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Synthesis of Cyclic and Bicyclic Polysilanes of Variable Ring Sizes

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Some trimethylsilyl-substituted cyclohepta-, cycloocta-, and cyclononasilanes were obtained by salt elimination reaction of α,ω-dipotassiotetrakis(trimethylsilyl)permethyloligosilanes with α,ω-dichloropermethyloligosilanes. Utilizing the same synthetic concept, the use of dianionic cyclooligosilanes led to the formation of various bicyclooligosilanes. The UV absorption behavior of the trimethylsilyl-substituted cyclosilanes is different from that of permethylated cyclosilanes of the same ring size. Spectroscopic analysis suggests that σ-electron delocalization occurs along chain segments in the ring reaching from one trimethylsilyl group to the other.

Introduction

The first reported synthesis of perphenylated cyclosilanes (with ring sizes from 4−6) was achieved as early as 1921 by Kipping.[1] It took almost another thirty years before dodecamethylcyclohexasilane, the first permethylated cyclosilane, was described.[2] Since then, methyl-substituted cyclosilanes have received much attention and have been studied in detail. Rings ranging in size from $(Me_2Si)_n$ $n = 4$ up to 35 have been reported.[3] A main interest in this class of compounds is associated with their unique properties due to electron delocalization in their σ-framework and their reactivity pattern.[3a,3b] While permethylated ring systems are the most studied ones, also perethyl- and ethylmethylcyclopolysilanes of ring sizes $n = 4-8$[4] and other peralkylcyclopolysilanes ($^nPr_2Si$, $^iPr_2Si$, $^nBu_2Si$, and $^iBu_2Si$)[5] have gained some interest. Structural information for cyclosilanes with ring sizes larger than 6 has been reported for the permethylated cyclopolysilanes $(Me_2Si)_7$, $(Me_2Si)_{13}$, and $(Me_2Si)_{16}$.[6] In addition the theoretical conformational analysis of $(Me_2Si)_8$ has been carried out.[6b]

Usually, cyclosilanes are prepared by alkali metal-mediated Wurtz-type coupling of diorganodihalosilanes. It is possible to run these reactions under kinetic control in order to obtain also compounds with ring sizes larger than 6. A serious problem of this approach, however, is associated with extremely disappointing yields, which are for ring sizes $n = 7-9$ between 2.6% and 0.8% and for the larger systems $n = 10-35$ as low as 0.2%.[3] Recently, we have introduced a straightforward way to obtain a number of different α,ω-dianionic polymethyloligosilanes.[7] These compounds are most useful synthetic building blocks for the synthesis of cyclic polysilanes. Their ring closure can be accomplished either by oxidative coupling[8] or by reaction with suitable dielectrophiles such as α,ω-dichloropermethyloligosilanes.[9] Employing these methods, we have reported the preparation of three- to seven-membered rings so far.[10]

Attempts to use the Wurtz-type conditions for the cross-coupling of diorganodichlorosilanes and organotrichlorosilanes for the synthesis of bicyclic oligosilane compounds unfortunately also yield only minute amounts of the desired products.[11,12] In order to get access to reasonable amounts of bicyclooligosilanes, we[9] and Kira's group[13] have recently developed strategies for the stepwise construction of these compounds.

In the study at hand, we want to present examples of the selective synthesis of medium-sized cyclosilanes and some new bicyclosilanes together with some unusual spectroscopic properties of these compounds.

Results and Discussion

A number of seven- (**1**, **2**), eight- (**3**, **4**), and nine-membered (**5**) rings were synthesized by reactions of α,ω-dipotassiotetrakis(trimethylsilyl)permethyloligosilanes with the corresponding α,ω-dichloropermethyloligosilanes in fair to excellent yields (Scheme 1). The selective synthesis of polysilanyl dianions[14] together with the use of suitable dielectrophiles enables the

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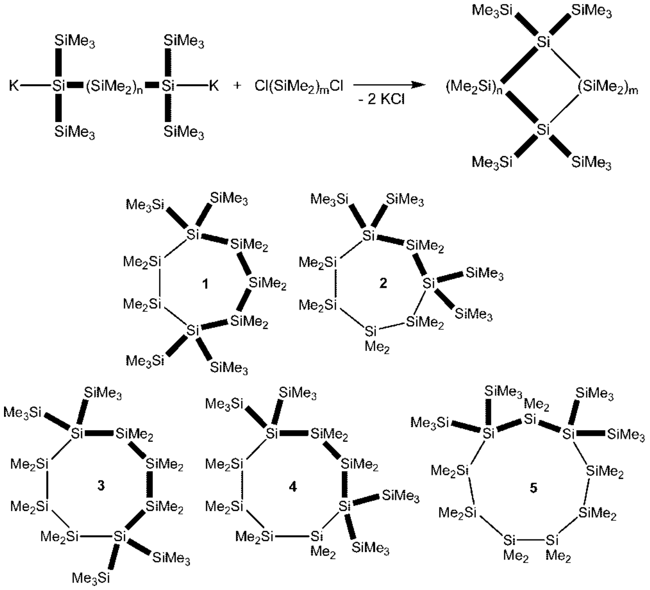
10.1021/om800842p CCC: $40.75

Scheme 1. Synthesis of Seven-, Eight-, and Nine-Membered Polysilanes[a]



[a] The bold backbone parts of the molecules indicate the used α,ω-dipotassiooligosilane starting materials.

formation of cyclosilanes with only one ring size. Depending on the numbers of silicon atoms in the dianionic starting material and the α,ω-dichlorosilane, different substitution patterns can be obtained. This feature allows access to different conformational motifs and is an important factor with respect to further derivatization reactions.

