Adamantanes, Nortricyclenes, and Dendrimers with Extended Silicon Backbones

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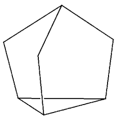
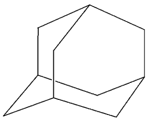
Abstract: By reaction of the hexabromoheptasilane $MeSi(SiMe_2SiMeBr_2)_3$ (**1a**) with H_2O, H_2S, NH_3, and H_2NMe the heptasilaadamantanes $MeSi(SiMe_2SiMeO)_3$ (**4**), $MeSi(SiMe_2SiMeS)_3$ (**5**), $MeSi(SiMe_2SiMeNH)_3$ (**6a**), and $MeSi(SiMe_2SiMeNMe)_3$ (**6b**), respectively, were prepared in good to moderate yields. Molecular structures of **4**, **5**, **6a**, and **6b** were determined by X-ray crystallography. The symmetry of the cages is approximately C_{3v}, and the geometry around the nitrogen atoms is essentially planar. Ab initio SCF/HF calculations with the 6-31G* basis set confirm these results. Reduction of $MeSi(SiMe_2SitBuBr_2)_3$ (**1b**) with lithium naphthalenide afforded the heptasilanortricyclene $MeSi(SiMe_2SitBu)_3$ (**7**). The ^{29}Si NMR spectrum of **7** consists of three signals with chemical shifts that agree closely with values predicted by ab initio calculations. ^{29}Si INADEQUATE spectra also strongly support the nortricyclene structure. Ab initio SCF/HF calculations were performed for the parent molecule Si_7H_{10}, and the ring strain of the cage was estimated as 168.8 $kJ\,mol^{-1}$ by using the homodesmic reaction $Si_7H_{10} + 3\,Si_2H_6 \rightarrow Si_{13}H_{28}$. Compound **1a** also served as the starting material for the preparation of first-generation dendrimer **2a** by reaction with six equivalents of $Ph_2MeSiLi$. Subsequent protodearylation with HBr and reaction with $(Me_2PhSi)_2SiMeK$ afforded second-generation dendrimer **3**. All dendrimers were characterized by multinuclear NMR spectroscopy.

Keywords: dendrimers • heptasilaadamantanes • heptasilanortricyclenes • polycycles • silanes

Introduction

In organic chemistry, the cage-shaped tricyclo[2.2.1.0^{2,6}]heptanes (nortricyclenes) and tricyclo[3.3.1.1^{3,7}]decanes (adamantanes) have long been known.[1] Many derivatives with various substitution patterns, including the parent hydrocarbons C_7H_{10} and $C_{10}H_{16}$ and compounds with backbones composed of carbon and first-row heteroatoms such as oxygen or nitrogen, have been described in the literature.[2]


Nortricyclene


Adamantane

Adamantanes and nortricyclenes are also common ring systems in the inorganic and organometallic chemistry of the heavier elements of Groups 15 and 16, such as phosphorus, arsenic, sulfur and selenium. Enumeration of a few examples of nortricyclenes such as P_7R_3,[3] As_7R_3,[4] P_4S_3,[5] P_4Se_3,[6] As_4S_3[7] and As_4Se_3[8] and of adamantanes such as P_4O_6 and P_4O_{10} may suffice here to demonstrate their widespread occurrence.

Due to its position in the Periodic Table, silicon is often compared with carbon. The importance of this “organic chemist’s” point of view for the development of organosilicon chemistry cannot be overemphasized and has led to many exciting discoveries. Indeed a close structural analogy between molecules with a carbon backbone C_n and a silicon backbone Si_n exists as long as only single bonds are present, and the similarity is even more striking when the substituents on the silicon atoms are organic groups such as methyl or phenyl. For instance, cyclohexane prefers the chair conformation, as do cyclohexasilane and dodecamethylcyclohexasilane.[9] One therefore would expect a highly stable molecule such as adamantane to have a counterpart in silicon chemistry. Impure $Si_{10}Me_{16}$ was in fact obtained from

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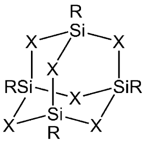
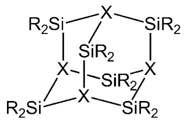
the reaction of a mixture of $MeSiCl_3$ and Me_2SiCl_2 with potassium in very low yield and was identified by its ^1H NMR spectrum.[10] Neither $Si_{10}H_{16}$ nor nortricyclenes Si_7R_{10} have been described so far. It is even more striking that adamantanes and nortricyclenes containing at least one silicon–silicon bond (except $Si_{10}Me_{16}$) are also unknown.

All known adamantanes with backbones partially composed of silicon atoms are characterized by alternating arrangements of Si and X atoms[11] and have the composition $(SiR)_4X_6$ (**A**: X=O, S, Se, NH, PPh) or $X_4(SiR_2)_6$ (**B**: X=P or As). The preparation of a number of fused adamantanes with an alternating arrangement of Si and C atoms by pyrolysis of, for instance, tetramethylsilane proves the exceptional stability of these carbosilane cages.[12]

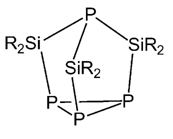


A

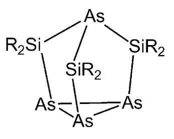


B

So far, only two nortricyclenes containing silicon atoms, namely, $P_4(SiMe_2)_3$ (**C**)[13] and $As_4(SiMe_2)_3$ (**D**),[14] have been synthesized and characterized by X-ray diffraction. These molecules contain three-membered P_3 or As_3 rings but no silicon–silicon bond.



C



D

Considering all these facts one could ask whether the nonexistence of adamantanes and nortricyclenes with silicon–silicon bonds reflects some inherent instability of these compounds or simply the difficulty of preparation due to the lack of suitable functional oligosilane starting materials. With these questions in mind we have set out to explore some synthetic pathways which eventually led us to the desired products.

The situation concerning dendrimers containing silicon–silicon bonds[15,16] is similar to that for the above-mentioned nortricyclanes and adamantanes. Dendrimers containing isolated silicon atoms in the backbone are quite well known, but again very few studies deal with compounds containing silicon–silicon bonds.[17] Nevertheless, the few publications on dendrimers with all-silicon scaffolds showed them to be potentially useful materials.[18] The spherical shape and high structural redundancy render them more robust compared to open-chain polysilanes. On searching for synthetic pathways towards oligosilane dendrimers it becomes clear that starting materials which are required for the construction of cage molecules can also be employed for the generation of dendrimeric structures.

