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Synthesis, Structures, and Unusual Photoluminescence of O- and N-Functional Cyclohexasilanes

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The reaction of chloropermethylcyclohexasilanes $Si_6Me_{12-n}Cl_n$ (n = 1−3) with lithium silanolates affords the siloxy derivatives $Si_6Me_{12-n}(OR)_n$ (n = 1−3; R = $SiMe_3$, $SiMe_2$-t-Bu). All compounds exhibit bathochromically shifted first UV absorption maxima and room-temperature photoluminescence in solution with emission maxima near 340 nm and remarkably enhanced luminescence intensity as compared to the data for Si_6Me_{12}. The solution photoemission spectra of the corresponding aminocyclohexasilanes $Si_6Me_{12-n}(NR_2)_n$ (n = 1, 2; R = $-SiMe_3$), which are accessible from $Si_6Me_{12-n}Cl_n$ and $LiN(SiMe_3)_2$, do not show any luminescence above 300 nm. Crystal structure analyses of the 1,3- and 1,4-disubstituted derivatives exhibit the cyclohexasilane ring in the chair conformation with the −OR or $-NR_2$ groups in either axial or equatorial positions, depending on the steric bulk of the hetero substituents.

Introduction

Crystalline silicon is the most widely used semiconductor material today, with a market share of above 90%. Due to its indirect electronic band structure, however, the material is not able to emit light effectively and, therefore, cannot be used for key applications such as light emitting diodes and lasers. Selected polysilane polymers such as linear or branched polysilylenes,[1] polysiloles,[2] and layered structures such as siloxene,[3] however, possess a direct band gap and therefore exhibit intense visible photoluminescence.

Siloxene, a two-dimensional layered polymer with the empirical formula $Si_6H_{6-n}(OH)_n$ consisting of stacked Si planes terminated by −H, −OH, or −O groups, is considered in particular as an alternative material for Si-based luminescent devices. When it is prepared by the topochemical hydrolysis reaction of $CaSi_2$ with aqueous HCl, its oxygen content and properties vary considerably with preparation conditions. It frequently has been argued that different structures might be responsible for this unusual behavior (compare A and B in Figure 1).[4]

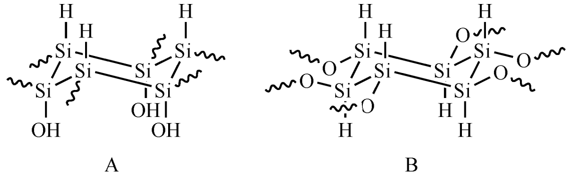

Figure 1. Structural models for Wöhler (A) and Kautsky (B) siloxene.

Only a few examples of nonpolymeric fluorescent Si−Si compounds are mentioned in the literature. The dual (locally excited (LE) and intramolecular charge transfer (ICT)) emission of phenylpentamethyldisilane was found in 1981[5] as a noticeable photophysical property of organosilicon compounds. Since then, the photophysical and photochemical properties of phenyldisilanes were investigated in detail mainly by the groups of Sakurai and Shizuka.[6,7] The fluorescence spectra of the permethylated oligosilanes Si_nMe_{2n+2} have been studied by the group of Michl in order to explain the fluorescence properties of poly(dialkylsilylenes).[8] Fluorescence of the cyclotetrasilanes $(R_2Si)_4$ (R = Me_3Si, Me_2SiEt, Me_3CCH_2, Me_2CH) with an extremely large Stokes shift has been observed in rigid matrixes at 77 K.[9] Matsumoto et al. studied the luminescence of

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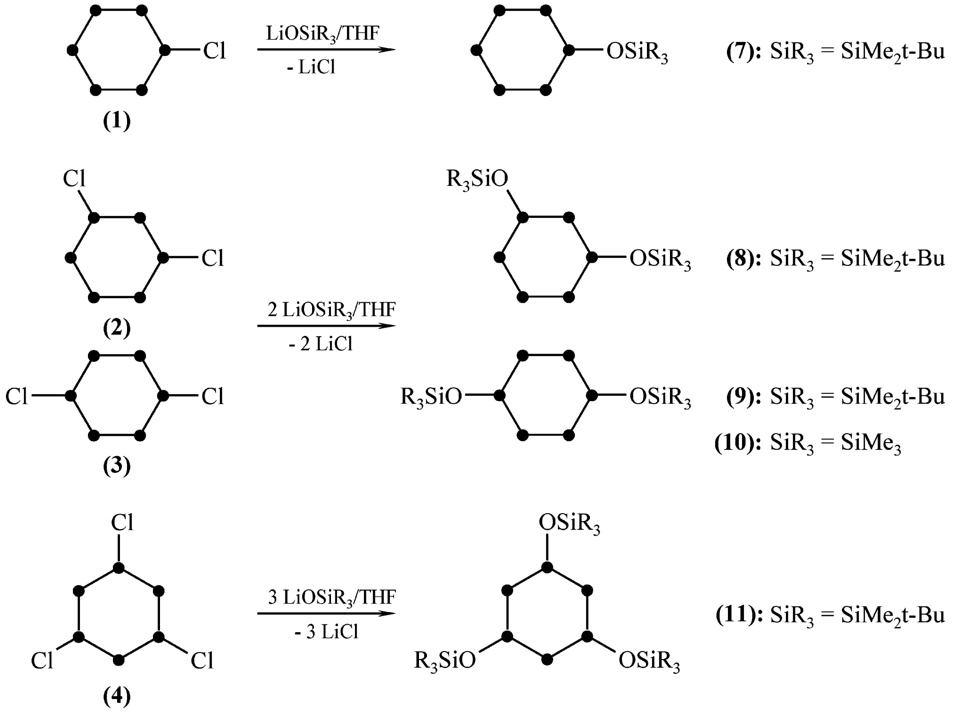
Scheme 1

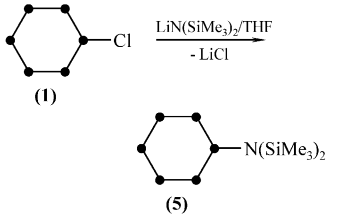


chemically synthesized Si_8 clusters with chain, ladder, and cubic structures and found the optical properties of Si_8 clusters to be strongly dependent on the shape of the Si−Si skeleton.[10] Finally, decaisopropyl-7-oxabicyclo[2.2.1]heptasilane was shown to exhibit relatively strong fluorescence with $\lambda_{max,em} = 337$ nm and a quantum yield of $\Phi_f = 0.014$.[11]

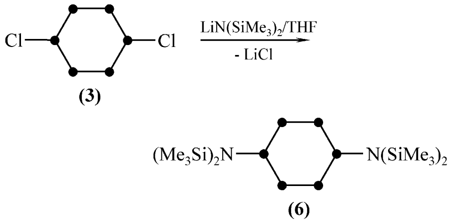
In a preceding study we were able to show that polysiloxane polymers with two-dimensional siloxene-like structures containing cyclosilanyl subunits are strongly photoluminescent.[12] Novel, luminescent materials, therefore, might be accessible on the basis of cyclohexasilanyl rings and oxygen-containing side groups. Thus, we decided to prepare a series of siloxy-substituted cyclohexasilanes of the general formula $Si_6Me_{12-n}(OSiR_3)_n$ as molecular model substances for the smallest structural subunit present in siloxene and to examine their photoluminescence properties. To investigate the influence of further hetero substituents on the luminescence behavior of cyclohexasilanes, the study additionally has been extended to the corresponding amino derivatives $Si_6Me_{12-n}(NR_2)_n$.