An effort to react 1,2-dipotassiotetrakis(trimethylsilyl)disilane[15] with 1,6-dichlorododecamethylhexasilane did not give the expected cyclooctasilane. This was somewhat unexpected, as the reaction of the same dianion with 1,4-dichlorooctamethyltetrasilane smoothly led to the formation of 1,1,2,2-tetrakis(trimethylsilyl)octamethylcyclohexasilane.[10]

1,1,2,2-Tetrakis(trimethylsilyl)hexamethylcyclopentasilane (**6**) is another new cyclosilane, which was synthesized by oxidative coupling of 1,5-dipotassio-1,1,5,5-tetrakis(trimethylsilyl)hexamethylpentasilane[7] employing a stoichiometric amount of 1,2-dibromoethane. In a clean reaction, **6** can be converted to the respective 1,2-dianionic compound **7** by conversion with 2 equiv of potassium *tert*-butoxide in the presence of 18-crown-6. Reactions of **7** with 1,3-dichlorohexamethyltrisilane and 1,4-dichlorooctamethyltetrasilane subsequently led to the formation of [3.3.0]bicyclooctasilane **8** and [4.3.0]bicyclononasilane **9**, respectively (Scheme 2). Starting from the known 1,1,3,3-tetrakis(trimethylsilyl)octamethylcyclohexasilane[10] the respective 1,3-dianionic compound **10** could be obtained. Reaction of **10** with 1,3-dichlorohexamethyltrisilane afforded [3.3.1]bicyclononasilane **11**, while its reaction with the respective 1,4-dichlorosilane led to [4.3.1]bicyclodecasilane **12** (Scheme 2).

Attempts to convert **8** to the respective dipotassium compound by reaction with 2 equiv of potassium *tert*-butoxide proved not to be successful. Instead of the expected bicyclic dianion, compound **7** was formed again. This result may be rationalized by the nucleophilic attack on the ring dimethylsilylene units rather than on the trimethylsilyl groups (Scheme 3). In a similar way, the reaction of cyclooctasilane **3** with 2 equiv of potassium *tert*-butoxide also gave **7** as the main product. In this case, a transannular attack of the initially formed monometalated compound is assumed.

Crystal Structure Analysis. Compounds **2**, **3**, **4**, and **8** could be subjected to crystal structure analysis. In accordance with the main occurrence of cyclosilanes with ring sizes up to six ring atoms, the structural properties of these compounds are relatively well understood.[3,10] Structural information on larger systems, however, is scarce, and only a few compounds have been studied by crystal structure [$(Me_2Si)_7$,[16] $(Me_2Si)_{13}$, and $(Me_2Si)_{16}$][3e] or conformational [$(Me_2Si)_8$][6] analysis.

Of the four known basic conformations for seven-membered rings, the permethylated cycloheptasilane $(Me_2Si)_7$ was found to exhibit a twist-chair conformation.[16] The solid-state structure of compound **2** (Figure 2), which features two crystallographically independent molecules in the asymmetric unit, also adopts this conformation. Average Si−Si bond distances of 2.35 Å [2.333(2)−2.3732(16) Å] indicate a nonstrained molecule. Si−Si−Si bond angles in the ring were found between 114.11(7)° and 125.59(6)°. For $(SiMe_2)_7$ the average bond angle was found to be 116.2°. The deviations of **2** are likely to be caused by the bulky trimethylsilyl substituents.

Theoretical considerations predict 10 different possible conformations for eight-membered rings.[17] For $(SiMe_2)_8$ the twist-chair-chair conformation was assumed to be most stable.[6] Cyclooctasilanes **3** (Figure 3) and **4** (Figure 4) cannot access this conformation because of the sterically demanding trimethylsilyl substituents in 1,1,5,5- and 1,1,4,4-position, respectively. Compound **3** was found to crystallize with an additional molecule of diethyl ether in the asymmetric unit, which is badly disordered. Measurement at 200 K was required, as the crystal was cracking at lower temperatures. The substitution pattern of **3** favors a chair conformation in the solid state. For the cyclooctasilane **4** again two crystallographically independent molecules were found in the asymmetric unit. The quality of the structure of **4** is poor, as indicated by rather high *R* values. Nevertheless, its conformation can be described as a skewed chair. Average Si−Si bond distances are around 2.37 Å for **3** and **4**. Si−Si−Si bond angles within the rings were found between 117.50(6)° and 118.65(8)° for **3** and 115.5(4)° and 121.6(4)° for **4**. Si−Si bond distances within the annulated five-membered rings of **8** (Figure 5) are between 2.355(2) and 2.365(2) Å, while the bridging atoms Si(1) and Si(5) are 2.372(2) Å apart. The torsional angle of the two $SiMe_3$ substituents along the bridge is 40.26(13)°, in accordance with the twisted *cisoid* configuration of the two rings.

UV Absorption Spectroscopy. UV absorption spectra of compounds **1**−**5** reveal some interesting aspects. From West's fundamental studies it is known that the UV absorption behavior of permethylated rings exhibits a trend of hypsochromic shifts for compounds with increasing ring sizes up to the cyclononasilane.[18] The low-energy transitions for cyclohepta-, cycloocta-, and cyclononasilanes were found at 249, 246, and 242 nm, respectively.[18] Compared to these values, the appearance of the spectra of compounds **1**−**5** is dramatically different (Figure 1). With the exception of cycloheptasilane **2** all compounds show at least three or four absorption bands. In contrast to the permethylated compounds, a marked bathochromic shift behavior with increasing ring size is observed. The strongest bathochromic shifted band for compound **5** is at 297 nm. In

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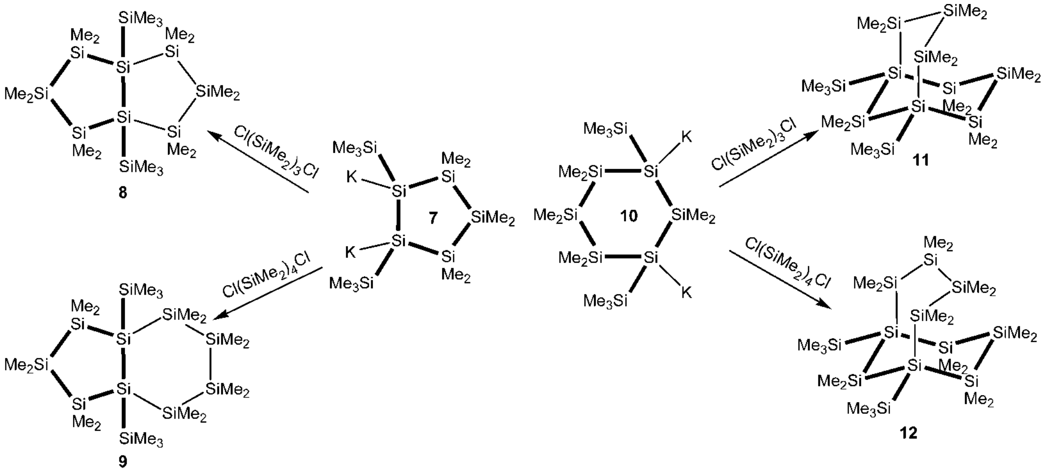
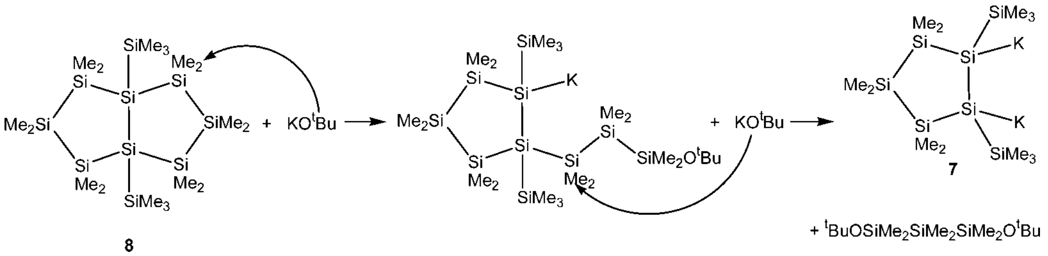
Scheme 2. Formation of Bicyclosilanes by Reaction of Cyclic Dianions with α,ω-Dichloropermethyloligosilanes[a]



