# Conformational Control of Polysilanes: Use of CH$_2$ Spacers in the Silicon Backbone

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S *Supporting Information*

ABSTRACT: By the reaction of a number of oligosilyl potassium compounds with (trimethylsilyl)chloromethane, derivatives containing the (trimethylsilyl)methyl substituent were prepared. Using X-ray single-crystal structure analysis and UV spectroscopy the conformational properties of some of the compounds were studied. It was found that the (trimethylsilyl)methylated examples exhibit UV absorption properties which correspond to lower energy transitions in comparison to those of analogous trimethylsilylated molecules. The influence of this effect decreases, however, with increasing chain lengths.
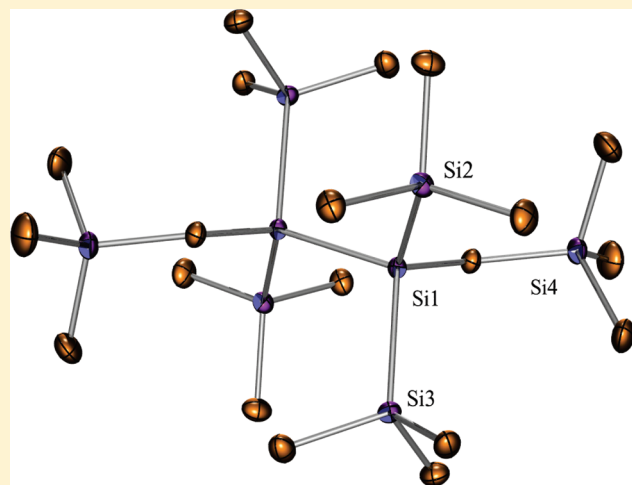
INTRODUCTION

In recent years small alkylated polysilanes[1] have been used to investigate the conformational dependency of the σ-bond electron delocalization of these compounds.[2−8] Some reports have dealt with branched derivatives of this substance class, which were either dendrimers[9−14] or linear silanes with branched end groups.[15−17] Comparing oligosilanes containing either tris(trimethylsilyl)silyl or bis-(trimethylsilyl)methylsilyl groups as terminating units, Krempner and Köckerling found that less branched silanes exhibited bathochromically shifted low-energy absorptions.[18] Our own studies, on the other hand, showed that the steric bulk of end groups is of importance for an all-transoid alignment of the main chain of polysilanes.[16,19,20]

With these two facts in mind, we decided to utilize the (trimethylsilyl)methyl group[21] in order to have the electronic properties of a methyl group which nevertheless is bulky enough to exercise sufficient steric influence onto the attached oligosilane unit. While these were the initial considerations for the synthesis of oligosilanes containing the (trimethylsilyl)methyl group, it later turned out that these materials were the most interesting starting materials for an AlCl$_3$-catalyzed rearrangement desilylative cyclization process, which leads to methylene containing cyclo- and bicyclosilanes.[22]

RESULTS AND DISCUSSION

Synthesis. Reaction of [tris(trimethylsilyl)silyl]potassium[23] (**1**) with (trimethylsilyl)chloromethane gave tris(trimethylsilyl)-[(trimethylsilyl)methyl]silane (**2**) in almost quantitative yield

(Scheme 1). In a similar way **2** could also be converted easily to the corresponding trisilanylpotassium compound **3** by reaction with potassium *tert*-butoxide. Introduction of another (trimethylsilyl)-methyl group was achieved again with (trimethylsilyl)chloromethane, yielding 2,2-bis[(trimethylsilyl)methyl]hexamethyltrisilane (**4**), which can be considered as a larger version of octamethyltrisilane. The additional steric bulk of **4** allowed us to obtain the disilanylpotassium compound **5** by removal of another trimethylsilyl group. Previous attempts to achieve the same transformation starting from octamethyltrisilane failed, likely because of the higher kinetic reactivity of (pentamethyldisilanyl)-potassium.[23] The reaction of **5** with (trimethylsilyl)chloromethane leading to 1,1,1-tris[(trimethylsilyl)methyl]trimethyldisilane (**6**) (Scheme 1) concluded the series of incremental introductions of the (trimethylsilyl)methyl group.

[Bis(trimethylsilyl)((trimethylsilyl)methyl)silyl]potassium (**3**) was then used to obtain further derivatives containing the bis(trimethylsilyl)[(trimethylsilyl)methyl]silyl group (Scheme 2). Oxidative coupling with 1,2-dibromoethane gave 1,2-bis[(trimethylsilyl)methyl]tetrakis(trimethylsilyl)disilane (**7**). Reaction with either pentamethylchlorodisilane or tris(trimethylsilyl)chlorosilane provided the expected compounds **13** and **14** as the products of salt elimination. When **3** was reacted with α,ω-dichloromethyloligosilanes, two bis(trimethylsilyl)[(trimethylsilyl)methyl]silyl

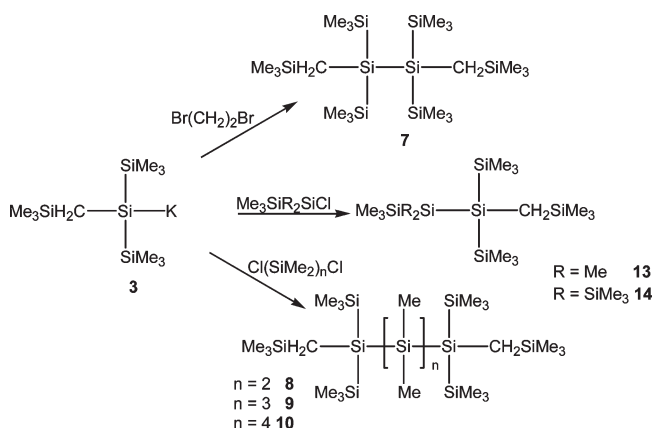**Scheme 1. Successive Replacement of Trimethylsilyl by (Trimethylsilyl)methyl Groups**
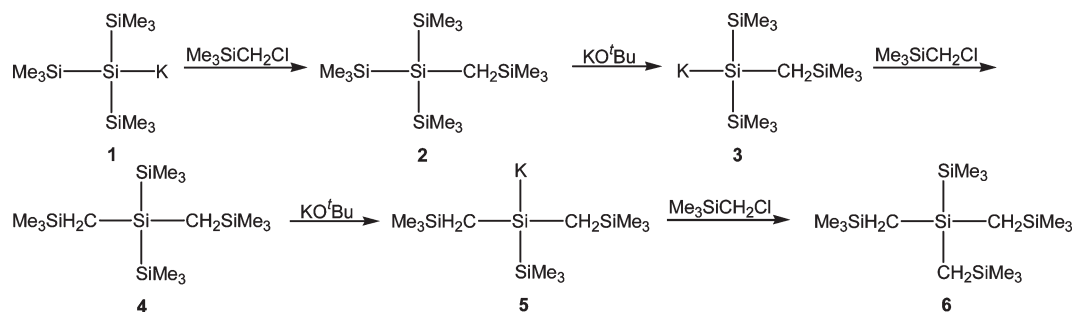
Scheme 2

groups were connected with methylated silanylene spacers of different lengths (**8**–**10**) (Scheme 2).

Further treatment of **14** with potassium *tert*-butoxide led to selective removal of a trimethylsilyl group from the more highly silylated silicon atom. The silylpotassium compound that formed was treated with either dimethyl sulfate or pentamethylchlorodisilane to give the respectively substituted derivatives **15** and **16** (Scheme 3).

In order to extend the series of permethyloligosilanylene-bridged compounds **8**–**10**, 1,6-bis[tris(trimethylsilyl)silyl]dodecamethylhexasilane[16,19] was converted into the 1,8-dianionic derivative, which upon treatment with (trimethylsilyl)chloromethane gave **11** (Scheme 4). In a similar way 1,2-bis[tris(trimethylsilyl)-silyl]tetramethyldisilane[24,25] was converted into the monopotassium species, which was then converted to a derivative with one (trimethylsilyl)methyl group (**17**) (Scheme 4).

