Organometallics **2008,** *27,* 5221–5229

Structure, Conformation, and UV Absorption Behavior of Partially Trimethylsilylated Oligosilane Chains

Andreas Wallner, Harald Wagner, Judith Baumgartner, Christoph Marschner,*
Henning W. Rohm, Martin Köckerling, and Clemens Krempner*

*Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria,
and Department of Chemistry, University of Rostock, A.-Einstein-Str. 3a, D-18059 Rostock, Germany*

Received May 14, 2008

A number of new oligosilane chains containing linear segments with up to 18 silicon atoms were prepared. Employing salt elimination reactions of oligosilylpotassium compounds and oligosilylhalides, we prepared a number of tris(trimethylsilyl)silyl-terminated chains with varying internal segments consisting of dimethylsilylene and bis(trimethylsilyl)silylene units. Single-crystal X-ray diffraction and UV spectroscopic analysis indicate that the oligosilanes thus obtained are conformationally highly constrained due to steric interactions between trimethylsilyl groups. The chains consist of all-*transoid*-oriented segments, capable of σ-bond electron delocalization, which are separated by *cisoid* turns.

Introduction

The property of σ-bond electron delocalization manifests poly- and oligosilanes as a class of compounds with unique properties. The degree of this delocalization, however, is highly dependent on the oligosilane silicon backbone conformation.[1] As rotational processes around Si−Si bonds are energetically very facile, polysilanes in solution often exist as mixtures of many conformers. For an effective delocalization, the silicon atoms need to be aligned as an all-*transoid* segment. Several methods to achieve this alignment have been investigated including the inclusion into cyclodextrins,[2] conformational locking by hydrogen bond interactions,[3] incorporation of pentacoordinate silicon atoms,[4] or incorporation into cyclic structures.[5] One way to control the conformation along a linear oligosilane chain unambiguously was studied by Tamao and Tsuji in a series of recent papers.[6] The introduction of oligosilane segments with a bicyclic alkylene backbone allowed the rotation around Si−Si bonds to be prevented. By the combination of different bicyclic backbone segments, it was possible to obtain chains either with all-*transoid* conformations or with only short *transoid* segments interrupted by *cisoid* turns.[7] UV spectroscopic examination of these chains revealed that the all-*transoid* chain exhibits an absorption maximum corresponding to the whole chain length. In contrast to this, the chain containing *cisoid* turns showed an absorption which can be attributed only to the short *transoid*-oriented segments of the chain. Thus, the effect of delocalization−rupture via a rotational turn which terminates the *transoid* arrangement was proven.

Recently, we reported that in the solid state tris(trimethylsilyl)silyl-terminated methylated oligosilanes adopt an all-*transoid* conformation.[8] Subsequent investigations of their UV spectroscopic properties in solution showed spectra containing two bands. The high energy band around 210 nm corresponds to the trisilanyl unit of the tris(trimethylsilyl)silyl group. The second band is associated with delocalization along the main chain with bathochromic shifts on increasing chain length. For the case of a chain length up to four dimethysilylene units, this band remains relatively sharp, indicating only one prevalent conformation. This was also supported by comparative Raman spectra of samples in the solid state and in solution.[9] In the meantime, we prepared another compound in the series with an internal chain length of six dimethysilylene units (**2**). Still

---

* Corresponding author. Tel: ++43-316-873-8209. Fax: ++43-316-873-8701. E-mail: christoph.marschner@tugraz.at. Tel: ++49-381-498-6406. Fax: ++49-381-498-6382. E-mail: clemens.krempner@uni-rostock.de.

(1) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359–1410. (b) West, R. Organopolysilanes. In *Comprehensive Organometallic Chemistry II*; Davies, A. G., Ed.; Pergamon: Oxford, 1994; Vol. 2, pp 77−110. (c) West, R. Polysilanes. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, UK, 1989; pp 1207−1240. (d) West, R. Polysilanes: Conformations, Chromotropism and Conductivity. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, UK, 2001; Vol. 3, pp 541−564. (e) Jones, R. G.; Ando, W.; Chojnowski, J. *Silicon-Containing Polymers*; Kluwer Academic Publisher: Dordrecht, The Netherlands, 2000.

(2) (a) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromol. Rapid Commun.* **2002**, *23*, 781–785. (b) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2003**, *36*, 6422–6429. (c) Sakamoto, T.; Naruoka, T.; Kira, M. *Chem. Lett.* **2003**, *32*, 380–380. (d) Sanji, T.; Yoshiwara, H.; Sakurai, H.; Tanaka, M. *Chem. Commun.* **2003**, 1506–1507. (e) Sanji, T.; Kato, N.; Kato, M.; Tanaka, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7301–7304. (f) Sanji, T.; Kato, M.; Tanaka, M. *Macromolecules* **2005**, *38*, 4034–4037.

(3) (a) Jäger-Fiedler, U.; Wulff, A.; Köckerling, M.; Ludwig, R.; Krempner, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6755–6759. (b) Krempner, C.; Flemming, A.; Köckerling, M.; Ludwig, R.; Miethchen, R. *Chem. Commun.* **2007**, 1810–1812.

(4) (a) El Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095–5096. (b) El Sayed, I.; Hatanaka, Y.; Onozawa, S.-Y.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **2001**, *123*, 3597–3598.

(5) (a) Mazieres, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682–6683. (b) Krempner, C.; Reinke, H. *Organometallics* **2007**, *26*, 2053–2057.

(6) (a) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3287–3290. (b) Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 7486–7487. (c) Tsuji, H.; Fukazawa, A.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *Organometallics* **2004**, *23*, 3375–3377. (d) Mallesha, H.; Tsuji, H.; Tamao, K. *Organometallics* **2004**, *23*, 1639–1642. (e) Fukazawa, A.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2006**, *128*, 6800–6801.

(7) The conformations are classified as *syn* (S, ~0°), *gauche* (G, ~60°), *ortho* (O, ~90°), *eclipsed* (E, ~120°), *deviant* (D, ~150°), *transoid* (T, ~170°), and *anti* (A, ~180°). See: Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *33*, 821–823.

(8) Baumgartner, J.; Frank, D.; Kayser, C.; Marschner, C. *Organometallics* **2005**, *24*, 750–761.

(9) Marschner, C.; Baumgartner, J.; Wallner, A. *Dalton Trans.* **2006**, 5667–5674.

10.1021/om8004383 CCC: $40.75

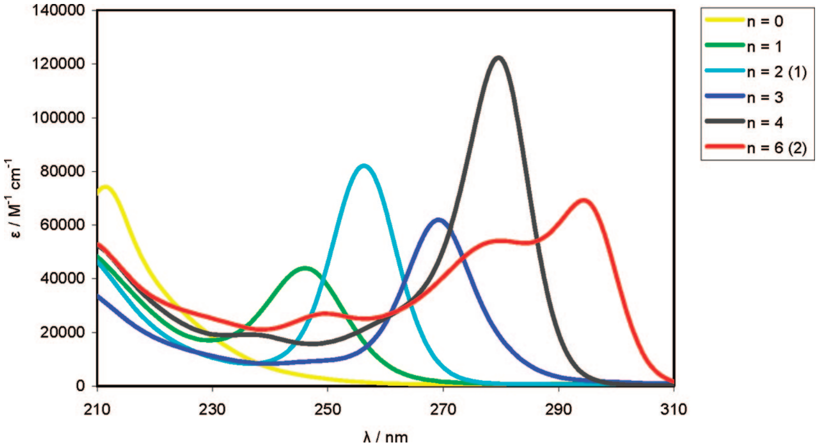


Figure 1. Comparison of UV spectra of compounds with the structure $(Me_3Si)_3Si(SiMe_2)_nSi(SiMe_3)_3$ (cf. ref 8 for $n = 1$, 2 (**1**), 3, 4, and 6 (**2**)).