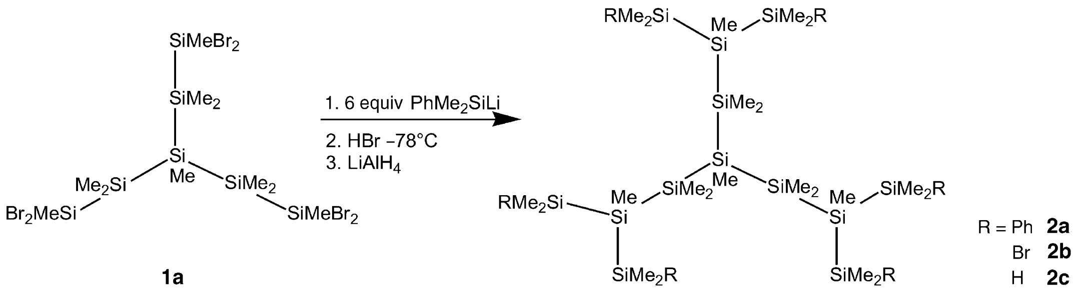
Results and Discussion

Syntheses

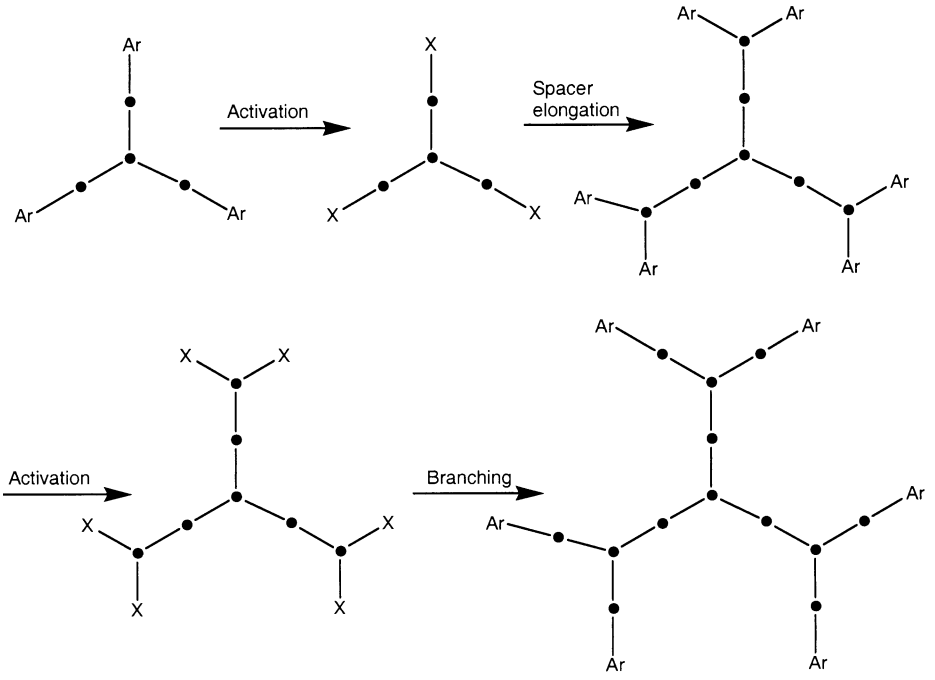
Dendrimers: Strategies for the synthesis of oligosilane dendrimers require similar intermediates to those for cage molecules with silicon–silicon bonds. In our case the common intermediate is hexabromoheptasilane **1a**. Its reaction with six equivalents of dimethylphenylsilyllithium generates the first-generation Si_{13} dendrimer **2a** (Scheme 1). The phenyl groups of **2a** can serve as masked functionalities and can easily be replaced by bromo groups to give **2b** by mild protodearylation with neat hydrogen bromide at −78°C. No $AlBr_3$ is required. The resulting hexafunctional dendrimer can then be converted to the corresponding hexahydrosilane **2c** by reaction with lithium aluminum hydride. Dendrimers with H-terminated branches may be useful for derivatization by hydrosilylation.

Compound **1a** was obtained from tris(dimethylphenylsilyl)methylsilane by protodearyation with hydrogen bromide, treatment with three equivalents of methyldiphenylsilyllithium[19] and another protodearylation step with hydrogen bromide. The synthetic strategy to construct dendrimers in one-atom steps (i.e., the branches grow by monosilyl units) therefore consists of repeated elongation and activation steps. It offers maximum flexibility with respect to substitution patterns and number of spacer atoms between branching points. However, it requires four reaction steps to grow the dendrimer one generation further (Scheme 2).

The number of steps between generations can be reduced to two if trisilanyl units are used instead of monosilyl groups. Such an approach can be realized by using isotetrasilane $(Me_2PhSi)_3SiMe$,[17b,20] which can provide the nucleus of the dendrimer by conversion to the corresponding tribromide.[21] In addition it also serves as a valuable source for



Scheme 1.



Scheme 2.

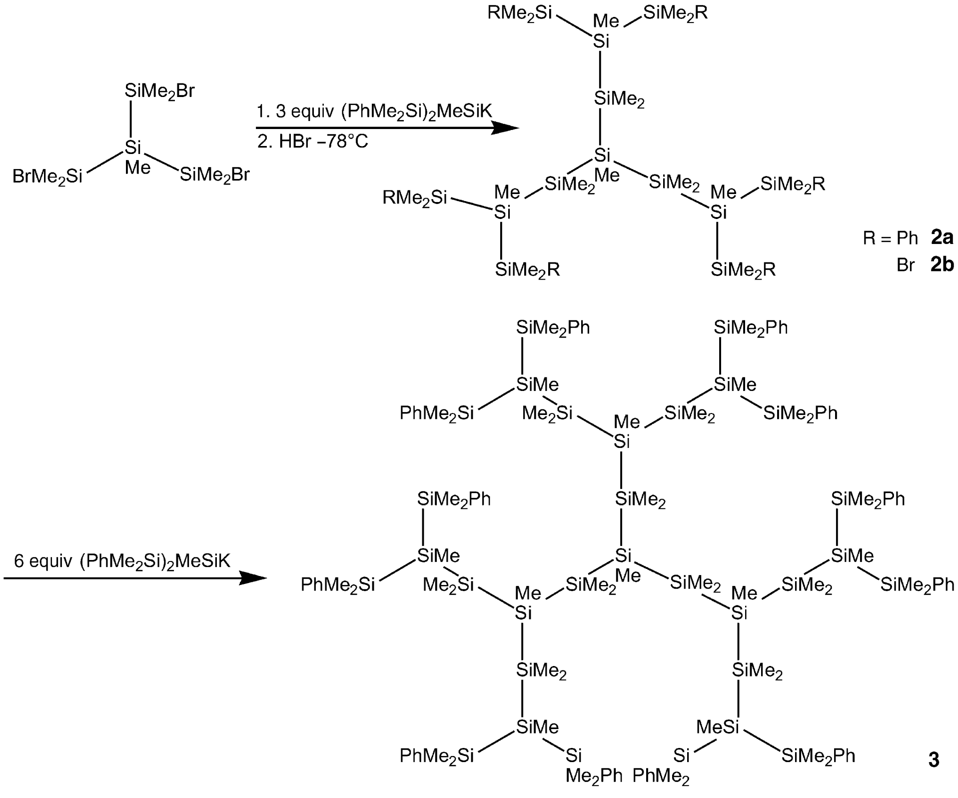
the generation of bis(dimethylphenylsilyl)methylsilylpotassium.[22] This compound can be prepared by simple treatment of tris(dimethylphenylsilyl)methylsilane with potassium *tert*-butoxide in THF.[23]

Reaction of three equivalents of the silyl potassium compound with tris(bromodimethylsilyl)methylsilane then gives the first-generation dendrimer **2a** in a single step (Scheme 3). As outlined above **2a** can be converted to the hexabromide **2b**, which reacts with six equivalents of the silyl potassium compound to give the second-generation Si_{31} dendrimer **3**.