Crystal Structure Analyses. Single-crystal structure analyses could be obtained for **7**–**10** and **12**. Compound **7** (Figure 1) crystallizes in the triclinic space group $P\overline{1}$ with an inversion center between the central Si–Si bond, in contrast to the case for hexakis(trimethylsilyl)disilane, which crystallizes in the trigonal space group $R\overline{3}c$.[26–29] The replacement of a trimethylsilyl group with a (trimethylsilyl)methyl group diminishes steric strain, as indicated by the shortening of the central Si–Si bond from 2.40 Å to 2.39 Å. This also affects the dihedral angle Me$_3$Si–Si–Si–SiMe$_3$, which would be 60° in a perfectly staggered conformation; the angles deviate to 43.3 and 76.6° in hexakis(trimethylsilyl)disilane,[26–29] whereas the values for **7** are 51.5 and 65.0°.

Compound **8** (Figure 2) and 1,1,1,4,4,4-hexakis(trimethylsilyl)-tetramethyltetrasilane[30] both crystallize in the triclinic space group $P\overline{1}$. However, while in the latter the inversion center resides at the middle of the central Si–Si bond, there is no symmetry in the asymmetric unit of **8**. As a consequence of this, 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane displays an all-transoid aligned conformation, whereas in **8** the torsion angle along the central Si–Si bond (Si(2)–Si(3)–Si(4)–Si(5)) is the rather unusual 129°. This can be seen from a Newman projection of **8** along the Si–Si skeleton, which shows an eclipsed conformation of the trimethylsilyl groups of the two branched shells for **8**, whereas 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane[30] has a staggered conformation.
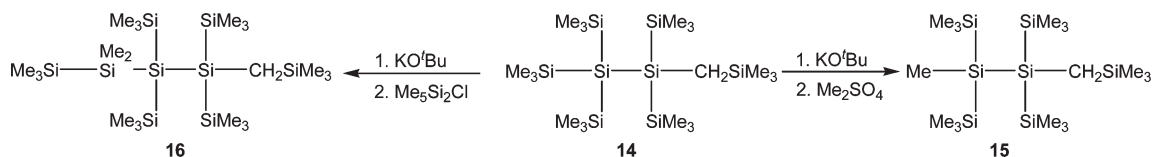
Compound **9** (Figure 3), with three dimethylsilylene units as a spacer, crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit. One of the two molecules exhibited a disorder in one of the bis(trimethylsilyl)[(trimethylsilyl)-methyl]silyl parts which required a number of restraints to resolve. Compound **10** (Figure 4), with four dimethylsilylene units as a spacer, crystallizes in the monoclinic space group $P2_1/n$. No unusually elongated Si–Si bonds were found. For the parent compound 1,1,1,6,6,6-hexakis(trimethylsilyl)octamethylhexasilane crystallization in the triclinic space group $P\overline{1}$ and a staggered conformation with respect to the tris(trimethylsilyl)silyl groups were found.[15]

In contrast to what was found for **8**, compounds **9** (the two crystallographically independent molecules show similar conformational properties) and **10** (which has an inversion center at the central Si–Si bond and hence a central torsion angle of 180°) feature all-transoid conformations with torsion angles close to 160°, which shows that with a growing number of dimethylsilylene spacers along the silicon skeleton the effect of the (trimethylsilyl)methyl group is diminishing.
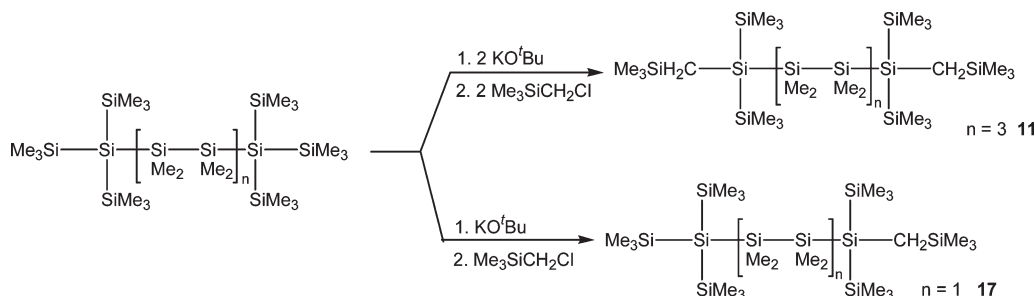
Compound **12** (Figure 5), with a 1,4-butanylene group as a spacer, crystallizes in the monoclinic space group $C2/c$. The structures of bis[tris(trimethylsilyl)silyl]methane,[31] bis[tris-(trimethylsilyl)silyl]ethane,[32] and bis[tris(trimethylsilyl)silyl]-propane[32] were determined before. The Si(1)–C(1) bond length in **12** (1.92 Å) is comparable to that in the other three structures mentioned above. The Si(1)–C(1)–C(2) bond angle of 117.8° is reduced compared to 136.2° in bis[tris-(trimethylsilyl)silyl]methane, 119.9° in bis[tris(trimethylsilyl)-silyl]ethane, and 118.1° in bis[tris(trimethylsilyl)silyl]propane. As in **10**, a staggered conformation with respect to the tris-(trimethylsilyl)silyl groups was found in **12**.

Spectroscopy. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of all new compounds were obtained and followed the expected trends for

Scheme 3

$$Me_3Si\text{—}\underset{\underset{Me_3Si}{\overset{Me_2}{|}}}{Si}\text{—}\underset{\underset{SiMe_3}{\overset{SiMe_3}{|}}}{Si}\text{—}\underset{\underset{SiMe_3}{\overset{Me_3Si}{|}}}{Si}\text{—}CH_2SiMe_3 \quad\xleftarrow[\text{2. } Me_5Si_2Cl]{\text{1. } KO^tBu}\quad Me_3Si\text{—}\underset{\underset{Me_3Si}{\overset{Me_3Si}{|}}}{Si}\text{—}\underset{\underset{SiMe_3}{\overset{SiMe_3}{|}}}{Si}\text{—}CH_2SiMe_3 \quad\xrightarrow[\text{2. } Me_2SO_4]{\text{1. } KO^tBu}\quad Me\text{—}\underset{\underset{Me_3Si}{\overset{Me_3Si}{|}}}{Si}\text{—}\underset{\underset{SiMe_3}{\overset{SiMe_3}{|}}}{Si}\text{—}CH_2SiMe_3$$

16   **14**   **15**

Scheme 4

Starting material: $Me_3Si\text{—}Si(SiMe_3)(SiMe_3)\text{—}[SiMe_2\text{—}SiMe_2]_n\text{—}Si(SiMe_3)(SiMe_3)\text{—}SiMe_3$

Top pathway: 1. 2 KO^tBu; 2. 2 Me_3SiCH_2Cl →
$Me_3SiH_2C\text{—}Si(SiMe_3)(SiMe_3)\text{—}[Si Me_2\text{—}Si Me_2]_n\text{—}Si(SiMe_3)(SiMe_3)\text{—}CH_2SiMe_3$ n = 3   **11**

Bottom pathway: 1. KO^tBu; 2. Me_3SiCH_2Cl →
$Me_3Si\text{—}Si(SiMe_3)(SiMe_3)\text{—}[Si Me_2\text{—}Si Me_2]_n\text{—}Si(SiMe_3)(SiMe_3)\text{—}CH_2SiMe_3$ n = 1   **17**

branched oligosilanes. Only the (trimethylsilyl)methyl group exhibited a very distinct spectroscopic pattern. For a 4-fold alkylated silicon atom a resonance close to 0 is expected in the ^{29}Si spectrum. Typically the respective peak was found at around +1.6 ppm for neutral compounds. In the proton and carbon spectra the methylene unit exhibited typical signatures with ^1H resonances ranging from −0.10 to +0.24 and ^{13}C values clustered around −6.5 ppm. The only exception from the ^{13}C trend can be found for compounds **4** and **6**, where two and three (trimethylsilyl)methyl groups are on the same silicon atom, and compounds **7** and **14**, both of which are sterically rather demanding branched compounds. The stronger steric strain present in these four compounds seems to be reflected in the observed downfield shifts.