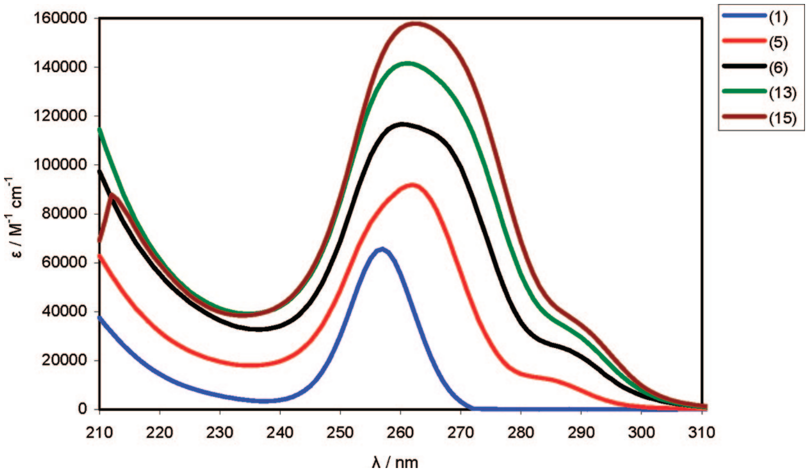


Figure 2. Comparison of UV spectra of compounds of the general formula $(Me_3Si)_3Si(Me_2Si)_2[(Me_3Si)_2Si(Me_2Si)_2]_nSi(SiMe_3)_3$ ($n = 0-4$) (**1**, **5**, **6**, **13**, **15**).

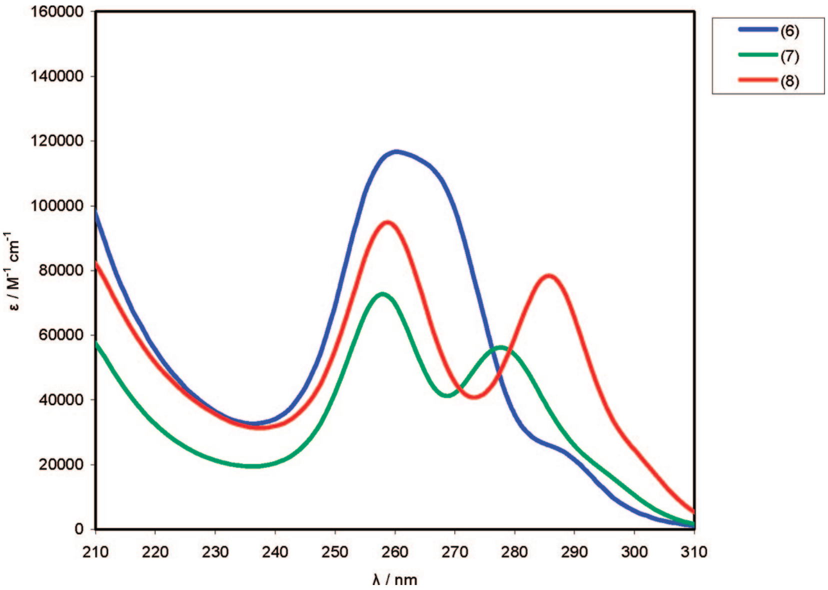


Figure 3. UV spectra of **6**, **7**, and **8**.

the crystal structure shows an all-*transoid* conformation with a helical twist in the solid state (Figure 4). A comparison of all solution UV spectra (Figure 1), however, showed a splitting of the low energy band for **2** into one band at the expected absorption wavelength of 294 nm, another one at 280 nm, and several other ones at higher energy. This splitting indicates that for the 1,6-permethylhexasilanylene spacer the steric influence of the two terminal tris(trimethylsilyl)silyl groups is not

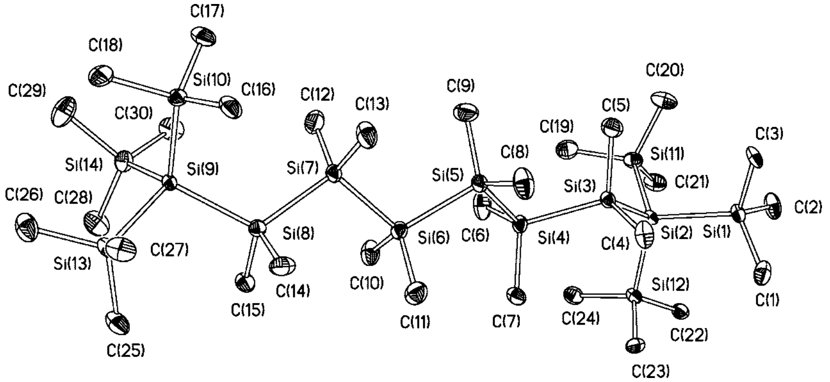


Figure 4. Molecular structure of **2** (thermal ellipsoids drawn at the 30% probability level; all hydrogen atoms were omitted for clarity). Selected bond lengths [Å] and bond angles [°] with standard deviation: Si(1)−C(1) 1.860(11), Si(1)−Si(2) 2.348(4), Si(1)−Si(2)−Si(3) 106.35(13), Si(4)−Si(3)−Si(2), 19.25(13), Si(3)−Si(4)−Si(5) 109.32(13), Si(6)−Si(5)−Si(4) 108.35(14), Si(5)−Si(6)−Si(7) 110.61(14), Si(6)−Si(7)−Si(8) 109.21(14), Si(9)−Si(8)−Si(7) 118.25(14), Si(11)−Si(2)−Si(1) 107.74(13), Si(11)−Si(2)−Si(12) 108.76(13), Si(1)−Si(2)−Si(12) 107.55(13), Si(11)−Si(2)−Si(3) 112.39(14), Si(12)−Si(2)−Si(3) 113.75(13), Si(14)−Si(9)−Si(13) 106.61(13), Si(14)−Si(9)−Si(10) 109.89(14), Si(13)−Si(9)−Si(10) 106.56(13), Si(14)−Si(9)−Si(8) 112.89(13), Si(13)−Si(9)−Si(8) 107.39(13), Si(10)−Si(9)−Si(8) 113.06(13).

sufficient to suppress rotation along the main chain effectively. The second band at 280 nm probably arises from a conformer which differs from the all-*transoid* arrangement by a rotation around the Si(3)−Si(4) bond. The longest all-*transoid* segment in this rotamer presumably contains eight silicon atoms and, hence, exhibit an absorption maximum close to the value for the compound with the tetrasilanylene spacer.

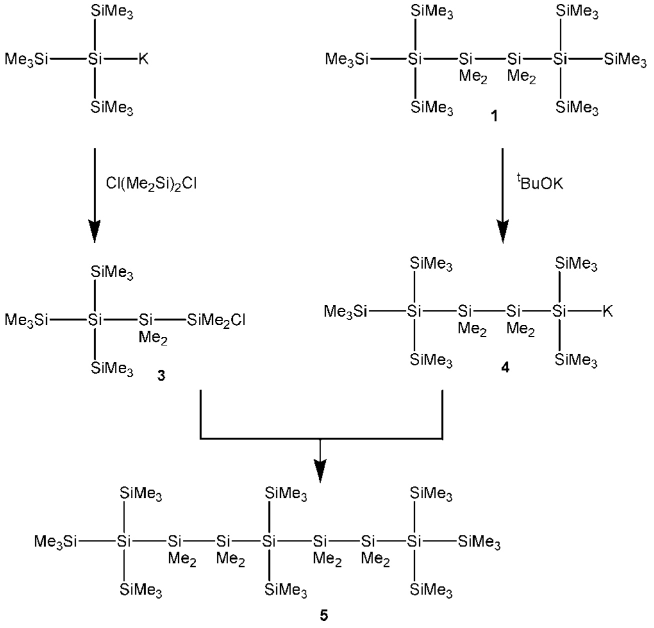
Results and Discussion

Synthesis of Longer Chains. To utilize the principle of conformational control employing trimethylsilyl substituents also for longer chains, we set out to prepare a series of polysilanes with internal trimethylsilyl substituents. Compound **5** as the first of these model substances was obtained by a two-step procedure. Reaction of tris(trimethylsilyl)silylpotassium[10] with 1,2-dichlorotetramethyldisilane gave the chlorinated compound **3**.[11] Reaction of **3** with the potassium compound **4**,[12] derived from the reaction of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane (**1**)[11] with potassium *tert*-butoxide, gave the desired nonasilane **5** (Scheme 1).

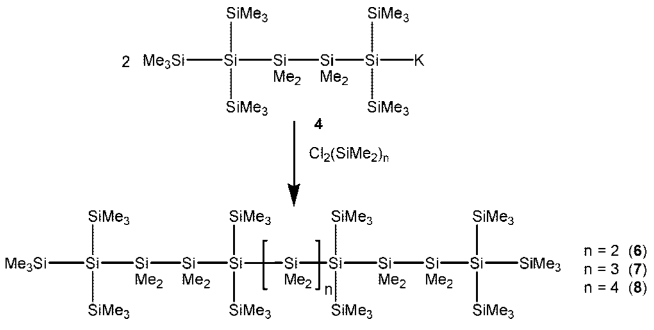
Reaction of 2 equiv of **4** with 1,2-dichlorotetramethyldisilane led to the formation of a similar compound (**6**) with three tetramethyldisilanylene units (Scheme 2). To obtain compounds with a variation of the internal spacer chain length, 2 equiv of **4** with either 1,3-dichlorohexamethyltrisilane or 1,4-dichlorooctamethyltetrasilane was reacted to yield compounds **7** and **8** (Scheme 2).