[a] The bold backbone parts of the molecules indicate the used starting materials.

Scheme 3. Proposed Mechanistic Rationale for the Formation of Dianion 7 from the Bicyclic Compound 8



addition, the extinction coefficients are markedly higher than reported for the permethylated compounds.

The decisive difference between the homocyclic compounds and compounds **1**−**5** comes from the presence of the trimethylsilyl groups. These groups may be considered to participate in the constitution of *transoid*-oriented segments within the ring. These segments then can be compared to open-chain permethylated oligosilanes. Absorption maxima of linear permethylated chains $Me(SiMe_2)_nMe$ have been found for $n = 3$ at 215 nm, $n = 4$ at 235 nm, $n = 5$ at 250 nm, $n = 6$ at 260 nm, $n = 7$ at 267 nm, $n = 8$ at 273 nm, $n = 10$ at 279 nm, and $n > 12$ at 288 nm.[18,19] It was also shown that segments oriented such that they are capable of σ-bond electron delocalization in larger molecules could be assigned this way.[20]

Comparison of the values derived from the spectra of Figure 1 (compiled in Table 1) with the absorption bands of permethyloligosilanes leads to the following: For **1** the two absorption bands at 255 and 275 nm seem to correspond to segments composed of six and eight silicon atoms. In contrast to this, the band at 242 nm for compound **2** seems to correspond to a pentasilane segment. For compound **3** we can assign the bands at 249 and 273 nm to penta- and heptasilane units. Compound **4** exhibits three bands at 245, 261, and 284 nm, which can be assigned to penta-, hexa-, and octasilane units. Finally, for compound **5** the absorption bands at 250, 278, and 297 nm correspond to penta-, hepta-, and decasilane units.

If we now consider that the segments in question include two trimethylsilyl end groups, we have *two* possibilities to arrange such a segment in a ring with different bridging segments: either along the shorter bridging unit, which intuitively seems to be the more likely possibility, or alternatively along the longer bridging section. The two cyclooctasilane molecules **3** and **4** would in this way give two heptasilane units for the more symmetric compound **3** and a hexa- and an octasilane unit for

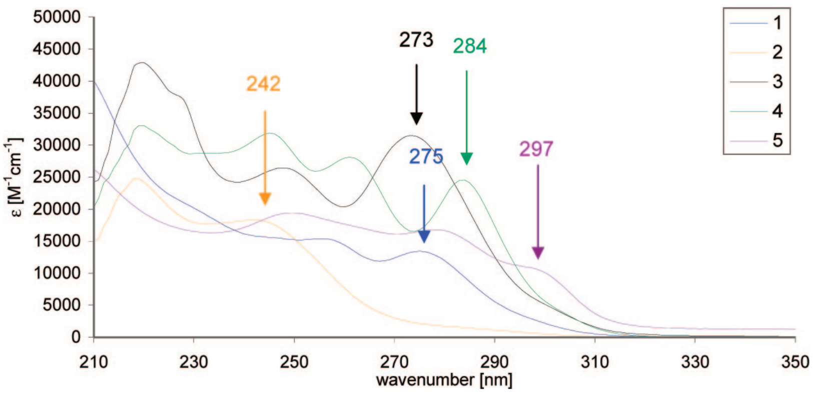


Figure 1. UV absorption spectra for compounds **1**−**5** with the lowest energy band for each compound marked.