As outlined in the Introduction, we were particularly interested in the UV absorption properties of the (trimethylsilyl)-methylated oligosilanes compared to those of their trimethylsilylated parent compounds. The fact that silyl substituents cause an increase in the absorption energy can easily be recognized by a comparison of trisilanes. While tetrakis(trimethylsilyl)silane and tris(trimethylsilyl)methylsilane both have their lowest energy absorption maxima below 210 nm, the corresponding band for octamethyltrisilane can be found at 215 nm.[33] Similar to that, we found the absorption band of **2** at 211 nm, whereas the double-(trimethylsilyl)methylated **4** exhibits a bathochromically shifted band at 222 nm.

Rather spectacular changes can be observed when the absorption spectra of permethyloligosilanylene-bridged bis[tris(trimethylsilylsilyl] compounds[19] are compared to the respective derivatives where two of the terminal trimethylsilyl groups are replaced by (trimethylsilyl)methyl substituents (Figure 6). While we observe the lowest energy transition for $[(Me_3Si)_3Si]_2(SiMe_2)_2$ at 256 nm, the respective band for **8** displays a bathochromic shift of 11 nm to 267 nm. The absorption maximum for **17**, which is a hybrid between **8** and the parent compound containing only one (trimethylsilyl)methyl group, lies expectedly at 262 nm. When the spacer between the branched units is increased by another dimethylsilylene unit, the comparison between the low-energy absorptions of
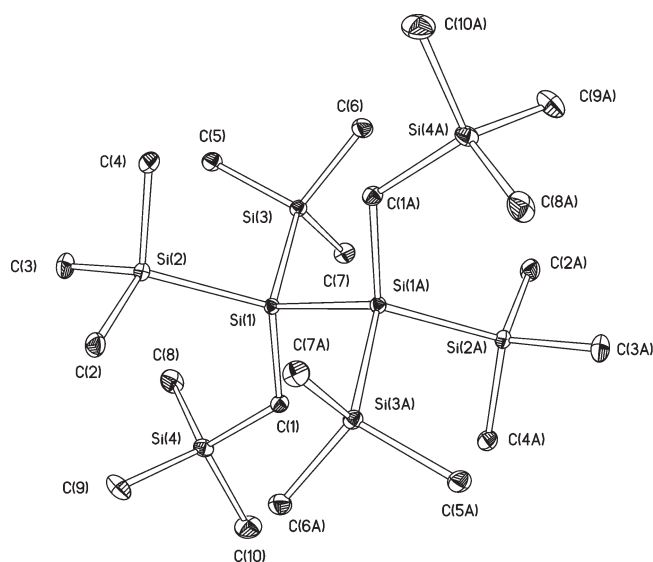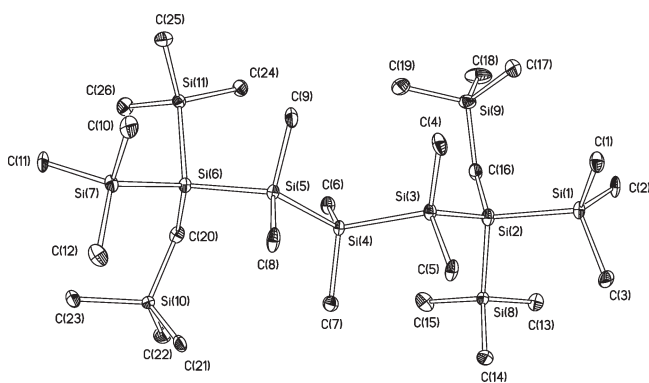

Figure 1. Molecular structure and numbering of **7** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)−C(1) = 1.908(3), Si(1)−Si(2) = 2.3683(12), Si(1)−Si(3) = 2.3764(12), Si(1)−Si(1A) = 2.3864(19), Si(2)−C(2) = 1.872(3); C(1)−Si(1)−Si(2) = 117.34(9), C(1)−Si(1)−Si(3) = 107.86(9), Si(2)−Si(1)−Si(3) = 105.38(4), C(1)−Si(1)−Si(1A) = 107.10(9), Si(2)−Si(1)−Si(1A) = 109.99(5), Si(3)−Si(1)−Si(1A) = 108.93(5), Si(4)−C(1)−Si(1) = 126.46(14).

$[(Me_3Si)_3Si]_2(SiMe_2)_3$ (269 nm) and **9** (276 nm) shows only a bathochromic shift of 7 nm. On going a step further with an octamethyltetrasilanylene spacer, the absorption bands of $[(Me_3Si)_3Si]_2(SiMe_2)_4$ (280 nm) and **10** (284 nm) are as close as 4 nm.

The UV spectrum of $[(Me_3Si)_3Si]_2(SiMe_2)_6$ displays two bands in the low-energy region (295/279 nm), which can be attributed to two conformations.[16,19] The absorption at 295 nm corresponds to the transoid-aligned decasilane conformer, whereas the conformer which absorbs at 279 nm contains a transoid-aligned
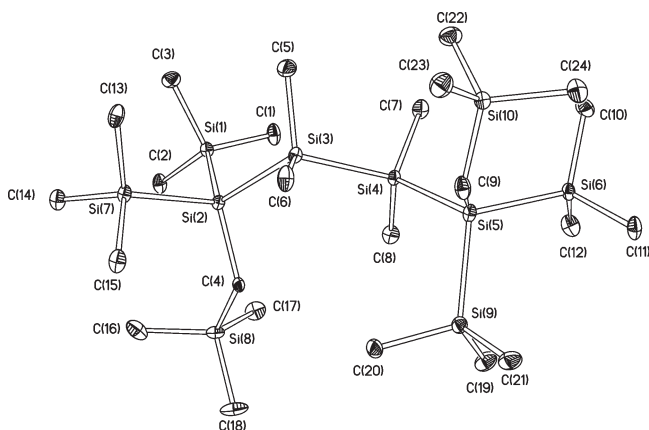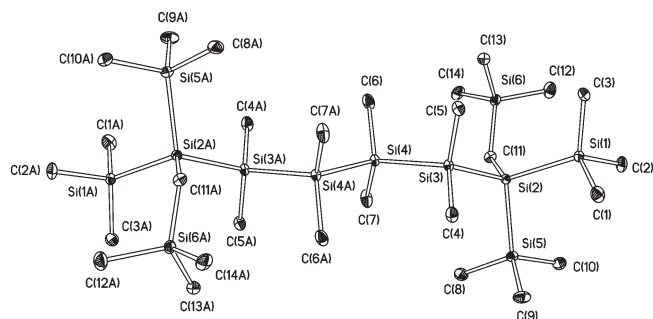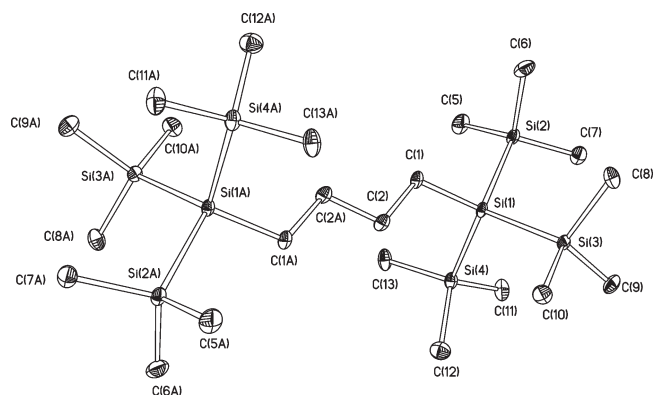
Figure 2. Molecular structure and numbering of **8** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å)] and bond angles (deg) with esd's: Si(1)−C(1) = 1.874(6), Si(1)−Si(2) = 2.358(2), Si(2)−C(4) = 1.911(6), Si(2)−Si(7) = 2.365(2), Si(2)−Si(3) = 2.367(2), Si(5)−C(9) = 1.894(6), Si(8)−C(4) = 1.860(6), Si(10)−C(9) = 1.861(7); C(4)−Si(2)−Si(1) = 120.36(19), Si(1)−Si(2)−Si(7) = 106.77(8), Si(1)−Si(2)−Si(3) = 108.84(9), Si(7)−Si(2)−Si(3) = 106.62(9), Si(2)−Si(3)−Si(4) = 114.51(9), Si(5)−Si(4)−Si(3) = 115.07(9), Si(6)−Si(5)−Si(4) = 110.08(9), C(9)−Si(5)−Si(9) = 102.1(2), Si(6)−Si(5)−Si(9) = 107.27(9), Si(4)−Si(5)−Si(9) = 107.56(9), Si(8)−C(4)−Si(2) = 125.4(3), Si(10)−C(9)−Si(5) = 124.1(3).