Results and Discussion

Preparation and Characterization. The methyl groups present in $(Me_2Si)_6$ can be substituted by halogen without destruction of the ring structure. With $SbCl_5$, either one, two, or three of the methyl groups can be replaced by chlorine, depending on the stoichiometric ratio of the reactants, thus giving the partially chlorinated derivatives $ClSi_6Me_{11}$ (**1**), 1,3-$Cl_2Si_6Me_{10}$ (**2**), 1,4-$Cl_2Si_6Me_{10}$ (**3**), and 1,3,5-$Cl_3Si_6Me_9Cl$ (**4**).[13] The reaction of **1**−**4** with various nucleophiles such as H^-, $[(CO)_2CpFe]^-$, RS^-, RO^-, and R^- subsequently can be utilized to synthesize the corresponding substitution products of the Si−Cl bond.[14] In a similar fashion the $(Me_3Si)_2N-$ derivatives **5** and **6** are obtained from **1** or **3** and $LiN(SiMe_3)_2$ (eqs 1 and 2).



(1)



(2)

The siloxy-substituted cyclohexasilanes **7**−**11** are easily accessible by reacting **1**−**4** with lithium silanolates according to Scheme 1.

All previously unknown compounds were fully characterized by spectroscopic means and elemental analyses. Analytical data (compare the Experimental Section) are consistent with the proposed structures in all cases. Marked electronic effects of the hetero substituents on the ring silicon atoms are apparent in the ^{29}Si NMR

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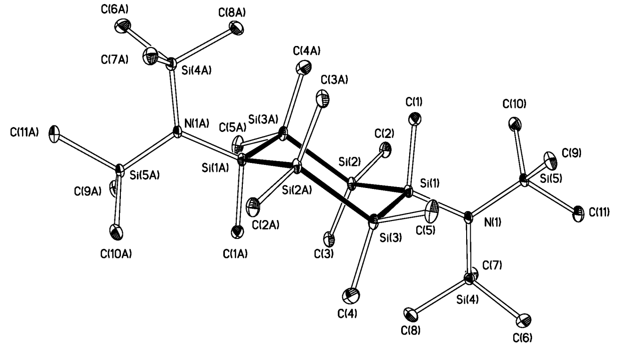

Figure 2. Molecular structure and numbering of **6**. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Si(1)−N(1) = 1.7751(14), Si(1)−Si(2) = 2.3638(8), Si(1)−Si(3) = 2.3701(8), Si(2)−Si(3)#1 = 2.3691(8), Si(4)−N(1) = 1.7534(15), Si(5)−N(1) = 1.7548(14); N(1)−Si(1)−C(1) = 111.06(7), N(1)−Si(1)−Si(2) = 114.16(5), N(1)−Si(1)−Si(3) = 115.22(5), Si(2)−Si(1)−Si(3) = 116.94(3), Si(1)−Si(2)−Si(3)#1 = 108.97(3), Si(2)#1−Si(3)−Si(1) = 110.85(3), Si(4)−N(1)−Si(5) = 119.77(8), Si(4)−N(1)−Si(1) = 118.98(8), Si(5)−N(1)−Si(1) = 120.98(8).

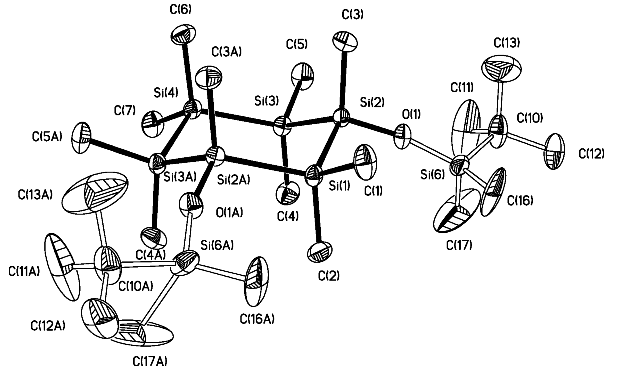

Figure 3. Molecular structure and numbering of **8**. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Si(6)−O(1) = 1.589(6), Si(5)−O(1) = 1.647(5), Si(1)−Si(2) = 2.3527(10), Si(2)−Si(3) = 2.3452(11), Si(3)−Si(4) = 2.3458(10); C(1)−Si(1)−Si(2) = 109.00(10), C(2)−Si(1)−Si(2)#1 = 109.10(9), C(1)−Si(1)−Si(2)#1 = 109.00(10), Si(2)−Si(1)−Si(2)#1 = 111.11(5), Si(3)−Si(2)−Si(1) = 112.00(4), Si(2)−Si(3)−Si(4) = 110.95(4), Si(3)−Si(4)−Si(3)#1 = 113.21(6), Si(6)−O(1)−Si(5) = 20.3(3).

spectra of **5**−**11**. Attachment of the −OR or $-NR_2$ groups to the cyclohexasilanyl ring causes a marked downfield shift of the α-Si resonances relative to Si_6Me_{12}[15] by about 26 ppm for **5** and **6** and at least 47 ppm for **7**−**11**. The additionally observed downfield shift of the *β*-Si resonance lines by approximately 5 ppm in the spectra of **5** and **6**, which is not observed for the −OR-substituted counterparts **7**−**11**, suggests significant electronic impact of the $-NR_2$ groups on the Si−Si skeleton.

