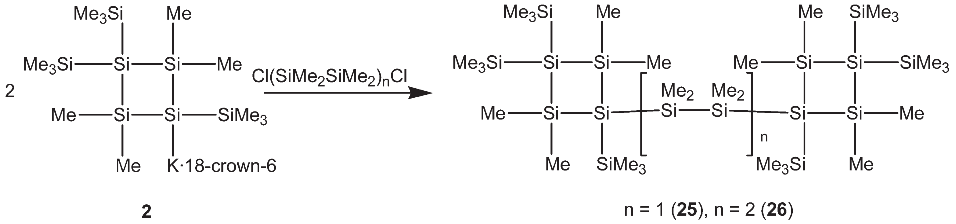
Scheme 4. Synthesis of Di- and Tetrasilanylene-Linked Bis{[2.2.2]bicyclooctasilanyl} Compounds 20 and 21



Scheme 5. Synthesis of Di- and Tetrasilanylene-Linked Bis{[2.2.1]bicycloheptasilanyl} Compounds 23 and 24



Scheme 6. Synthesis of Di- and Tetrasilanylene-Linked Bis(cyclotetrasilanyl) 25 and 26



tetra-, and hexasilanylene-linked bis[1,4,4-tris(trimethylsilyl)-octamethylcyclohexasilanyl] compounds **13**, **14**, and **15**, respectively (Scheme 3).

In an analogous manner 2 equiv of the monopotassium derivative of **19** with 1,2- and 1,4-dichloropermethylsilanes gave the di- and tetrasilanylene-linked bis{[2.2.2]bicyclooctasilanyl} compounds **20** and **21** (Scheme 4).

Similarly to the synthesis of **20** and **21**, the monopotassium derivative of **22** could be utilized to obtain di- and tetrasilanylene-linked bis{[2.2.1]bicycloheptasilanyl} compounds **23** and **24** (Scheme 5).

For the introduction of four-membered rings 2 equiv of compound **2** was reacted with 1,2- and 1,4-dichloropermethyldi- and -tetrasilanes (Scheme 6).

Crystal Structure Analyses. On previous occasions we have seen that the conformations of highly branched oligosilanes are very similar in solid state and in solution.[18a] Hence it was especially interesting to obtain crystals from compounds containing connected ring systems, but we succeeded only in **11**, **13**, and **14**.

The cyclotetrasilane **1** crystallizes in the triclinic space group *P*$\bar{1}$. In **1** (Figure 1), as already shown for similar compounds,[5b] there is only a slight difference between endocyclic Si−Si (2.37 Å) and exocyclic Si−SiMe$_3$ (2.35 Å) bond lengths. For **2** (Figure 2) all Si−Si distances are shortened for the exocyclic to 2.33 Å, and the endocyclic are in the range 2.35 to 2.37 Å.

The two starting materials **4** and **5** crystallize in the triclinic space group *P*$\bar{1}$ and in the monoclinic space group *P*2(1)/*c*, respectively. In tetrakis(trimethylsilyl)silane the Si−Si bonds are 2.34 Å long and the bond angles (Si−Si−Si) are 109.3° and 109.7°.[26] Exchanging two methyl groups for phenyl in **4** (Figure 3) elongates the Si−Si bonds to 2.36 Å and increases the bond angles between the central silicon and the two SiMe$_2$Ph groups to 112.6°. In **5** all Si−Si bond distances are

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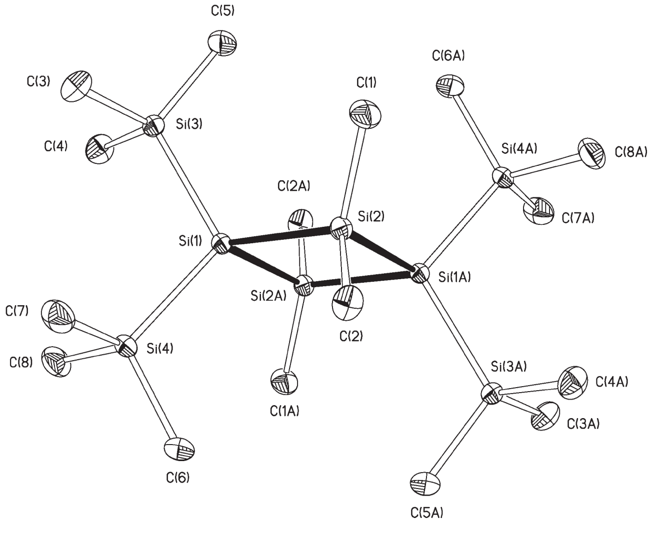

Figure 1. Molecular structure and numbering of **1** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Si(1)−Si(3) 2.3463(10), Si(1)−Si(4) 2.3465(12), Si(1)−Si(2) 2.3664(9), Si(1)−Si(2A) 2.3681(8), Si(2)−C(1) 1.879(2), Si(3)−Si(1)−Si(4) 109.90(4), Si(3)−Si(1)−Si(2) 116.33(4), Si(4)−Si(1)−Si(2) 114.25(4), Si(2)−Si(1)−Si(2A) 89.03(4), Si(2A)−Si(1)−Si(2)−Si(1A) 0.0.

in a normal range between 2.36 and 2.39 Å, but the steric strain of the two trimethylsilyl groups at the central silicon increases the bond angles along the silicon backbone from the ideal 109.5° to 127.8° (Si2−Si3−Si4) and 129.0° (Si4−Si5−Si6). The bond angles around the central silicon atom in the chain are in a range between 104.0° and 113.6°, whereas these angles around the central silicon atoms of the two terminal tris(trimethylsilyl)silyl groups are between 101.9° and 120.1° around Si2 and 103.5° and 121.9° around Si6. These strong deviations lead to a bending of the silicon backbone, shown in Figure 4 (lower part).

The crown ether adducts of **10** and **2** crystallize in the monoclinic space groups *P*2(1)/*n* and *P*2(1)/*c*, respectively. **10** is the first example of a trisilylated silyl anion with an attached cyclosilanyl substituent. The ring exhibits a perfect chair conformation with the metalated silicon atom in the expected equatorial position (Figure 7). Si−Si bond distances within the molecule are fairly short, mostly around 2.34 Å. The Si−K distances of 3.52 Å for **10** and 3.55 Å for **2** fall into the range 3.45 to 3.60 Å found in the other characterized cases of oligosilyl potassium crown-ether adducts.[27] The introduction of a negative charge onto a ring atom, as in **2** (Figure 2), causes a folding of the previously planar ring of **1** (Figure 1) by 20°. A folding by 31° was also found comparing the planar ring of octakis(trimethylsilyl)-cyclotetrasilane to the heptakis(trimethylsilyl)cyclotetrasilanyl sodium DME adduct.[5b] The packing pattern of **2** shows a band-shaped supramolecular arrangement with a coordination of the potassium atom toward a methyl group (C32) of a neighboring molecule. This motif is predominant in cases of silyl potassium crown ether adducts.[28] The distances in this series of coordinating carbon and potassium atoms can range from as small as 2.89 Å up to 3.6 Å; thus here we are in this range with 3.3 Å.

The six-membered ring **6** crystallizes in the orthorhombic space group *Pna*2(1), bearing two independent molecules in the asymmetric unit. The ring exhibits a twisted boat conformation with Si−Si bond lengths between 2.35 and 2.39 Å within the ring and also for the exocyclic bonds (Figure 5). The bond angles between all quaternary silicon atoms (Si6−Si1−Si2, Si2−Si3−Si4, Si4−Si5−Si6) are widened to about 117°.

Compound **8** crystallizes in the monoclinic space group *P*2(1). The cyclohexasilane part adopts a not quite regular chair conformation with ring bond angles between 108.1° and 116.5° (Figure 6). Si−Si bond lengths are between 2.33 and 2.38 Å within the ring and between 2.36 and 2.40 Å along the backbone.

Compound **11** crystallizes in the triclinic space group $P\overline{1}$ with an inversion center between the two dimethylsilylene spacer silicon atoms. Again, the Si−Si bond lengths along the backbone are slightly elongated (between 2.39 and 2.40 Å) compared to the ring distances. The cyclohexasilane part shows bond angles between 104.2° and 114.3°, and the rings adopt a *trans* position to each other (Figure 8). In analogy with the parent molecule of dodecamethylcyclohexasilane[29] **8** and **11** show all the cyclohexasilanyl units to exhibit chair conformations, with the sterically more demanding substituents occupying the equatorial positions. The structures of **8** and **11** are quite illustrative with respect to the conformational possibilities of the compounds (Figure 11). As can be seen in Figure 6 (lower part) molecule **8** contains two *transoid*-aligned chain segments. One segment consists of a hexasilane unit, which is present in a similar conformation to that found for **16**.[30] The second segment is a pentasilane unit, which includes a trisilane moiety from the cyclohexasilane and two silicon atoms from the bis(trimethylsilyl)silyl section. The two segments are oriented perpendicular to each other. For compound **11** a different conformation was found. Here the two undecamethylcyclohexasilanyl rings are oriented in a way to extend the aligned chain, which is similar to what has been observed for **16**, by addition of a trisilanyl unit (Figure 8, bottom).

The comparison of the two compounds **13** and **14** (Figures 9 and 10) is also interesting. Si−Si bond distances are in the range between 2.34 and 2.38 Å, and the bond angles are unexceptional. Again the *transoid* alignment of the main chain extends into the cyclohexasilanyl units. Like the parent compound 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane[31] all the six-membered rings in both molecules adopt a twist conformation. The interesting feature that distinguishes the structures of **13** and **14** is that the *transoid* alignment of **13** includes two additional ring atoms (Figure 9, bottom right), while for compound **14** the participation of only one additional atom is found (Figure 10, bottom). The explanation for this somewhat strange finding is that the rings in **13** and **14** do not feature the

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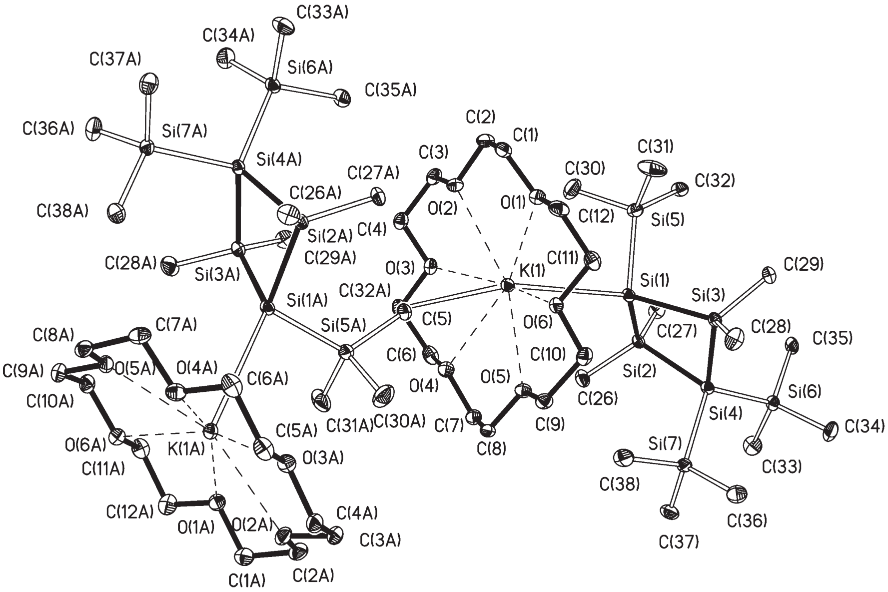

Figure 2. Molecular structure and numbering of **2** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Si(1)−Si(5) 2.325(2), Si(1)−Si(3) 2.347(2), Si(1)−Si(2) 2.350(2), Si(1)−K(1) 3.5531(18), Si(2)−C(26) 1.889(5), Si(2)−Si(4) 2.367(2), Si(3)−Si(4) 2.359(2), Si(4)−Si(7) 2.333(2), Si(4)−Si(6) 2.334(2), K(1)−C(32A) 3.331(5), Si(3)−Si(1)−Si(2) 84.56(7), Si(3)−Si(1)−K(1) 137.75(7), Si(2)−Si(1)−K(1) 123.96(6), Si(1)−Si(2)−Si(4) 91.93(8), Si(1)−Si(3)−Si(4) 92.20(7), Si(3)−Si(4)−Si(2) 83.92(7), C(32A)−K(1)−Si(1) 160.21(11), Si(3)−Si(1)−Si(2)−Si(4) 20.40(7).

same twist conformation. Switching of **14** to the second twist conformer would cause the same extension of alignment as was found for **13**.