Figure 3. Molecular structure and numbering of **9** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)−Si(2) = 2.368(2), Si(2)−C(16) = 1.879(6), Si(1)−C(3) = 1.873(6), Si(2)−Si(3) = 2.358(2), Si(6)−C(20) = 1.919(6), Si(6)−Si(11) = 2.379(2); C(16)−Si(2)−Si(3) = 117.1(2), C(16)−Si(2)−Si(1) = 109.6(2), Si(3)−Si(2)−Si(1) = 109.49(9), C(16)−Si(2)−Si(8) = 103.5(2), Si(3)−Si(2)−Si(8) = 111.77(9), Si(1)−Si(2)−Si(8) = 104.60(9), C(20)−Si(6)−Si(5) = 113.39(19), C(20)−Si(6)−Si(7) = 117.16(19), Si(5)−Si(6)−Si(7) = 107.77(9), C(20)−Si(6)−Si(11) = 103.59(19), Si(5)−Si(6)−Si(11) = 109.24(8), Si(7)−Si(6)−Si(11) = 105.09(8).

octasilane segment. The situation for compound **11** is quite similar. Two absorption bands are observed (293/283 nm) which are nearly identical with those of $[(Me_3Si)_3Si]_2(SiMe_2)_6$. As could be expected from the trend described above, an increase of the spacer lengths by another two dimethylsilylene units further diminishes the influence of the (trimethylsilyl)methyl units. The absorption intensities of the two bands of $[(Me_3Si)_3Si]_2$-$(SiMe_2)_6$ are different, with the lower energy band being stronger, indicating that the aligned decasilane unit exists in a greater


Figure 4. 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 esd's: Si(1)−Si(2) = 2.3629(12), Si(2)−C(11) = 1.907(3), Si(2)−Si(3) = 2.3708(12), Si(2)−Si(5) = 2.3736(14), Si(3)−Si(4) = 2.3696(12), Si(4)−Si(4A) = 2.3562(15), Si(6)−C(11) = 1.875(3); C(11)−Si(2)−Si(1) = 114.71(10), C(11)−Si(2)−Si(3) = 113.13(10), Si(1)−Si(2)−Si(3) = 110.39(4), C(11)−Si(2)−Si(5) = 103.06(10), Si(1)−Si(2)−Si(5) = 105.20(4), Si(3)−Si(2)−Si(5) = 109.70(5), Si(4)−Si(3)−Si(2) = 114.77(4), Si(4A)−Si(4)−Si(3) = 110.01(5), Si(6)−C(11)−Si(2) = 124.74(16).

Figure 5. Molecular structure and numbering of **12** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)−C-(1) = 1.920(5), Si(1)−Si(2) = 2.352(2), Si(1)−Si(4) = 2.357(2), Si(1)−Si(3) = 2.362(2), Si(2)−C(5) = 1.890(7), C(1)−C(2) = 1.533(8), C(2)−C(2A) = 1.532(11); C(1)−Si(1)−Si(2) = 106.45(18), C(1)−Si(1)−Si(4) = 109.57(18), Si(2)−Si(1)−Si(4) = 108.02(8), C(2)−C(1)−Si(1) = 117.7(4), C(2A)−C(2)−C(1) = 113.7(6).

proportion. In contrast to this, we observe nearly identical absorption intensities for the two bands of **11**, hinting at similar numbers of transoid-aligned octasilane and decasilane conformers. This difference between $[(Me_3Si)_3Si]_2(SiMe_2)_6$ and **11** clearly points at a diminished steric influence of the $(Me_3Si)_2(Me_3SiCH_2)Si$ group compared to the $(Me_3Si)_3Si$ unit. As a final observation, it may also be worth mentioning that the absorption intensities of substances of the type $[(Me_3Si)_3Si]_2(SiMe_2)_n$ are substantially higher than those of compounds **9**−**11**. The reason for this is not quite clear yet but may be connected to the fact that rotation of the $(Me_3Si)_2(Me_3SiCH_2)Si$ group yields only two out of three conformers with all-transoid σ-bond conjugation.

■ CONCLUSION

α,ω-Bis[tris(trimethylsilyl)silyl]-substituted methylated oligosilanes were shown to exhibit a strong tendency to engage in
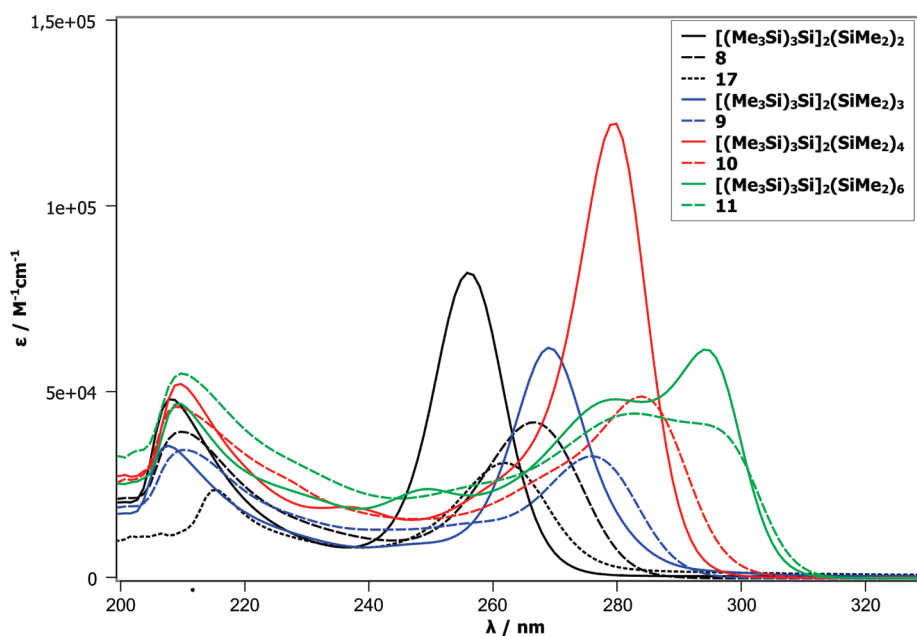
Figure 6. Comparison of UV absorption spectra of bis[tris(trimethylsilyl)silyl]-substituted permethyloligosilanes with those of the respective (trimethylsilyl)methyl derivatives **8**−**11** and **17**.