The introduction of the bulky *t*-$BuMe_2SiO-$ substituent significantly facilitates crystallization and, hence, purification of the obtained crude reaction products. While in the Me_3SiO- series only compound **10** could be isolated in a pure state, the *t*-$BuMe_2SiO$-substituted derivatives **7**−**9** and **11** are easily obtained after repeated recrystallization. In case of the di- and trisubstituted compounds **6** and **8**−**11** one isomer crystallizes selectively from the originally obtained statistical mixture of cis and trans isomers. The stereochemistry of the obtained crystalline fractions of **6** and **8**−**10** was determined by X-ray crystallography. ORTEP views of the compounds are shown in Figures 2−5 together with a listing of selected bond lengths and angles. In the case of **11** suitable crystals for an X-ray structure analysis could not be obtained. Its molecular structure, however, was unequivocally assigned by ^{29}Si NMR spectroscopy. The experimental spectrum exhibits two resonance lines, what is only consistent with the cis,cis structure containing two nonequivalent silicons.

The cyclohexasilane rings of **6** and **8**−**10** adopt slightly distorted chair conformations. Both hetero substituents are attached to the Si_6 moiety either in axial or in equatorial positions, resulting in a cis conformation for **8** and in trans conformations for **6**, **9**, and **10**. The bulky $(Me_3Si)_2N-$ and *t*-$BuMe_2SiO-$ groups in **6** and **8**, respectively, occupy equatorial sites in order to minimize nonbonding interactions, while the smaller Me_3SiO- groups in **10** are arranged diaxially, in line with earlier studies of the solid-state structures of disubstituted cyclohexasilanes.[16] Small substituents usually prefer axial positions at the cyclohexasilane ring, while bulky side groups are preferably attached equatorially. An intermediate case is obviously found in the structure of **9** (compare Figure 4), where the a,a and the e,e forms of the trans isomer cocrystallize within one crystal lattice. The oxygen atom apparently acts as a spacer, pushing the bulky *t*-$BuMe_2Si-$ groups away from the Si_6 skeleton, thus diminishing their steric influence. **8**−**10** exhibit average Si−Si distances of 2.34 Å, close to those of elemental silicon (2.35 Å),[17] 1,4-Ph_2-Si_6Me_{10} (2.35 Å), and Si_6Me_{12} (2.338 Å).[18] These distances agree well with the Si−Si covalent bond length of 2.34 Å. The geometry around the endocyclic silicon atoms of **8**−**10** is approximately tetrahedral. The average Si−Si−Si bond angles are close to the respective angles found in other cyclohexasilane structures.[16−19] For **8**−**10** rather wide Si−O−Si bond angles (156.3° for **8**, 163.9° for **9**, and 151.8° for **10**) are observed, as is common for compounds containing the Si−O−Si moiety. Disiloxanes of the general formula $X_3SiOSiX_3$ (X = H, halogen, Me, Ph), for instance, exhibit Si−O−Si bond angles between 142.2 and 180°.[20] Unusual structural features are observed for compound **6**. The average Si−Si bond length (2.37 Å) is significantly increased, and the environment of the silicon atoms bearing the $-N(SiMe_3)_2$ groups is more trigonal pyramidal than tetrahedral ($\angle N_1{-}Si_1{-}Si_2 = 114.2°$; $\angle N_1{-}Si_1{-}Si_3 = 115.2°$; $\angle Si_2{-}Si_1{-}Si_3 = 116.9°$; $\angle C_1{-}Si_1{-}Si_2 = 97.8°$; $\angle C_1{-}Si_1{-}Si_3 = 98.7°$). This could at least to some extent be a consequence of an electronic N→Si−Si backbone interaction. The nitrogen atoms in the crystal structure

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[20] For an excellent discussion on that topic compare: Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; p 227.

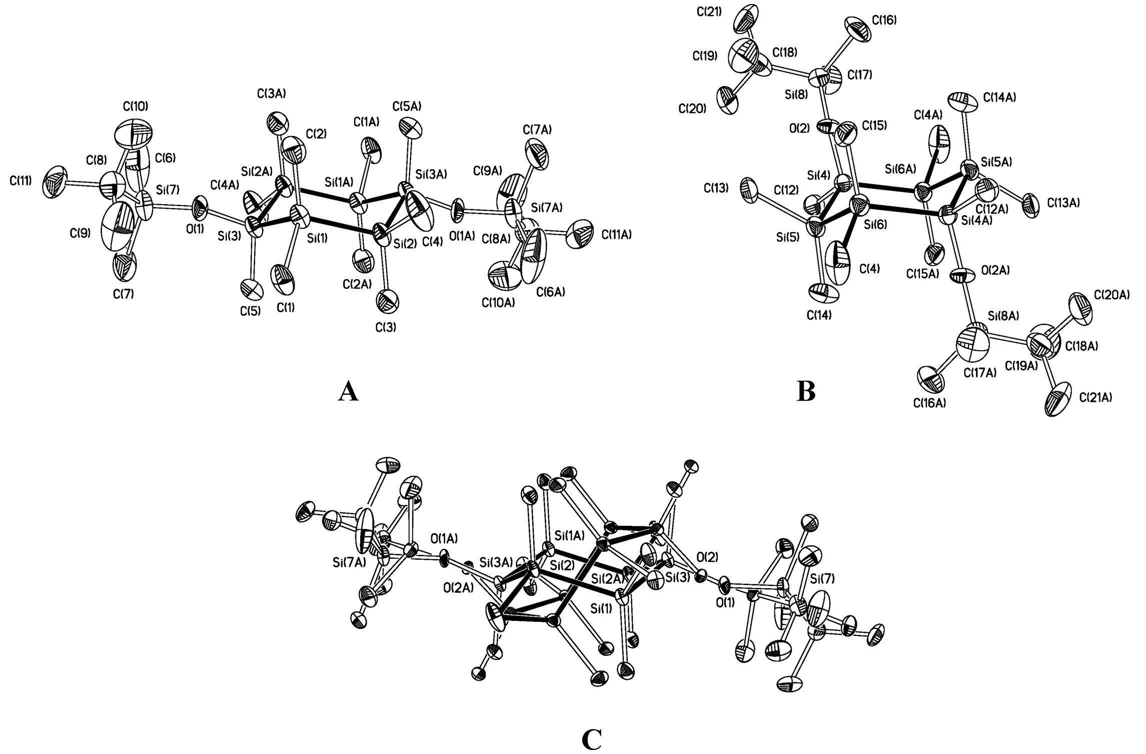

Figure 4. Molecular structure and numbering of **9**. The e,e (A) and aa forms (B) of *trans*-**9** cocrystallize to form mixed crystals (C) containing equal amounts of each conformer. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Si(1)−Si(2) = 2.3386(17), Si(1)−Si(3) = 2.3489(17), Si(2)−Si(3)#1 = 2.3440(17), Si(3)−O(1) = 1.637(5), Si(7)−O(1) = 1.613(4), Si(4)−O(2) = 1.676(6), Si(4)−Si(6)#1 = 2.352(2), Si(4)−Si(5) = 2.353(3), Si(5)−Si(6) = 2.342(2), Si(8)−O(2) = 1.606(7); Si(2)−Si(1)−Si(3) = 111.40(8), Si(1)−Si(2)−Si(3)#1 = 111.73(8), O(1)−Si(3)−Si(2)#1 = 109.1(2), O(1)−Si(3)−Si(1) = 107.4(2), Si(2)#1−Si(3)−Si(1) = 111.76(7), Si(7)−O(1)−Si(3) = 154.6(4), O(2)−Si(4)−Si(6)#1 = 111.5(3), O(2)−Si(4)−Si(5) = 107.6(3), Si(6)#1−Si(4)−Si(5) = 110.70(9), Si(6)−Si(5)−Si(4) = 111.20(9), Si(5)−Si(6)−Si(4)#1 = 111.51(10), Si(8)−O(2)−Si(4) = 147.4(4).