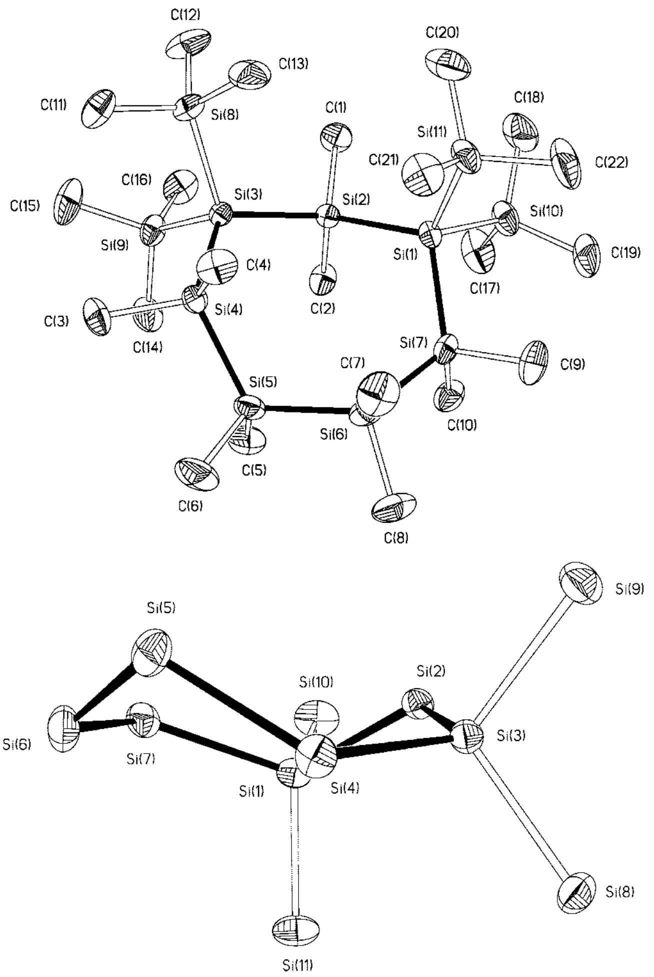


Figure 2. (Top) Molecular structure and numbering of **2** (only one of two crystallographically independent molecules shown). (Bottom) Oligosilane backbone with methyl groups omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Si(1)−Si(2) 2.3732(16), Si(7)−Si(1)−Si(2) 112.91(6), Si(3)−Si(2)−Si(1) 125.59(6), Si(4)−Si(3)−Si(2) 116.06(6), Si(5)−Si(4)−Si(3) 119.81(6), Si(6)−Si(5)−Si(4) 114.11(7), Si(5)−Si(6)−Si(7) 118.55(7), Si(6)−Si(7)−Si(1) 121.84(6), Si(11)−Si(1)−Si(7) 111.06(7), Si(11)−Si(1)−Si(2) 117.40(7), Si(11)−Si(1)−Si(10) 104.70(7), Si(7)−Si(1)−Si(10) 104.57(7), Si(2)−Si(1)−Si(10) 104.78(6), Si(4)−Si(3)−Si(8) 106.29(6), Si(4)−Si(3)−Si(9) 107.99(6), Si(8)−Si(3)−Si(9) 106.19(6), Si(8)−Si(3)−Si(2) 113.77(6), Si(9)−Si(3)−Si(2) 106.01(6).

4. This corresponds quite well with the found bands and suggests that also along the longer bridging section there would be some sort of delocalization, even if it were rather unlikely that an all- *transoid*-oriented conformation can be acquired. Cyclononasilane **5** is an even more striking example, as it clearly exhibits an absorption band that may be assigned to a decasilane unit (arrangement from one trimethylsilyl group along the long bridging unit to the other trimethylsilyl group).

The only compound that does not really fit into this view is compound **2**, which should exhibit not only an absorption band corresponding to a pentasilane unit but also another one that would resemble an octasilane. However, it may be that the 1,3-interactions of the trimethylsilyl groups strongly favor a certain conformation, which is likely to be the one that is present in the solid-state structure. Although compound **5** possesses the 1,1,3,3-tetrakis(trimethylsilyl) structural unit as well, it seems to be able to exhibit different conformations, as the larger ring size provides more flexibility.

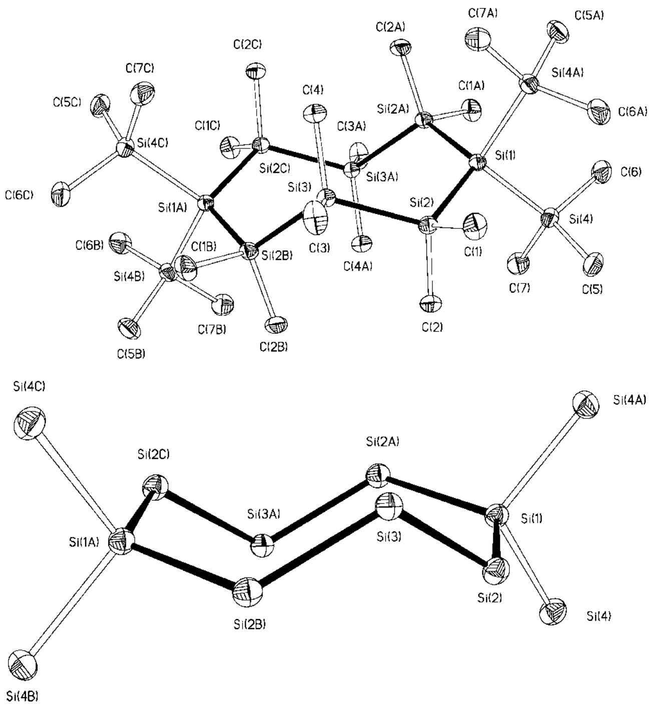


Figure 3. (Top) Molecular structure and numbering of **3**. (Bottom) Oligosilane backbone with methyl groups omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Si(1)−Si(4) 2.3659(14), Si(4A)-Si(1)−Si(4) 105.21(8), Si(4A)-Si(1)−Si(2) 109.73(4), Si(4)−Si(1)−Si(2) 106.38(4), Si(4A)-Si(1)-Si(2A) 106.38(4), Si(4)−Si(1)−Si(2A) 109.73(4), Si(2)−Si(1)−Si(2A) 118.65(8), Si(1)−Si(2)−Si(3) 117.50(6), Si(2B)-Si(3)−Si(2) 118.56(8).

NMR Spectroscopy. The NMR spectroscopic behavior of the obtained compound resembles very much that of related compounds. As usual, ^{29}Si NMR data proved to be most useful for the assignment of structures.[21] The spectroscopic data compiled in Table 3 show a trend commonly found in cyclosilanes, that resonances corresponding to silicon atoms in a sterically more crowded environment experience a downfield shift. For the $SiMe_2$ units this means that they approach the resonance value for permethylated cyclosilanes (around −42 ppm) if located in the middle segment of a longer bridge. If this group is neighbored by two quaternary silicon atoms, it experiences a shift to values above −30 ppm. This trend is further amplified if the neighboring atoms bear negative charges such as in **10**, where the resonance for the dimethylsilylene unit is found at −19.2 ppm. The situation for the quaternary silicon atoms is quite similar, and downfield shifts are found for cases of more distorted environments. This again is in accordance with previous observations.[21]

Conclusion

Medium-sized cyclooligosilanes with $n = 7, 8, 9$ could be synthesized by reaction of α,ω-dipotassiumoligosilanes with the corresponding α,ω-dichlorooligosilanes. Also bicyclic oligosilanes could be easily achieved by reaction of cyclic dipotas-