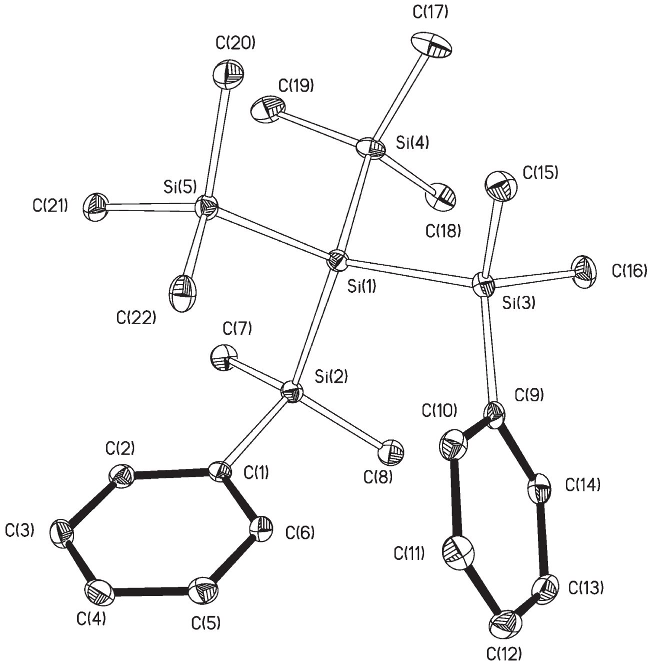

Figure 3. Molecular structure and numbering of **4** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Si(1)−Si(4) 2.3494(10), Si(1)−Si(5) 2.3520(13), Si(1)−Si(2) 2.3529(8), Si(1)−Si(3) 2.3604(9), Si(2)−C(7) 1.8750(19), Si(4)−Si(1)−Si(5) 109.22(4), Si(4)−Si(1)−Si(2) 108.51(3), Si(5)−Si(1)−Si(2) 108.62(4), Si(4)−Si(1)−Si(3) 106.01(4), Si(5)−Si(1)−Si(3) 111.80(4), Si(2)−Si(1)−Si(3) 112.56(4).

UV Spectroscopy. The influence of the six-membered rings on the UV absorption properties of compounds **8** and **11** can be estimated from the comparison with 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane (**16**) in Figure 12. The replacement of one trimethylsilyl group of **16** by the cyclohexasilanyl unit in **8** induces a bathochromic shift of the low-energy absorption (maximum at 261 nm ($\varepsilon = 4.8 \times 10^4$) and a shoulder at 281 nm). This trend is further enforced by the addition of another ring in compound **11** (maximum at 270 nm ($\varepsilon = 3.6 \times 10^4$) and two shoulders at 241 and 286 nm). The sharp bands of **16** are replaced by broader bands for **8** and **11**. These can be attributed to a higher degree of conformational flexibility as the cyclohexasilanyl units might undergo fast conformational changes.

Figure 13 compares the UV spectra of the di-, tetra-, and hexasilanylene-linked bis[1,4,4-tris(trimethylsilyl)octamethylcyclohexasilanyl] compounds **13**, **14**, and **15** with the respective tris(trimethylsilyl)silyl-terminated analogues (**16**, **17**, **18**). Compound **13**, with two silicon atoms between the cyclic building blocks, exhibits two different bathochromic shifted maxima at longer wavelengths, 265 nm ($\varepsilon = 3.8 \times 10^4$) and 289 nm ($\varepsilon = 3.6 \times 10^4$), compared to the linear compound **16**. The bathochromic shift may be interpreted by the extension of the *transoid*-aligned segments into the cyclic parts. Compound **14**, with four silicon atoms as spacers, shows only one strongly bathochromic shifted maximum at 297 nm ($\varepsilon = 5.5 \times 10^4$) comparable to 1,1,1,6,6,6-hexakis(trimethylsilyl)octamethylhexasilane (**17**) (Figure 13). The one narrow band of **17** indicates one predominant conformation, and the same seems to be true for **14**. The six-membered rings should maintain their *trans* position (Figure 5) also in solution. An additional shoulder at 273 nm may be attributed to a less abundant conformer. The two maxima of 1,1,1,8,8,8-hexakis(trimethylsilyl)dodecamethyloctasilane (**18**) show the limit of the conformational control gained by tris(trimethylsilyl)silyl units as end-groups.[18] The steric demand of these groups is not sufficient to conformationally confine a spacer consisting of six dimethylsilylene

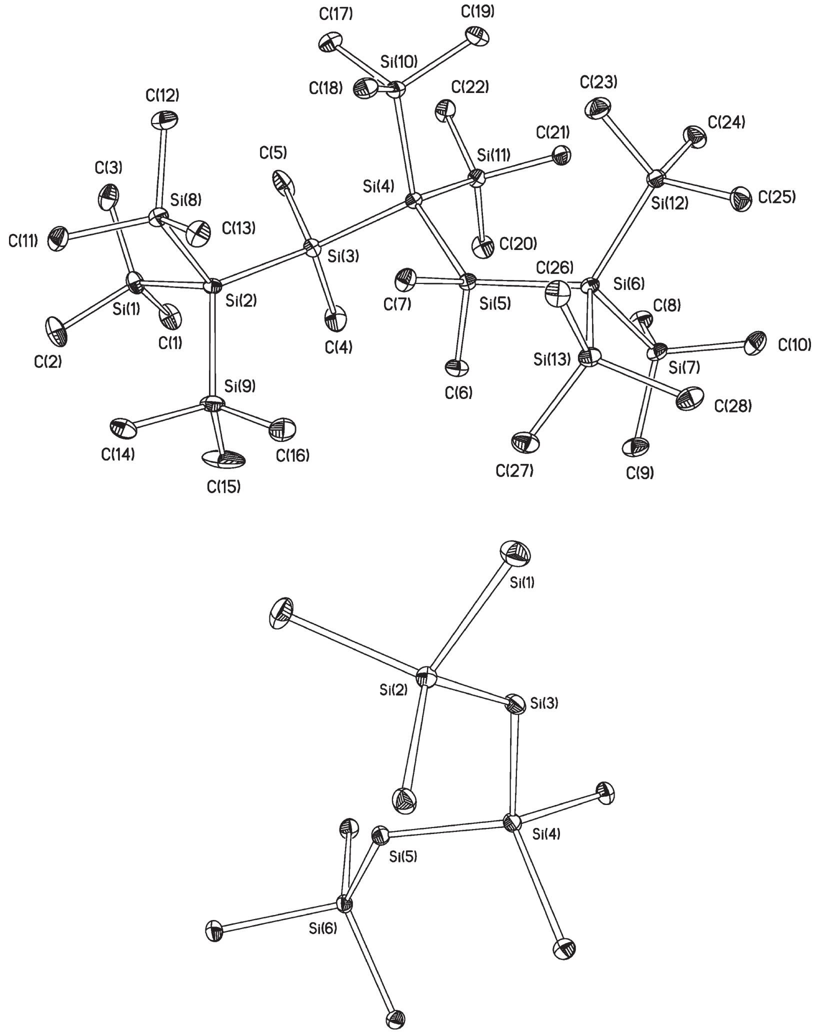

Figure 4. Molecular structure and numbering of **5** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Si(1)−C(1) 1.884(3), Si(1)−Si(2) 2.3790(11), Si(2)−Si(3) 2.3899(11), Si(3)−Si(4) 2.3874(11), Si(4)−Si(5) 2.3742(11), Si(5)−Si(6) 2.3857(11), Si(6)−Si(7) 2.3584(11), Si(1)−Si(2)−Si(3) 101.89(4), Si(2)−Si(3)−Si(4) 127.82(4), Si(3)−Si(4)−Si(5) 108.13(4), Si(4)−Si(5)−Si(6) 129.01(4), Si(5)−Si(6)−Si(7) 112.12(4).

units to one conformer. This can be seen by the occurrence of a second band in the UV spectrum. The comparable compound **15** shows a bathochromic maximum at 303 nm ($\varepsilon_1 = 7.3 \times 10^4$ $M^{-1}cm^{-1}$) and a shoulder around 290 nm (Figure 13), which also indicates the existence of two conformers in solution. The crystal structures of **13** and **14** show that both compounds have *transoid*-aligned octasilane segments. However, the conformational change of the two twist conformers would extend the segment of **14** by two silicon atoms. This process is facile,[21,32] and it is therefore likely that all ring conformers are present in solution. At the same instance it is also valid to expect conformers of **12** in solution, which contain the other twist conformers and thus have shortened *transoid*-aligned segments.

Compounds **20** and **21** differ from **13** and **14** by the introduction of the tetramethyldisilanylene bridge sections, which generates a [2.2.2]bicyclooctasilane cage and thus locks the conformation of the cyclohexasilane system. This seems to result in mainly one conformer existing in solution, as only one low-energy band can be observed in each of the UV spectra (Figure 14) of **20** (288 nm) and **21** (299 nm). The positions of these absorption maxima do not differ substantially from those for **13** and **14**.

Compounds **23** and **24** are very similar to **20** and **21** in a sense that the [2.2.2]bicyclooctasilane units are replaced by [2.2.1]-bicycloheptasilane entities. The reason for this change was that it can be expected that the [2.2.1]bicycloheptasilane might allow conjugation over the dimethylsilylene bridge unit. However, the spectra of **23** and **24** (Figure 15) are fairly similar to those of **20** and **21**. The low-energy absorption band of **23** (290 nm) is somewhat broader compared to the spectrum of **20**.

Changing from the cyclohexasilane units to cyclotetrasilanyl moieties changes the UV absorption behavior in an unexpected way (Figure 16). The comparison with the acyclic reference compounds **16** and **17** shows that the bands at 255 nm (**25**) and 275 nm (**26**) correspond to *transoid*-aligned hexa- and octasilanyl fragments composed of the spacer and the attached isotetrasilanyl units. The more astonishing feature of both **25** and **26** is an absorption band around 323 nm. This particular band is not found in the spectrum of compound **1**, which is shown for comparison (Figure 16).