Table 1. Comparison of Low-Energy Absorption Maxima (nm) and Dihedral Angles (deg) of Main Chains Derived from the Crystal Structures of 8−11 and 17 with Those of the Respective (Me$_3$Si)$_3$Si-Terminated Compounds

compd	λ_{max}	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	conformation
[(Me$_3$Si)$_3$Si]$_2$(SiMe$_2$)$_2$	256	159	180	159					*TAT*
8	267	166	128	156					*TET*
17	262								
[(Me$_3$Si)$_3$Si]$_2$(SiMe$_2$)$_3$	269	161	160	167	164				*TTTT*
9	276	157/159[a]	165/157[a]	160/159[a]	174/171[a]				*TTTT*
[(Me$_3$Si)$_3$Si]$_2$(SiMe$_2$)$_4$	280	162	159	180	159	162			*TTATT*
10	284	158	158	180	158	158			*TTATT*
[(Me$_3$Si)$_3$Si]$_2$(SiMe$_2$)$_6$	295/279	161	168	161	155	167	164	164	*TTTTTTT*
11	293/283								

[a] two molecules in the asymmetric unit.

all-transoid conformations.[19] Upon the replacement of one or two terminal trimethylsilyl by (trimethylsilyl)methyl groups in these compounds, the conformational properties were not shown to change much. Nevertheless, a comparison of the two types of compounds did show some interesting details (Table 1). The most pronounced differences are between [(Me$_3$Si)$_3$Si]$_2$(SiMe$_2$)$_2$ and compound **8**. The low-energy absorption maximum of **8** is red-shifted 11 nm. In addition the crystal structure of **8** does not exhibit the expected all-transoid conformation but features a torsion angle around the central Si−Si bond of 128°. This is unusual, as it clearly points at a much higher flexibility of the main chain. The bathochromically shifted absorption maximum indicates that in solution a strong preference still exists for an all-transoid orientation. With increasing spacer lengths the differences with respect to both solid-state behavior and absorption properties become smaller. For compound **11**, with a hexasilanylene spacer, clearly the bulk of the end groups is no longer sufficient to make the all-transoid conformation the preferred one in solution.

■ EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of nitrogen or argon using either Schlenk techniques or a glovebox. Solvents were dried using a column solvent purification system.[34] Potassium *tert*-butoxide was purchased from Merck. All other chemicals were used as received from chemical suppliers.

Aqueous workup was performed by pouring the reaction mixture into 2 M H$_2$SO$_4$, followed by separation of the layers. Subsequently the aqueous phase was extracted twice. The combined organic extracts were washed with a saturated aqueous sodium hydrogen carbonate solution and then dried over sodium sulfate.

^{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 spectrometer. If not noted otherwise, C$_6$D$_6$ was used as solvent for all samples. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence was used for the amplification of the signal.[35,36]

Elemental analyses were done using a Heraeus Vario Elementar EL apparatus. Analysis values for carbon show values that are consistently

Table 2. Crystallographic Data for Compounds 7−10 and 12

	7	8	9	10	12
empirical formula	$Si_8C_{20}H_{58}$	$Si_{10}C_{24}H_{70}$	$Si_{22}C_{524}H_{152}$	$Si_{12}C_{28}H_{82}$	$Si_8C_{22}H_{62}$
M_w	523.38	639.70	1395.72	756.02	551.44
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)
size (mm)	$0.40 \times 0.30 \times 0.20$	$0.50 \times 0.40 \times 0.25$	$0.35 \times 0.24 \times 0.16$	$0.34 \times 0.26 \times 0.20$	$0.45 \times 0.36 \times 0.30$
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$C2/c$
a (Å)	9.5214(2)	10.918(2)	19.020(4)	8.0514(2)	15.188(3)
b (Å)	9.955(2)	13.549(3)	16.414(3)	32.411(7)	9.960(2)
c (Å)	10.396(2)	15.158(3)	29.778(6)	9.924(2)	25.704(5)
α (deg)	93.09(3)	79.34(3)	90	90	90
β (deg)	111.65(3)	77.65(3)	99.97(3)	111.07(3)	103.36(3)
γ (deg)	107.06(3)	75.41	90	90	90
V (Å^3)	860.9(3)	2099.3(7)	9156(3)	2416.4(8)	3783.1(2)
Z	1	2	4	2	4
ρ_{calcd} (g cm^{-3})	1.010	1.012	1.012	1.039	0.968
abs coeff (mm^{-1})	0.319	0.326	0.328	0.339	0.293
$F(000)$	290	708	3088	836	1224
θ range (deg)	$2.14 < \theta < 26.31$	$1.39 < \theta < 24.00$	$1.09 < \theta < 25.00$	$2.29 < \theta < 26.38$	$1.63 < \theta < 23.50$
no. of collected/unique rflns	6877/3450	13 941/6580	64 873/16 131	18 871/4935	11 475/2791
completeness to θ (%)	98.5	99.5	100	99.8	100
no. of data/restraints/params	3450/0/136	6580/0/329	16 131/150/851	4935/0/194	2791/0/145
goodness of fit on F^2	1.24	1.26	1.14	1.11	1.35
final R indices ($I > 2\sigma(I)$)	R1 = 0.056, wR2 = 0.116	R1 = 0.092, wR2 = 0.183	R1 = 0.100, wR2 = 0.178	R1 = 0.060, wR2 = 0.116	R1 = 0.093, wR2 = 0.198
R indices (all data)	R1 = 0.063, wR2 = 0.119	R1 = 0.112, wR2 = 0.191	R1 = 0.148, wR2 = 0.199	R1 = 0.081, wR2 = 0.124	R1 = 0.099, wR2 = 0.201
largest diff peak/hole (e/Å^3)	0.51/−0.28	0.77/−0.49	0.70/−0.46	0.50/−0.34	0.91/−0.42

too low, which is attributed to the formation and incomplete combustion of silicon carbide. Lengthening the combustion times could be used to obtain slightly improved values.

GC analyses were carried out on an HP 5890 series II instrument equipped with an HP-1 ms capillary column (25 m × 0.251 mm; 0.33 μm) and an HP 5971 mass spectrometer. UV−vis absorption spectra were recorded on a Perkin−Elmer Lambda 35 spectrometer in pentane solution. QtiPlot was used for analysis and plotting of the spectra.[37]

For X-ray structure analyses crystals were mounted onto the tips of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[38] and SADABS,[39,40] respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).[41] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters.

Crystallographic data (excluding structure factors) for the structures of compounds 7−10 and 12 reported in this paper (Table 2) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-670861 (7), -670859 (8), -793979 (9), -670863 (10), and -670860 (12). Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

Tris(trimethylsilyl)silylpotassium (1),[23] 1,4-bis[tris(trimethylsilyl)silyl]-butane (12),[42] dichlorotetramethyldisilane,[43] 1,3-dibromohexamethyl-trisilane,[44] 1,4-dichlorooctamethyltetrasilane,[45] 1,1,1,8,8,8-hexakis(trimethylsilyl)dodecamethyloctasilane,[16] chloropentamethyldisilane,[46] and 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane[24,25]

were prepared and have spectral properties in accord with those published.

Tris(trimethylsilyl)[(trimethylsilyl)methyl]silane (2). At 0 °C a suspension of 1 (2.08 g, 3.78 mmol) in benzene (20 mL) was added slowly to chloromethyltrimethylsilane (0.464 g, 3.78 mmol) in benzene (20 mL). The reaction mixture remained colorless during the whole addition process, and a white precipitate was formed. After 2 h at 0 °C the suspension was warmed to room temperature followed by an aqueous workup (diethyl ether). A colorless viscous liquid of 2 (1.19 g, 94%) was obtained. ^{1}H NMR (δ, ppm): 0.24 (s, 27H, Me_3Si), 0.11 (s, 9H, Me_3Si), −0.10 (s, 2H, CH_2). ^{13}C NMR (δ, ppm): 1.6 (Me_3SiCH$_2$), 1.3 (Me_3Si), −8.3 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.8 (Me_3SiCH$_2$), −12.9 (Me_3Si), −85.1 (Me_3SiSi). MS (70 eV; m/z (%)): 334 (5.5) [M$^+$], 261 (23.9) [M$^+$ − SiMe$_3$], 231 (8.3) [M$^+$ − SiMe$_5$], 187 (89.0) [M$^+$ − Si$_2$Me$_6$H], 131 (14.1) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$]. Anal. Calcd for C$_{13}$H$_{38}$Si$_5$ (334.87 g/mol): C, 46.63; H, 11.44. Found: C, 46.87; H, 11.25. UV absorption: λ_1 211 nm (ε_1 = 1.2 × 10^4 M^{-1} cm^{-1}).