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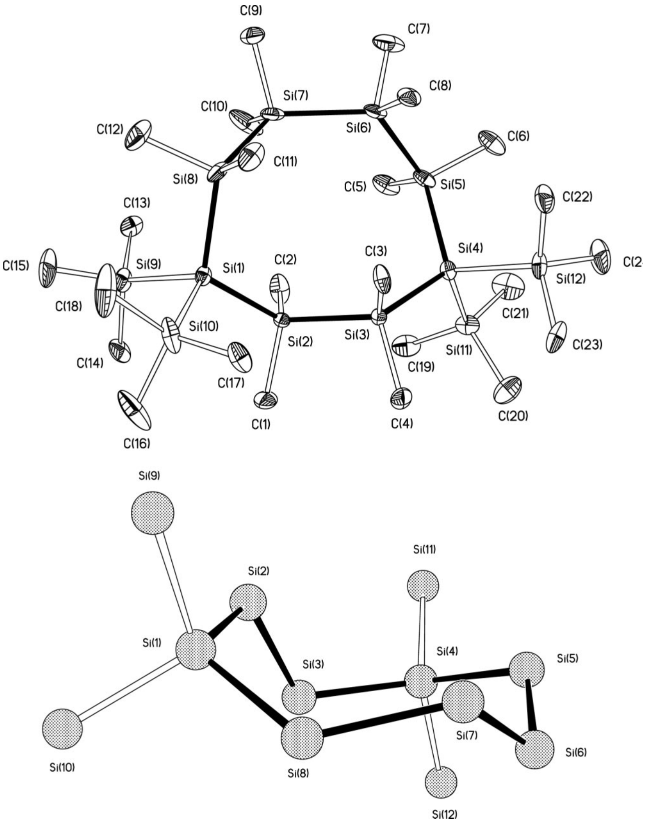

Figure 4. (Top) Molecular structure and numbering of **4**. (Bottom) Oligosilane backbone with methyl groups omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Si(1)−Si(2) 2.349(10), Si(2)−Si(1)−Si(10) 111.7(4), Si(2)−Si(1)−Si(8) 115.5(4), Si(10)−Si(1)−Si(8) 110.2(5), Si(2)−Si(1)−Si(9) 106.4(4), Si(10)−Si(1)−Si(9) 105.0(4), Si(8)−Si(1)−Si(9) 107.1(4), Si(1)−Si(2)−Si(3) 117.3(3), Si(4)−Si(3)−Si(2) 118.2(3), Si(3)−Si(4)−Si(5) 115.5(4), Si(3)−Si(4)−Si(11) 111.5(4), Si(5)−Si(4)−Si(11) 109.5(4), Si(3)−Si(4)−Si(12) 106.4(4), Si(5)−Si(4)−Si(12) 108.2(4), Si(11)−Si(4)−Si(12) 105.2(4), Si(6)−Si(5)−Si(4) 119.8(4), Si(7)−Si(6)−Si(5) 121.1(4), Si(6)−Si(7)−Si(8) 121.6(4), Si(7)−Si(8)−Si(1) 120.6(5).

siumoligosilanes with the corresponding α,ω-dichlorooligosilanes. UV spectra of the obtained rings show an unusual feature. Contrary to what was found by West and co-workers,[18] no hypsochromic shift of the low-energy bands was observed with increasing ring size. Instead, a marked bathochromic shift behavior was detected, which seems to be suggestive of σ-bond electron delocalization along segments starting from one trimethylsilyl group along both sides of the ring to another trimethylsilyl group. It is likely that the different bands observed for the rings are to be attributed to different conformations. The fact that the conformationally more confined cycloheptasilane **2** exhibits only one of the two bands, which might be assigned to the two ways to run a chain from one trimethylsilyl group to the other through the ring, seems to support this assumption.

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.[22] Potassium *tert*-butanolate was purchased from Merck.

^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. Samples for ^{29}Si spectra were dissolved in either deuterated benzene or chloroform or, in case 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.[23] Elementary analysis was carried out using a Heraeus VARIO Elementar instrument (in cases of bad carbon values WO_3 was added to facilitate complete combustion and to suppress silicon carbide formation).

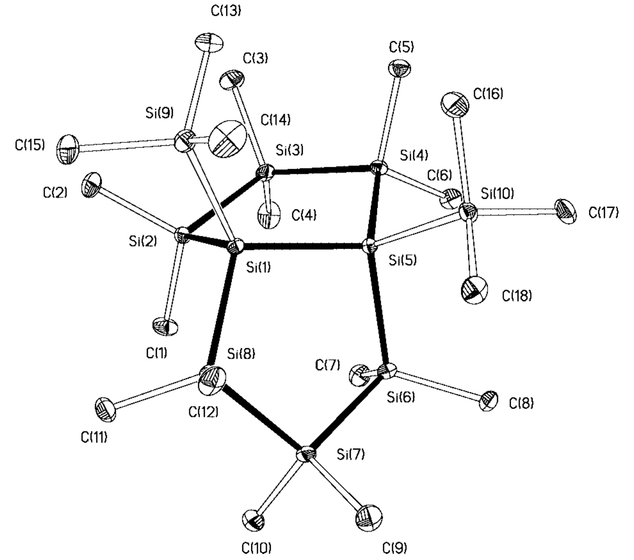

Figure 5. Molecular structure and numbering of **8**. Selected bond lengths [Å] and bond angles [deg]: Si(1)−Si(9) 2.346(2), Si(1)−Si(2) 2.365(2), Si(1)−Si(5) 2.372(2), Si(9)−Si(1)−Si(8) 110.63(9), Si(9)−Si(1)−Si(2) 109.34(9), Si(8)−Si(1)−Si(2) 111.12(9), Si(9)−Si(1)−Si(5) 117.65(9), Si(8)−Si(1)−Si(5) 106.00(8), Si(2)−Si(1)−Si(5) 101.76(8), Si(3)−Si(2)−Si(1) 107.29(9), Si(4)−Si(3)−Si(2) 107.37(8).