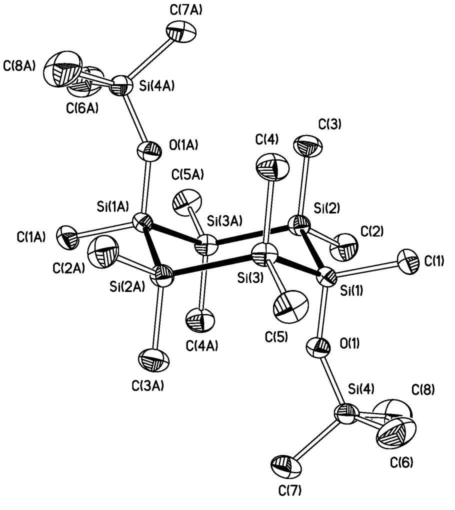

Figure 5. Molecular structure and numbering of **10**. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Si(1)−O(1) = 1.644(2), Si(1)−Si(2) = 2.3394(14), Si(1)−Si(3) = 2.3440(13), Si(2)−Si(3)#1 = 2.3366(13), Si(3)−Si(2)#1 = 2.3366(13), Si(4)−O(1) = 1.625(2); O(1)−Si(1)−Si(2) = 107.69(9), Si(2)−Si(1)−Si(3) = 112.72(5), Si(3)#1−Si(2)−Si(1) = 109.16(5), Si(2)#1−Si(3)−Si(1) = 109.61(5), Si(4)−O(1)−Si(1) = 148.41(14).

of **6** adopt a nearly perfectly planar configuration, which is in line with structural data for other trisilylamines.[21]

Table 1. Absorption and Emission Data (C_6H_{12} Solution)

compd	$\lambda_{\mathrm{max,abs}}$ (nm) (ϵ (L mol^{-1} cm^{-1}))[a]	$\lambda_{\mathrm{max,em}}$ (nm)[b]
5	264 (1900)	
6	266 (2300), 260 (2500)	
7	269 (870), 233 (5200)	353 sh, 342
cis-**8**	280 (700), 253 (2250), 236 (5940)	344, 332
trans-**9**	275 (890), 250 (2950), 228 sh (7800)	340
trans-**10**	275 (930), 252 (3000)	340
cis,cis-**11**	295 (390), 255 (2250), 234 (7900)	340 sh, 333

[a] Conditions: $c = 2 \times 10^{-4}$ mol/L. [b] Conditions: room temperature; $c = 5 \times 10^{-4}$ mol/L; $\lambda_{\mathrm{ex}} = 288$ nm.

UV/Vis Absorption and Photoluminescence Spectra. Room-temperature solution UV absorption and photoluminescence emission data of compounds **5**−**11** are listed in Table 1 together with the corresponding data for dodecamethylcyclohexasilane.

The UV absorption spectra of all compounds exhibit several overlapping bands at the low-energy side, which at least in part is attributable to the presence of conformational isomers, as demonstrated previously for open-chained permethyloligosilanes[8b,22] and by the results of DFT calculations showing contributions of different conformers to the UV absorption spectra of OR- or NR_2-substituted permethylcyclohexasilanes.[23]

Upon hetero substitution a significant shift to the red relative to Si_6Me_{12} is found for the first absorption maxima (compare Figure 6). Excitation energies ad-

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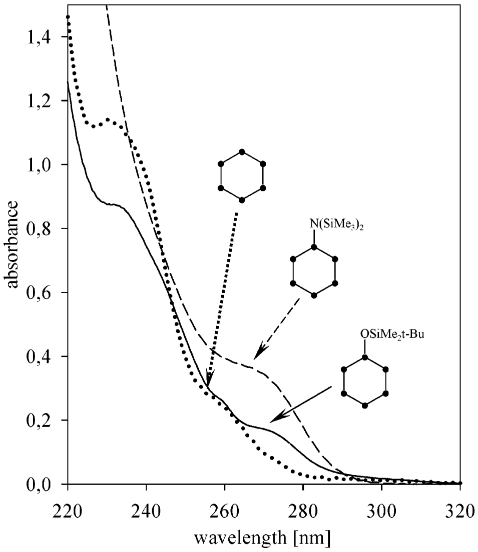

Figure 6. UV absorption spectra of Si_6Me_{12}, **5**, and **7** (C_6H_{12} solution, $c = 2 \times 10^{-4}$ mol/L). The first absorption maximum is shifted to lower energy upon hetero substitution.

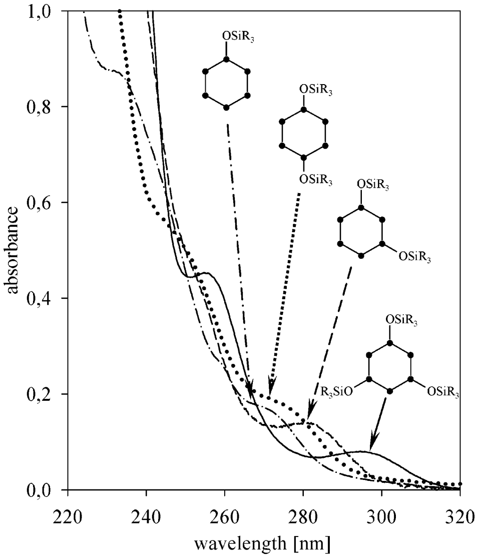

Figure 7. UV absorption spectra of **7**−**10** (C_6H_{12} solution, $c = 2 \times 10^{-4}$ mol/L). The first absorption maximum is shifted to lower energy with an increasing number of −OSiMe₂-*t*-Bu groups.