Conclusion. A number of compounds where cyclosilanes are connected with silanylene spacers of different lengths

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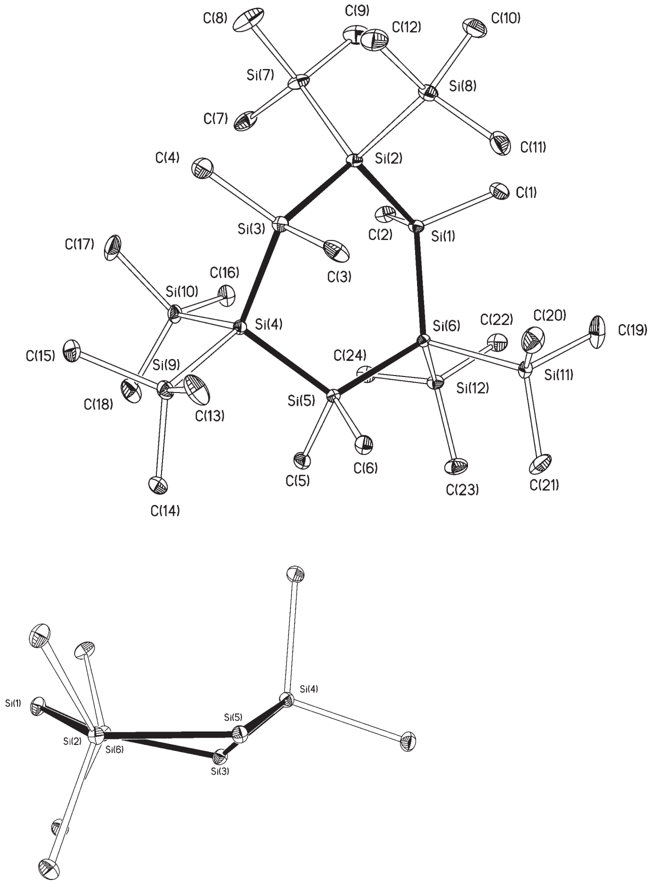

Figure 5. Molecular structure and numbering of **6** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Si(1)−Si(2) 2.3767(16), Si(1)−Si(6) 2.3823(16), Si(2)−Si(3) 2.3594(16), Si(2)−Si(7) 2.3711(17), Si(3)−Si(4) 2.3456(14), Si(4)−Si(5) 2.3544(14), Si(5)−Si(6) 2.3864(15), Si(2)−Si(1)−Si(6) 117.67(7), Si(3)−Si(2)−Si(1) 113.90(6), Si(4)−Si(3)−Si(2) 117.06(6), Si(3)−Si(4)−Si(5) 108.32(6), Si(3)−Si(4)−Si(9) 108.26(7), Si(5)−Si(4)−Si(9) 107.90(6), Si(4)−Si(5)−Si(6) 116.62(6), Si(1)−Si(6)−Si(5) 117.25(6).

were synthesized. Due to their cyclic nature, the cyclosilane parts of these molecules have only restricted conformational freedom. On the basis of our recent studies concerning the alignment of methylated polysilane chains using bulky end-groups such as the tris(trimethylsilyl)silyl group, we decided to study the use of cyclosilanes for this purpose. As these also consist of catenated silicon atoms, it was expected that the conjugation of the polysilane chain would be extended into the cyclosilane. As can be seen in Figure 17 a *transoid*-aligned dodecasilane chain would be present in compound **24**, whereas only decasilane units might be expected for **11**, **14**, and **21**. Comparison of UV absorption behavior of the obtained compounds with the respective tris(trimethylsilyl)-silyl-terminated ones is interesting. It shows that in almost all cases the introduction of a cyclosilane unit causes a marked bathochromic shift. Compared to the tris(trimethylsilyl)silyl-terminated compounds, the substances with the 1,4,4,-tris-(trimethylsilyl)cyclohexasilanyl and the [2.2.2]bicyclooctasilanyl units would be expected to contain two additional silylene units in the *transoid*-aligned segment. If the positions of the absorption maxima are compared to the tris-(trimethylsilyl)silyl-terminated compounds with spacers that contain two additional silylene units, the cyclosilane-containing compounds exhibit bathochromic shift behavior. The comparison of the low-energy absorption maxima of the 1,4,4,-tris(trimethylsilyl)cyclohexasilanyl-, the [2.2.2]bicyclooctasilanyl-, and the [2.2.1]bicycloheptasilanyl-connected compounds shows *no* marked differences. The non-bicyclic compounds exhibit additional bands that can be attributed to conformational flexibility in the cyclohexasilane unit. Although a longer *transoid*-aligned segment was expected for the compounds containing the [2.2.1]bicycloheptasilanyl unit, no clear bathochromic shift was observed. A possible explanation for this arises from a comparison of the UV spectra of **19** and **22**. It was assumed that **22**, which contains one *transoid*-aligned pentasilane unit, would exhibit a clearly red-shifted absorption behavior compared to **19**. However, the spectrum of **22** is rather similar to that of **19**, with the expected pentasilanes absorption around 250 nm only visible as a shoulder.

Surprisingly, it was found that the structurally very similar compounds containing the 1,3,3-tris(trimethylsilyl)tetramethylcyclotetrasilanyl units show the most bathochromic shifted bands. The fact that both compounds of this type show the low-energy band at about the same wavelength, irrespective of the spacer unit, suggests that this particular band is associated with the cyclotetrasilane unit. Absorption at comparatively low energy is also known for peralkylated cyclotetrasilanes.[33]

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. Solvents were dried using a column solvent purification system.[34] Potassium *tert*-butanolate was purchased exclusively from Merck. All other chemical were bought from different suppliers and were used without further purification.

^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian Unity INOVA 300. Samples for ^{29}Si spectra were either dissolved in deuterated solvents or in cases of reaction samples measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence was used for the amplification of the signal.[35] If not noted otherwise, the used solvent was C_6D_6 and all samples were measured at rt.

Elementary analysis was carried out using a Heraeus Vario Elementar EL apparatus. In cases of low carbon values, which is attributed to the formation and incomplete combustion of silicon carbide, the combustion time was raised to 30 s.

UV−vis absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer in spectroscopy grade pentane or heptane solutions.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[36] and SADABS,[37] respectively. Structures were solved by direct methods and

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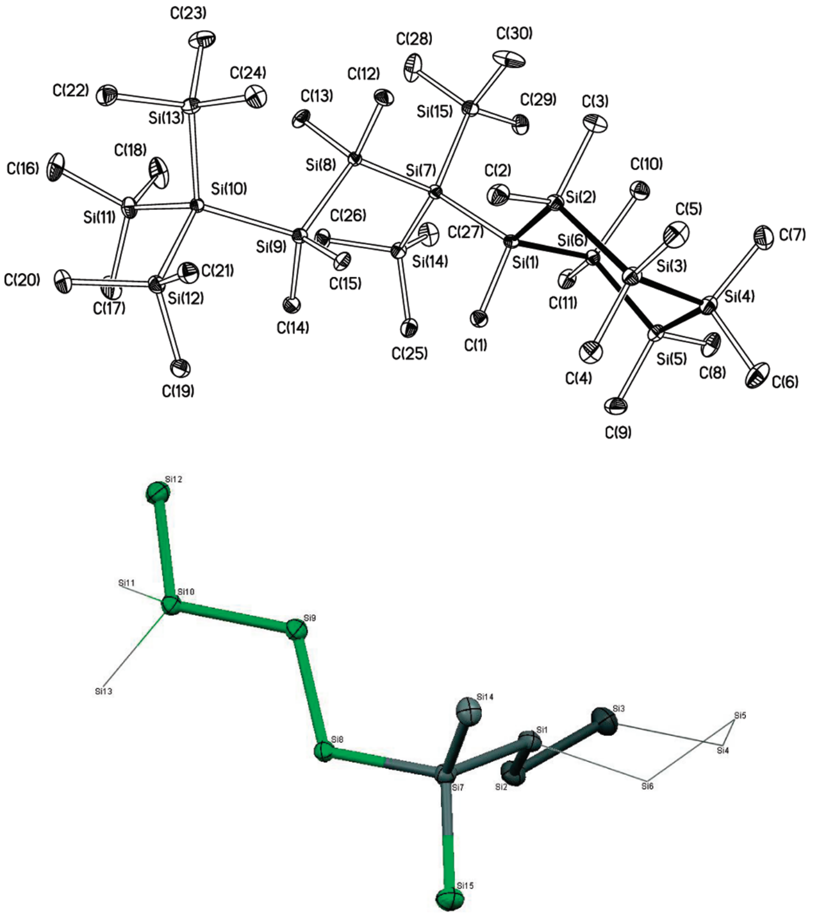

Figure 6. (Top) Molecular structure and numbering of **8** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: Si(1)−C(1) 1.910(5), Si(1)−Si(6) 2.3614(19), Si(1)−Si(2) 2.3790(19), Si(6)−Si(1)−Si(2) 104.45(7), Si(6)−Si(1)−Si(7) 111.47(7), Si(2)−Si(1)−Si(7) 122.36(7), Si(3)−Si(2)−Si(1) 110.23(7), Si(4)−Si(3)−Si(2) 116.50(8), Si(3)−Si(4)−Si(5) 108.04(8), Si(6)−Si(5)−Si(4) 109.84(7), Si(5)−Si(6)−Si(1) 111.72(7), Si(15)−Si(7)−Si(8) 105.26(7), Si(15)−Si(7)−Si(14) 107.33(7), Si(8)−Si(7)−Si(14) 108.91(7), Si(15)−Si(7)−Si(1) 111.60(7), Si(8)−Si(7)−Si(1) 111.70(7), Si(14)−Si(7)−Si(1) 111.73(7), Si(9)−Si(8)−Si(7) 116.22(7), Si(10)−Si(9)−Si(8) 113.88(7), Si(13)−Si(10)−Si(11) 111.82(7), Si(13)−Si(10)−Si(9) 113.57(7), Si(11)−Si(10)−Si(9) 114.35(7), Si(13)−Si(10)−Si(12) 104.83(7), Si(11)−Si(10)−Si(12) 105.26(7), Si(9)−Si(10)−Si(12) 105.98(7). (Bottom) Wireframe model with *transoid*-aligned segments highlighted.

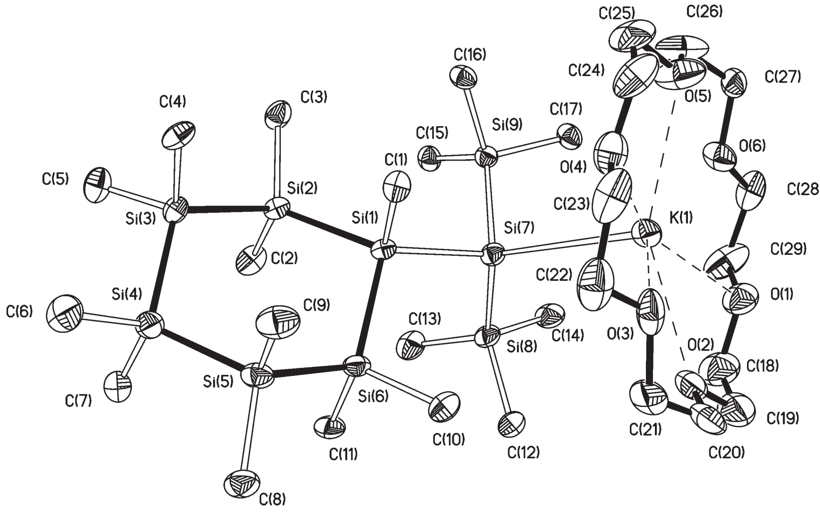

Figure 7. Molecular structure and numbering of **10** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: K(1)−O(1) 2.806(7), K(1)−Si(7) 3.523(3), Si(1)−C(1) 1.913(8), Si(1)−Si(6) 2.344(3), Si(1)−Si(7) 2.346(3), Si(1)−Si(2) 2.362(3), Si(6)−Si(1)−Si(7) 108.31(11), Si(6)−Si(1)−Si(2) 105.26(12), Si(7)−Si(1)−Si(2) 127.62(12), Si(3)−Si(2)−Si(1) 112.66(12), Si(4)−Si(3)−Si(2) 114.80(12), Si(5)−Si(4)−Si(3) 110.80(13), Si(4)−Si(5)−Si(6) 110.63(13), Si(5)−Si(6)−Si(1) 115.57(12), Si(8)−Si(7)−Si(9) 100.98(12), Si(8)−Si(7)−Si(1) 101.15(11), Si(9)−Si(7)−Si(1) 109.74(12).