Figure 1 shows the ^{29}Si NMR spectrum of **3**, which exhibits three groups of signals for atoms attached to three ($\delta = -60$ to -80 ppm), two ($\delta = -25$ to -30 ppm), or one ($\delta = -15$ ppm) silicon atom. The chemical shifts are in good agreement with the values observed for the permethylated compound.[16b]

Our synthetic approach resembles that of Sekiguchi et al.,[17b,d] which utilizes the reaction of triflates with 2-lithiotrisilanes. However, for a number of reasons the reaction scheme described here represents a substantial improvement. The use of bromides instead of triflates avoids the frequently encountered side reactions of strong nucleophiles with triflates.[24] The main advantage, however, is the use of silylpotassium compounds.[25] The reaction of suitable precursors with potassium alkoxides provides access to silyl anions in almost quantitative yield.[23] In addition, the potassium compounds are also more reactive than the lithium compounds. While this is not a major issue for normal types of reactions, it is of importance in dendrimer synthesis, where completeness of reaction makes the difference between a perfect dendrimer and by-products that are so similar to the product that they can hardly be removed. It is this final argument that we think makes our approach very attractive.

Adamantanes and nortricyclenes: Adamantanes are closely related to nortricyclenes, since the (formal) insertion of three atoms into the three-membered ring transforms the latter into the former. We therefore chose hexafunctional heptasilanes of the type $MeSi(SiMe_2SiRBr_2)_3$ (**1a**: R = Me; **1b**: R = *t*Bu) as suitable precursors which could furnish nor-



Scheme 3.

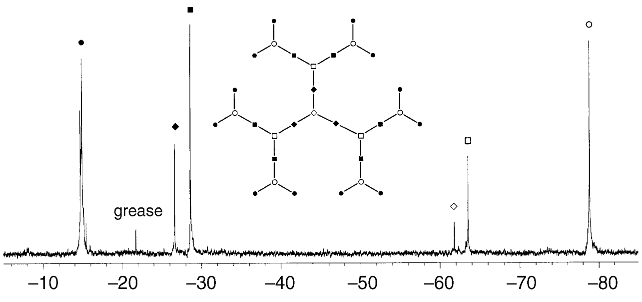
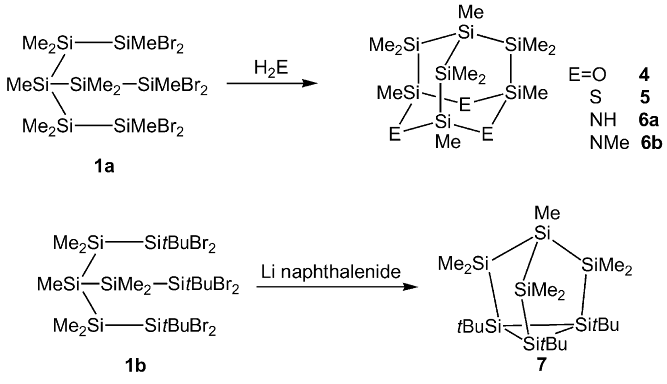


Figure 1. ^{29}Si NMR spectrum of **3**.

tricyclenes on reduction with alkali metals or related reducing agents, or adamantanes Si_7X_3 on reaction with hydrides of oxygen, sulfur, nitrogen, and phosphorus. To stabilize the three-membered ring of the nortricyclenes, the bulky *tert*-butyl group was introduced as substituent R, whereas methyl groups were chosen for preparation of the adamantanes (Scheme 4).



Scheme 4.

The reaction of **1a** with three equivalents of H_2O and triethylamine as trapping agent for hydrogen bromide does not result in formation of the trioxaadamantane $MeSi(SiMe_2SiMeO)_3$ (**4**). Instead extensive silicon–silicon cleavage gives a plethora of products. With six equivalents of H_2O and imidazole instead of triethylamine the reaction proceeds smoothly with yields near 80%. Compound **4** can be crystallized from *n*-pentane or diethyl ether.

The reaction of **1b** with water did not result in the formation of a trioxaadamantane. The ^{29}Si NMR spectrum of the reaction mixture displayed a considerable number of signals, which could not be assigned.

With H_2S and in the presence of imidazole, **1a** reacts smoothly to give trithiaheptasilaadamantane **5**, which can be purified by crystallization from *n*-pentane.

When **1a** is treated with an ample excess of NH_3, **6a** is formed in quantitative yield without any detectable by-products. Here, ammonia also serves as a base to remove hydrogen bromide as ammonium bromide.

With an excess of $MeNH_2$ the reaction does not proceed as smoothly as with NH_3. Still, **6b** can be obtained in moderate yield by crystallization from *n*-pentane. The ^{29}Si NMR spectrum of the residue consists of a fairly large number of lines indicative of intermolecular SiNSi bond formation. No attempts were made to identify or separate these products from the reaction mixture.