Reaction of only 1 equiv of **4** with 1,2-dichlorotetramethyldisilane gave the monochlorinated compound **9**. Reaction of tris(trimethylsilyl)silylpotassium with 1-chloro-2-phenyltetramethyldisilane resulted in the formation of **10**. Conversion to the corresponding silylpotassium compound by reaction with potassium *tert*-butoxide and its subsequent reaction with **9** yielded the terminally phenyl-substituted compound **11**. Dephenylation by means of reaction with triflic acid[13] and conversion of the obtained triflate with lithium chloride gave silyl chloride **12**. Again the sequence is finished by reaction of **12** with **4** (Scheme 3).

Scheme 1



Scheme 2



The synthetic procedure for the final compound with five disilanylene units follows a similar strategy. Again compound **10** was converted to the respective anion, which subsequently was reacted with 0.5 equiv of 1,2-dichlorotetramethyldisilane to give compound **14**. Addition of 2 equiv of triflic acid generates the ditriflate which upon reaction with 2 equiv of **4** gave **15**, which contains a linear Si_{18} segment (Scheme 4).

---

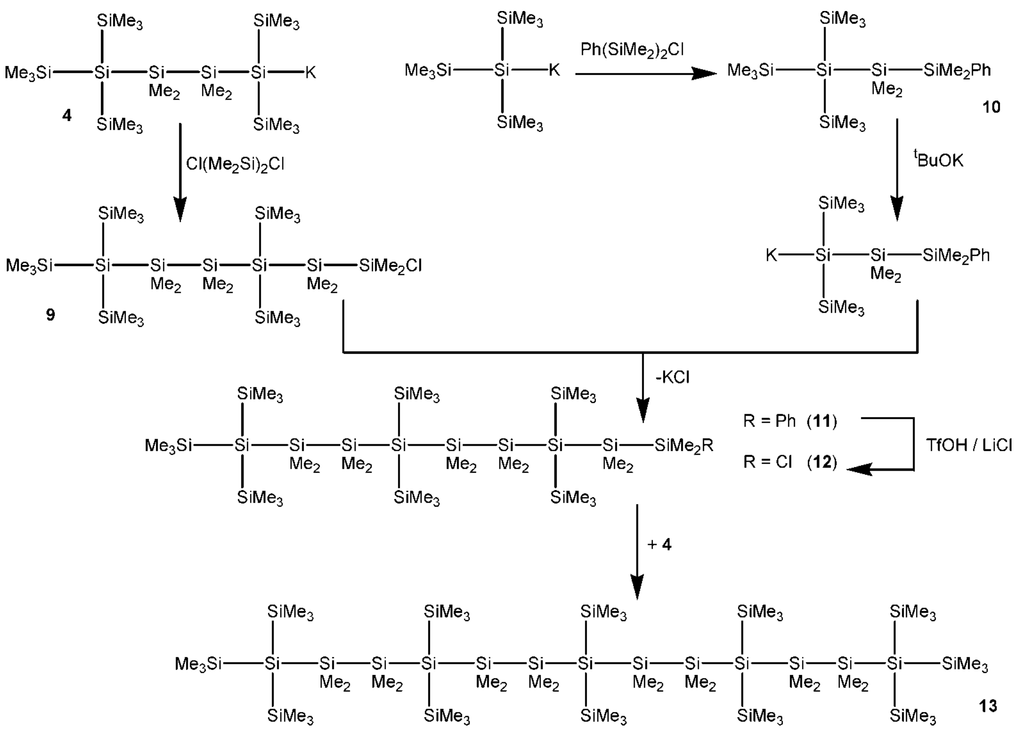
(10) Marschner, C *Eur. J. Inorg. Chem.* **1998**, 221–226.

(11) Whittaker, S. M.; Brun, M. C.; Cervantes-Lee, F.; Pannell, K. H. *J. Organomet. Chem.* **1995**, *499*, 247–252.

(12) Kayser, C.; Kickelbick, G.; Marschner, C. *Angew. Chem.* **2002**, *114*, 1031−1034; *Angew. Chem., Int. Ed.* **2002**, *41*, 989−992.

(13) Uhlig, W. *J. Organomet. Chem.* **1992**, *421*, 189–197.

Scheme 3



Scheme 4

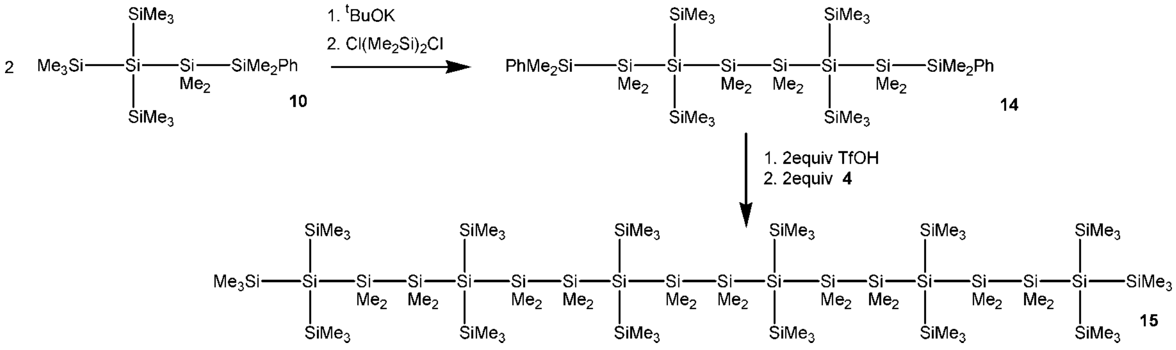


Table 1. UV Spectroscopic Data of Some Selected Oligosilanes

compound	oligosilane chain length	λ_1 (nm)	ϵ_1 (M^{-1} cm^{-1})	λ_2 (nm)	ϵ_2 (M^{-1} cm^{-1})	λ_3 (nm)	ϵ_3 (M^{-1} cm^{-1})
1	6	257	6.6×10^4	–	–	–	–
(*n* = 3)	7	269	6.2×10^4	–	–	–	–
(*n* = 4)	8	280	1.2×10^5	–	–	–	–
5	9	~284 (sh)	1.2×10^4	–	–	262	9.2×10^4
2	10	294	6.9×10^4	280	5.4×10^4	250	2.7×10^4
6	12	~289 (sh)	2.3×10^4	–	–	259	7.4×10^4
7	13	~295 (sh)	1.8×10^4	278	5.6×10^4	258	7.3×10^4
8	14	~303 (sh)	1.8×10^4	286	7.8×10^4	259	9.5×10^4
13	15	~289 (sh)	3.1×10^4	–	–	261	1.4×10^5
15	18	~291 (sh)	3.3×10^4	–	–	262	1.6×10^5

UV Spectroscopic Properties. The degree of σ-bond electron delocalization can be determined by UV spectroscopy. As outlined above, we extended the numbers of silicon atoms in the spacer of the permethyloligosilanylene unit between the tris(trimethylsilyl)silyl units. As a function of this extension, a bathochromic shift of the low energy band was observed (Table 1). Considering this behavior, it could be expected that compounds **5**, **6**, **13**, and **15** should exhibit bands with a successively bathochromic shift compared to the absorption of 257 nm for **2**. However, as can be seen from Figure 2, only the band of **5** is substantially shifted to lower energy (262 nm). In addition, a shoulder around 286 nm can be observed. For compounds **6**, **13**, and **15**, the situation is very similar to **5**. However, while the absorption maxima remain around 261 nm, they become stronger and broader with increasing number of silicon atoms. In addition the shoulder moves to lower energy (292 nm for **15**).

In Figure 3, the comparison of compounds **6**, **7**, and **8** is shown. Here the situation is different as we observe a splitting into two low energy bands for **7** and **8**. The band at higher energy remains at the same position where the absorption for **5**, **6**, **13**, and **15** was observed. For **7**, the new band is observed at 278 nm, while for **8**, it is shifted to 286 nm.