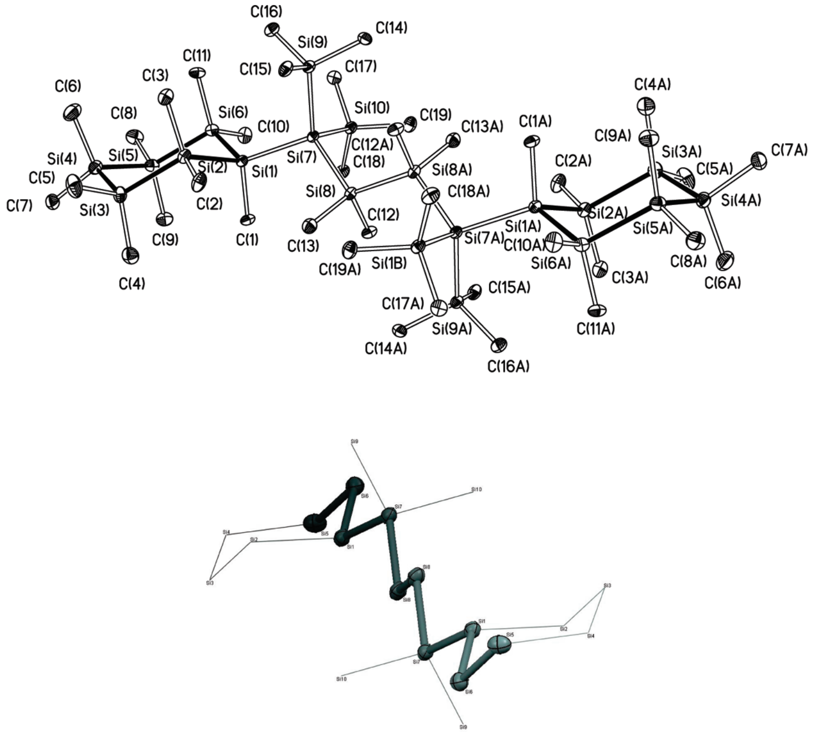

Figure 8. (Top) Molecular structure and numbering of **11** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: Si(1)−C(1) 1.904(5), Si(1)−Si(2) 2.369(2), Si(1)−Si(6) 2.385(2), Si(2)−Si(1)−Si(6) 104.15(8), Si(2)−Si(1)−Si(7) 115.45(8), Si(6)−Si(1)−Si(7) 118.28(8), Si(3)−Si(2)−Si(1) 112.90(8), Si(4)−Si(3)−Si(2) 111.89(9), Si(5)−Si(4)−Si(3) 108.98(9), Si(4)−Si(5)−Si(6) 114.28(9), Si(5)−Si(6)−Si(1) 111.15(8), Si(9)−Si(7)−Si(10) 107.87(8), Si(9)−Si(7)−Si(8) 115.17(8), Si(10)−Si(7)−Si(8) 106.84(8), Si(9)−Si(7)−Si(1) 110.68(8), Si(10)−Si(7)−Si(1) 106.22(8), Si(8)−Si(7)−Si(1) 109.60(8). (Bottom) Wireframe model with *transoid*-aligned segment highlighted.

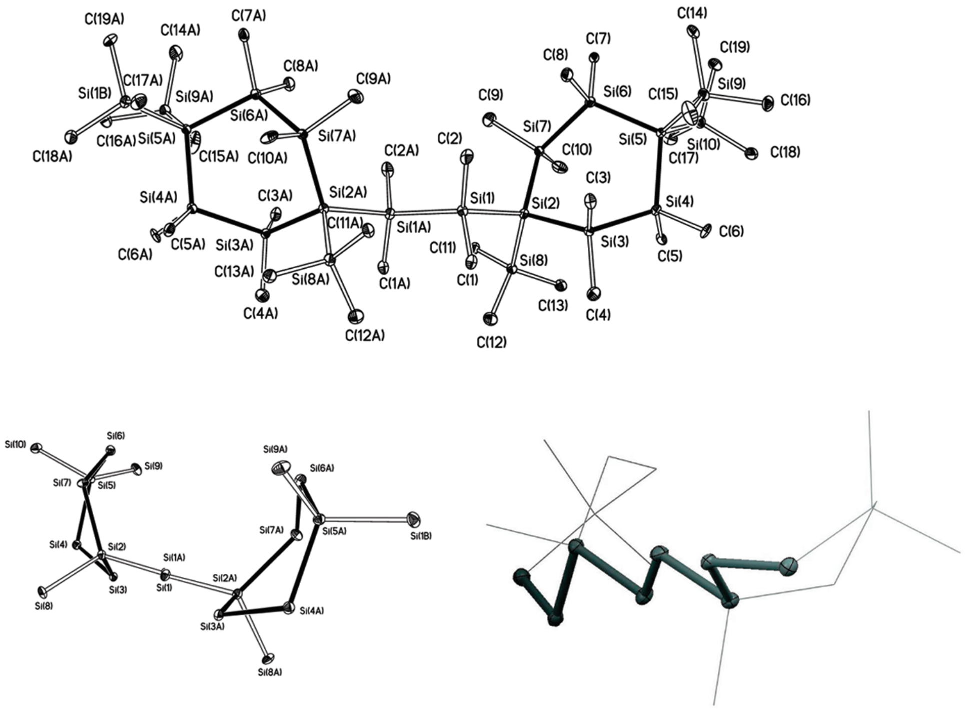

Figure 9. (Top) Molecular structure and numbering of **13** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: Si(1)−C(1) 1.884(8), Si(1)−Si(2) 2.388(3), Si(2)−Si(8) 2.350(3), Si(8)−Si(2)−Si(3) 109.30(12), Si(8)−Si(2)−Si(7) 107.36(11), Si(3)−Si(2)−Si(7) 107.71(11), Si(8)−Si(2)−Si(1) 109.04(12), Si(3)−Si(2)−Si(1) 105.46(11), Si(7)−Si(2)−Si(1) 117.77(12), Si(4)−Si(3)−Si(2) 115.20(11), Si(3)−Si(4)−Si(5) 112.27(12), Si(6)−Si(5)−Si(10) 110.40(12), Si(6)−Si(5)−Si(9) 110.21(12), Si(10)−Si(5)−Si(9) 105.38(12), Si(6)−Si(5)−Si(4) 110.81(11), Si(10)−Si(5)−Si(4) 108.35(11), Si(9)−Si(5)−Si(4) 111.53(12), Si(7)−Si(6)−Si(5) 113.38(12), Si(6)−Si(7)−Si(2) 115.33(11). (Bottom left) Polysilane skeleton with methyl groups omitted for clarity. (Bottom right) Wireframe model with *transoid*-aligned segment highlighted.

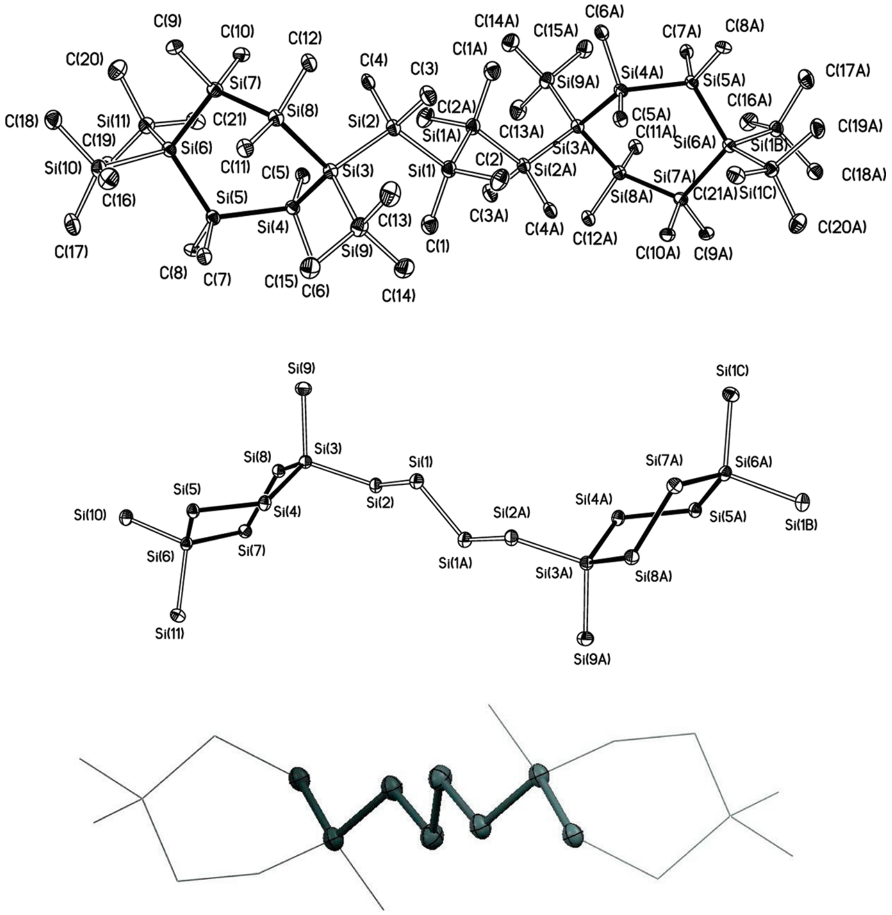

Figure 10. (Top) Molecular structure and numbering of **14** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: Si(1)−C(1) 1.889(6), Si(1)−Si(2) 2.372(3), Si(3)−Si(2)−Si(1) 116.96(10), Si(9)−Si(3)−Si(4) 112.15(10), Si(9)−Si(3)−Si(2) 109.56(10), Si(4)−Si(3)−Si(2) 109.02(9), Si(9)−Si(3)−Si(8) 108.06(9), Si(4)−Si(3)−Si(8) 109.21(9), Si(2)−Si(3)−Si(8) 108.78(10), Si(5)−Si(4)−Si(3) 112.87(9), Si(4)−Si(5)−Si(6) 116.02(9), Si(11)−Si(6)−Si(5) 110.82(9), Si(11)−Si(6)−Si(10) 107.72(10), Si(5)−Si(6)−Si(10) 106.31(9), Si(11)−Si(6)−Si(7) 108.74(9), Si(5)−Si(6)−Si(7) 109.90(9), Si(10)−Si(6)−Si(7) 113.33(9), Si(8)−Si(7)−Si(6) 113.23(9), Si(7)−Si(8)−Si(3) 116.44(9). (Middle) Polysilane skeleton with methyl groups omitted for clarity. (Bottom) Wireframe model with *transoid*-aligned segment highlighted.

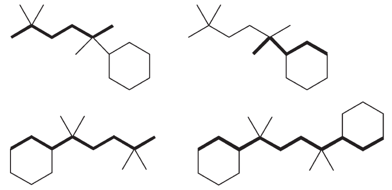

Figure 11. (Top) 2-D representation of the polysilane backbone of the conformer found in the crystal structure of compound **8** (highlighted bonds indicate *transoid*-aligned segments). (Bottom) On the left side another possible conformer of **8** where the *transoid* alignment extends from the chain into the ring in the same way as found for **11**; on the right the *transoid*-aligned chain elements are highlighted.

refined by full-matrix least-squares method (SHELXL97).[38] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and hydrogen atoms were omitted for clarity. Unfortunately, the obtained crystal quality of some substances was poor. This fact is reflected by quite high *R* and low θ values (Tables 1 and 2).