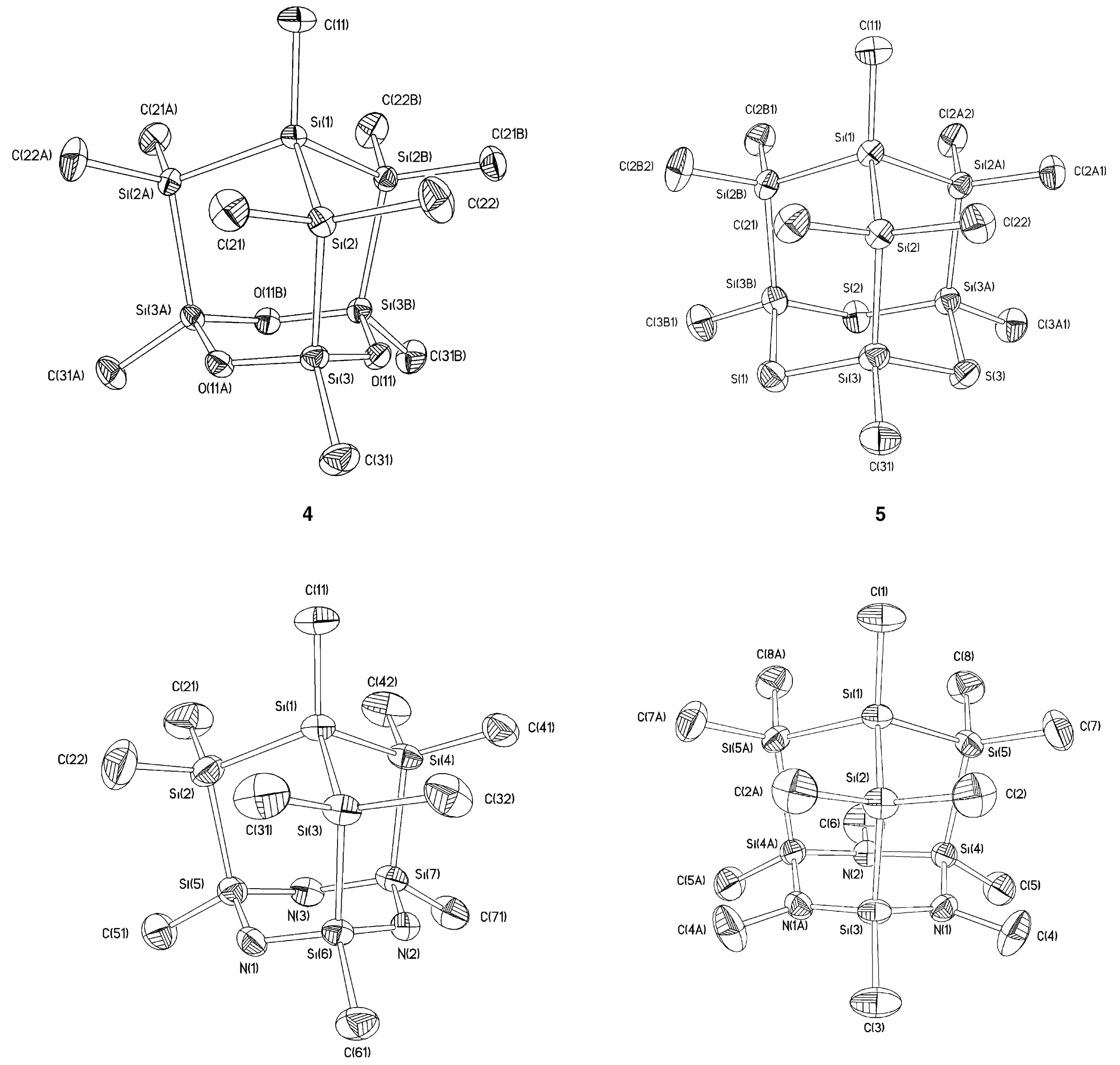
Both hexa-*tert*-butylcyclotrisilane[26] and hexakis(trimethylsilyl)cyclotrisilane[27] are stable compounds, and hence provide support for the expectation that cyclotrisilanes bearing *tert*-butyl or trimethylsilyl groups will also be stable. We therefore expected that the three-membered ring in heptasilanortricyclene would be stabilized by introduction of *tert*-butyl groups. It is also known from the work of Weidenbruch et al.[28] that the reduction of di-*tert*-butyldichlorosilane does not result in the formation of a cyclotrisilane. However, reduction of di-*tert*-butyldibromosilane gives the cyclotrisilane in good yield, possibly due to the lower Si–Br bond energy. We therefore chose tri-*tert*-butylheptamethylhexabromoheptasilane **1b** as a promising starting material which could afford a heptasilanortricyclene on reduction.

Reducing agents such as C_8K and sodium/potassium alloy led to the formation of polymers. The reaction with lithium naphthalenide proceeded differently and gave the desired nortricyclene **7** as the only detectable product. Compound **7** was identified by its ^{29}Si NMR spectrum, which consists of three lines with chemical shifts that agree excellently with those obtained from ab initio calculations (see "NMR spectroscopy" below). It was not possible to grow crystals of the compound because of naphthalene present in the reaction mixture. Attempts to remove the naphthalene by sublimation resulted in decomposition, probably due to the formation of silylenes from the cyclotrisilane, a process which can occur at temperatures as low as 40°C, depending on the type of substituents.[29]

X-ray crystallography: The molecular structures of **4**, **5**, **6a** and **6b** were determined by single-crystal X-ray diffraction (Figure 2). SCF/HF ab initio calculations at the 6-31G* level predict C_{3v} symmetry for **4**, **5**, **6a** and **6b**. Due to packing effects the molecular symmetry of the cages is lowered in the crystal, although the deviations from C_{3v} are fairly small. Average bond lengths, bond angles, and torsion angles are therefore listed in Table 1.

For instance, the C1-Si1-Si2-Si3, C1-Si1-Si2A-Si3A, and C1-Si1-Si2B-Si3B dihedral angles, which can be used to assess deviations of the Si_7X_3 core from C_{3v} symmetry, do not differ from 180° by more than ±2.8°. Deviations from C_{3v} symmetry can also be quantified by comparing the C21-Si2-Si1 and C22-Si2-Si1 angles of the $SiMe_2$ groups. The differences of less than 2° indicate just a slight twisting of the $SiMe_2$ groups. Moreover, equivalent bond lengths generally are identical within fractions of a picometer. The different molecular symmetries observed in the crystals—**4** belongs to point group C_3, **5** and **6a** to C_1 and **6b** to C_s—reflect subtle differences in the packing forces.

Table 1 reveals some interesting differences between the geometries of the cages with X = O, N and X = S. The comparatively short Si–O and Si–N bonds result in a small $(SiN/O)_3$ six-membered ring in which the Si1-Si2-Si3 bond angles are as small as 102–104°. This is accompanied by flattening of the $(SiN/O)_3$ ring, as indicated by dihedral angles of around ±40° (Table 1), which distributes the resulting strain over a larger number of bond angles. With X = S, the



4 **5**

6a **6b**

Figure 2. Molecular structures of **4**, **5**, **6a**, and **6b** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

strain is considerably reduced due to the longer Si–S bond. Consequently, the Si1-Si2-Si3 bond angle (108.1°) is close to the tetrahedral angle of 109.5°. Notably, the geometry around the nitrogen atoms in **6b** is nearly planar. The sum of the relevant bond angles is 354.9° (av).

NMR spectroscopy: Table 2 summarizes the ^{29}Si, ^{13}C, and ^{1}H chemical shifts of the adamantanes **4**, **5**, **6a**, and **6b.** The numbering of atoms is given in Figure 2. Shift values for Si1 (which is surrounded by three silicon atoms) are fairly constant throughout the series, ranging from $\delta = -80.0$ to -86.9 ppm. The corresponding value for $MeSi(SiMe_3)_3$ is $\delta = -87.9$ ppm.[30] The data clearly indicate that the Si-Si1-Si angles do not differ dramatically within the series, which is confirmed by the results of the X-ray investigations. The range of shifts for Si2 is larger ($\delta = -31.6$ to -44.4 ppm), which is partly due to the differing electronegativities of O, S, and N, which are just two bonds away from Si2, and also by variations in the Si1-Si2-Si3 bond angles. For instance, the values for **6a** and **6b** are 103.5° and 101.7°, respectively, and that for **5** is 108.1°. It is also not surprising that the largest variations are observed for Si3, which shows resonances over a range of nearly 30 ppm.