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[24] and SADABS,[25] respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).[26] 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. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **2**, **3**, **4**, and **8** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-666916 (**2**), 666914 (**3**), 666915 (**4**), and 695767 (**8**). Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

The following compounds were synthesized according to the reported procedures: 1,1,1,3,3,3-hexakis(trimethylsilyl)dimethyltrisilane,[27]1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane,[7]1,1,1,5,5,5-hexakis(trimethylsilyl)hexamethylpentasila-

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Table 1. UV Absorption Maxima [nm] and Molar Extinctions [M^{-1} cm^{-1}] of Cyclosilanes 1−5

	λ_1 [nm]	ϵ_1 [M^{-1} cm^{-1}]	λ_2 [nm]	ϵ_2 [M^{-1} cm^{-1}]	λ_3 [nm]	E_3 [M^{-1} cm^{-1}]	λ_4 [nm]	ϵ_4 [M^{-1} cm^{-1}]
1	209	4.1×10^4	255	1.5×10^4	275	1.3×10^4		
2	219	2.5×10^4	242	1.8×10^4				
3	220	4.3×10^4	249	2.6×10^4	273	3.1×10^4		
4	220	3.3×10^4	245	3.2×10^4	261	2.8×10^4	284	2.5×10^4
5	209	2.4×10^4	250	1.8×10^4	278	1.6×10^4	297	1.1×10^4

Table 2. ^{29}Si NMR Shifts (ppm) of the Obtained Cyclic and Bicyclic Polysilanes

	δ $SiMe_3$	δ $SiMe_2$	δ Si		δ $SiMe_3$	δ $SiMe_2$	δ Si
1	−8.3	−31.6/−35.4/−35.5	−130.2	**7**	−3.5	−24.4/−40.2	−175.6
2	−8.3	−27.3/−36.5/−38.0	−118.4	**8**	−7.3	−28.3/−40.7	−118.6
3	−8.2	−33.9/−37.5	−124.9	**9**	−7.2	−28.3/−34.9/−41.4/−42.1	−121.6
4	−8.5	−31.9/−34.1/−37.5	−124.4	**10**	−3.2	−19.2/−27.7/−45.7	−173.0
5	−9.3	−24.8/−30.7/−34.6/−35.0	−106.7	**11**	−4.9	−29.3/−35.5/−44.2	−125.6
6	−8.1	−30.1/−41.3	−123.6	**12**	−6.1	−31.3/−36.5/−37.9/−38.3	−122.5

Table 3. Crystallographic Data for Compounds 2, 3, 4, and 8

	2	**3**	**4**	**8**
empirical formula	$Si_{22}C_{44}H_{132}$	$Si_{12}OC_{30}H_{72}$	$Si_{24}C_{48}H_{144}$	$Si_{20}C_{36}H_{105}$
M_w	1279.48	785.96	1395.79	1100.00
temperature [K]	100(2)	200(2)	100(2)	100(2)
size [mm]	0.33 × 0.28 × 0.25	0.42 × 0.34 × 0.22	0.40 × 0.30 × 0.26	0.42 × 0.35 × 0.22
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*Ibma*	*P*2(1)/*c*	*P*2(1)/*n*
a [Å]	17.892(4)	10.329(2)	22.842(5)	18.509(4)
b [Å]	18.938(4)	15.447(3)	16.013(3)	21.689(4)
c [Å]	25.108(5)	31.058(6)	26.748(5)	19.166(4)
α [deg]	90	90	90	90
β [deg]	94.27(3)	90	109.36(3)	114.73(3)
γ [deg]	90	90	90	90
V [$Å^3$]	8484(3)	4955(2)	9230(3)	6988(2)
Z	4	4	4	4
ρ_{calc} [gcm^{-3}]	1.002	1.054	1.004	1.046
absorp coeff [mm^{-1}]	0.349	0.334	0.350	0.382
F(000)	2816	1712	3072	2404
θ range	$1.35 < \theta < 26.38$	$2.37 < \theta < 26.36$	$0.94 < \theta < 24.00$	$1.28 < \theta < 25.00$
reflns collected/unique	67 433/17 339	18 749/2587	60 613/14 482	49 989/12 303
completeness to θ [%]	99.8	99.7	100	100
data/restraints/params	17 339/0/639	2587/0/123	14 482/6/697	12 303/0/540
goodness of fit on F^2	0.92	1.27	1.09	1.3
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.062, wR2 = 0.127	R1 = 0.084, wR2 = 0.173	R1 = 0.149, wR2 = 0.285	R1 = 0.099, wR2 = 0.178
R indices (all data)	R1 = 0.141, wR2 = 0.151	R1 = 0.093, wR2 = 0.178	R1 = 0.187, wR2 = 0.308	R1 = 0.126, wR2 = 0.189
largest diff peak/hole [$e^-/Å^3$]	0.34/−0.23	0.46/−0.88	1.50/−1.58	0.94/−0.50

ne,[27] 1,1,3,3-tetrakis(trimethylsilyl)octamethylcyclohexasilane,[7] 1,1,4,4-tetrakis(trimethylsilyl)decamethylcycloheptasilane (**1**),[10] 1,2-dichlorotetramethyldisilane,[28,29] 1,3-dichlorohexamethyltrisilane,[29] 1,4-dichlorooctamethyltetrasilane,[29] and 1,6-dichlorodecamethylhexasilane.[29]

1,1,3,3-Tetrakis(trimethylsilyl)decamethylcycloheptasilane (2). 1,1,1,3,3,3-Hexakis(trimethylsilyl)dimethyltrisilane (0.300 g, 0.542 mmol) was dissolved in toluene (3 mL), and 18-crown-6 (0.301 g, 1.138 mmol) and KO^tBu (0.128 g, 1.138 mmol) were added. The red solution was stirred for 16 h and then added to a solution of 1,4-dichlorooctamethyltetrasilane (0.165 g, 0.542 mmol) in toluene (5 mL). After stirring for 3 days the reaction mixture was poured on aqueous sulfuric acid (0.5 M), washed with brine, and extracted with ether. The organic phase was dried over sodium sulfate, and the solvent was removed under vacuum. Colorless crystals of **2** were obtained after recrystallization from CH_2Cl_2 at −30 °C (0.328 g, 95%). Mp: 171−174 °C. NMR (δ in ppm): ^{29}Si (C_6D_6) −8.3, −27.3, −36.5, −38.0, −118.4; ^1H (C_6D_6) 0.61 (s, 6H, Si*Me*$_2$), 0.41 (s, 12H, 2×Si*Me*$_2$), 0.36 (s, 36H, 4×Si*Me*$_3$), 0.26 (s, 12H, 2×Si*Me*$_2$); ^{13}C (C_6D_6) 5.4, 4.5, −0.3, −4.8. Anal. Calcd for $C_{22}H_{66}Si_{11}$ (639.70): C 41.31, H 10.40. Found: C, 40.96, H 10.37. UV absorption: $\lambda_1 = 219$ nm ($\epsilon_1 = 2.5 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 242$ nm ($\epsilon_2 = 1.8 \times 10^4$ [M^{-1} cm^{-1}]).