Crystallographic data (excluding structure factors) for the structures of compounds **2**, **4**, **5**, **6**, **7**, **8**, **10**, **11**, **13**, and **14** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 741866 (**2**), 741864 (**4**), 741865 (**5**), 741867 (**6**), 741863 (**7**), 663890 (**8**), 663889 (**10**), 663891 (**11**), 663893 (**13**), and 663892 (**14**). Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

1,1,4,4,4-Pentakis(trimethylsilyl)tetramethyltetrasilanylpotassium$\cdot$18-crown-6 (**7**),[39] 1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilanyldipotassium$\cdot$(18-crown-6)$_2$ (**9**),[39,40] bis(trimethylsilyl)undecamethylcyclohexasilanylsilanylpotassium$\cdot$18-crown-6 (**10**),[4a] 1,4,4-tris(trimethylsilyl)octamethylcyclohexasilanylpotassium$\cdot$18-crown-6 (**12**),[4a] 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane (**16**),[41] 1,1,1,6,6,6-hexakis(trimethylsilyl)octamethylhexasilane (**17**),[19] 1,1,1-trimethylsilyldodecamethylbicyclo[2.2.2]octasilanylpotassium$\cdot$18-crown-6 (**19**),[4a] diphenylbis(trimethylsilyl)silane,[42] decamethyl-1,4,-bis(trimethylsilyl)bicyclo[2.2.1]heptasilane,[4,43]

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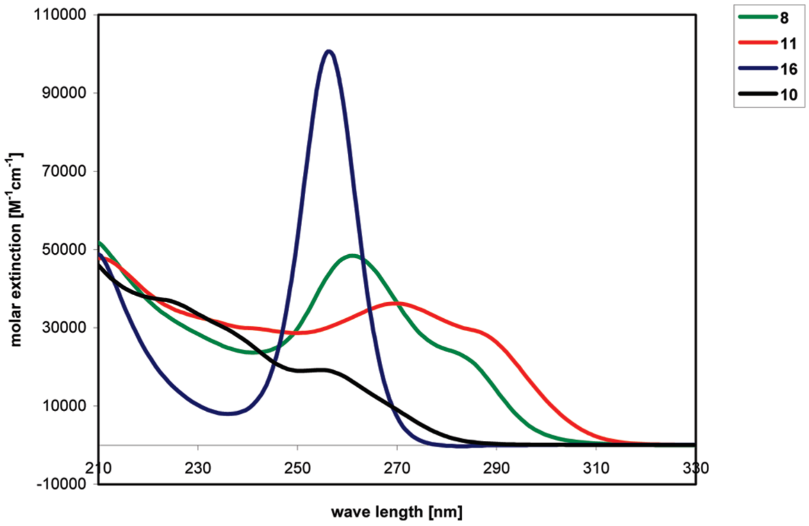

Figure 12. Comparison of the UV spectra of **8**, **11**, and **16**. Spectrum of tris(trimethylsilyl)silylundecamethylcyclohexasilane (**10**) shown for comparison.

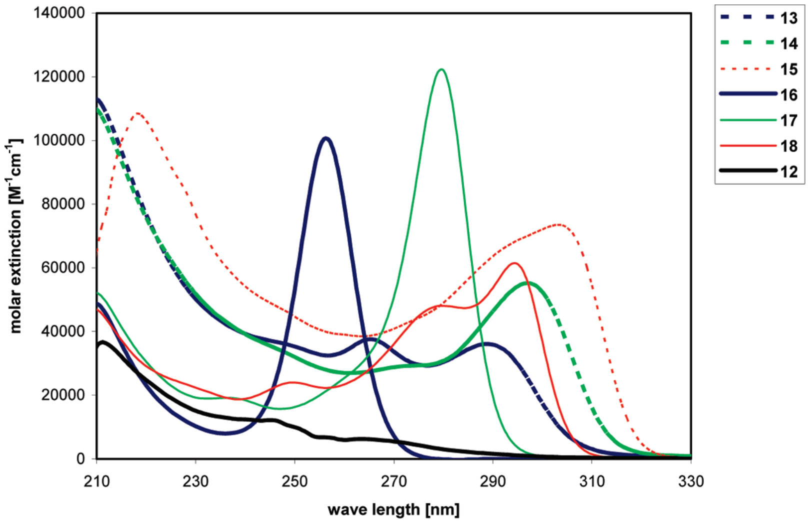

Figure 13. Comparison of UV spectra of methylated isotetrasilanyl and 1,4,4-tris(trimethylsilyl)cyclohexasilanyl units connected with compounds with disilanylene (**16**, **13**), tetrasilanylene (**17**, **14**), and hexasilanylene spacers (**18**, **15**). Spectrum of 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (**12**) shown for comparison.

bromoundecamethylcyclohexasilane,[44] 1,4-dichlorooctamethyltetrasilane,[45] 2,2-dimethyl-1,1,3,3-tetrakis(trimethylsilyl)trisilanyl dipotassium·(18-crown-6)$_2$,[5b] and 1,6-dichlorododecamethylhexasilane[46] were prepared according to reported procedures.

Aqueous workup was performed by pouring the reaction mixture on aqueous H_2SO_4 (0.5 or 2 M). After separation of the layers the aqueous layer was extracted twice with the organic solvent. The combined organic layers were first washed with a saturated aqueous sodium hydrogen carbonate solution and then dried over sodium sulfate.

1,1,3,3-Tetrakis(trimethylsilyl)tetramethylcyclotetrasilane (1). A solution of dimethyl-1,1,3,3-tetrakis(trimethylsilyl)trisilanyldipotassium·(18-crown-6)$_2$ (0.860 mmol) in toluene (20 mL) was added slowly to dichlorodimethylsilane (122 mg, 0.946 mmol) in toluene (40 mL) at 0 °C. The reaction mixture remained colorless during the whole addition process, and a white precipitate was formed. Stirring was continued for 5 h at rt, and then the reaction mixture was subjected to an aqueous workup with ice/diethyl ether/0.5 M H_2SO_4. Compound **1** was obtained as a colorless solid, which was further purified by recrystallization from diethyl ether/acetone (380 mg, 95%). Mp: 183−187 °C. NMR (δ in ppm): ^{1}H ($CDCl_3$) 0.22 (s, 36H), 0.50 (s, 12H); ^{13}C ($CDCl_3$) 2.5, 3.2; ^{29}Si ($CDCl_3$) −8.2 (Me$_3$*Si*), −25.5 (Me$_2$*Si*), −95.0 (*Si$_q$*). Anal. Calcd for $C_{16}H_{48}Si_8$ (465.24): C 41.31, H 10.40. Found: C 41.08, H 10.44. UV absorption: λ_1 = 217 nm (ε_1 = 5.4×10^4 [M^{-1} cm^{-1}]), λ_2 = 238 nm (ε_2 = 2.0×10^4 [M^{-1} cm^{-1}]), λ_3 = 253 nm (ε_3 = 9.3×10^3 [M^{-1} cm^{-1}]).

1,3,3-Tris(trimethylsilyl)tetramethylcyclotetrasilanylpotassium·18-crown-6 (2) and 1,1,3-Tris(trimethylsilyl)pentamethylcyclotetrasilane (3). A solution of **1** (150 mg, 0.322 mmol) in toluene (12 mL) was treated with potassium *tert*-butoxide (38 mg, 0.338 mmol) and 18-crown-6 (89 mg, 0.338 mmol). After 2 h the reaction was complete [NMR (δ in ppm): ^{1}H 0.62 (s, 18H), 0.65 (s, 9H), 0.96 (s, 12 H); ^{29}Si δ −5.9 (Me$_3$*Si*SiK), −10.7 (Me$_3$*Si*Si), −26.0 (Me$_2$*Si*); −98.6 (*Si$_q$*); −136.8 (*Si*K)]. This reaction mixture

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Table 1. Crystallographic Data for Compounds 1, 2, 4, 5, and 6

	1	2	4	5	6
empirical formula	$C_{16}H_{48}Si_8$	$C_{25}H_{62}KO_6Si_7$	$C_{22}H_{40}Si_5$	$C_{28}H_{84}Si_{13}$	$C_{48}H_{144}Si_{24}$
M_w	465.26	694.48	444.99	786.12	1395.79
temperature [K]	150(2)	100(2)	100(2)	100(2)	100(2)
size [mm]	0.35 × 0.28 × 0.22	0.40 × 0.28 × 0.25	0.32 × 0.28 × 0.20	0.40 × 0.30 × 0.25	0.40 × 0.36 × 0.30
cryst syst	triclinic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$	$Pca21$
a [Å]	9.119(2)	10.366(2)	9175(2)	9.740(2)	24.391(5)
b [Å]	9.407(2)	19.171(4)	9.561(2)	31.897(6)	19.863(4)
c [Å]	9.870(2)	21.170(4)	18.183(4)	16.617(3)	18.147(4)
α [deg]	76.07(3)	90	75.97(3)	90	90
β [deg]	81.57(3)	96.37(3)	81.92(3)	94.52(3)	90
γ [deg]	65.31(3)	90	62.00(3)	90	90
V [Å^3]	746(2)	4207(2)	1366(2)	5146(2)	8792(3)
Z	1	4	2	4	4
ρ_{calc} [g cm^{-3}]	1.036	1.096	1.082	1.015	1.055
absorp coeff [mm^{-1}]	0.361	0.356	0.268	0.342	0.368
$F(000)$	256	1508	484	1736	3072
θ range	$2.13 < \theta < 26.35$	$1.43 < \theta < 25.00$	$2.31 < \theta < 26.37$	$1.28 < \theta < 26.38$	$1.67 < \theta < 28.35$
reflns collected/unique	5952/3004	29 669/7384	710 973/5496	40 646/10 494	72 642/20 647
completeness to θ [%]	98.4	99.7	98.6	99.7	96.5
data/restraints/params	3004/0/117	7384/0/364	5496/0/254	10 494/0/398	20 647/1/650
goodness of fit on F^2	1.11	1.15	1.03	1.08	1.04
final R indices [$I > 2\sigma(I)$]	R1 = 0.037, wR2 = 0.089	R1 = 0.082, wR2 = 0.173	R1 = 0.039, wR2 = 0.097	R1 = 0.054, wR2 = 0.104	R1 = 0.0566 wR2 = 0.1154
R indices (all data)	R1 = 0.040, wR2 = 0.092	R1 = 0.115, wR2 = 0.188	R1 = 0.048, wR2 = 0.103	R1 = 0.078, wR2 = 0.111	R1 = 0.0790 wR2 = 0.1231
largest diff peak/hole [e$^-$/Å^3]	0.36/−0.18	0.65/−0.44	0.60/−0.21	0.54/−0.31	0.56/−0.33