Table 2 also includes the observed ^{29}Si shifts for the nortricyclene **7** (Figure 3), which consists of three lines, as expected for a nortricyclene structure. The observed shifts of $\delta = -80.6$ (Si3) and $\delta = -87.4$ ppm (Si1) clearly rule out a chain-like structure. The proposed assignment is based solely on the results of the ab initio calculations (next below). Attempts to record proton-coupled spectra, which would provide an unambiguous assignment, were not successful due to the low concentration of **7** in the reaction mixture. The proton-decoupled INEPT–INADEQUATE spectrum, part of which is shown in Figure 4, also confirms the Si_7 cage structure. The following Si–Si coupling constants were obtained (the numbering of the atoms is given in Figure 6):

$^{1}J_{Si(1),Si(2)} = 52.7$, $^{1}J_{Si(2),Si(3)} = 48.4$, $^{2}J_{Si(1),Si(3)} = 9.6$, $^{2}J_{Si(3),Si(2')} = 8.6$ Hz.

To obtain further evidence for the nortricyclene-structure of **7**, ab initio calculations of ^{29}Si chemical shifts were performed for **4**, **5**, **6a** and **7** by the GIAO-SCF method (see below). Figure 5 shows the correlation between the calculated absolute shifts and the experimental shifts relative to TMS. The important result is that the shift for Si3 of **7** lies exactly on the least-squares fit, leaving little doubt that Si3 is indeed part of a three-membered ring. From the least-squares fit, an absolute shift value for TMS of 441.5 ppm was obtained, which compares well with the value of 461.1 ppm given in the literature.[31]

Table 1. Selected average bond lengths [pm], angles [°] and torsion angles [°] for **4**, **5**, **6a**, and **6b**. The labelling of structure **4** is also valid for **5**, **6a**, and **6b**.

	4	**5**	**6a**	**6b**
		Bond lengths		
Si1–Si2	235.40(2)	233.53(19)	234.29(10)	235.42(10)
Si2–Si3	234.36(5)	233.92(20)	234.67(10)	235.95((10)
Si–X	165.47(19)	215.08(20)	172.80(10)	172.48(16)
		Angles		
Si2-Si1-Si2A	105.183(16)	106.15(7)	105.43(4)	106.85(4)
Si1-Si2-Si3	102.130(19)	108.10(7)	103.53(3)	101.70(3)
Si2-Si3-X1	106.09(4)	112.67(8)	107.15(7)	107.07(6)
Si2-Si3-X3	109.28(4)	111.92(8)	108.93(7)	107.98(6)
X-Si3-X	106.61(7)	112.20(9)	107.04(9)	107.01(10)
Si3-X-Si3A	125.60(6)	105.07(8)	123.47(11)	124.97(12)
C1-Si2-Si3	113.479(14)	112.62(20)	113.26(9)	111.98(11)
C21-Si2-Si1	111.69(6)	112.45(20)	111.37(12)	110.83(10)
C22-Si2-Si1	113.91(6)	112.88(20)	112.66(12)	110.83(10)
C21-Si2-Si3	109.62(5)	106.65(20)	112.43(13)	113.57(10)
C22-Si2-Si3	111.90(7)	107.75(20)	110.17(12)	113.79(10)
C3-Si3-Si2	116.87(6)	110.77(20)	113.82(10)	114.76(10)
		Torsion angles		
C1-Si1-Si2-C21	64.47(6)	62.20(30)	57.80(17)	60.42(15)
C1-Si1-Si2-C22	−57.63(7)	−61.01(30)	−62.79(17)	−58.66(15)
Si3-X1-Si3B-X2	38.72(11)	63.13(10)	44.21(15)	41.60(16)
X1-Si3B-X2-Si3A	−38.72(11)	−62.14(11)	−43.17(15)	−39.90(14)
Si3B-X2-Si3A-X3	38.72(11)	61.57(11)	41.13(14)	38.25(17)
X2-Si3A-X3-Si3	−38.72(11)	−61.01(10)	−40.25(14)	−38.25((17)
Si3A-X3-Si3-X1	38.72(11)	61.56(10)	41.64(13)	39.90(14)
X3-Si3-X1-Si3B	−38.72(11)	−62.75(10)	−43.52(14)	−41.60(16)

Table 2. Experimental δ(^{29}Si), δ(^{13}C) and δ(^{1}H) values [ppm versus TMS] for the heptasilaadamantanes **4**, **5**, **6a** **6b** and for the heptasilanortricyclene **7**. The numbering of the atoms is $MeSi(1)[Si(2)Me_2Si(3)MeX]_3$ for the heptasilaadamantanes and $MeSi(1)[Si(2)Me_2Si(3)tBu]_3$ for the heptasilanortricyclene.

	Si(1)			Si(2)			Si(3)		
	δ(^{29}Si)	δ(^{13}C)	δ(^{1}H)	δ(^{29}Si)	δ(^{13}C)	δ(^{1}H)	δ(^{29}Si)	δ(^{13}C)	δ(^{1}H)
4	−80.1	−13.9	0.26	−40.3	−4.3	0.33	1.0	2.6	0.42
5	−78.4	−12.7	0.16	−31.6	−3.7	0.31	13.4	4.7	0.70
6a[a]	−80.0	−13.1	0.34	−38.9	−3.6	0.32	−0.7	2.1	0.11/(0.44)
6b[b]	−86.9	−13.5	0.34	−44.4	−2.7	0.40	−5.2	−1.7/(30.9)	0.35/(2.45)
7	−87.4			−14.6			−80.6		

[a] Value in parentheses is for the hydrogen atoms on nitrogen. [b] Values in parentheses are for the methyl groups on nitrogen

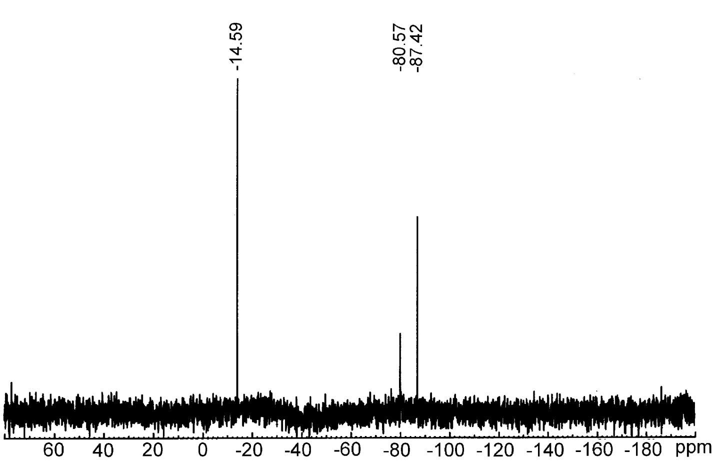


Figure 3. ^{29}Si{^{1}H} NMR spectrum of **7** recorded with the INEPT pulse sequence.