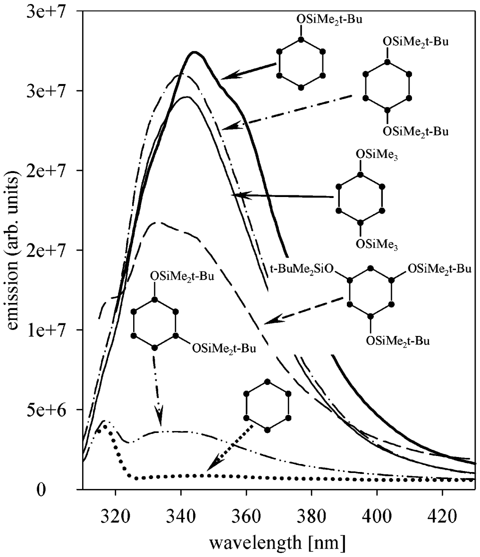

Figure 8. Photoemission spectra of Si_6Me_{12} and **7**−**11** (room temperature, C_6H_{12} solution, $c = 5 \times 10^{-4}$ mol/L, λ_{ex} = 288 nm). The emission intensity markedly increases in the presence of $-OSiR_3$ groups.

ditionally decrease with an increasing number of hetero substituents (compare Figure 7). Similar bathochromic shifts upon hetero substitution have been observed for permethoxycyclopolysilanes $[Si(OMe)_2]_n$[24] and 2-substituted derivatives of heptamethyltrisilane.[25] UV absorption maxima of alkoxy-substituted polysilane high polymers were also found to be red-shifted relative to their alkyl-substituted counterparts.[26] The low-energy absorption bands appearing in the UV spectra of permethylcyclopolysilanes $(SiMe_2)_n$ are generally assigned to $\sigma\sigma^*$-type excitations of highly delocalized Si−Si σ electrons within the Si−Si backbone.[27] Substituent effects as apparent in the absorption spectra of **5**−**11** are consistent with earlier interpretations in terms of σ−n interactions between the lone pair of electrons on the hetero substituent and the Si−Si backbone electronic structure, leading to a potential reduction of the HOMO−LUMO gap.[23,24,28]

The most striking property of the emission spectra is the occurrence of relatively strong emission bands in the spectra of the siloxy-substituted cyclohexasilanes **7**−**11**. Room-temperature hydrocarbon solutions of **7**−**11** exhibit fluorescence emission at around 340 nm (see Figure 8), giving a Stokes shift of about 60 nm, which is an intermediate value between the Stokes shifts observed for poly(dialkyl)silylenes[1a] and short-chain permethylated linear oligosilanes.[8b] The position of the fluorescence bands appearing in the spectra of **7**−**11** is only slightly influenced by the kind and number of the OR groups attached to the cyclohexasilane ring. Fluorescence intensity varies considerably with the number of hetero substituents and with the substitution pattern within the series **7**−**11**. Although fluorescence quantum yields have not been determined quantitatively, so far a marked increase of emission intensity upon oxygen substitution is apparent in all cases. Particularly strong fluorescence is observed for **7**, **9**, and **10**, while the parent Si_6Me_{12} and the amino derivatives **5** and **6**, just like the permethyloligosilanes Si_nMe_{2n+2},[8] are essentially nonluminescent at room temperature.

Conclusions

In summary, we have investigated the structures and the UV absorption/emission characteristics of a number of OR- and NR_2-substituted permethylcyclohexasilanes in order to explain the origin of the outstanding photoemission of siloxene, a two-dimensional solid-state silicon polymer. Our results clearly demonstrate that room-temperature photoluminescence is also an intrin-

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sic molecular property of siloxycyclohexasilanes. This is certainly an important finding, because photoluminescence can be traced down to the smallest subunit present in the structure of siloxene according to Kautsky: that is, the cyclohexasilane ring linked to other silyl groups by oxygen bridges (compare B in Figure 1). Detailed theoretical and experimental studies of the observed photoluminescence properties, including fluorescence quantum yields, are currently in progress.

Experimental Section

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried with sodium−potassium alloy and distilled under nitrogen prior to use. Commercially available $Me_3SiOSiMe_3$ and t-$BuMe_2SiOH$ were purified by distillation prior to use. $(Me_3Si)_2NLi$[29] and the cyclohexasilane derivatives Si_6Me_{12},[30] 1,3- and 1,4-$Cl_2Si_6Me_{10}$,[13a,31] 1,3,5-$Cl_3Si_6Me_9$,[13b] and $MeOSi_6Me_{11}$[32] were synthesized as previously reported. ^1H (300.13 MHz), ^{29}Si (59.62 MHz), and ^{13}C NMR spectra (75.4 MHz) were recorded on a Bruker 300-MSL spectrometer in C_6D_6 solution versus external TMS. Mass spectra were run either on a HP 5971/A/5890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm poly(dimethylsiloxane)) or on a Kratos Profile mass spectrometer equipped with a solids probe inlet. Infrared spectra were obtained in Nujol mulls on a Perkin-Elmer 883 spectrometer. UV/vis absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer. Photoluminescence spectra were obtained in solution on a JOBIN YVON SPEX Fluoromax 2 spectrometer. Melting points were determined using a Büchi apparatus according to the method of Dr. Tottoli and are uncorrected. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus.

Chloroundecamethylcyclohexasilane (1). A 12 mL portion (13.9 mmol) of triflic acid was added to a solution of 40.0 g (11.5 mmol) of dodecamethylcyclohexasilane in 250 mL of heptane at 0 °C over a period of 3 h, and the mixture was stirred at room temperature for 48 h. Subsequently a further 7 mL (8.1 mmol) of triflic acid was added and the mixture was continuously stirred until all of the Si_6Me_{12} had been consumed (monitoring performed by hydrogenation of small samples with $LiAlH_4$ followed by acid hydrolysis and GC/MS analysis of the resulting HSi_6Me_{11}). After removal of the solvent and excess triflic acid under vacuum, 200 mL of diethyl ether and 10.0 g (24.0 mmol) of anhydrous LiCl was added at 0 °C and the mixture was stirred for another 3 days at room temperature. Finally the solvent was replaced by 100 mL of petroleum ether and the lithium salts were filtered. Subsequent removal of the solvent, sublimation of the resulting oily residue under vacuum (90 °C/0.05 mbar), and crystallization of the crude product from 20 mL of heptane at −30 °C yielded 26 g (61%) of the white crystalline title compound. ^{29}Si NMR (heptane/D_2O, external TMS, ppm): −40.32; −41.34; −41.38; −41.77 (consistent with the literature[33]).