Table 2. Crystallographic Data for Compounds 8, 10, 11, 13, and 14

	8	10	11	13	14
empirical formula	$C_{30}H_{90}Si_{15}$	$C_{29}H_{75}KO_6Si_9$	$C_{38}H_{114}Si_{20}$	$C_{19}H_{57}Si_{10}$	$C_{42}H_{126}Si_{22}$
M_w	872.37	811.80	1133.09	566.55	1249.41
temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
size [mm]	0.52 × 0.40 × 0.25	0.42 × 0.32 × 0.28	0.32 × 0.20 × 0.18	0.40 × 0.32 × 0.26	0.48 × 0.30 × 0.22
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2(1)$	$P2(1)/n$	$P\bar{1}$	$C2$	$P2(1)/n$
a [Å]	15.993(3)	10.144(2)	9.946(2)	16.160(3)	9.4839(2)
b [Å]	9.880(2)	21.284(4)	13.658(3)	10.545(2)	24.749(5)
c [Å]	18.665(4)	22.641(5)	15.241(3)	22.036(4)	16.970(3)
α [deg]	90	90	105.86(3)	90	90
β [deg]	107.97(3)	96.56(3)	99.83(3)	106.59(3)	93.36(3)
γ [deg]	90	90	111.00(3)	90	90
V [Å^3]	2795(2)	4856(2)	1774(6)	3599(2)	3977(2)
Z	2	4	1	4	2
ρ_{calc} [g cm^{-3}]	1.037	1.110	1.060	1.046	1.044
absorp coeff [mm^{-1}]	0.361	0.364	0.378	0.373	0.371
$F(000)$	960	1768	622	1244	1372
θ range	$1.34 < \theta < 25.00$	$1.32 < \theta < 23.00$	$1.71 < \theta < 26.37$	$1.93 < \theta < 24.50$	$1.46 < \theta < 25.00$
reflns collected/unique	20 169/9710	28 805/6750	14 250/7139	12 583/5908	28 357/6993
completeness to θ [%]	99.8	100	98.6	99.9	99.8
data/restraints/params	9710/1/437	6750/0/423	7139/0/281	5908/1/282	6993/0/310
goodness of fit on F^2	0.98	1.12	0.96	1.10	0.85
final R indices [$I > 2\sigma(I)$]	R1 = 0.058, wR2 = 0.127	R1 = 0.107, wR2 = 0.211	R1 = 0.081, wR2 = 0.154	R1 = 0.086, wR2 = 0.149	R1 = 0.069, wR2 = 0.111
R indices (all data)	R1 = 0.074, wR2 = 0.133	R1 = 0.151, wR2 = 0.237	R1 = 0.146, wR2 = 0.176	R1 = 0.108, wR2 = 0.158	R1 = 0.200, wR2 = 0.142
largest diff peak/hole [e$^-$/Å^3]	0.57/−0.31	0.88/−0.41	0.57/−0.37	0.49/−0.48	0.45/−0.41

was added dropwise slowly to dimethyl sulfate (41 mg, 0.322 mmol) in diethyl ether at 0 °C. After stirring for 3 h at rt an aqueous workup was carried out to yield a colorless oil of **3** (98 mg, 75%). NMR (δ in ppm): ^{1}H 0.22 (s, 9H), 0.29 (s, 9H), 0.31 (s, 9H), 0.38 (s, 3H), 0.44 (s, 6H), 0.52 (s, 6H); ^{29}Si −8.3 (Me$_3$*Si*Si), −8.9 (Me$_3$*Si*Si), −11.9 (Me$_3$*Si*SiMe), −25.1 (Me$_2$*Si*), −50.0 (Me$_3$Si*Si*Me), −102.9 (Me$_3$Si*Si*). Anal. Calcd for $C_{14}H_{42}Si_7$ (407.08): C 41.31, H 10.40. Found: C 40.98, H 10.32.

Bis(dimethylphenylsilyl)bis(trimethylsilyl)silane (4). To an ice bath cooled solution of diphenylbis(trimethylsilyl)silane (163 mg, 0.487 mmol) in toluene (2 mL) was added trifluoromethanesulfonic acid (146 mg, 0.976 mmol). The cooling bath was removed and stirring continued overnight. After ^{29}Si NMR indicated complete conversion [NMR (δ in ppm): ^{29}Si δ +38.8 (TfO*Si*), −12.2 (Me$_3$*Si*Si)] the solution was cooled to −78 °C and a solution of dimethylphenylsilyllithium (prepared from finely cut lithium wire (32 mg, 4.6 mmol) and dimethylphenylchlorosilane (167 mg, 0.976 mmol) in THF) was added dropwise in a way that the triflate solution was allowed to warm when the solution stopped decolorizing. After complete addition stirring was continued for 16 h at rt. After aqueous workup colorless crystals of **4** (149 mg, 68%) were obtained. Mp: 364−368 °C. NMR (δ in ppm): ^{1}H 7.42 (m, 4H), 7.17(m, 6H), 0.43 (s, 12H), 0.17 (s, 18H); ^{29}Si −9.6 (Me$_3$*Si*Si), −13.2 (Me$_2$Ph*Si*Si), −132.8 (Me$_3$Si*Si*). Anal. Calcd for $C_{22}H_{40}Si_5$ (444.98): C 59.38, H 9.06. Found: C 59.17, H 8.98.

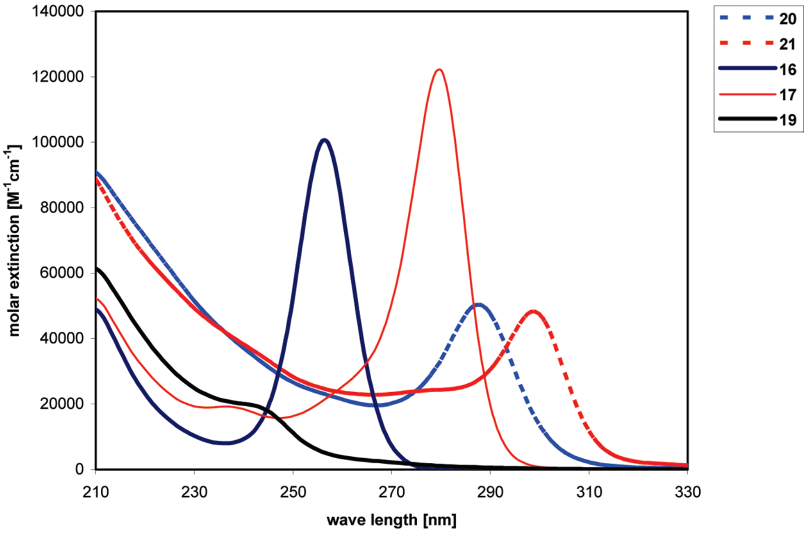

Figure 14. Comparison of UV spectra of methylated isotetrasilanyl and [2.2.2]bicyclooctasilanyl units connected with disilanylene (**16**, **20**) and tetrasilanylene spacers (**17**, **21**). Spectrum of 1,4-bis(trimethylsilyl)dodecamethylbicyclo[2.2.2]heptasilane (**19**) shown for comparison.

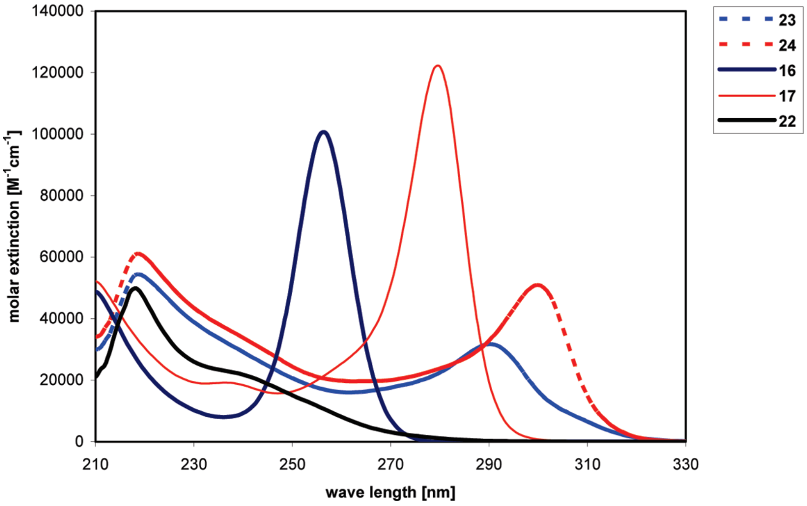

Figure 15. Comparison of UV spectra of methylated isotetrasilanyl and [2.2.1]bicycloheptasilanyl units connected with disilanylene (**16**, **23**) and tetrasilanylene spacers (**17**, **24**). Spectrum of 1,4-bis(trimethylsilyl)decamethylbicyclo[2.2.1]heptasilane (**22**) shown for comparison.

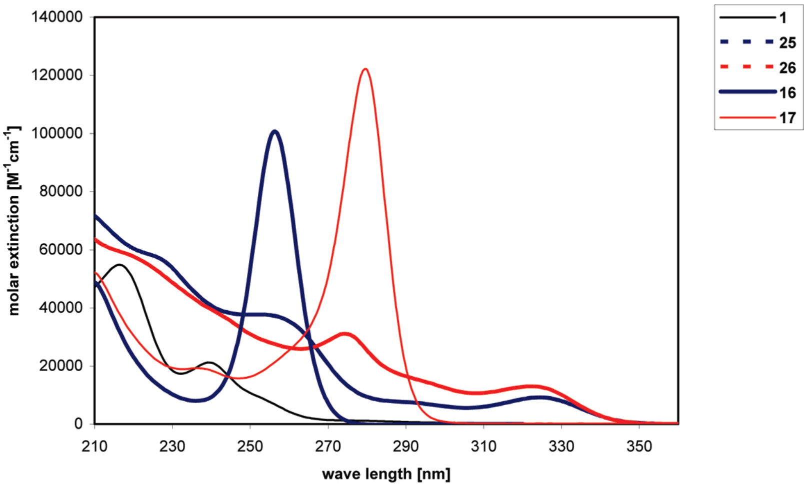

Figure 16. Comparison of UV spectra of methylated isotetrasilanyl and 1,3,3-tris(trimethylsilyl)octamethylcyclotetrasilanyl units connected with disilanylene (**16**, **25**) and tetrasilanylene spacers (**17**, **26**). Spectrum of 1,1,3,3-tetrakis(trimethylsilyl)octamethylcyclotetrasilane (**1**) shown for comparison.

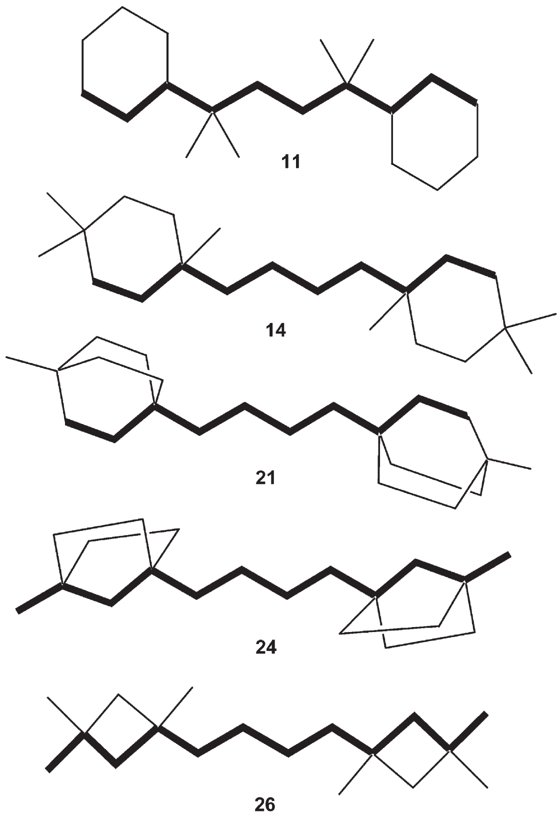

Figure 17. 2-D representations of the polysilane backbones of **11** and the compounds with the tetrasilanylene spacers highlighting the best achievable all-*transoid*-aligned conformation.