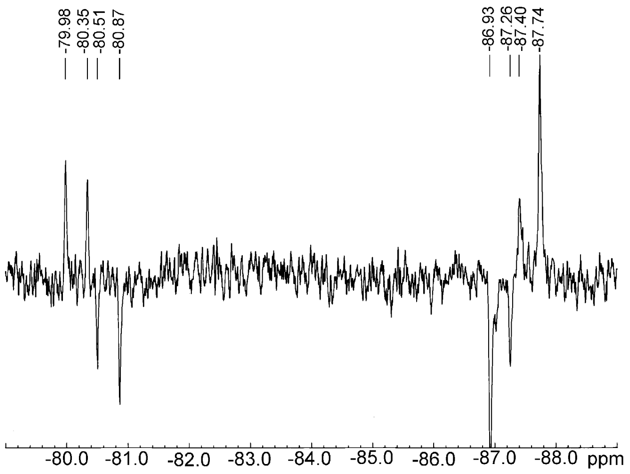


Figure 4. Part of the INADEQUATE spectrum of **7** in the range between $\delta = -80$ and -90 ppm.

Ab initio calculations

Adamantanes: Ab initio geometry optimizations predict C_{3v} symmetry for **4**, **5**, **6a** and **6b**. The calculated equilibrium bond lengths, bond angles and dihedral angles closely match the experimental values given in Table 1, and thus also confirm the approximate planar geometry of the nitrogen atoms in **6a** and **6b**. Moreover, predicted bond lengths and

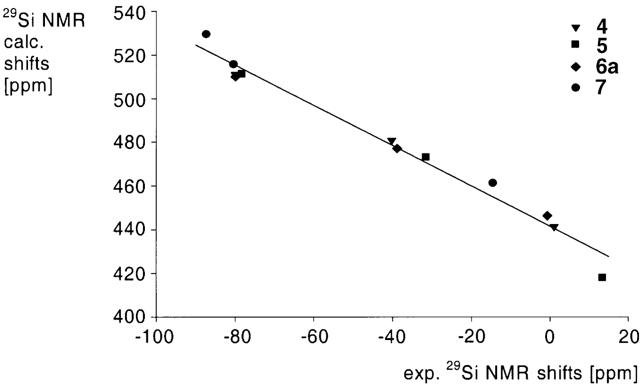


Figure 5. Correlation between observed and calculated ^{29}Si chemical shifts for **4**, **5**, **6a**, and **7**.

angles for $Si_7O_3H_{10}$ and for the partially methylated species $Si_7O_3H_6Me_4$ and $Si_7O_3H_4Me_6$ do not differ significantly from those calculated for $Si_7O_3Me_{10}$ itself. Detailed results of the calculations can be obtained from the authors on request.

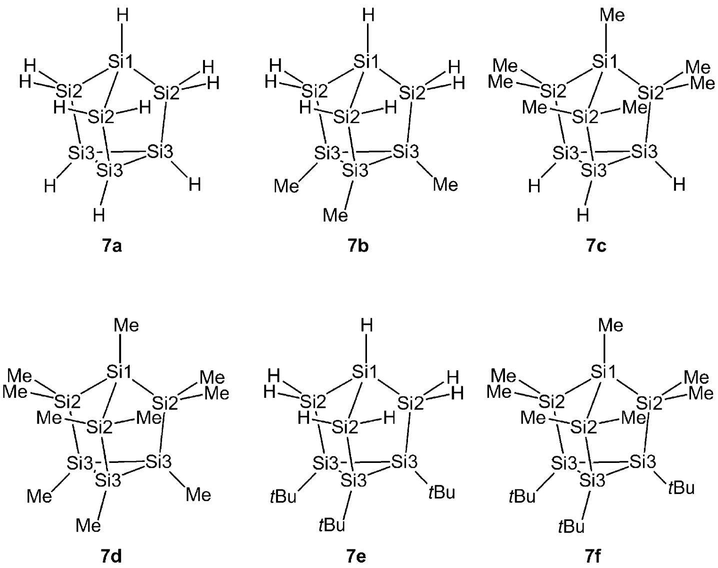


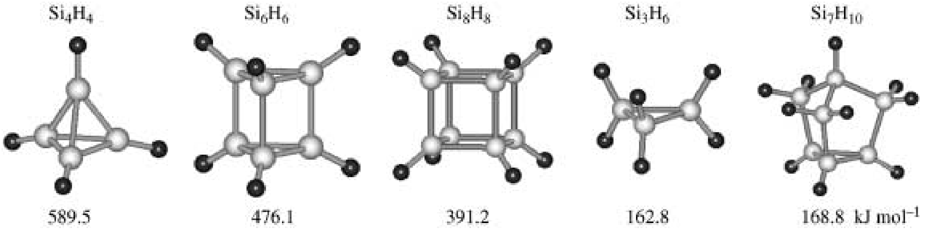
Figure 6. Heptasilanortricyclanes for which geometry optimizations were performed.

Table 3. Selected average bond lengths [pm], angles [°] and torsion angles [°] for the heptasilanortricyclenes **7**–**7e**, as predicted by ab initio calculations

	7a C_{3v}	**7b** C_{3v}	**7c** C_{3v}	**7d** C_{3v}	**7e** C_3	**7** C_3
Si1–Si2	237.3	237.1	239.4	239.2	236.1	237.8
Si2–Si3	235.1	235.3	235.8	235.9	236.5	237.7
Si3–Si3	235.1	236.0	235.5	236.3	238.1	238.9
Si3–X	147.3	190.3	147.7	190.8	194.0	194.7
Si3-Si3′-Si3″	60	60	60	60	60	60
Si1-Si2-Si3	96.6	97.1	95.5	96.0	98.8	97.4
Si2-Si1-Si2′	102.4	102.1	102.9	102.7	101.2	102.3
Si2-Si3-Si3′	106.6	106.4	107.1	106.9	105.8/105.3	106.3/105.8
X-Si1-Si2	115.9	116.1	115.4	115.6	116.8	116.0
X-Si2-X	108.5	107.8	106.1	105.6	107.4	105.4
Si2-Si3-X	123.1	121.7	124.1	122.7	115.1	116.2
X-Si3-Si2-Si1	180.0	180.0	180.0	180.0	179.9	–178.6

Nortricyclenes: Geometry optimizations were performed for a series of heptasilanortricyclenes Si_7H_{10} (**7a**), $Si_7Me_3H_7$ (**7b**), $Si_7Me_7H_3$ (**7c**), Si_7Me_{10} (**7d**), $Si_7tBu_3H_7$ (**7e**) and $Si_7tBu_3Me_7$ (**7**), as shown in Figure 6, to arrive at some understanding of the geometrical changes taking place on stepwise replacement of hydrogen atoms by larger groups such as methyl and *tert*-butyl.