(Bis(trimethylsilyl)amino)undecamethylcyclohexasilane (5). A solution of 0.88 g (2.4 mmol) of **1** and 0.68 g (2.6 mmol) of $LiN(SiMe_3)_2{\cdot}Et_2O$ in 10 mL of THF was heated to 90 °C in a closed, thick-walled Schlenk tube until complete conversion was achieved (approximately 24 h, reaction monitored by GC/MS). After removal of the solvent under vacuum, the remaining yellow semisolid residue was extracted with 20 mL of pentane and filtered. Removal of pentane under vacuum and Kugelrohr distillation at 215 °C and 0.03 mbar gave 0.5 g (40%) of pure **5** as a white waxy solid. Bp: 215 °C (0.03 mbar). Anal. Found: C, 41.12; H, 10.35; N 2.72. Calcd for $C_{17}H_{51}NSi_8$: C, 41.31; H, 10.40; N, 2.83. IR (Nujol mull): ν_{as}(Si−N−Si) 909 cm^{-1} (vs). ^{29}Si NMR (C_6D_6, external TMS, ppm): 2.32 ($SiMe_3$); −15.73 ($Si_{Ring}MeNR_2$); −38.63, −42.02, −43.72 ($Si_{Ring}Me_2$). ^1H NMR (C_6D_6, external TMS, ppm, relative intensity): 0.27 (s, 18H, $Si(CH_3)_3$, 0.65 (s, 3H), 0.38 (s, 6H), 0.29 (s, 6H), 0.25 (s, 6H), 0.23 (s, 3H), 0.22 (s, 6H), 0.21 (s, 3H), ($Si_{Ring}CH_3$). ^{13}C NMR (C_6D_6, external TMS, ppm): 6.04, 5.29 ($NSi_{Ring}CH_3$, $NSi(CH_3)_3$); −2.07, −4.36, −5.04, −5.28, −5.41, −5.73 ($Si_{Ring}(CH_3)_2$). MS (m/e (relative intensity)): 493 (3%, M^+).

1,4-Bis(bis(trimethylsilyl)amino)decamethylcyclohexasilane (6). A solution of 2.66 g (6.8 mmol) of **3** and 2.3 g (13.6 mmol) of $LiN(SiMe_3)_2{\cdot}Et_2O$ in 30 mL of THF were heated to 90 °C in a closed, thick-walled Schlenk tube until complete conversion was achieved (approximately 72 h, reaction monitored by ^{29}Si NMR). After removal of the solvent under vacuum the remaining yellow semisolid residue was extracted with 30 mL of pentane and filtered. Removal of pentane under vacuum and Kugelrohr distillation at 180 °C and 0.03 mbar gave 1.4 g (32%) of white crystalline **6** (mixture of cis and trans isomers). The pure trans isomer was obtained by repeated crystallization from diethyl ether (−30 °C).

Data for the trans isomer are as follows. Mp: 242−243 °C. Anal. Found: C, 41.21; H, 10.21; N, 4.27. Calcd for $C_{22}H_{66}N_2Si_{10}$: C, 41.31; H, 10.40; N, 4.38. IR (Nujol mull): ν_{as}(Si−N−Si) 899 cm^{-1} (vs). ^{29}Si NMR (C_6D_6, external TMS, ppm): 2.37 ($SiMe_3$); −15.38 ($Si_{Ring}MeNR_2$); −37.05 ($Si_{Ring}Me_2$). ^1H NMR (C_6D_6, external TMS, ppm, relative intensity): 0.28 (s, 36H, $Si(CH_3)_3$, 0.70 (s, 6H), 0.40 (s, 12H), 0.33 (s, 12H) ($Si_{Ring}CH_3$). ^{13}C NMR (C_6D_6, external TMS, ppm): 6.12, 5.67 ($NSi_{Ring}CH_3$, $NSi(CH_3)_3$); −1.17, −4.06 ($Si_{Ring}(CH_3)_2$). MS (m/e (relative intensity)): 638 (36%, M^+).

Data for the cis isomer are as follows. ^{29}Si NMR (C_6D_6, external TMS, ppm): 2.29 ($SiMe_3$); −15.77 ($Si_{Ring}MeNR_2$); −36.30 ($Si_{Ring}Me_2$).

***(tert*-Butyldimethylsiloxy)undecamethylcyclohexasilane (7).** A 4.05 mL portion (8.1 mmol) of a 2 M solution of butyllithium in pentane was added within 1 h to a stirred solution of 1.1 g (8.24 mmol) of t-$BuMe_2SiOH$ in 10 mL of THF at −80 °C. The resulting yellow solution of t-$BuMe_2SiOLi$ was warmed to room temperature, diluted to 40 mL with THF, and added to a refluxing solution of 2.8 g (7.6 mmol) of **1** in 100 mL of THF over a period of 5 h. The resulting mixture was refluxed until complete conversion had been achieved (approximately 18 h, reaction monitored by GC/MS). After aqueous workup with 1 M H_2SO_4 and extraction with petroleum ether the combined organic layers were dried over Na_2SO_4. Removal of the solvent and excess $BuMe_2SiOH{\cdot}0.5H_2O$ under vacuum gave 2.7 g (77%) of crude **7** as a slightly yellow oil. Chromatography of 0.5 g of the crude product on an RP-18 column (50 cm length, 2.5 cm diameter) developed by a mixture of methanol and 2-propanol (4:1) afforded 0.4 g (60% based on $Si_6Me_{11}Cl$) of pure, oily, and colorless **7**. Anal. Found: C, 43.77; H, 10.30. Calcd for $C_{17}H_{48}OSi_7$: C, 43.83; H, 10.40. IR (neat): ν_{as}(Si−O−Si) 1033 cm^{-1} (vs, b). ^{29}Si NMR (C_6D_6, external TMS, ppm): 11.32 ($SiMe_2$-t-Bu); 6.06 ($Si_{Ring}MeOR$); −41.93, −42.19, −43.11 ($Si_{Ring}Me_2$). ^1H NMR ($CDCl_3$, external TMS, ppm, relative intensity): 0.86 (s, 9H, $C(CH_3)_3$); 0.38, 0.20, 0.15, 0.14, 0.13, 0.12, 0.09, 0.01 (s, 39H, $Si(CH_3)$). ^{13}C NMR ($CDCl_3$, external TMS, ppm): 25.96 ($C(CH_3)_3$); 18.44 ($C(CH_3)_3$); 1.68 ($OSi_{Ring}CH_3$); −2.37 ($OSi(CH_3)_2$); −5.48; −5.69; −6.49 ($Si_{Ring}(CH_3)_2$). MS (m/e (relative intensity)): 464 (44%, M^+).