[Bis(trimethylsilyl)((trimethylsilyl)methyl)silyl]potassium−18-crown-6 (3). Compound 2 (9.13 g, 27.3 mmol), KO^{t}Bu (3.102 g, 27.3 mmol), and 18-crown-6 (7.30 g, 27.3 mmol) were dissolved in benzene (50 mL). The cleavage reaction proceeded within 4 h and yielded 3 as a red solution. ^{1}H NMR (δ, ppm): 3.20 (s, 24H, 18-crown-6), 0.51 (s, 18H, Me_3Si), 0.32 (s, 9H, Me_3Si), 0.24 (s, 2H, CH_2). ^{13}C NMR (δ, ppm): 69.9 (18-crown-6), 4.5 (Me_3Si), 1.7 (Me_3SiCH$_2$), −7.5 (CH$_2$). ^{29}Si NMR (δ, ppm): 0.8 (Me_3SiCH$_2$), −6.6 (Me_3Si), −128.6 (Me_3SiSi).

Bis(trimethylsilyl)bis((trimethylsilyl)methyl)silane (4). The same procedure as described for 2 was used, with 3 (2.37 mmol) and chloromethyltrimethylsilane (0.291 g, 2.37 mmol). A colorless viscous

liquid of **4** (0.743 g, 90%) was obtained. ^{1}H NMR (δ, ppm): 0.22 (s, 18H, Me_3Si), 0.13 (s, 18H, Me_3SiCH$_2$), −0.01 (s, 4H, CH_2). ^{13}C NMR (δ, ppm): 2.1 (Me_3Si), −0.1 (Me_3SiCH$_2$), −1.6 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.2 (Me$_3$SiCH$_2$), −16.7 (Me$_3$Si), −43.9 (Me$_3$SiSi). MS (70 eV; m/z (%)): 348 (0.6) [M$^+$], 275 (6.1) [M$^+$ − SiMe$_3$], 245 (2.8) [M$^+$ − SiMe$_5$], 187 (100) [M$^+$ − Si$_2$Me$_7$], 131 (22.3) [Si$_2$Me$_5^+$], 73 (52.0) [SiMe$_3^+$]. Anal. Calcd for C$_{14}$H$_{40}$Si$_5$ (348.89 g/mol): C, 48.19; H, 11.56. Found: C, 48.16; H, 11.45. UV absorption: λ_1 208 nm (ε_1 = 5.5 × 10^3 M^{-1} cm^{-1}), λ_2 222 nm (ε_2 = 7.1 × 10^3 M^{-1} cm^{-1}).

[Bis((trimethylsilyl)methyl)(trimethylsilyl)silyl]potassium−18-crown-6 (5). The same procedure as described for **3** was used, with **4** (7.82 g, 22.5 mmol), KO^{t}Bu (2.52 g, 22.5 mmol), and 18-crown-6 (5.94 g, 22.5 mmol). ^{1}H NMR (δ, ppm): 3.19 (s, 24H, 18-crown-6), 0.25 (s, 9H, Me_3Si), 0.22 (s, 18H, Me_3SiCH$_2$), −0.04 (s, 4H, CH_2). ^{13}C NMR (δ, ppm): 69.9 (18-crown-6), 2.5 (Me_3Si), 1.0 (Me_3SiCH$_2$), −1.5 (CH$_2$). ^{29}Si NMR (δ, ppm): 0.0 (Me$_3$SiCH$_2$), −12.0 (Me$_3$Si), −66.5 (Me$_3$SiSi).

Tris[(trimethylsilyl)methyl](trimethylsilyl)silane (6). The same procedure as described for **2** was used, with **5** (0.792 g, 1.361 mmol) and chloromethyltrimethylsilane (0.167 g, 1.361 mmol). A colorless viscous liquid of **6** (0.403 g, 81%) was obtained. ^{1}H NMR (δ, ppm): 0.21 (s, 9H, Me_3Si), 0.14 (s, 27H, Me_3SiCH$_2$), 0.03 (s, 6H, CH_2). ^{13}C NMR (δ, ppm): 4.3 (Me_3Si), 2.2 (Me_3SiCH$_2$), −0.8 (CH$_2$). ^{29}Si NMR (δ, ppm): 0.2 (Me$_3$SiCH$_2$), −15.9 (Me$_3$Si), −20.2 (Me$_3$SiSi). MS (70 eV; m/z (%)): 362 (0.3) [M$^+$], 289 (3.0) [M$^+$ − SiMe$_3$], 259 (1.0) [M$^+$ − SiMe$_5$], 201 (100) [M$^+$ − Si$_2$Me$_7$], 73 (40.7) [SiMe$_3^+$]. Anal. Calcd for C$_{15}$H$_{42}$Si$_5$ (362.92 g/mol): C, 49.64, H, 11.66. Found: C, 49.56; H, 11.49. UV absorption: λ_1 198 nm (ε_1 = 1.6 × 10^4 M^{-1} cm^{-1}), shoulder at λ_2 221 nm (ε_2 = 1.8 × 10^3 M^{-1} cm^{-1}).

1,1,2,2-Tetrakis(trimethylsilyl)-1,2-bis[(trimethylsilyl)methyl]-disilane (7). A procedure similar to that described for **2** was used, with **3** (1.91 mmol) and dibromoethane (0.179 g, 0.955 mmol) in 150 mL of diethyl ether. The reaction was carried out at −78 °C instead of 0 °C. Compound **7** (0.473 g, 95%) was obtained as a colorless crystalline solid (mp 48−51 °C). ^{1}H NMR (δ, ppm): 0.35 (s, 36H, Me_3Si), 0.17 (s, 4H, Me$_3$SiCH_2), 0.15 (s, 18H, Me_3SiCH$_2$). ^{13}C NMR (δ, ppm): 2.9 (Me_3Si), 1.9 (Me_3SiCH$_2$), −1.6 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.3 (Me$_3$SiCH$_2$), −12.8 (Me$_3$Si), −72.6 (Me$_3$SiSi). MS (70 eV; m/z (%)): 522 (0.9) [M$^+$], 449 (1.3) [M$^+$ − SiMe$_3$], 362 (1.4) [M$^+$ − Si$_2$Me$_6$CH$_2$], 347 (4.8) [M$^+$ − Si$_2$Me$_7$CH$_2$], 289 (4.5) [Si$_5$Me$_9$CH$_2^+$], 261 (36.8) [Si$_4$Me$_9$CH$_2^+$], 246 (80.9) [Si$_4$Me$_8$CH$_2^+$], 187 (88.8) [Si$_3$Me$_6$CH$_2^+$], 173 (33.5) [Si$_3$Me$_5$CH$_2^+$], 131 (14.1) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$]. Anal. Calcd for C$_{20}$H$_{58}$Si$_8$ (523.36 g/mol): C, 45.90, H, 11.17. Found: C, 45.41; H, 11.08. UV absorption: λ_1 211 nm (ε_1 = 5.2 × 10^4 M^{-1} cm^{-1}), shoulders at λ_2 230 nm and λ_3 245 nm.