Crystal Structure Analyses. The compounds dealt with in this study are nonpolar. With longer chain length, they become

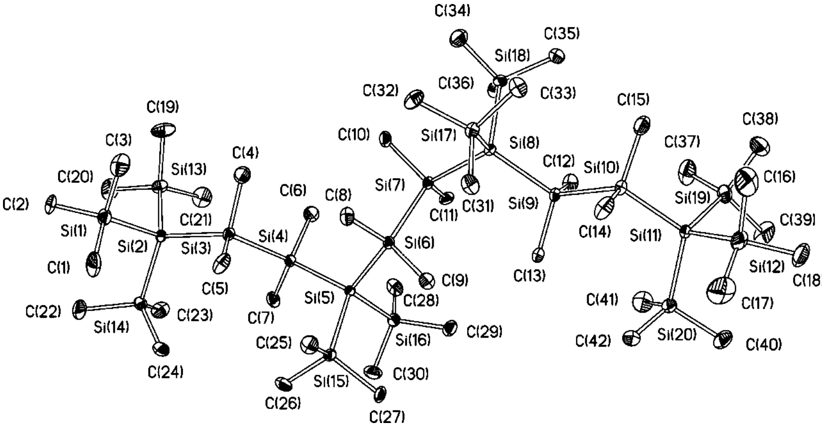


Figure 5. Molecular structure of **6** (thermal ellipsoids drawn at the 30% probability level, all hydrogen atoms were omitted for clarity). Selected bond lengths [Å] and bond angles [°] with standard deviation: Si(1)−C(1) 1.872(16), Si(1)−Si(2) 2.349(5), Si(1)−Si(2)−Si(3) 105.43(18), Si(4)−Si(3)−Si(2) 118.37(18), Si(3)−Si(4)−Si(5) 118.05(17), Si(6)−Si(5)−Si(4) 116.47(17), Si(5)−Si(6)−Si(7) 118.52(17), Si(8)−Si(7)−Si(6) 117.72(17), Si(7)−Si(8)−Si(9) 109.37(17), Si(10)−Si(9)−Si(8) 118.72(18), Si(9)−Si(10)−Si(11) 115.98(18), Si(12)−Si(11)−Si(10) 106.7(2), Si(1)−Si(2)−Si(13) 108.42(19).

also less soluble. This is known from the chemistry of polysilanes, and it does not facilitate crystallization. Obtaining single crystals of good quality therefore is rather difficult. Nonetheless, compounds **2**, **6**, and **8** could be subjected to crystal structure analysis. While the diffraction data were not of high quality in all three cases, a clear-cut picture of the conformational situation in the solid state could be obtained.

In analogy to the compounds with shorter spacer lengths,[8] compound **2** (Figure 4) exhibits a regular all-*transoid* arrangement of the spacer segment. Due to 1,3- and 1,4-steric interactions, the *anti*-conformation in the chain is disfavored and torsional angles of around 160° are observed. The deviation from 180°, always in the same direction, causes a helical twist to the molecule, which is in accordance with what is reported for polysilane polymers.[1] Si−Si bond lengths are close to 2.36 Å, which is typical for related compounds.

The structural properties of compounds **6** and **8** are of interest as they should provide an explanation for the observed UV spectroscopic properties. Analysis of the two structures shows an interesting feature. For both compounds (**6**, **8**), we observe that the main chain is divided into three segments with all-*transoid* conformational arrangement. After the bis(trimethylsilyl)silyl unit, the chain makes a turn, adopting a torsional angle of around 80°. A description of the *transoid* conformational segments as planes through all involved silicon atoms reveals that these planes are oriented close to orthogonal to each other. The outer *transoid* segments of compound **6** (Figure 5) are different; both consist of six silicon atoms: one outer trimethylsilyl group, the quaternary silicon atom and four additional silicon atoms. However, these four atoms are part of the main chain for one segment but include one of the internal trimethylsilyl groups for the other segment. The inner transoid Si_6 segment consists of the four inner silicon atoms and two of the internal trimethylsilyl groups (Figure 7).

For compound **8** (Figure 6), the outer segments also consist of six silicon atoms. In contrast to **6**, the inner terminal silicon atoms of the outer segments are not part of the main chain but consist of trimethylsilyl groups. Now the inner *transoid* segment of **8**, which consists of eight silicon atoms, reaches along the main chain without any involvement of the internal trimethylsilyl groups (Figure 8). Dihedral angles of the polysilane framework are listed in Table 2. From the sign of the dihedral angle, it can be concluded that there is a helical arrangement of the *transoid* aligned segments in **2** and **8**. Compound **6** seems to be fairly distorted. For the three conjugated segments of **6**, only one shows a helical alignment.

Conclusion

The UV spectra of a series of oligosilane chains consisting of the general formula $(Me_3Si)_3Si(Me_2Si)_2[(Me_3Si)_2Si(Me_2Si)_2]_n$-$Si(SiMe_3)_3$ ($n = 0{-}4$) (**3**, **5**, **6**, **13**, **15**) have been prepared and studied using UV spectroscopy. Interestingly, no distinct bathochromic shift of the lowest energy absorption band was observed with increasing chain length. The absorption maximum remains in the same region (around 260 nm) for all compounds of the series (Figure 2). Only a shoulder of the band reaches to lower energy. In contrast to this, the extinction grows linearly as the number of silicon atoms increases. Compounds **7** and **8**, which have spacer chains with a larger number of silicon atoms compared to **6**, exhibit a splitting of the low energy band into one band at the same wavelength as found for the described series and a second band with a bathochromic shift corresponding to the elongated middle segment of the chain.

The spectral characteristics of compounds **1**, **5**, **6**, **7**, **8**, **13**, and **15** can be interpreted in a similar fashion as the compounds studied recently by Tamao et al.[6] In a way, comparable to polysilane chains consisting of blocks of constrained oligosilanyl units, the trimethylsilyl substituents suppress the conformational flexibility of the main chain. Compounds with trimethylsilyl groups only at the ends of the main chain feature an all-*transoid* arrangement. In contrast to this, internal trimethylsilyl groups force *cisoid* turns. As a consequence, depending on the chain length, several *transoid*-oriented segments of the same length contribute to absorption at about the same wavelength. Compared to the use of bicyclic building blocks,[6] the conformational control is less strict. Conformers with segments that are longer than the preferred six silicon atoms seem also to be present to some small extent. Their contribution can be estimated from the growing shoulders in the range from 280 to 290 nm (Figure 2).

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. All solvents besides $CDCl_3$ were dried over sodium/potassium alloy under

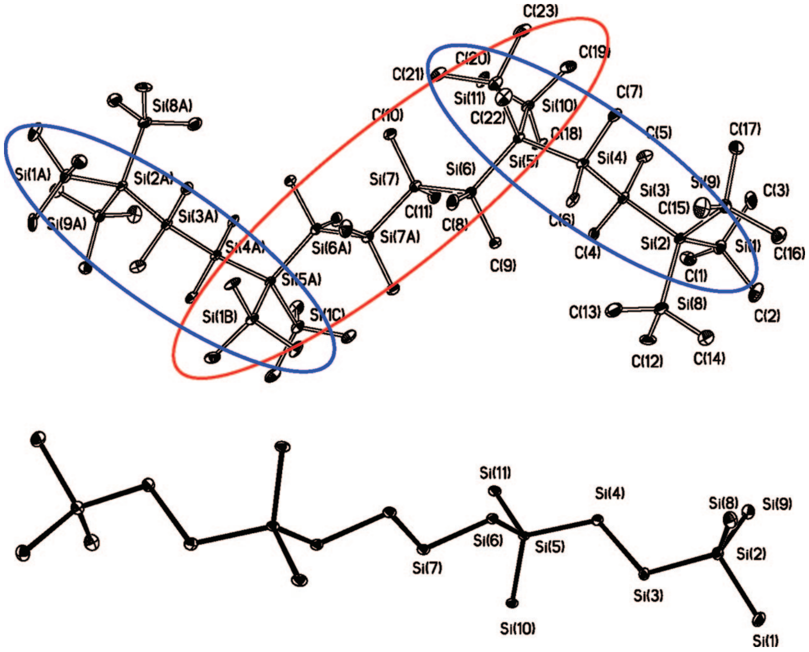


Figure 6. Molecular structure of **8** (thermal ellipsoids drawn at the 30% probability level; all hydrogen atoms were omitted for clarity). Top: structure with methyl groups and marked *transoid* segments. Bottom: all-silicon backbone of the molecule. Selected bond lengths [Å] and bond angles [°] with standard deviation: Si(1)−C(3) 1.862(10), Si(1)−Si(2) 2.358(4), Si(2)−Si(8) 2.342(4), Si(8)−Si(2)−Si(3) 112.33(14), Si(3)−Si(2)−Si(1) 105.54(13), Si(2)−Si(3)−Si(4) 116.55(13), Si(3)−Si(4)−Si(5) 116.23(13), Si(6)−Si(5)−Si(4) 109.22(13), Si(7)−Si(6)−Si(5) 118.86(13), Si(6)−Si(7)−Si(7A) 109.30(16), Si(8)−Si(2)−Si(9) 110.27(14), Si(3)−Si(2)−Si(9) 116.08(14), Si(8)−Si(2)−Si(1) 105.55(13), Si(9)−Si(2)−Si(1) 106.21(13), Si(10)−Si(5)−Si(6) 115.71(13), Si(10)−Si(5)−Si(11) 106.86(13), Si(6)−Si(5)−Si(11) 106.87(13), Si(10)−Si(5)−Si(4) 111.26(13), Si(11)−Si(5)−Si(4) 106.40(12).