As long as the substituents are hydrogen or methyl, all nortricyclenes are predicted to possess C_{3v} symmetry, which is broken to C_3 with the introduction of bulky *tert*-butyl groups. Table 3 summarizes the most important equilibrium bond lengths and angles for **7**–**7e**. In Si_7H_{10} the predicted Si–Si distance in the three-membered ring (Si3–Si3′) is smaller by 2–4 pm than the bonds which involve the equatorial silicon atoms (Si1–Si2, Si2–Si3). In nortricyclane itself, the C–C bonds in the cyclopropane ring are longer than the equatorial bonds by about 4 pm.[32] The same pattern is also observed for $P_7(SiMe_3)_3$.[33] It is only with the introduction of the *tert*-butyl substituents that a lengthening of the Si–Si bond of the three-membered ring occurs due to the mutual repulsion of the substituents. Calculations of Si–Si valence force constants, which were obtained by transforming the Hessian matrices defined in Cartesian coordinates into valence force fields by use of symmetry coordinates, predict a decrease in *f*(SiSi) upon replacing H or Me substituents with *t*Bu groups. It is also noteworthy that the Si–Si force constants of the apical bonds of **7a** and **7b** are considerably larger (by about 0.5 N cm^{-1}, unscaled) than those in the Si_3 ring, despite the longer bond (Table 3).



Si_7H_{10} is a strained system due to the three-membered ring. To estimate the total strain energy, the homodesmic reaction $Si_7H_{10} + 3\,Si_2H_6 \rightarrow Si_{13}H_{28}$ was used. The energies of the starting material and products were calculated at the SCF level with the 6-31G* basis set and corrected for the zero-point energy. The result can be compared with energies for other strained silicon hydrides such as Si_4H_4, Si_6H_6, Si_8H_8 and Si_3H_6, which were calculated by Nagase et al.[34] at the same level of theory, also with the 6-31G* basis set. The difference of just 6 kJ mol^{-1} between Si_3H_6 and Si_7H_{10} indicates that the predominant part of the strain energy comes from the three-membered ring.

The introduction of *tert*-butyl groups increases the strain energy due to their mutual repulsion and thus lengthen the Si–Si bonds and decreases the Si2-Si3-X bond angle by roughly 8° (Table 3).

Experimental Section

Ab initio calculations: All calculations were performed with Gaussian 94[35]at the HF/SCF level of theory with the 6-31G* basis set. Geometry optimizations were followed by calculations of second derivatives of the electronic energies as a check for true local minima. The Hessian matrices describing the harmonic force constants in terms of Cartesian coordinates were then transformed into symmetry force constants defined by symmetry coordinates, and normal-coordinate analyses were finally performed. For these steps, the program ASYM40[36] was used. The calculations of NMR chemical shifts were performed by employing the GIAO-SCF method as implemented in Gaussian 94.

Spectroscopy: NMR spectra were recorded with a Bruker MSL 300 or a Varian Unity Inova 300 spectrometer. The ^{29}Si spectra were measured in in THF or toluene in 10 mm tubes with capillaries containing D_2O as external lock. The ^{1}H and ^{13}C spectra were recorded in C_6D_6.

IR spectra were recorded with a Perkin Elmer model 883 grating spectrometer in the range 4000–250 cm^{-1}. The spectra were recorded as films between CsBr plates for liquid compounds and as Nujol mulls for solid substances. Nujol was distilled under vacuum from sodium/potassium alloy prior to use.

GC-MS spectra were recorded with a Hewlett Packard HP5890-II, coupled with a mass-selective detector HP 5971. A fused-silica column (DB 14T) with a length of 25 m (diameter 0.251 mm) was used.

X-ray structure analysis: Crystals were mounted onto the tip of a glass fiber, and data were collected with a Bruker-AXS SMART APEX CCD diffractometer. Graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm) was used for the measurements. The data were reduced to F_o^2 and corrected for absorption effects with SAINT[37] and SADABS,[38] respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).[39] 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. Crystallographic data are listed in Table 4.

General synthetic methods: All syntheses and manipulations were carried out under an inert atmosphere of N_2 or Ar by standard Schlenk techniques. Solvents were distilled from sodium, potassium, sodium/potassium alloy or $LiAlH_4$ prior to use. Amines such as NEt_3 were dried over molecular sieves. Elemental analyses were performed with a Heraeus Vario Elementar. Due to facile formation of silicon carbide during the combustion process the carbon values of the polysilane dendrimers tend to be too low.[17e]

The preparation of the heptasilanes $MeSi(SiMe_2SiMeBr_2)_3$ (**1a**) and $MeSi(SiMe_2Si\mathit{t}BuBr_2)_3$ (**1b**) and their precursors will be described in a forthcoming paper[40] and are not reported here again. $(PhMe_2Si)_2SiMeK$ was prepared as described previously.[22]

4-(2-Dimethylphenylsilyl-3-phenylpentamethyltrisilanyl)-2,6-bis(dimethylphenylsilyl)-1,7-diphenylundecamethylheptasilane (2a): A solution of phenyldimethylsilylchloride (4.00 g, 23.6 mmol) in THF (50 mL) with added lithium powder (0.40 g, 57.6 mmol) was stirred for 16 h and then filtered over glass wool. The solvent was removed in vacuum and the residue dissolved in toluene (50 mL). This solution was added dropwise to a solution of **1a** (3.00 g, 3.58 mmol) in toluene (50 mL) at −30 °C. After complete addition the completeness of conversion was checked by ^{29}Si NMR spectroscopy of an aliquot. The solution was poured onto ice/2 N HCl, and the aqueous layer, after being saturated with sodium chloride, was extracted with diethyl ether (2 × 50 mL). After drying over sodium sulfate the solvent was removed, and the residual brown oil was subjected to chromatography on silica gel (toluene/heptane 1/20) to give pure

Table 4. Crystallographic data for the heptasilaadamantanes **4**, **5**, **6a**, and **6b**.