1,1,4,4-Tetrakis(trimethylsilyl)-1,4-bis[(trimethylsilyl)methyl]-tetramethyltetrasilane (8). A procedure similar to that described for **2** was used, with **3** (1.60 mmol) and 1,2-dichlorotetramethyldisilane (0.150 g, 0.801 mmol). Compound **8** (0.490 g, 96%) was obtained as a colorless crystalline solid (mp 56−59 °C). ^{1}H NMR (δ, ppm): 0.45 (s, 12H, Me_2Si), 0.28 (s, 36H, Me_3Si), 0.13 (s, 18H, Me_3SiCH$_2$), 0.03 (s, 4H, CH_2). ^{13}C NMR (δ, ppm): 2.3 (Me_3Si), 1.9 (Me_3SiCH$_2$), −0.2 (Me_2Si), −6.1 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.6 (Me$_3$SiCH$_2$), −12.6 (Me$_3$Si), −32.5 (Me$_2$Si), −77.7 (Me$_3$SiSi). MS (70 eV; m/z (%)): 638 (2.0) [M$^+$], 377 (17.4) [Si$_6$Me$_{13}$CH$_2^+$], 319 (18.9) [Si$_5$Me$_{11}$CH$_2^+$], 304 (18.3) [Si$_5$Me$_{10}$CH$_2^+$], 232 (24.6) [Si$_4$Me$_8^+$], 131 (39.5) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$]. Anal. Calcd for C$_{24}$H$_{70}$Si$_{10}$ (639.67 g/mol): C, 45.06; H, 11.03. Found: C, 44.88; H, 10.95. UV absorption: λ_1 210 nm (ε_1 = 3.9 × 10^4 M^{-1} cm^{-1}), λ_2 267 nm (ε_2 = 4.2 × 10^4 M^{-1} cm^{-1}).

1,1,5,5-Tetrakis(trimethylsilyl)-1,5-bis[(trimethylsilyl)methyl-hexamethylpentasilane (9). A procedure similar to that described for **2** was used, with **3** (3.27 mmol) and 1,3-dibromohexamethyltrisilane (0.545 g, 1.63 mmol). Compound **9** (1.08 g, 95%) was obtained as a colorless crystalline solid (mp 65−68 °C). ^{1}H NMR (δ, ppm): 0.50 (s, 6H, Me_2Si),

0.48 (s, 12H, Me_2Si), 0.32 (s, 36H, Me_3Si), 0.16 (s, 18H, Me_3SiCH$_2$), 0.08 (s, 4H, CH_2). ^{13}C NMR (δ, ppm): 2.1 (Me_3Si), 1.8 (Me_3SiCH$_2$), −0.8 (Me_2Si), −2.0 (Me_2Si), −6.1 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.6 (Me$_3$SiCH$_2$), −12.6 (Me$_3$Si), −32.9 (Me$_2$Si), −35.8 (Me$_2$Si), −78.0 (Me$_3$SiSi). Anal. Calcd for C$_{26}$H$_{76}$Si$_{11}$ (697.82 g/mol): C, 44.75; H, 10.98. Found: C, 45.11; H, 11.02. UV absorption: λ_1 211 nm (ε_1 = 3.4 × 10^4 M^{-1} cm^{-1}), shoulder at λ_2 256 nm, λ_3 276 nm (ε_3 = 3.3 × 10^4 M^{-1} cm^{-1}).

1,1,6,6-Tetrakis(trimethylsilyl)-1,6-bis[(trimethylsilyl)methyl-octamethylhexasilane (10). A procedure similar to that described for **2** was used, with **3** (0.509 g, 0.901 mmol) and 1,4-dichlorooctamethyltetra-silane (0.136 g, 0.451 mmol). Compound **10** (0.313 g, 92%) was obtained as a colorless crystalline solid (mp 167−169 °C). ^{1}H NMR (δ, ppm): 0.47 (s, 12H, Me_2Si), 0.45 (s, 12H, Me_2Si), 0.32 (s, 36H, Me_3Si), 0.16 (s, 18H, Me_3SiCH$_2$), 0.17 (s, 4H, CH_2). ^{13}C NMR (δ, ppm): 2.1 (Me_3Si), 1.8 (Me_3SiCH$_2$), −0.7 (Me_2Si), −2.8 (Me_2Si), −6.2 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.6 (Me$_3$SiCH$_2$), −12.6 (Me$_3$Si), −33.6 (Me$_2$Si), −35.8 (Me$_2$Si), −78.0 (Me$_3$SiSi). Anal. Calcd for C$_{28}$H$_{82}$Si$_{12}$ (755.98 g/mol): C, 44.49; H, 10.93. Found: C, 44.62; H, 10.93. UV absorption: λ_1 209 nm (ε_1 = 4.6 × 10^4 M^{-1} cm^{-1}), λ_2 284 nm (ε_2 = 4.9 × 10^4 M^{-1} cm^{-1}).

1,1,8,8-Tetrakis(trimethylsilyl)-1,8-bis[(trimethylsilyl)methyl-dodecamethyloctasilane (11). The dianion derived from 1,1,1,8,8,8-hexakis(trimethylsilyl)-dodecamethyloctasilane was prepared according to the procedure described for **3** using the octasilane (0.311 g, 0.368 mmol), KO^{t}Bu (83 mg, 0.74 mmol), and 18-crown-6 (196 mg, 0.74 mmol). The reaction of the dianion was done according to a procedure similar to that described for **2** using chloromethyltrimethylsilane (91 mg, 2 equiv). Compound **11** (290 mg, 90%) was obtained as a colorless crystalline solid (mp 70−75 °C) after recrystallization (Et$_2$O/isopropyl alcohol). ^{1}H NMR (δ, ppm): 0.47 (s, 12H, Me_2Si), 0.44 (s, 12H, Me_2Si), 0.40 (s, 12H, Me_2Si), 0.32 (s, 36H, Me_3Si), 0.17 (s, 18H, Me_3SiCH$_2$), 0.08 (s, 4H, CH_2). ^{13}C NMR (δ, ppm): 2.1 (Me_3Si), 1.8 (Me_3SiCH$_2$), −0.8 (Me_2Si), −2.8 (Me_2Si), −3.4 (Me_2Si), −6.2 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.6 (Me$_3$SiCH$_2$), −12.6 (Me$_3$Si), −33.8 (Me$_2$Si), −36.3 (Me$_2$Si), −36.5 (Me$_2$Si), −78.4 (Me$_3$SiSi). Anal. Calcd for C$_{32}$H$_{94}$Si$_{14}$ (872.29 g/mol): C, 44.06; H, 10.86. Found: C, 43.73; H, 10.83. UV absorption: λ_1 210 nm (ε_1 = 5.5 × 10^4 M^{-1} cm^{-1}), λ_2 = 283 nm (ε_2 = 4.4 × 10^4 M^{-1} cm^{-1}), λ_3 293 nm (ε_3 = 4.2 × 10^4 M^{-1} cm^{-1}).

1,4-Bis[tris(trimethylsilyl)silyl]butane (12). 1 (1.09 mmol) in THF (10 mL) was added slowly to a stirred solution of 1,4-ditosylbu-tane (0.56 mmol, 223 mg) in THF (10 mL). After 12 h at room temperature, the reaction mixture was subjected to an aqueous workup (diethyl ether). Compound **12** (258 mg, 88%) was obtained as a colorless crystalline solid (mp 165−166 °C). ^{1}H NMR (δ, ppm): 1.68 (m, 4H), 1.02 (m, 4H), 0.25 (s, 54H). ^{13}C NMR (δ, ppm): 34.4 (SiCH$_2$CH_2), 7.6 (SiCH$_2$), 1.3 (Me$_3$Si). ^{29}Si NMR (δ, ppm): −13.1 (Me$_3$Si), −81.9 (Me$_3$SiSi). Anal. Calcd for C$_{22}$H$_{62}$Si$_8$ (551.41 g/mol): C, 47.92; H, 11.33. Found: C, 48.08; H, 11.60. UV absorption: λ_1 211 nm (ε_1 = 1.6 × 10^4 M^{-1} cm^{-1}), shoulder at λ_2 228 nm (ε_2 = 5.2 × 10^3 M^{-1} cm^{-1}).