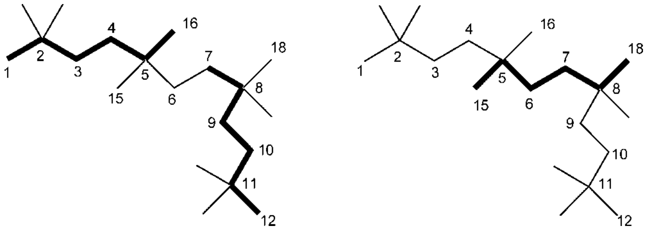


Figure 7. Two-dimensional representation of the silicon scaffold of **6**. The outer *transoid* aligned Si_6 segments drawn bold on the left side. The middle *transoid* aligned Si_6 segment drawn bold on the right side.

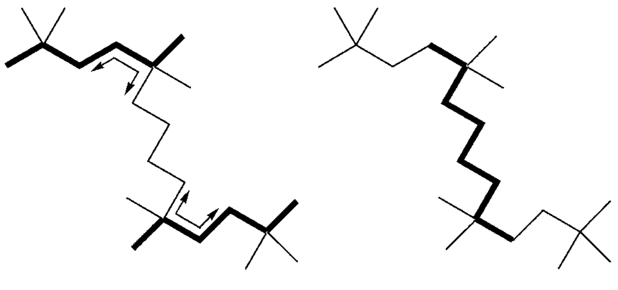


Figure 8. Two-dimensional representation of the silicon scaffold of **8**. The outer *transoid* aligned Si_6 segments drawn bold on the left side. The middle *transoid* aligned Si_8 segment drawn bold on the right side. The *cisoid* turns (indicated on the left side) of the main chain are in the outer segments.

nitrogen and were freshly distilled prior to use. Potassium *tert*-butoxide was purchased from Merck. All other chemical were purchased from different suppliers and were used without further purification.

^1H NMR (300 MHz), ^{13}C NMR (75.4 MHz), and ^{29}Si NMR (59.3 MHz) spectra were recorded either on a Varian INOVA 300 spectrometer or, if noted, on Bruker AC 250, or ARX 300 and 400 spectrometers. If not noted otherwise, for all NMR samples, C_6D_6 was used as solvent. Some ^{29}Si spectra of the reaction solution were 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.[14] Elemental analyses were carried out using a Heraeus VARIO ELEMENTAR. In some cases, the addition of WO_3 was required to suppress SiC formation. UV absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer in pentane solution or on a Perkin-Elmer Lambda 2 spectrometer in heptane solution with a quartz cell of 1.0 cm length. Mass spectra (EI) were measured on an Intectra AMD 402. GC analyses were carried out on a HP 5890 series II (capillary column DB-1HT; 15 m × 0.251 mm; 0.1 μm) with a flame ionization detector or a HP 5890 series II coupled to a mass spectrometer HP 5971A.

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^2_o and corrected for absorption effects with SAINT[15] and SADABS,[16] respectively. The structures were solved by direct methods and refined by full-matrix least-squares method.[17] Measuring compounds **2** and **6** at higher degrees than 100 K was necessary because the crystals lost their integrity at lower temperature. If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles.

---

[14] (a) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760–762. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877–879.

[15] *SAINTPLUS: Software Reference Manual*, version 6.45; Bruker-AXS: Madison, WI, 1997−2003.

[16] Blessing, R. H. *Acta Crystallogr. A* **1995**, *51*, 33−38; *SADABS*, version 2.1; Bruker-AXS: Madison, WI, 1998.

[17] Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112–122.

Table 2. Dihedral Angles in the Silicon Skeleton of Compounds 2, 6, and 8[a]

2		6		8	
Si atoms	angle (deg)	Si atoms	angle (deg)	Si atoms	angle (deg)
1−2−3−4	***−161.0***	***1−2−3−4***	***+170.6***	***1−2−3−4***	***−163.1***
2−3−4−5	***−167.7***	***2−3−4−5***	***−151.4***	***2−3−4−5***	***−165.9***
3−4−5−6	***−161.1***	**3−4−5−16**	**+171.7**	**3−4−5−11**	**−159.9**
4−5−6−7	***−155.3***	*3−4−5−6*	*−61.5*	*3−4−5−6*	*+85.1*
5−6−7−8	***−167.5***	3−4−5−15	+60.2	3−4−5−10	−43.8
6−7−8−9	***−164.0***	*4−5−6−7*	*−67.2*	***4−5−6−7***	**−161.1**
7−8−9−13	***−164.1***	**15−5−6−7**	**+167.1**	***5−6−7−7A***	**−167.0**
		5−6−7−8	***−156.9***	***6−7−7A-6A***	**+180.0**
		6−7−8−18	**−161.7**	***7−7A-6A-5A***	**−167.0**
		6−7−8−9	*+82.5*	***7A-6A-5A-4A***	**−161.1**
		6−7−8−14	−48.1		
		17−8−9−10	−32.5		
		18−8−9−10	+86.4		
		7−8−9−10	**−159.9**		
		8−9−10−11	**−176.9**		
		9−10−11−12	**−159.8**		

[a] Bold areas correspond to *anti* or *transoid* aligned segments, italic segments are in the main chain.

Table 3. Crystallographic Data for Compounds 2, 6, and 8

	2	6	8
empirical formula	$Si_{14}C_{30}H_{90}$	$Si_{10}C_{21}H_{63}$	$Si_{22}C_{46}H_{138}$
M_w	844.28	596.61	1309.54
temperature [K]	200(2)	250(2)	100(2)
size [mm]	0.44 × 0.38 × 0.20	0.42 × 0.32 × 0.25	0.40 × 0.28 × 0.18
crystal system	triclinic	triclinic	triclinic
space group	$P1$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.5206(2)	9.832(2)	9.2052(2)
b [Å]	14.645(3)	14.033(3)	9.6344(2)
c [Å]	20.701(4)	29.483(6)	27.109(5)
α [°]	81.88(3)	89.14(3)	94.89(3)
β [°]	89.20(3)	83.87(3)	95.07(3)
γ [°]	84.67(3)	75.44(3)	116.65(3)
V [Å ^{3}]	2845(2)	3914(2)	2119(2)
Z	2	4	1
ρ_{calcd} [g cm^{-3}]	0.986	1.012	1.026
absorption coefficient [mm^{-1}]	0.333	0.345	0.351
F(000)	932	1316	722
θ range	$0.99 < \theta < 22.50$	$0.69 < \theta < 22.00$	$1.52 < \theta < 22.50$
reflections collected/unique	16273/7393	21693/9585	12305/5534
completeness to θ [%]	99.4	99.7	99.8
data/restraints/parameters	7393/0/427	9585/0/601	5534/0/330
goodness of fit on F^2	1.24	1.21	1.16
final R indices [$I > 2\sigma(I)$]	$R1 = 0.108$, $wR2 = 0.214$	$R1 = 0.129$, $wR2 = 0.256$	$R1 = 0.099$, $wR2 = 0.199$
R indices (all data)	$R1 = 0.133$, $wR2 = 0.226$	$R1 = 0.169$, $wR2 = 0.273$	$R1 = 0.143$, $wR2 = 0.215$
largest diff. peak/hole [e$^-$/ Å^3]	0.53/−0.40	0.61/−0.40	0.69/−0.42

Crystallographic data (excluding structure factors) for the structures of compounds **2**, **6**, and **8** reported in this paper (Table 3) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 670359 (**2**), CCDC-670358 (**6**), and 670357 (**8**). Copies of the data can be obtained free of charge on application at www.ccdc.cam.ac.uk/products/csd/request.