1,1,5,5-Tetrakis(trimethylsilyl)dodecamethylcyclooctasilane (3). The procedure for the synthesis of **2** was followed using 1,1,1,5,5,5-hexakis(trimethylsilyl)hexamethylpentasilane (1.000 g, 1.493 mmol) in benzene (10 mL), 18-crown-6 (0.789 g, 2.986 mmol), and KO^tBu (0.335 g, 2.986 mmol) to produce the dipotassium compound. 1,3-Dichlorohexamethyltrisilane (0.366 g, 1.493 mmol) in benzene (10 mL) was used as the dielectrophile. **3** was obtained as colorless crystals after recrystallization from Et_2O/acetone at rt (0.989 g, 95%). NMR (δ in ppm): ^{29}Si (C_6D_6) −8.2, −33.9, −37.5, −124.9; ^1H (C_6D_6) 0.37 (s, 4H, 4×Si*Me*$_2$), 0.29 (s, 36H, 4×Si*Me*$_3$), 0.24 (s, 12H, 2×Si*Me*$_2$); ^{13}C (C_6D_6) 4.3, 1.0, −2.6. Anal. Calcd for $C_{24}H_{72}Si_{12}$ (697.85): C 41.31, H 10.40. Found: C 41.37, H 10.26. UV absorption: $\lambda_1 = 220$ nm ($\epsilon_1 = 4.3 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 249$ nm ($\epsilon_2 = 2.6 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_3 = 273$ nm ($\epsilon_3 = 3.1 \times 10^4$ [M^{-1} cm^{-1}]), shoulder 228 nm.

1,1,4,4-Tetrakis(trimethylsilyl)dodecamethylcyclooctasilane (4). The procedure for the synthesis of **2** was followed using 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane (0.500 g, 0.817 mmol) in toluene (5 mL), 18-crown-6 (0.443 g, 1.676 mmol), and KO^tBu (0.188 g, 1.676 mmol) to produce the dipotassium compound. 1,4-Dichlorooctamethyltetrasilane (0.248 g, 0.817 mmol) in toluene (5 mL) was used as the dielectrophile. Colorless crystals of **4** were obtained after recrystallization from Et_2O/acetone (0.225 g, 40%). Mp: 158−160 °C. NMR (δ in ppm): ^{29}Si (C_6D_6) −8.5, −31.9, −34.1, −37.5, −124.4; ^1H (C_6D_6) 0.41 (s, 12H, 2×Si*Me*$_2$), 0.35 (s, 12H, 2×Si*Me*$_2$), 0.29 (s, 36H, 4×Si*Me*$_3$), 0.22 (s, 12H,

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2×Si*Me*$_2$); ^{13}C (C_6D_6) 4.2, 2.0, 0.2, −3.8. Anal. Calcd for $C_{24}H_{72}Si_{12}$ (697.85): C 41.31, H 10.40. Found: C 41.04, H 10.35. UV absorption: $\lambda_1 = 220$ nm ($\epsilon_1 = 3.3 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 245$ nm ($\epsilon_2 = 3.2 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_3 = 261$ nm ($\epsilon_3 = 2.8 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_4 = 284$ nm ($\epsilon_4 = 2.5 \times 10^4$ [M^{-1} cm^{-1}]).

1,1,3,3-Tetrakis(trimethylsilyl)tetradecamethylcyclononasilane (5). The procedure for the synthesis of **2** was followed using 1,1,1,3,3,3-hexakis(trimethylsilyl)dimethyltrisilane (0.150 g, 0.271 mmol) in benzene (7 mL), 18-crown-6 (0.143 g, 0.542 mmol), and KO^{t}Bu (0.061 g, 0.542 mmol) to produce the dipotassium compound. 1,6-Dichlorododecamethylhexasilane (0.114 g, 0.271 mmol) in benzene (7 mL) was used as the dielectrophile. Compound **5** was obtained as semicrystalline residue (0.155 g, 76%). NMR (δ in ppm): ^{29}Si ($CDCl_3$) −9.2, −24.8, −30.7, −34.6, −35.0, −106.7; ^{1}H ($CDCl_3$) 0.60 (s, 6H, Si*Me*$_2$), 0.47 (s, 12H, 2×Si*Me*$_2$), 0.35 (s, 36H, 4×Si*Me*$_3$), 0.32 (s, 12H, 2×Si*Me*$_2$), 0.31 (s, 12H, 2×Si*Me*$_2$); ^{13}C (C_6D_6) 4.8, −2.2, −2.3, −5.8, −12.1. Anal. Calcd for $C_{26}H_{78}Si_{13}$ (756.01): C 41.31, H 10.40. Found: C 39.5, H 10.10. UV absorption: $\lambda_1 = 209$ nm ($\epsilon_1 = 2.4 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_2 = 250$ nm ($\epsilon_2 = 1.8 \times 10^4$ [M^{-1} cm^{-1}]), $\lambda_3 = 278$ nm ($\epsilon_3 = 1.6 \times 10^4$ [M^{-1} cm^{-1}]), shoulder 298 nm.

1,1,2,2-Tetrakis(trimethylsilyl)hexamethylcyclopentasilane (6). 1,1,1,5,5,5-Hexakis(trimethylsilyl)hexamethylpentasilane (1.500 g, 2.239 mmol) was dissolved in toluene (10 mL), and 18-crown-6 (1.243 g, 4.703 mmol) and KO^{t}Bu (0.528 g, 4.703 mmol) were added. The red solution was stirred for 16 h, and Et_2O (10 mL) was added. Then at −70 °C a solution of 1,2-dibromoethane (0.442 g, 2.35 mmol) in Et_2O (10 mL) was slowly added. The reaction mixture was allowed to reach rt and then stirred for 20 h before it was subjected to a workup analogous to that for **2**. The obtained residue was dissolved in pentane and filtered through silica gel. Again, the solvent was removed under vacuum, and 1,1,2,2-tetrakis(trimethylsilyl)hexamethylcyclopentasilane **6** was obtained as a white solid (0.969 g, 83%). NMR (δ in ppm): ^{29}Si (C_6D_6) −8.1, −30.1, −41.3, −123.6; ^{1}H (C_6D_6) 0.38 (s, 12H, 2×Si*Me*$_2$), 0.34 (s, 36H, 4×Si*Me*$_3$), 0.21(s, 6H, 1×Si*Me*$_2$); ^{13}C (C_6D_6) 4.4, −0.7, −5.8. Anal. Calcd for $C_{18}H_{54}Si_9$ (523.39): C 41.31, H 10.40. Found: C 41.01, H 10.32.