1,3-Bis(*tert*-butyldimethylsiloxy)decamethylcyclohexasilane (8). The procedure followed was that used for **7** with 5.8 g (43.8 mmol) of t-$BuMe_2SiOH$, 21.5 mL of 2 M butyllithium in pentane, and 8.0 g (20.5 mmol) of **2** (reaction time under reflux to complete conversion approximately 48 h). Yield: 9.1 g (76%) of a colorless oil (isomeric mixture of *cis*-

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Table 2. Crystallographic Data for Compounds 6 and 8−10

	6	**8**	**9**	**10**
empirical formula	$C_{22}H_{66}N_2Si_{10}$	$C_{22}H_{60}O_2Si_8$	$C_{22}H_{60}O_2Si_8$	$C_{16}H_{48}O_2Si_8$
fw	639.67	581.42	581.42	497.26
T (K)	100(2)	213(2)	200(2)	200(2)
size (mm)	0.48 × 0.36 × 0.28	0.44 × 0.28 × 0.22	0.44 × 0.34 × 0.24	0.38 × 0.30 × 0.18
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	*Pnma*	$P2_1/c$	$P2_1/n$
a (Å)	12.356(3)	14.398(3)	12.628(3)	10.014(2)
b (Å)	8.4870(17))	25.476(5)	10.543(2)	10.973(2)
c (Å)	18.520(4)	10.577(2)	14.917(3)	14.842(3)
α (deg)	90	90	90	90
β (deg)	91.90(3)	90	106.36(3)	97.02(3)
γ (deg)	90	90	90	90
V (Å ^{3})	1940.9(7)	3879.5(13)	1905.5(7)	1618.6(6)
Z	2	4	2	2
ρ_{calcd} (g cm^{-3})	1.095	0.995	1.013	1.020
μ (mm^{-1})	0.354	0.292	0.298	0.341
F(000)	704	1280	640	544
θ range (deg)	$1.65 < \theta < 26.37$	$1.60 < \theta < 26.43$	$1.68 < \theta < 26.37$	$2.31 < \theta < 26.35$
no. of collected/unique rflns	14 908/3971	29 332/4057	14 886/3905	12 560/3290
completeness to θ (%)	99.6	99.3	99.9	99.6
no. of data/restraints/params	3971/0/165	4057/18/191	3905/204/299	3290/0/126
GOF on F^2	1.06	1.02	1.035	0.961
R indices ($I > 2\sigma(I)$)	R1 = 0.039, wR2 = 0.106	R1 = 0.066, wR2 = 0.187	R1 = 0.062, wR2 = 0.16	R1 = 0.056, wR2 = 0.123
R indices (all data)	R1 = 0.042, wR2 = 0.107	R1 = 0.092, wR2 = 0.204	R1 = 0.10, wR2 = 0.18	R1 = 0.099, wR2 = 0.1338
largest diff peak/hole (e/Å^3)	0.84/−0.31	0.77/−0.21	0.44/−0.37	0.33/−0.23

and *trans*-**8**). After repeated crystallization from acetone (−80 °C), diethyl ether (−30 °C), and finally pentane (−30 °C), 5.1 g (46%) of pure white crystalline *cis*-**8** was obtained. The trans isomer can be enriched in the filtrate by removing the less soluble cis isomer by repeated crystallization and is obtained as a colorless oil, which could not be crystallized or purified.

Data for the cis isomer are as follows. Mp: 129−130 °C. Anal. Found: C, 45.46; H, 10.39. Calcd for $C_{22}H_{60}O_2Si_8$: C, 45.45; H, 10.40. IR (Nujol mull): ν_{as}(Si−O−Si) 1044 cm^{-1} (vs, b). ^{29}Si NMR (C_6D_6, external TMS, ppm): 11.35 (*Si*Me$_2$-*t*-Bu); 6.32 (*Si*$_{Ring}$MeOR); −42.58, −42.82, −48.40 (*Si*$_{Ring}$Me$_2$). ^{1}H NMR (CDCl$_3$, external TMS, ppm, relative intensity): 0.86 (s, 18H, C(C*H*$_3$)$_3$); 0.34, 0.30, 0.23, 0.22, 0.17, 0.14, 0.03, 0.02 (s, 42H, Si(C*H*$_3$)). ^{13}C NMR (CDCl$_3$, external TMS, ppm): 25.85 (C(*C*H$_3$)$_3$); 18.35 (*C*(CH$_3$)$_3$); 2.00 (OSi$_{Ring}$*C*H$_3$); −2.51 (OSi(*C*H$_3$)$_2$); −5.21, −5.66, −7.21, −7.91 (Si$_{Ring}$(*C*H$_3$)$_2$). MS (*m*/*e* (relative intensity)): 580 (5%, M$^+$).

Data for the trans isomer are as follows. ^{29}Si NMR (C_6D_6, external TMS, ppm): 10.98 (*Si*Me$_2$-*t*-Bu); 5.91 (*Si*$_{Ring}$MeOR); −43.49, −44.91, −48.64 (*Si*$_{Ring}$Me$_2$).

1,4-Bis(*tert*-butyldimethylsiloxy)decamethylcyclohexasilane (9). The procedure followed was that used for **7**, with 3.5 g (26.3 mmol) of *t*-BuMe$_2$SiOH, 13 mL of 2 M butyllithium in pentane, and 5.0 g (12.8 mmol) of **3** (reaction time under reflux to complete conversion approximately 60 h). Yield: 7.2 g (96%) of a colorless oil (isomeric mixture of *cis*- and *trans*-**9** + byproducts). Repeated crystallization from acetone (−30 °C) and pentane (−30 °C) afforded 2.2 g (31%) of pure white crystalline *trans*-**9**. The cis isomer could be enriched in the filtrate by removing the less soluble trans isomer by repeated crystallization and was obtained as a colorless oil, which could not be crystallized or purified.

Data for the trans isomer are as follows. Mp: 191−193 °C. Anal. Found: C, 45.54; H, 10.28. Calcd for $C_{22}H_{60}O_2Si_8$: C, 45.45; H, 10.40. IR (Nujol mull): ν_{as}(Si−O−Si) 1034 cm^{-1} (vs, b). ^{29}Si NMR (C_6D_6, external TMS, ppm): 11.59 (*Si*Me$_2$-*t*-Bu); 6.56 (*Si*$_{Ring}$MeOR); −44.44 (*Si*$_{Ring}$Me$_2$). ^{1}H NMR (CDCl$_3$, external TMS, ppm, relative intensity): 0.86 (s, 18H, C(C*H*$_3$)$_3$); 0.41, 0.18, 0.17, 0.01 (s, 42H, Si(C*H*$_3$)). ^{13}C NMR (CDCl$_3$, external TMS, ppm): 25.83 (C(*C*H$_3$)$_3$); 18.29 (*C*(CH$_3$)$_3$); 1.86 (OSi$_{Ring}$*C*H$_3$); −2.51 (OSi(*C*H$_3$)$_2$); −5.63, −7.07 (Si$_{Ring}$(*C*H$_3$)$_2$). MS (*m*/*e* (relative intensity)): 580 (12%, M$^+$).