Tris(trimethylsilyl)silylpotassium,[10,18] 1,1,2,2-tetramethylphenyldisilane,[19] 1,2-dichlorotetramethyldisilane,[20] 1,3-dichlorohexamethyltrisilane,[20] 1,4-dichlorooctamethyltetrasilane,[20] and 1,1,1,3,3,4,4,6,6,6-decamethyl-2,2,5,5-tetrakis(trimethylsilyl)hexasilane (**1**)[11] were prepared according to literature procedures. $PhMe_2Si-SiMe_2Cl$ was obtained by heating (90 °C, 3 days) a solution of $PhMe_2Si-SiMe_2H$ in dry CCl_4 and subsequent distillation in vacuum (70−80 °C, 1 mbar). Analytical data obtained were identical to those given in the literature.[21]

General Procedure for the Preparation of Silylpotassium Compounds: The silane was dissolved in toluene or THF, and 18-crown-6 and ^{t}BuOK were added. The solution turned immediately orange and was stirred for 2 h at rt until the reaction was complete (checked by ^{29}Si NMR). The obtained silyl anion could be used either directly in solution or alternatively could be isolated by removal of the solvent.

1,1,1,3,3,4,4,5,5,6,6,7,7,8,8,10,10,10-Octadecamethyl-2,2,9,9-tetrakis(trimethylsilyl)decasilane (2): A THF solution of $KSi(SiMe_3)_3$ [prepared from $Si(SiMe_3)_4$ (1.51 g, 4.70 mmol) and ^{t}BuOK (0.532 g, 1.01 equiv)] was added dropwise over a period of 30 min to an ice cooled THF solution of 1,6-dichlorododecamethylhexasilane (5.37 mmol, 0.5 equiv). The mixture was allowed to warm to rt and was then subjected to an aqueous workup (0.5 M H_2SO_4/Et_2O). The combined organic extracts were dried over $MgSO_4$ and concentrated, and after recrystallization of the initially isolated solid from Et_2O, pure **2** (1.79 g, 90%) was obtained as a colorless solid (mp 218−221 °C): ^{1}H NMR (δ ppm) 0.50 (s, $SiMe_3$, 54 H), 0.43, 0.39, 0.34 (3s, $SiMe_2$, 3 × 12 H); ^{13}C NMR (δ ppm) 3.4, 0.9, −2.8, −3.3; ^{29}Si NMR (δ ppm) −9.8 ($SiMe_3$), −32.1, −36.0, −36.6 ($SiMe_2$), −129.1 ($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{30}H_{90}Si_{14}$ (844.238):

---

(18) Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. *Organometallics* **2002**, *21*, 1023–1030.

(19) Cartledge, F. K.; Riedel, K. H. *J. Organomet. Chem.* **1972**, *34*, 11–15.

(20) Gilman, H.; Inoue, S. *J. Org. Chem.* **1964**, *29*, 3418–3419.

(21) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478–484.

C, 42.68; H, 10.75. Found: C, 41.92; H, 10.72. UV λ_{max} (ϵ): 294 nm (6.1×10^4); 280 nm (4.8×10^4); 250 nm (2.4×10^5); 210 nm (4.7×10^5).

1-Chloro-1,1,2,2,4,4,4-heptamethyl-3,3-bis(trimethylsilyl)tetrasilane (3): A pentane solution of $KSi(SiMe_3)_3$ [prepared from $Si(SiMe_3)_4$ (1.05 g, 3.27 mmol) and ^{t}BuOK (0.385 g, 3.44 mmol)] was slowly added to a vigorously stirred *n*-pentane solution of 1,2-dichlorotetramethyldisilane (1.00 mL, 5.37 mmol) at −78 °C. Stirring was continued for 30 min at −78 °C, and the mixture was allowed to warm up to rt within 2 h. After filtration and removal of the solvent, the crude product was distilled using a Kugelrohr furnace (130 °C, 0.01 mbar) to yield **3** (1.02 g, 77%) as a colorless semisolid: ^{1}H NMR (250 MHz, δ ppm) 0.50 (s, $SiMe_2Cl$, 6 H), 0.39 (s, $SiMe_2$, 6 H), 0.27 (s, $SiMe_3$, 27 H); ^{13}C NMR (δ ppm) 3.6 ($SiMe_2Cl$), 3.1 ($SiMe_3$), −1.5 ($SiMe_2$); ^{29}Si NMR (δ ppm) 26.8 ($SiMe_2Cl$), −9.4 ($SiMe_3$), −37.3 ($SiMe_2$), −132.4 ($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{13}H_{39}ClSi_6$ (399.41): C, 39.09; H, 9.84. Found: C, 39.04; H, 9.87.

1,1,1,3,3,4,4,6,6,7,7,9,9,9-Tetradecamethyl-2,2,5,5,8,8-hexakis(trimethylsilyl)nonasilane (5): A solution of **3** (400 mg, 1.0 mmol) in pentane (10 mL) was added to a solution of the silylpotassium reagent **4** [derived from **1** (675 mg, 1.10 mmol) and ^{t}BuOK (125 mg, 1.11 mmol)] via cannula at −78 °C. Stirring was continued for 30 min at −78 °C, and the mixture was allowed to warm to rt within 2 h. After adding water to the stirred suspension, the organic layer was separated and the aqueous layer was extracted twice with pentane. The combined organic extracts were dried over $MgSO_4$, filtered, concentrated, and dried under vacuum at 100 °C. Recrystallization from acetone gave pure **5** (705 mg, 78%) as colorless crystals (mp 235−237 °C): ^{1}H NMR (250 MHz, δ ppm) 0.64, 0.61 (2s, $SiMe_2$, 2 × 12 H), 0.42 (s, $SiMe_3$, 18 H), 0.35 (s, $SiMe_3$, 54 H); ^{13}C NMR (δ ppm) 3.8 ($Si(SiMe_3)_3$), 4.6 ($Si(SiMe_3)_2$), 2.7, 1.9 ($SiMe_2$); ^{29}Si NMR (δ ppm) −9.3, −9.6 ($SiMe_3$), −27.8, −29.3 ($SiMe_2$), −118.1 ($\underline{Si}(SiMe_3)_2$), −127.4 ($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{32}H_{96}Si_{15}$ (902.39): C, 42.59; H, 10.72. Found: C, 42.89; H, 10.76.

1,1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,12-Octadecamethyl-2,2,5,5,8,8,11,11-octakis(trimethylsilyl)dodecasilane (6): Method A: The procedure for compound **5** was followed using **1** (2.1 g, 3.4 mmol), ^{t}BuOK (0.39 g, 3.5 mmol), and 1,2-dichlorotetramethyldisilane (0.30 mL, 1.6 mmol). Recrystallization from toluene gave **6** (1.2 g, 61%) as a white solid. Crystals suitable for X-ray analysis were obtained from toluene.

Method B: A solution of **4** (569 mg, 0.68 mmol) in toluene (10 mL) was added slowly to a solution of 1,2-dichlorotetramethyldisilane (63 mg, 0.34 mmol) in toluene (10 mL). After stirring for 2 h, the mixture was subjected to an aqueous workup (toluene/0.5 M H_2SO_4) to give **6** (376 mg, 93%) as a white solid (mp 249−252 °C): ^{1}H NMR (THF-*d*$_8$, δ ppm) 0.41, 0.38, 0.37 (3s, $SiMe_2$, 3 × 12 H), 0.22 (s, $Si(SiMe_3)_2$, 36 H), 0.18 (s, $Si(SiMe_3)_3$, 54 H); ^{1}H NMR (C_6D_6, δ ppm) 0.70, 0.65, 0.61 (3s, $SiMe_2$, 3 × 12 H), 0.40 (s, $SiMe_3$, 36 H), 0.34 (s, $SiMe_3$, 54 H); ^{29}Si NMR (δ ppm) −9.3, −9.7 ($SiMe_3$), −27.7, −27.8, −29.4 ($SiMe_2$), −117.5 (($\underline{Si}(SiMe_3)_2$), −127.5 (($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{42}H_{126}Si_{20}$ (1193.17): C, 42.28; H, 10.64. Found: C, 42.13; H, 10.56. UV absorption: $\lambda_1 = 211$ nm ($\epsilon_1 = 5.9 \times 10^4$ M^{-1} cm^{-1}), $\lambda_2 = 259$ nm ($\epsilon_2 = 7.4 \times 10^4$ M^{-1} cm^{-1}), shoulder 289 nm.