1,2-Dipotassium-1,2-bis(trimethylsilyl)hexamethylcyclopentasilane (7). To a solution of **6** (0.150 g, 0.287 mmol) in benzene (4 mL) were added 18-crown-6 (0.152 g, 0.573 mmol) and KO^{t}Bu (0.064 g, 0.573 mmol). The solution turned red, and complete conversion was detected after 4 h. After removal of the solvent the residue was dissolved in a mixture of pentane and toluene to give orange crystals of **7** after cooling to −70 °C. NMR (δ in ppm): ^{29}Si (C_6D_6) −3.5, −24.4, −40.2, −175.6; ^{1}H (C_6D_6) 3.33 (s, 48H), 0.80 (s, 12H), 0.76 (s, 18H), 0.69 (s, 6H); ^{13}C (C_6D_6) 70.0, 9.0, 8.2, −3.4.

1,5-Bis(trimethylsilyl)bicyclo[3.3.0]dodecamethyloctasilane (8). To a solution of *in situ* prepared **7** (0.890 mmol) was added dropwise a solution of 1,3-dichlorohexamethyltrisilane (0.218 g, 0.890 mmol) in benzene (10 mL) at 0 °C. The reaction mixture was stirred for 18 h and was then subjected to the same isolation procedure as described for **6**. Colorless crystals of **8** were obtained (0.184 g, 37%). NMR (δ in ppm): ^{29}Si (C_6D_6) −7.3, −28.3, −40.7, −118.6; ^{1}H (C_6D_6) 0.38(s, 24H), 0.33 (s, 18H), 0.25 (s, 6H), 0.13 (s, 6H); ^{13}C (C_6D_6) 3.7, −1.3, −6.3. Anal. Calcd for $C_{18}H_{54}Si_{10}$ (551.48): C 39.20, H 9.87. Found: C39.04, H 9.52.

1,5-Bis(trimethylsilyl)bicyclo[3.4.0]tetradecamethylnonasilane (9). The procedure for the synthesis of **8** was followed using *in situ* prepared **7** (0.085 g, 0.086 mmol) in benzene (4 mL) and a solution of 1,4-dichlorooctamethyltetrasilane (0.026 g, 0.086 mmol) in benzene (7 mL). A colorless oil of **9** was obtained (0.045 g, 85%). NMR (δ in ppm): ^{29}Si (C_6D_6) −7.2, −28.3, −34.9, −41.4, −42.1, −121.6; ^{1}H (C_6D_6) 0.43 (s, 6H), 0.40 (s, 6H), 0.39 (s, 6H); 0.37 (s, 9H), 0.36 (s, 9H), 0.29 (s, 6H), 0.26 (s, 6H), 0.24 (s, 6H), 0.22 (s, 6H). Anal. Calcd for $C_{20}H_{60}Si_{11}$ (609.63): C 39.40, H 9.92. Found: C 39.69, H 10.07.

1,3-Dipotassium-1,3-bis(trimethylsilyl)octamethylcyclohexasilane (10). To a solution of 1,1,3,3-tetrakis(trimethylsilyl)octamethylcyclohexasilane (0.060 g, 0.103 mmol) in benzene (2 mL) were added 18-crown-6 (0.055 g, 0.206 mmol) and KO^{t}Bu (0.023 g, 0.206 mmol). The orange solution was stirred for 16 h, after which complete conversion was detected. The solvent was removed under vacuum, and **10** was obtained as a red oil. NMR (δ in ppm): ^{29}Si (C_6D_6) −4.4, −10.9, −31.3, −37.1, −40.7, −43.3, −125.5, −189.3; ^{1}H (C_6D_6) 3.20 (s, 24H), 0.79 (s, 6H), 0.72 (s, 6H), 0.68 (s, 9H), 0.65 (s, 18H), 0.54 (s, 6H), 0.49 (s, 6H); ^{13}C (C_6D_6) 69.9, 9.2, 4.8, 4.3, 0.2, −4.0, −4.4.

1,5-Bis(trimethylsilyl)bicyclo[3.3.1]tetradecamethylnonasilane (11). The procedure for the synthesis of **8** was followed using *in situ* prepared **10** (0.103 mmol) in benzene (4 mL) and a solution of 1,3-dichlorohexamethyltrisilane (0.025 g, 0.103 mmol) in benzene (4 mL). **11** was obtained as a white solid (0.060 g, 97%). NMR (δ in ppm): ^{29}Si ($CDCl_3$) −4.9, −29.3, −35.5, −44.2, −125.6; ^{1}H ($CDCl_3$) 0.46 (s, 6H), 0.37 (s, 12H), 0.36 (s, 12H), 0.33 (s, 18H, SiMe$_3$), 0.22 (s, 6H), 0.20 (s, 6H); ^{13}C ($CDCl_3$) 4.7, 2.9, 0.8, −0.5, −3.5, −5.0. Anal. Calcd for $C_{20}H_{60}Si_{11}$ (609.63): C 39.40, H 9.92. Found: C 38.81, H 9.89.

1,5-Bis(trimethylsilyl)bicyclo[3.4.1]hexadecamethyldecasilane (12). The procedure for the synthesis of **8** was followed using *in situ* prepared **10** (0.103 mmol) in benzene (4 mL) and a solution of 1,4-dichlorooctamethyltetrasilane (0.031 g, 0.103 mmol) in benzene (4 mL). **12** was obtained as semicrystalline residue (0.062 g, 90%). NMR (δ in ppm): ^{29}Si ($CDCl_3$) −6.1, −31.3, −36.5, −37.9, −38.3, −45.5, −122.5; ^{1}H ($CDCl_3$) 0.46 (s, 3H), 0.43 (s, 3H), 0.34 (s, 12H), 0.33 (s, 6H), 0.32 (s, 6H), 0.30 (s, 18H), 0.24 (s, 6H), 0.20 (s, 6H), 0.19 (s, 3H), 0.11 (s, 3H); ^{13}C ($CDCl_3$) 4.8, 4.5, 0.5, 0.3 (2×), 0.2, −4.2, −4.3, −12.1. Anal. Calcd for $C_{22}H_{66}Si_{12}$ (667.79): C 39.57, H 9.96. Found: C 39.47, H 10.12.

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Supporting Information Available: X-ray crystallographic information for compounds **2**, **3**, **4**, and **8** in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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