1,1,1,3,3,5,5,5-Octakis(trimethylsilyl)-2,2,4,4-tetramethylpentasilane (5). To a solution of bis(trimethylsilyl)bis(dimethylphenylsilyl)silane (**4**) (2.05 g, 4.65 mmol) in toluene (10 mL) at 0 °C was added trifluoromethylsulfonic acid (1.39 g, 9.29 mmol). After removal of the ice bath stirring was continued for 16 h to achieve complete conversion [NMR (δ in ppm): ^{29}Si +5.9 ($\mathrm{TfO}\mathit{Si}\mathrm{Me_2}$), −9.9 ($\mathrm{Me_3}\mathit{Si}\mathrm{Si}$), −131.1 ($\mathrm{Me_3Si}\mathit{Si}$)]. After cooling the solution to 0 °C again tris(trimethylsilyl)silylpotassium (9.29 mmol) in THF (10 mL) was added dropwise. A precipitate was observed, and stirring was continued at rt for 10 h. Aqueous workup was followed by drying over sodium sulfate and removal of the solvent. The residue was sublimed at 70 °C/0.7 mbar and crystallized from pentane to give **5** (1.050 g, 29%) as colorless crystals. Mp: 170−171 °C. NMR (δ in ppm): ^{1}H 0.76 (s, 12H, $\mathrm{Si}\mathit{Me_2}$), 0.44 (s, 18H, $\mathrm{Si}\mathit{Me_3}$), 0.38 (s, 54H, $\mathrm{Si}\mathit{Me_3}$); ^{13}C 7.8 ($\mathrm{Si}\mathit{Me_2}$), 5.1 [$(\mathit{Me_3}\mathrm{Si})_2\mathrm{Si}$], 4.4 [$(\mathit{Me_3}\mathrm{Si})_3\mathrm{Si}$]. ^{29}Si −9.4 [$(\mathrm{Me_3}\mathit{Si})_3\mathrm{Si}$], −9.8 [$(\mathrm{Me_3}\mathit{Si})_2\mathrm{Si}$], −23.7 ($\mathrm{Me_2}\mathit{Si}$), −94.0 [$(\mathrm{Me_3Si})_2\mathit{Si}$], −116.8 [$(\mathrm{Me_3Si})_3\mathit{Si}$]. Anal. Calcd for $C_{28}H_{84}Si_{13}$ (786.08): C 42.78, H 10.77. Found: C 42.31, H 10.56.

1,1,3,3,5,5-Hexakis(trimethylsilyl)-2,2,4,4,6,6-hexamethylcyclohexasilane (6). To an ice cold solution of **4** (984 mg, 1.78 mmol) in toluene (45 mL) was added dropwise trifluoromethanesulfonic acid (534 mg, 3.56 mmol). The stirring was continued at rt for 4 h, and after complete conversion (controlled by NMR) the solution was diluted with toluene (20 mL) and cooled to 0 °C again. At this temperature 2,2-dimethyl-1,1,3,3-tetrakis(trimethylsilyl)trisilanyldipotassium·(18-crown-6)$_2$ [obtained from hexakis(trimethylsilyl)-2,2-dimethyltrisilane (984 mg, 1.78 mmol), KO^{t}Bu (399 mg, 3.55 mmol), 18-crown-6 (940 mg, 3.55 mmol)] in toluene (55 mL) was added dropwise, and the stirring was continued for another 12 h at rt. After subjecting the mixture to an aqueous workup the obtained residue was recrystallized from ethyl acetate, yielding **6** as a white crystalline solid (360 mg, 29%). Mp: 329−332 °C. NMR (δ in ppm): ^{1}H NMR ($CDCl_3$) 0.32 (s, 54H), 0.52 (s, 18H); ^{13}C ($CDCl_3$) 4.9, 5.1; ^{29}Si ($CDCl_3$) −7.6 ($\mathrm{Me_3}\mathit{Si}$), −31.1 ($\mathrm{Me_2}\mathit{Si}$), −124.1. Anal. Calcd for $C_{24}H_{72}Si_{12}$ (697.85): C 41.31, H 10.40. Found: C 40.88, H 10.44. UV absorption: $\lambda_1 = 203$ nm ($\varepsilon_1 = 2.3 \times 10^5$ [M^{-1} cm^{-1}]), $\lambda_2 = 239$ nm ($\varepsilon_2 = 6.1 \times 10^3$ [M^{-1} cm^{-1}]).

1,1,4,4,4-Pentakis(trimethylsilyl)-1-undecamethylcyclohexasilanyltetramethyltetrasilane (8). To a solution of bromoundecamethylcyclohexasilane (209 mg, 0.508 mmol) in benzene (10 mL) at rt was added a solution of 1-potassium-1,1,4,4,4-pentakis-(trimethylsilyl)tetramethyltetrasilane (427 mg, 1 equiv) (**7**) in benzene (10 mL). The reaction mixture remained colorless during the whole addition process, and a white precipitate was formed. After complete addition the reaction mixture was stirred for 2 h and then subjected to an aqueous workup with heptane/0.5 M H_2SO_4. After drying with sodium sulfate the solvent was removed, yielding a colorless solid of **8** (370 mg, 84%). Mp: 156−159 °C. NMR (δ in ppm): ^{1}H 0.66 (s, 6H), 0.61 (s, 6H), 0.54 (s, 3H), 0.49 (s, 6H), 0.43 (s, 18H), 0.43 (s, 6H), 0.35 (s, 27H), 0.26 (s, 6H), 0.25 (s, 6H), 0.23 (s, 6H); ^{13}C 4.7, 3.8, 3.2, 2.0, −1.4, −2.1, −2.6, −4.3, −5.2, −5.9, −6.5. ^{29}Si (D_2O cap) −9.2 ($\mathrm{Me_3}\mathit{Si}$), −9.3 ($\mathrm{Me_3}\mathit{Si}$), −25.9 ($\mathrm{Me_2}\mathit{Si}$), −29.9 ($\mathrm{Me_2}\mathit{Si}$), −34.5 ($\mathrm{Me_2}\mathit{Si}$), −38.6 ($\mathrm{Me_2}\mathit{Si}$), −43.5 ($\mathrm{Me_2}\mathit{Si}$), −67.9 ($\mathrm{Me}\mathit{Si}$), −113.1 ($\mathrm{Me_3Si}\mathit{Si}$), −126.2 ($\mathrm{Me_3Si}\mathit{Si}$). Anal. Calcd for $C_{30}H_{90}Si_{15}$ (872.33): C 41.31, H 10.40. Found: C 41.62, H 10.39. UV absorption: $\lambda_1 = 209$ nm ($\varepsilon_1 = 5.2 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 261$ nm ($\varepsilon_2 = 4.8 \times 10^4$ [M^{-1} cm^{-1}]), shoulder 281 nm.

1,1,4,4-Tetrakis(trimethylsilyl)-1,4-bis(undecamethylcyclohexasilanyl)tetramethyltetrasilane (11). The same procedure as described for **8** was used with bromoundecamethylcyclohexasilane (966 mg, 2.34 mmol) and **9** (1.253 g, 1.172 mmol). Compound **11** was obtained as a colorless solid (710 mg, 53%). Mp: 218−223 °C. NMR (δ in ppm): ^{1}H 0.75 (s, 6H), 0.57 (s, 6H), 0.49 (s, 12H), 0.44 (s, 12H), 0.43 (s, 36H), 0.39 (s, 18H), 0.27 (s, 12H), 0.23 (s, 12H); ^{29}Si (D_2O cap) −9.4 ($\mathrm{Me_3}\mathit{Si}$), −26.8 ($\mathrm{Me_2}\mathit{Si}$), −34.2 ($\mathrm{Me_2}\mathit{Si}$), −38.5 ($\mathrm{Me_2}\mathit{Si}$), −43.6 ($\mathrm{Me_2}\mathit{Si}$), −67.6 ($\mathrm{Me}\mathit{Si}$), −111.2 ($\mathrm{Me_3Si}\mathit{Si}$). Anal. Calcd for $C_{38}H_{114}Si_{20}$ (1133.04): C 40.28, H 10.14. Found: C 39.95, H 9.87. UV absorption: $\lambda_1 = 210$ nm ($\varepsilon_1 = 4.8 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 270$ nm ($\varepsilon_2 = 3.6 \times 10^4$ [M^{-1} cm^{-1}]), shoulder 241 nm, 286 nm.

1,2-Bis[1′,4′,4′-tris(trimethylsilyl)octamethylcyclohexasilanyl]-tetramethyldisilane (13). The same procedure as described for **8** was used with **12** (1.17 g, 1.45 mmol) and 1,2-dichlorotetramethyldisilane (136 mg, 0.732 mmol) and a reaction time of 18 h. Compound **13** was obtained as a colorless solid (713 mg, 87%). Mp: 227−231 °C. NMR (δ in ppm): ^{1}H 0.68 (s, 12H), 0.51 (s, 12H), 0.47 (s, 12H), 0.43 (s, 24H), 0.41 (s, 18H), 0.34 (s, 36H); ^{29}Si −8.1 ($\mathrm{Me_3}\mathit{Si}$), −8.6 ($\mathrm{Me_3}\mathit{Si}$), −9.2 ($\mathrm{Me_3}\mathit{Si}$), −26.6 ($\mathrm{Me_2}\mathit{Si}$), −37.7 ($\mathrm{Me_2}\mathit{Si}$), −38.1 ($\mathrm{Me_2}\mathit{Si}$), −119.8 ($\mathrm{Me_3Si}\mathit{Si}$), −132.1 ($\mathrm{Me_3Si}\mathit{Si}$). Anal. Calcd for $C_{38}H_{114}Si_{20}$ (1133.03): C 40.28, H 10.14. Found: C 39.97, H 10.07. UV absorption: $\lambda_1 = 210$ nm ($\varepsilon_1 = 11.3 \times 10^4$ [$M^{-1}cm^{-1}$]), $\lambda_2 = 265$ nm ($\varepsilon_2 = 3.8 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_3 = 289$ nm ($\varepsilon_3 = 3.6 \times 10^4$ [M^{-1} cm^{-1}]).

1,4-Bis[1′,4′,4′-tris(trimethylsilyl)octamethylcyclohexasilanyl]-octamethyltetrasilane (14). The same procedure as described for **8** was used with **12** (754 mg, 0.931 mmol) and 1,4-dichloro octamethyltetrasilane (140 mg, 0.462 mmol) and a reaction time of 18 h. Compound **14** was obtained as a colorless solid (490 mg, 85%). Mp: 209−214 °C. NMR (δ in ppm): ^{1}H 0.60 (s, 12H), 0.52 (s, 12H), 0.49 (s, 12H), 0.46 (s, 12H), 0.43 (s, 18H), 0.39 (s, 18H), 0.34 (s, 30H), 0.32 (12H); ^{29}Si −8.2 ($\mathrm{Me_3}\mathit{Si}$), −8.6 ($\mathrm{Me_3}\mathit{Si}$), −9.0 ($\mathrm{Me_3}\mathit{Si}$), −29.2 ($\mathrm{Me_2}\mathit{Si}$), −34.7 ($\mathrm{Me_2}\mathit{Si}$), −37.9 ($\mathrm{Me_2}\mathit{Si}$), −38.4 ($\mathrm{Me_2}\mathit{Si}$), −121.7 ($\mathrm{Me_3Si}\mathit{Si}$), −132.1 ($\mathrm{Me_3Si}\mathit{Si}$). Anal. Calcd for $C_{42}H_{126}Si_{22}$ (1249.35): C 40.38, H 10.16. Found: C 40.24, H 9.73. UV absorption: $\lambda_1 = 209$ nm ($\varepsilon_1 = 10.9 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 297$ nm ($\varepsilon_2 = 5.5 \times 10^4$ [M^{-1} cm^{-1}]), shoulder 273 nm.