1,1,1,3,3,4,4,6,6,7,7,8,8,10,10,11,11,13,13,13-Eicosamethyl-2,2,5,5,9,9,12,12-octakis(trimethylsilyl)tridecasilane (7): Following the procedure for **6** (method B) using **4** (0.57 g, 0.68 mmol), 1,3-dichlorohexamethyltrisilane (0.083 g, 0.34 mmol), and benzene instead of toluene, **7** (0.36 g, 84%) was obtained as a colorless solid (mp 216−219 °C): ^{1}H NMR (δ ppm) 0.63, 0.61, 0.60 (3s, $SiMe_2$, 3 × 12 H), 0.54 (s, $SiMe_2$, 6 H), 0.40 (s, $SiMe_3$, 36 H), 0.33 (s, $SiMe_3$, 54 H); ^{29}Si (D_2O, δ ppm) −9.1, −9.4 ($SiMe_3$), −28.0 −28.7, −29.2, −35.5 ($SiMe_2$), −117.4 ($\underline{Si}(SiMe_3)_2$), −127.2 ($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{44}H_{132}Si_{21}$ (1250.89): C, 42.21; H, 10.64. Found: C, 41.86; H, 10.62. UV absorption: $\lambda_1 = 208$ nm ($\epsilon_1 = 6.0 \times 10^4$ M^{-1} cm^{-1}), $\lambda_2 = 258$ nm ($\epsilon_2 = 7.3 \times 10^4$ M^{-1} cm^{-1}), $\lambda_3 = 278$ nm ($\epsilon_3 = 5.6 \times 10^4$ M^{-1} cm^{-1}).

1,1,1,3,3,4,4,6,6,7,7,8,8,9,9,11,11,12,12,14,14,14-Docosamethyl-2,2,5,5,10,10,13,13-octakis(trimethylsilyl)tetradecasilane (8): Following the procedure for **6** (method B) using **4** (1.14 g, 1.36 mmol), 1,4-dichlorooctamethyltetrasilane (206 mg, 0.68 mmol), and benzene instead of toluene, **8** (810 mg, 91%) was obtained as a colorless solid (mp 243−245 °C). Crystals suitable for X-ray analysis were obtained from *n*-heptane: ^{1}H NMR (δ ppm) 0.63, 0.61, 0.59, 0.51 (4s, $SiMe_2$, 4 × 12 H,), 0.41 (s, $SiMe_3$ 36 H), 0.35 (s, $SiMe_3$, 54 H); ^{29}Si NMR (D_2O, δ ppm) −9.0, −9.2 ($SiMe_3$), −28.0, −29.0, −30.0, −34.2 ($SiMe_2$), −118.2 ($\underline{Si}(SiMe_3)_2$), −127.0 ($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{46}H_{138}Si_{22}$ (1309.49) C, 42.19; H, 10.62. Found: C, 42.06; H, 10.67. UV absorption: $\lambda_1 = 209$ nm ($\epsilon_1 = 8.4 \times 10^4$ M^{-1} cm^{-1}), $\lambda_2 = 259$ nm ($\epsilon_2 = 9.5 \times 10^4$ M^{-1} cm^{-1}), $\lambda_3 = 286$ nm ($\epsilon_3 = 7.8 \times 10^4$ M^{-1} cm^{-1}).

1-Chloro-1,1,2,2,4,4,5,5,7,7,7-undecamethyl-3,3,6,6-tetrakis(trimethylsilyl)heptasilane (9): Following the procedure for compound **3** using **1** (5.03 g, 8.23 mmol), ^{t}BuOK (0.95 g, 8.48 mmol), and 1,2-dichlorotetramethyldisilane (3.00 mL, 16.1 mmol), crude **9** was obtained after Kugelrohr distillation (195−205 °C, 0.01 mbar) as a liquid that slowly solidified upon standing at room temperature. After grinding crude **9** in a mortar, the resulting powder was suspended in dry acetonitrile, filtered, and dried under vacuum to afford pure **9** (4.51 g, 80%): ^{1}H NMR (250 MHz, δ ppm) 0.58, 0.56, 0.55, 0.48 (4s, $SiMe_2$, 4 × 6 H), 0.35 (s, $Si(SiMe_3)_2$, 18 H), 0.34 (s, $Si(SiMe_3)_3$, 27 H); ^{13}C NMR (δ ppm) 4.1, 3.8 ($SiMe_3$), 4.0 ($SiMe_2Cl$), 2.1, 1.7, −0.3 ($SiMe_2$); ^{29}Si NMR (δ ppm) 27.5 ($SiMe_2Cl$), −9.2, −9.5 ($SiMe_3$), −29.8, −29.1, −36.1 ($SiMe_2$), −122.9 ($\underline{Si}(SiMe_3)_2$), −127.7 ($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{23}H_{69}ClSi_{11}$ (690.19): C, 40.03; H, 10.08. Found: C, 39.94; H, 10.16.

1-Phenyl-1,1,2,2,4,4,4-heptamethyl-3,3-bis(trimethylsilyl)tetrasilane (10): Following the procedure for compound **3** using $Si(SiMe_3)_4$ (12.00 g, 37.42 mmol), ^{t}BuOK (4.20 g, 37.42 mmol), and 1-chloro-2-phenyltetramethyldisilane (8.13 g, 35.55 mmol), **10** was obtained after Kugelrohr distillation (140 °C, 0.01 mbar) as a colorless liquid (13.81 g, 88%): ^{1}H NMR (250 MHz, δ ppm) 7.49−7.45, 7.27−7.19 (2m, CH-Ph, 5 H), 0.47, 0.32 (2s, $SiMe_2$, 2 × 6 H), 0.25 (s, $SiMe_3$, 27 H); ^{13}C NMR (75.5 MHz, δ ppm): 139.5, 134.3, 128.8, 128.1 (C-Ph.), 3.2 ($SiMe_3$), −0.9, −2.3 ($SiMe_2$); ^{29}Si NMR (δ ppm) −9.5 ($SiMe_3$), −17.9 ($SiMe_2Ph$), −39.3 ($SiMe_2$), −131.3 ($\underline{Si}(SiMe_3)_3$). Anal. Calcd for $C_{19}H_{44}Si_6$ (441.07): C, 51.74; H, 10.05. Found: C, 51.59; H, 10.04.

1-Phenyl-1,1,2,2,4,4,5,5,7,7,8,8,10,10,10-pentadecamethyl-3,3,6,6,9,9-hexakis(trimethylsilyl)decasilane (11): In a Schlenk flask with a magnetic stirrer were placed **10** (1.49 g, 3.38 mmol) and ^{t}BuOK (380 mg, 3.39 mmol). The flask was evacuated and refilled with argon three times, THF (ca. 20 mL) was added at 0 °C, and the resulting yellow solution was stirred for 12 h at rt. After removal of the solvent and other volatiles under vacuum, the oily residue was dissolved in pentane (ca. 20 mL) and cooled to 0−5 °C. Solid **9** (2.10 g, 3.04 mmol) was added in one portion, and stirring was continued for another 12 h at rt. After addition of water to the stirred suspension, the organic layer was separated and the aqueous layer was extracted twice with pentane. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated, and all volatiles were removed under vacuum. The crude product was purified by flash chromatography (silica gel, *n*-heptane) and recrystallization from acetonitrile to afford pure **11** (2.40 g, 77%) as a white solid (mp 105−108 °C): ^{1}H NMR ($CDCl_3$, 250 MHz, δ ppm) 7.45, 7.32 (2m, CH-Ph, 5 H), 0.45, 0.40, 0.40, 0.39, 0.35, 0.22 (6s, $SiMe_2$, 6 × 6 H), 0.27, 0.20 (2s, $Si(SiMe_3)_2$, 2 × 18 H), 0.24 (s, $Si(SiMe_3)_3$, 27 H); ^{13}C NMR ($CDCl_3$, δ ppm) 139.7 (ipso-C), 134.1, 128.4, 127.6 (CH-Ph), 4.4, 3.9 ($Si(SiMe_3)_2$), 3.6 ($Si(SiMe_3)_3$), 2.3, 2.2, 1.8, 1.4, 0.0, −2.1 ($SiMe_2$); ^{29}Si NMR ($CDCl_3$, 59.6 MHz, δ ppm)

−9.2, −9.4, −9.5 (SiMe$_3$), −17.2, −28.0 (2 signals), −28.8, −29.6, −38.7 (SiMe$_2$), −117.8, −120.6 ($\underline{\mathrm{Si}}$(SiMe$_3$)$_2$), −127.3 ($\underline{\mathrm{Si}}$(SiMe$_3$)$_3$). Anal. Calcd for $C_{39}H_{104}Si_{16}$ (1022.62): C, 45.81; H, 10.25. Found: C, 45.82; H, 10.22.