Data for the cis isomer are as follows. ^{29}Si NMR (C_6D_6, external TMS, ppm): 11.39 (*Si*Me$_2$-*t*-Bu); 6.13 (*Si*$_{Ring}$MeOR); −44.04 (*Si*$_{Ring}$Me$_2$).

1,4-Bis(trimethylsiloxy)decamethylcyclohexasilane (10). A 20 mL portion (32.0 mmol) of a 1.6 M solution of methyllithium in diethyl ether was slowly added to a stirred solution of 5.5 g (33.9 mmol) of Me$_3$SiOSiMe$_3$ in 80 mL of THF at room temperature, and the resulting solution was refluxed for 2 h. After diethyl ether and Me$_4$Si were removed by distillation, the mixture was refluxed for another 12 h, subsequently diluted to 100 mL with THF, and added dropwise to a refluxing solution of 5.8 g (15.0 mmol) of **3** in 50 mL of THF over a period of 3 h. The resulting mixture was refluxed until complete conversion has been achieved (approximately 12 h, reaction monitored by GC/MS). After aqueous workup with 1 M H_2SO_4 and extraction with petroleum ether, the combined organic layers were dried over Na_2SO_4. Removal of the solvent under vacuum gave 3.5 g (90%) of crude **10** as a colorless oil (isomeric mixture of *cis*- and *trans*-**10** + byproducts), from which 1.3 g (37%) of pure white crystalline *trans*-**10** can be isolated by repeated crystallization from 2-propanol (−20 °C), acetone (−30 °C), and pentane (−30 °C). The cis isomer could be enriched in the filtrate by removing the less soluble trans isomer by repeated crystallization and was obtained as a colorless oil, which could not be crystallized or purified.

Data for the trans isomer are as follows. Mp: 109−111 °C. Anal. Found: C, 38.83; H, 9.72. Calcd for $C_{16}H_{48}O_2Si_8$: C, 38.65; H, 9.73. IR (Nujol mull): ν_{as}(Si−O−Si) 1032 cm^{-1} (vs, b). ^{29}Si NMR (C_6D_6, external TMS, ppm): 8.56 (*Si*Me$_3$); 6.45 (*Si*$_{Ring}$MeOR); −44.88 (*Si*$_{Ring}$Me$_2$). ^{1}H NMR (CDCl$_3$, external TMS, ppm, relative intensity): 0.40 (s, 6H, Si$_{Ring}$C*H*$_3$O), 0.21 (s, 12H, Si$_{Ring}$(C*H*$_3$)$_2$), 0.13 (s, 12H, Si$_{Ring}$(C*H*$_3$)$_2$), 0.04 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, external TMS, ppm): 2.27, 0.63 (OSi$_{Ring}$*C*H$_3$, OSi(CH$_3$)$_3$); −6.51, −6.62 (Si$_{Ring}$(*C*H$_3$)$_2$). MS (*m*/*e* (relative intensity)): 496 (8%, M$^+$).

Data for the cis isomer are as follows. ^{29}Si NMR (C_6D_6, external TMS, ppm): 8.51 (*Si*Me$_3$); 6.28 (*Si*$_{Ring}$MeOR); −44.13 (*Si*$_{Ring}$Me$_2$).

1,3,5-Tris(*tert*-butyldimethylsiloxy)decamethylcyclohexasilane (11). The procedure followed was that used for **7**, with 5.6 g (42.3 mmol) of *t*-BuMe$_2$SiOH, 20 mL of 2 M butyllithium in pentane, and 5.2 g (12.7 mmol) of **4** (reaction time under reflux to complete conversion approximately 160 h). Yield: 8.0 g (90%) of an orange oil (isomeric mixture of crude *cis,cis*- and *cis,trans*-**11** + byproducts). Separation of the isomers was performed by chromatography of 0.5 g of the crude product on an RP-18 column (50 cm length, 2.5 cm diameter) developed by a mixture of methanol and 2-propanol (5:1) (fraction 1 contains the crude cis,trans isomer and fraction 2 the cis,cis isomer). A 0.14 g portion (28%) of pure white crystalline *cis,cis*-**11** could be recovered from fraction 2 after removal of the solvents and crystallization from acetone/methanol (3:1). Crystallization and purification of *cis,trans*-**11** could not be achieved.

Data for the cis,cis isomer are as follows. Mp: 154−156 °C. Anal. Found: C, 46.25; H, 10.40. Calcd for $C_{27}H_{72}O_3Si_9$: C, 46.48; H, 10.40. IR (Nujol mull): ν_{as}(Si−O−Si) 1031 cm^{-1} (vs, b). ^{29}Si NMR (C_6D_6, external TMS, ppm): 11.68 (*Si*Me$_2$-*t*-Bu); 4.94 (Si_{Ring}MeOR); −44.27 ($Si_{Ring}Me_2$). ^1H NMR ($CDCl_3$, external TMS, ppm, relative intensity): 0.88 (s, 27H, C(CH_3)$_3$); 0.36, 0.35, 0.23, 0.03 (s, 45H, Si(CH_3)). ^{13}C NMR ($CDCl_3$, external TMS, ppm): 25.96 (C(CH$_3$)$_3$); 18.47 (**C**(CH$_3$)$_3$); 2.01 (OSi$_{Ring}$$CH_3$); −2.38 (OSi($CH_3$)$_2$); −5.12, −7.29 (Si$_{Ring}$($CH_3$)$_2$). MS (*m/e* (relative intensity)): 596 (32%, M^+).

X-ray Crystallography. Suitable crystals of **6** and **8**−**10** were grown by cooling pentane solutions slowly at −80 °C. For X-ray structure analysis 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 (0.710 73 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[34] and SADABS[35] (except **3**), respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).[36] 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. Unfortunately the obtained crystal quality of some substances was poor, a fact which is reflected in quite high *R* values and low θ values. Crystals measured at temperatures higher than 100 K undergo a phase transition at lower temperature, which destroyed the crystal.

Crystallographic data for compounds **6** and **8**−**10** are given in Table 2.

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Supporting Information Available: CIF files for the structures of compounds **6** and **8**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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