1,6-Bis[1′,4′,4′-tris(trimethylsilyl)octamethylcyclohexasilanyl]-dodecamethylhexasilane (15). The same procedure as described for **8** was used with **12** (418 mg, 0.516 mmol) and 1,6-dichlorododecamethylhexasilane (108 mg, 0.257 mmol) and a reaction time of 12 h. Compound **15** was obtained as a colorless solid (347 mg, 99%). Mp: 207−212 °C. NMR (δ in ppm): ^{1}H 0.58 (s, 12H), 0.50 (s, 12H), 0.49 (s, 12H), 0.46 (s, 12H), 0.44 (s, 12H), 0.43 (s, 24H), 0.39 (s, 18H), 0.34 (s, 36H); ^{13}C 4.7, 3.9, 3.8, 2.2, −0.1,

−0.4, −0.6, −2.4, −3.1; ^{29}Si −8.2 (Me$_3$*Si*), −8.5 (Me$_3$*Si*), −9.0 (Me$_3$*Si*), −30.0 (Me$_2$*Si*), −35.3 (Me$_2$*Si*), −35.7 (Me$_2$*Si*), −37.9 (Me$_2$*Si*), −38.5 (Me$_2$*Si*), −122.2 (Me$_3$Si*Si*), −132.2 (Me$_3$Si*Si*). Anal. Calcd for $C_{46}H_{138}Si_{24}$ (1365.65): C 40.46, H 10.18. Found: C 40.73, H 9.94. UV absorption: $\lambda_1 = 303$ nm ($\varepsilon_1 = 7.3 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 218$ nm ($\varepsilon_2 = 1.1 \times 10^5$ [M^{-1} cm^{-1}]).

1,2-Bis(4′-trimethylsilyldodecamethylbicyclo[2.2.2]octasilanyl)-tetramethyldisilane (20). The same procedure as described for **8** was used with **19** (297 mg, 0.381 mmol) and 1,2-dichlorotetramethyldisilane (36 mg, 0.192 mmol), a reaction time of 4 h, and aqueous workup with toluene/0.5 M H_2SO_4. Compound **20** was obtained as a colorless solid (181 mg, 89%). Mp: > 300 °C. NMR (δ in ppm): ^{1}H (CDCl$_3$) 0.46 (s, 12H), 0.36 (s, 36H), 0.32 (s, 36H), 0.28 (s, 18H); ^{13}C (CDCl$_3$) 3.7, 1.9, −0.1, −0.8; ^{29}Si (CDCl$_3$) 0.1 (Me$_3$*Si*), −26.0 (Me$_2$*Si*), −37.2 (Me$_2$*Si*), −37.9 (Me$_2$*Si*), −121.8 (Si*Si*), −131.5 (Me$_3$Si*Si*). Anal. Calcd for $C_{34}H_{102}Si_{20}$ (1072.90): C 38.06, H 9.58. Found: C 38.01, H 9.76. UV absorption: $\lambda_1 = 209$ nm ($\varepsilon_1 = 9.1 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 288$ nm ($\varepsilon_2 = 5.0 \times 10^4$ [M^{-1} cm^{-1}]).

1,4-Bis(4′-trimethylsilyldodecamethylbicyclo[2.2.2]octasilanyl)-octamethyltetrasilane (21). The same procedure as described for **8** was used with **19** (270 mg, 0.353 mmol) and 1,4-dichlorooctamethyltetrasilane (52 mg, 0.171 mmol) and a reaction time of 18 h. Compound **21** was obtained as a colorless solid (200 mg, 98%). Mp: > 300 °C. NMR (δ in ppm): ^{1}H 0.58 (s, 12H), 0.49 (s, 12H), 0.48 (s, 36H), 0.41 (s, 36H), 0.33 (s, 18H); ^{29}Si (D$_2$O-cap) −5.8 (Me$_3$*Si*), −26.1 (Me$_2$*Si*), −36.6 (Me$_2$*Si*), −37.1 (Me$_2$*Si*), −37.7 (Me$_2$*Si*), −122.1 (Si*Si*), −130.9 (Me$_3$Si*Si*). Anal. Calcd for $C_{38}H_{114}Si_{22}$ (1189.21): C 38.38, H 9.66. Found: C 37.91, H 9.52. UV absorption: $\lambda_1 = 208$ nm ($\varepsilon_1 = 9.1 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 299$ nm ($\varepsilon_2 = 4.8 \times 10^4$ [M^{-1} cm^{-1}]).

1,2-Bis(4′-trimethylsilyldecamethylbicyclo[2.2.1]heptasilanyl)-tetramethyldisilane (23). At rt a mixture of 1,4-bis(trimethylsilyl)-decamethylbicyclo[2.2.1]heptasilane (**22**) (309 mg, 0.627 mmol), potassium *tert*-butoxide (74 mg, 0.659 mmol), and 18-crown-6 (174 mg, 0.659 mmol) was dissolved in benzene (10 mL). The solution immediately turned yellow, and complete conversion was achieved after 2 h [NMR (δ in ppm): ^{1}H 3.13 (s, 24H), 0.69 (s, 6H), 0.67 (s, 12H), 0.62 (s, 6H), 0.49 (s, 9H), 0.47 (s, 6H); ^{29}Si 1.0 (Me$_3$*Si*), −8.1 (Me$_2$*Si*), −18.8 (Me$_2$*Si*), −27.9 (Me$_2$*Si*), −113.6 (Me$_3$Si*Si*), −177.7 (K*Si*)]. Using the obtained solution the same procedure as described for **8** was followed with 1,2-dichlorotetramethyldisilane (62 mg, 0.329 mmol) to give **23** (285 mg, 95%) as a colorless solid. Mp: > 300 °C. NMR (δ in ppm): ^{1}H 0.59 (s, 12H), 0.54 (s, 12H), 0.50 (s, 12H), 0.45 (s, 12H), 0.41 (s, 12H), 0.40 (s, 12H), 0.34 (s, 18H). ^{13}C 4.5, 4.4, 2.6, 2.2, 1.2, 1.1, −0.7; ^{29}Si −5.3 (Me$_3$*Si*), −14.1 (Me$_2$*Si*), −26.8 (Me$_2$*Si*), −31.4 (Me$_2$*Si*), −31.6 (Me$_2$*Si*), −80.6 (Me$_3$Si*Si*), −118.5 (Me$_2$Si*Si*). Anal. Calcd for $C_{30}H_{90}Si_{18}$ (956.58): C 37.67, H 9.48. Found: C 37.52, H 9.48. UV absorption: $\lambda_1 = 219$ nm ($\varepsilon_1 = 5.4 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 290$ nm ($\varepsilon_2 = 3.2 \times 10^4$ [M^{-1} cm^{-1}]).

1,4-Bis(4′-trimethylsilyldecamethylbicyclo[2.2.1]heptasilanyl)-octamethyltetrasilane (24). The same procedure as described for **23** employing **22** (404 mg, 0.559 mmol) and 1,4-dichlorooctamethyltetrasilane (90 mg, 0.296 mmol) was used. Compound **24** (273 mg, 91%) was obtained as a colorless solid. Mp: 248−253 °C. NMR (δ in ppm): ^{1}H 0.59 (s, 12H), 0.54 (s, 12H), 0.50 (s, 12H), 0.45 (s, 12H), 0.43 (s, 12H), 0.41 (s, 12H), 0.40 (s, 12H), 0.34 (s, 18H); ^{13}C 3.4, 1.6, 0.9, −0.1, −0.7, −1.1, −1.6, −3.6. ^{29}Si −5.5 (Me$_3$*Si*), −14.4 (Me$_2$*Si*), −25.2 (Me$_2$*Si*), −31.7 (Me$_2$*Si*), −31.9 (Me$_2$*Si*), −38.7 (Me$_2$*Si*), −119.2 (Me$_3$Si*Si*), −123.5 (Me$_2$Si)$_4$*Si*. Anal. Calcd for $C_{34}H_{102}Si_{20}$ (1040.73): C 38.06, H 9.58. Found: C 37.66, H 9.60. UV absorption: $\lambda_1 = 219$ nm ($\varepsilon_1 = 6.1 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 300$ nm ($\varepsilon_2 = 5.1 \times 10^4$ [M^{-1} cm^{-1}]).

1,2-Bis[1,3,3-tris(trimethylsilyl)tetramethylcyclotetrasilanyl]-tetramethyldisilane (25). A solution of 1,3,3-tris(trimethylsilyl)-tetramethylcyclotetrasilanylpotassium·18-crown-6 (0.430 mmol) in benzene (2 mL) was slowly added (within 15 min) to a stirred solution of 1,2-dichlorotetramethyldisilane (0.226 mmol) in benzene (5 mL). The resulting clear and colorless reaction mixture was stirred for 2 h. The solution was poured into a mixture of H_2SO_4 (0.5 M solution) and diethyl ether. After separation of the layers the aqueous phase was extracted several times with diethyl ether, and the combined organic layers were dried over sodium sulfate. After removal of solvent **25** was obtained as a white solid (185 mg, 96%).

NMR (δ in ppm): ^{1}H 0.70 (s, 12H), 0.65 (s, 12H), 0.61 (s, 12H), 0.22 (s, 18H), 0.35(s, 18H), 0.34 (s, 18H). ^{13}C 4.2, 3.6, 3.5, 3.4, 3.0, 1.0; ^{29}Si −7.8, −8.5, −9.0, −24.2, −28.8, −90.6, −95.7. Anal. Calcd for $C_{30}H_{90}Si_{16}$ (900.40): C 40.02, H 10.07. Found: C 39.73, H 10.17. UV absorption: $\lambda_1 = 255$ nm ($\varepsilon_1 = 3.7 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 292$ nm ($\varepsilon_1 = 7.4 \times 10^3$ [M^{-1}cm^{-1}]), $\lambda_3 = 325$ nm ($\varepsilon_1 = 9.2 \times 10^3$ [M^{-1} cm^{-1}]).

1,4-Bis[1,3,3-tris(trimethylsilyl)tetramethylcyclotetrasilanyl]-octamethyltetrasilane (26). A solution of 1,3,3-tris(trimethylsilyl)tetramethylcyclotetrasilanylpotassium·18-crown-6 (0.430 mmol) in benzene (2 mL) was slowly added (within 15 min) to a stirred solution of 1,4-dichlorooctamethyltetrasilane (69 mg, 0.23 mmol) in benzene (5 mL). During the addition a white precipitate was formed. The resulting colorless reaction mixture was stirred for 2 h. Then the solution was poured into a mixture of H_2SO_4 (0.5 M solution) and diethyl ether. The layers were separated, the aqueous phase was extracted several times with diethyl ether, and combined organic layers were dried over sodium sulfate. After removing the solvent a white solid was obtained (193 mg, 88%), which was insoluble in C_6D_6 and only slightly soluble in CDCl$_3$.

NMR (δ in ppm): ^{1}H (CDCl$_3$) 0.56 (s, 12H), 0.55 (s, 12H), 0.53 (s, 12H), 0.41 (s, 12H), 0.29 (s, 18H), 0.26 (s, 18H), 0.26 (s, 18H); ^{13}C (CDCl$_3$) 3.9, 3.4, 3.4, 3.3, 2.8, 2.5, 1.0; ^{29}Si (CDCl$_3$) −7.6, −8.2, −8.7, −23.7, −28.5, −37.6, −90.9, −95.3. Anal. Calcd for $C_{34}H_{102}Si_{18}$ (1016.71): C 40.17, H 10.11. Found: C 39.66, H 10.00. UV absorption: $\lambda_1 = 274$ nm ($\varepsilon_1 = 3.1 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 325$ nm ($\varepsilon_1 = 1.3 \times 10^4$ [M^{-1} cm^{-1}]), shoulder 296 nm.

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Supporting Information Available: X-ray crystallographic information in CIF format and copies of ^{1}H NMR spectra of all new compounds are available free of charge via the Internet at http://pubs.acs.org.