1-Chloro-1,1,2,2,4,4,5,5,7,7,8,8,10,10,10-pentadecamethyl-3,3,6,6,9,9-hexakis(trimethylsilyl)decasilane (12): Triflic acid (0.20 mL, 2.28 mmol) was added to a stirred solution of **11** (1.58 g, 1.55 mmol) in pentane (ca. 10 mL) at 0−5 °C. After stirring had been continued for 2 h, the solvent was removed, a 3-fold excess of LiCl was added, and the mixture was suspended in ether at 0−5 °C. After it had been stirred for 12 h at rt, the solvent was replaced by *n*-pentane, the mixture was filtered, and all volatiles were removed under vacuum. The crude product was suspended in dry acetonitrile, filtered, and dried under vacuum to afford **12** (1.45 g, 96%) as a white powder: ^{1}H NMR (250 MHz, δ ppm) 0.65, 0.64 (2 signals), 0.61, 0.55, 0.49 (6s, SiMe$_2$, 6 × 6 H), 0.41, 0.36 (2s, Si(SiMe$_3$)$_2$, 2 × 18 H), 0.35 (s, Si(SiMe$_3$)$_3$, 27 H); ^{13}C NMR (δ ppm) 4.7, 4.2 (Si(SiMe$_3$)$_2$), 4.1 (SiMe$_2$Cl), 3.9 (Si(SiMe$_3$)$_3$), 2.8, 2.7, 2.3, 1.9, 0.0, −0.2 (SiMe$_2$); ^{29}Si NMR (δ ppm) 27.5 (SiMe$_2$Cl), −9.1, −9.2, −9.4 (SiMe$_3$), −27.3, −27.7, −28.6, −29.2, −36.1 (SiMe$_2$), −117.7, −122.1 ($\underline{\mathrm{Si}}$(SiMe$_3$)$_2$), −127.3 ($\underline{\mathrm{Si}}$(SiMe$_3$)$_3$).

1,1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15,15-Docosamethyl-2,2,5,5,8,8,11,11,14,14-decakis(trimethylsilyl)pentadecasilane (13): Compound **12** (0.4 g, 0.41 mmol) was added in one portion to a solution of **4** [derived from **1** (0.27 g, 0.44 mmol) and ^{t}BuOK (0.051 g, 0.46 mmol)] in heptane, and the mixture was stirred for 12 h at rt. After it had been refluxed for 10 min, the hot suspension was filtered through Celite and allowed to cool to rt, after which time colorless crystals began to form. After storing in a freezer for a day, the crystals were collected and dried under vacuum to give pure **13** (0.50 g, 83%, mp 249−251 °C): ^{1}H NMR (250 MHz, δ ppm) 0.72 (s, SiMe$_2$, 2 × 6 H), 0.66, 0.62 (2s, SiMe$_2$, 2 × 6 H), 0.44 (s, Si(SiMe$_3$)$_2$, 18 H), 0.43 (s, Si(SiMe$_3$)$_2$, 36H), 0.36 (s, Si(SiMe$_3$)$_3$, 54 H); ^{13}C NMR (THF-d_8, 313 K, δ ppm) 2 × 4.8, 3.9 (SiMe$_3$), 3.2, 3.1, 3.0, 2.1 (SiMe$_2$); ^{29}Si NMR (THF-d_8, 59.3 MHz, 313 K, δ ppm) −9.0, −9.1, −9.4 (SiMe$_3$), −27.3, −27.4, −27.6, −29.2 (SiMe$_2$), −115.5, −116.3 ($\underline{\mathrm{Si}}$(SiMe$_3$)$_2$), −126.5 ($\underline{\mathrm{Si}}$(SiMe$_3$)$_3$). Anal. Calcd for $C_{52}H_{156}Si_{25}$ (1483.94): C, 42.09; H, 10.60. Found: C, 41.88; H, 10.51.

1,8-Diphenyl-1,1,2,2,4,4,5,5,7,7,8,8-dodecamethyl-3,3,6,6-tetrakis(trimethylsilyl)octasilane (14): In a Schlenk flask with a magnetic stirrer were placed **10** (3.07 g, 6.96 mmol) and ^{t}BuOK (0.80 g, 7.13 mmol). The flask was evacuated and refilled with argon three times, THF (20 mL) was added at 0 °C, and the resulting yellow solution was stirred for 12 h at rt. After removal of the solvent and other volatiles in vacuum, the oily residue was dissolved in pentane (20 mL) and cooled to −78 °C, and 1,2-dichlorotetramethyldisilane (0.62 mL, 3.33 mmol) was added. Stirring was continued for 30 min at −78 °C. The mixture was allowed to warm to rt within 2 h. After addition of water to the stirred suspension, the organic layer was separated and the aqueous layer was extracted twice with pentane. The combined organic extracts were dried over MgSO$_4$, filtered, and concentrated, and volatile byproducts were removed under vacuum. The crude product was purified by flash chromatography (*n*-heptane/silica gel) and subsequently recrystallized from ethanol to afford pure **14** (1.85 g, 65%) as a white solid (mp 124−126 °C): ^{1}H NMR (CDCl$_3$, 250 MHz, δ ppm) 7.45, 7.32 (2m, CH-Ph, 10 H), 0.45, 0.32, 0.22 (3s, SiMe$_2$, 3 × 12 H), 0.2 (s, Si(SiMe$_3$)$_2$, 36 H); ^{13}C NMR (CDCl$_3$, δ ppm) 139.7 (ipso-C), 134.1, 128.4, 127.6 (CH-Ph), 3.9 (SiMe$_3$), 1.7, −0.1, −2.1 (SiMe$_2$); ^{29}Si NMR (CDCl$_3$, δ ppm) −9.4 (SiMe$_3$), −17.3, −28.9, −38.7 (SiMe$_2$), −121.0 ($\underline{\mathrm{Si}}$(SiMe$_3$)$_2$). Anal. Calcd for $C_{36}H_{82}Si_{12}$ (852.07): C, 50.75; H, 9.70. Found: C, 50.58; H, 9.84.

1,1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15,16,16,18,18,18-Hexaeicosamethyl-2,2,5,5,8,8,11,11,14,14,17,17-dodekakis(trimethylsilyl)octadecasilane (15): Triflic acid (0.15 mL, mmol) was added to a stirred solution of **14** (0.65 g, 0.76 mmol) in pentane (20 mL) at 0 °C. After stirring had been continued for 1 h, a pentane solution of **4** derived from **1** (1.12 g, mmol) and ^{t}BuOK (206 mg, mmol) in THF was added via cannula. After stirring for 12 h, water was added to the suspension and the remaining white precipitate was filtered, washed twice with water, acetone, and pentane, and dried under vacuum. Recrystallization from toluene or THF gave analytically pure **15** (0.67 g, 50%) as a white solid (mp 246−249 °C): ^{1}H NMR (toluene-d_8, 400 MHz, 360 K, δ ppm) 0.67 (s, SiMe$_2$, 18 H), 0.62, 0.59 (2s, SiMe$_2$, 2 × 6 H), 0.40 (s, Si(SiMe$_3$)$_2$, 36 H), 0.33 (s, Si(SiMe$_3$)$_3$, 27 H). Anal. Calcd for $C_{62}H_{186}Si_{30}$ (1774.72): C, 41.96; H, 10.56. Found: C, 41.72; H, 10.32.

Acknowledgment. This study was supported by the Austrian Fonds zur Förderung der Wissenschaften (FWF) via the projects Y-120 and P-18538. C.K. gratefully acknowledges support of this work by the Deutsche Forschungsgemeinschaft (DFG).

Supporting Information Available: X-ray crystallographic information for compounds **2**, **6**, and **8** in CIF format are available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8004383