1,1-Bis(trimethylsilyl)-1-[(trimethylsilyl)methyl]pentamethyl-trisilane (13). A procedure similar to that described for **2** was used, with **3** (1.07 mmol) and chloropentamethyldisilane (0.179 g, 1.07 mmol). Instead of benzene THF was used, and no 18-crown-6 was required. Compound **13** (330 mg, 78%) was obtained as a colorless liquid. ^{1}H NMR (δ, ppm): 0.28 (s, 6H, Me_2Si), 0.25 (s, 18H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.10 (s, 9H, Me_3Si), −0.05 (s, 2H, CH_2). ^{13}C NMR (δ, ppm): 1.9 (Me_3Si), 1.8 (Me_3Si), 0.6 (Me_3Si), −2.7 (Me_2Si), −6.7 (CH$_2$). ^{29}Si NMR (δ, ppm): 1.6 (Me$_3$SiCH$_2$), −12.3 (Me$_3$Si), −14.7 (Me$_3$Si), −40.7 (Me$_2$Si), −80.8 (Me$_3$SiSi). Anal. Calcd for C$_{15}$H$_{44}$Si$_6$ (393.02 g/mol): C, 45.84; H, 11.28. Found: C, 46.19; H, 11.28. UV absorption: λ_1 215 nm (ε_1 = 1.3 × 10^4 M^{-1} cm^{-1}), λ_2 227 nm (ε_2 = 1.1 × 10^4 M^{-1} cm^{-1}).

1,1,1,2,2-Pentakis(trimethylsilyl)-2-bis[(trimethylsilyl)methyl]-disilane (14). Similar procedure as described for **13** starting from

hexakis(trimethylsilyl)disilane (345 mg, 0.696 mmol) and KO^{t}Bu (79 mg, 0.70 mmol) followed by addition to chloromethyltrimethylsilane (86 mg, 0.70 mmol). Compound **14** (290 mg, 82%) was obtained as a colorless crystalline solid (mp: decomposition at 180 °C). ^{1}H NMR (δ, ppm): 0.32 (s, 27H, Me_3Si), 0.31 (s, 18H, Me_3Si), 0.12 (s, 9H, Me_3Si), 0.09 (s, 2H, CH_2). ^{13}C NMR (δ, ppm): 4.3 (Me_3Si), 3.0 (Me_3Si), 2.0 (Me_3Si), 0.1 (CH_2). ^{29}Si NMR (δ, ppm): 1.2 (Me_3SiCH$_2$), −9.9 (Me_3Si), −13.3 (Me_3Si), −71.2 (Me_2Si), −123.0 (Me_3SiSi). Anal. Calcd for C$_{19}$H$_{56}$Si$_8$ (509.33 g/mol): C, 44.80; H, 11.08. Found: C, 44.60; H, 11.01. UV absorption: λ_1 216 nm (ε_1 = 2.3 × 10^4 M^{-1} cm^{-1}).

1,1,2,2-Tetrakis(trimethylsilyl)-1-bis[(trimethylsilyl)methyl]-2-methyldisilane (15). A procedure similar to that described for **2** was used, starting with **14** (406 mg, 0.797 mmol) and KO^{t}Bu (89 mg, 0.80 mmol) followed by addition to dimethyl sulfate (101 mg, 1.01 equiv). Instead of benzene THF was used, and no 18-crown-6 was required. Compound **15** (315 mg, 88%) was obtained as a colorless oil. ^{1}H NMR (δ, ppm): 0.32 (s, 3H, MeSi), 0.30 (s, 18H, Me_3Si), 0.27 (s, 18H, Me_3Si), 0.19 (s, 2H, CH_2), 0.14 (s, 9H, Me_3Si). ^{13}C NMR (δ, ppm): 2.3 (Me_3Si), 1.9 (Me_3Si), 1.7 (Me_3Si), 0.4 (MeSi), −8.5 (CH_2). ^{29}Si NMR (δ, ppm): 1.4 (Me_3SiCH$_2$), −11.8 (Me_3Si), −12.8 (Me_3Si), −76.1 (Me_3SiSi), −78.1 (Me_3SiSi). Anal. Calcd for C$_{17}$H$_{50}$Si$_7$ (451.18 g/mol): C, 45.26; H, 11.17. Found: C, 45.26; H, 10.75. UV absorption: λ_1 216 nm (ε_1 = 1.4 × 10^4 M^{-1} cm^{-1}).

1,1,2,2-Tetrakis(trimethylsilyl)-1-[(trimethylsilyl)methyl]-pentamethyltetrasilane (16). A procedure similar to that described for **13** was used, starting with **14** (696 mg, 1.366 mmol) and KO^{t}Bu (153 mg, 1.36 mmol) followed by addition to chloropentamethyldisilane (228 mg, 1.36 mmol). Compound **16** (720 mg, 93%) was obtained as a colorless crystalline solid (mp: 130−140 °C). ^{1}H NMR (δ, ppm): 0.39 (s, 6H, Me_2Si), 0.35 (s, 18H, Me_3Si), 0.33 (s, 18H, Me_3Si), 0.20 (s, 9H, Me_3Si), 0.14 (s, 9H, Me_3Si), 0.09 (s, 2H, CH_2). ^{29}Si NMR (δ, ppm): 1.2 (Me_3SiCH$_2$), −10.0 (Me_3Si), −13.1 (Me_3Si), −13.2 (Me_3Si), −38.2 (Me_2Si), −69.7 (Me_3SiSi), −115.2 (Me_3SiSi). Anal. Calcd for C$_{21}$H$_{62}$Si$_9$ (567.49 g/mol): C, 44.45; H, 11.01. Found: C, 44.46; H, 10.83. UV absorption: λ_1 216 nm (ε_1 = 1.9 × 10^4 M^{-1} cm^{-1}).

1,1,1,4,4-Pentakis(trimethylsilyl)-4-[(trimethylsilyl)methyl-tetramethyltetrasilane (17). A procedure similar to that described for **2** was used, starting with 1,1,1,4,4,4-hexakis(trimethylsilyl)-tetramethyltetrasilane (391 mg, 0.639 mmol), 18-crown-6 (169 mg, 0.639 mmol), and KO^{t}Bu (72 mg, 0.639 mmol) followed by addition to chloromethyltrimethylsilane (79 mg, 1.01 equiv). Compound **17** (360 mg, 90%) was obtained as a colorless crystalline solid (mp: 203−206 °C). ^{1}H NMR (δ, ppm): 0.54 (s, 6H, Me_2Si), 0.49 (s, 6H, Me_2Si), 0.33 (s, 27H, Me_3Si), 0.31 (s, 18H, Me_3Si), 0.15 (s, 9H, Me_3Si), 0.07 (s, 2H, CH_2). ^{13}C NMR (δ, ppm): 3.6 (Me_3Si), 2.3 (Me_3Si), 1.8 (Me_3SiCH$_2$), 1.6 (Me_2Si), −0.3 (Me_2Si), −6.0 (CH_2). ^{29}Si NMR (δ, ppm): 1.6 (Me_3SiCH$_2$), −9.7 (Me_3Si), −12.6 (Me_3Si), −29.8 (Me_2Si), −32.7 (Me_2Si), −77.5 (Me_3SiSi), −128.3 (Me_3SiSi). Anal. Calcd for C$_{23}$H$_{68}$Si$_{10}$ (625.64 g/mol): C, 44.15; H, 10.96. Found: C, 43.74; H, 10.87. UV absorption: λ_1 215 nm (ε_1 = 2.4 × 10^4 M^{-1} cm^{-1}), λ_2 262 nm (ε_2 = 3.1 × 10^3 M^{-1} cm^{-1}).

ASSOCIATED CONTENT

ⓢ **Supporting Information.** CIF files giving X-ray crystallographic data for **7**−**10** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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