	4	**5**	**6a**	**6b**
empirical formula	$C_{10}H_{30}O_3Si_7$	$C_{10}H_{30}S_3Si_7$	$C_{10}H_{33}N_3Si_7$	$C_{13}H_{36}N_3Si_7$
M_r	394.95	443.15	392.02	434.08
T [K]	293(2)	233(2)	296(2)	296(2)
crystal size [mm]	0.55 × 0.20 × 0.16	0.41 × 0.37 × 0.16	0.66 × 0.21 × 0.18	0.75 × 0.32 × 0.10
crystal system	cubic	monoclinic	monoclinic	monoclinic
space group	$I\bar{4}3d$	*Cc* (no. 9)	*P*2(1)/*n*	*C*2/*m*
a [Å]	20.8722(5)	17.136(3)	10.6367(13)	15.8806(8)
b [Å]	20.8722(5)	9.6333(19)	14.2734(17)	16.3684(8)
c [Å]	20.8722(5)	15.982(3)	15.6011(19)	10.1566(5)
α [°]	90	90	90	90
β [°]	90	111.23(3)	93.687(2)	95.6980(10)
γ [°]	90	90	90	90
V [Å^3]	9092.9(4)	2459.4(8)	2363.7(5)	2627.1(2)
Z	12	4	4	6
ρ_{calcd} [g cm^{-3}]	1.154	1.197	1.102	1.098
absorption coefficient [mm^{-1}]	0.423	0.634	0.400	0.366
F(000)	3392	944	848	944
θ range	$2.39 \leq \theta \leq 28.31$	$2.47 \leq \theta \leq 29.31$	$1.94 \leq \theta \leq 28.35$	$1.79 \leq \theta \leq 28.27$
h, k, l indices range	$-27 < h < 27$, $-12 < k < 27$, $-27 < l < 27$,	$-18 < h < 12$, $-10 < k < 10$, $-16 < l < 17$,	$-14 < h < 14$ $-13 < k < 19$, $-20 < l < 20$,	$-21 < h < 21$, $-0 < k < 21$, $0 < l < 13$,
reflections collected/unique	30 500/1901	5236/2435	16 435/5887	3331/3331
completeness to $\theta = 28.35°$ [%]	99.8	98.9	99.7	98.9
data/restraints/parameters	1901/0/62	2435/2/192	5887/0/182	3331/0/124
GOF on F^2	1.088	1.053	1.016	1.056
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0203$ $wR2 = 0.0505$	$R1 = 0.0345$ $wR2 = 0.0899$	$R1 = 0.0410$ $wR2 = 0.1036$	$R1 = 0.0396$ $wR2 = 0.1116$
R indices (all data)	$R1 = 0.0233$ $wR2 = 0.0527$	$RI = 0.0356$ $wR2 = 0.0896$	R1 = 0.0750 $wR2 = 0.1181$	$R1 = 0.0506$ $wR2 = 0.1220$
extinction coefficient	0.00031(5)	0.0000(2)	0.0006(5)	0.0011(4)
largest diff. peak/hole [e Å^{-3}]	0.204/−0.204	0.251/−0.186	0.320/−0.311	0.341/−0.319

2a as a colorless oil (1.80 g, 1.55 mmol, 43 %). ^{1}H and ^{13}C NMR spectra were in full accordance with literature data.[16b] ^{29}Si NMR (C_6D_6): $\delta = -14.5, -28.5, -63.9, -78.3$ ppm.

4-(2-Bromodimethylsilyl-3-bromopentamethyltrisilanyl)-2,6-bis(bromodimethylsilyl)-1,7-dibromoundecamethylheptasilane (2b): Compound **2a** (0.52 g, 0.45 mmol) was placed in 25 mL flask and approx. 10 mL of neat dry hydrogen bromide was condensed onto the compound by using a reflux condenser cooled to −78 °C and a cooling bath with methanol/liquid nitrogen. After complete condensation the bath was removed and the reaction mixture was refluxed for two hours. The excess hydrogen bromide was transferred in vacuum to a nitrogen-cooled trap, and the residue dissolved in pentane. After cooling to −35 °C the product was obtained as white crystals (0.44 g, 0.37 mmol, 83 %). ^{1}H NMR (C_6D_6): $\delta = 0.70$ (s, 36 H), 0.60 (s, 18 H), 0.51 (s, 9 H), 0.44 ppm (s, 3 H); ^{13}C NMR (C_6D_6): $\delta = 5.9, 2.0, -0.1, -8.2$ ppm; ^{29}Si NMR (toluene): $\delta = 21.8, -29.7, -64.4, -71.6$ ppm; elemental analysis (%) calcd for $C_{22}H_{66}Br_6Si_{13}$ (1167.73): C 22.03, H 5.61; found: C 22.48, H 5.66.

4-(2-Dimethylsilyl-1,1,2,3,3-pentamethyltrisilanyl)-2,6-bis(dimethylsilyl)-1,1,2,3,3,4,5,5,6,7,7-undecamethylheptasilane (2c): Compound **2b** (446 mg, 0.38 mmol) in diethyl ether (10 ml) was cooled in an ice bath, and $LiAlH_4$ in diethyl ether (0.76 mL, 1.5 M, 1.14 mmol) was added dropwise over 60 min. After allowing the reaction mixture to warm to RT the mixture was poured onto ice/10 % H_2SO_4. The aqueous layer wa extracted twice with diethyl ether and the combined ethereal extracts were dried over sodium sulfate. After removal of the solvent in vacuum a colorless oil was obtained (220 mg, 0.31 mmol, 83 %). ^{1}H NMR (C_6D_6): $\delta = 4.31$ (m, 6 H), 0.62 (s, 3 H), 0.56 (s, 18 H), 0.34 (s, 9 H), 0.31 ppm (s, 36 H); ^{13}C NMR: (C_6D_6) $\delta = 1.0, -3.4$ and -3.7 (diastereotopic carbon atoms), $-6.2, -9.7$ ppm; ^{29}Si NMR: (C_6D_6) $\delta = -30.9, -33.3$ (d, $J = 178$ Hz), $-65.3, -81.5$ ppm; elemental analysis (%) calcd for $C_{22}H_{72}Si_{13}$ (701.92): C 36.91; H 10.41; found: C 37.64, H 10.34. Alternatively, **2b** can be prepared from $(PhMe_2Si)_2MeSiK$ and $(BrMe_2Si)_3SiMe$, analogous to **3**, in 74 % yield.

Second-generation dendrimer 3: Compound **2b** (0.30 g, 0.67 mmol) in pentane (15 mL) was cooled to −70 °C, and a solution of bis(phenyldimethylsilyl)methylsilylpotassium (generated from $(PhMe_2Si)_3SiMe$ (1.21 g, 2.70 mmol) and KO*t*Bu[22] (303 mg, 2.70 mmol)) in THF (10 mL) was added dropwise. The degree of conversion of the reaction was monitored by ^{29}Si NMR spectroscopy on aliquots of the reaction solution. After complete conversion was observed the solution was poured onto ice/10 % H_2SO_4. The organic layer was dried over sodium sulfate. After removal of solvent in vacuum the residue was subjected to Kugelrohr distillation to remove phenyldimethylsilyl *tert*-butyl ether. The remaining oil was subjected to chromatography on silica gel (toluene/heptane 1/3) to give **3** (710 mg, 0.28 mmol, 41 %) as a colourless oil (pure according to ^{1}H and ^{29}Si NMR spectroscopy). ^{1}H NMR (C_6D_6): $\delta = 7.40$ (m, 24 H), 7.32 (m, 36 H), 0.41 (s, 3 H), 0.37 (s, 36 H), 0.36 (s, 36 H), 0.35 (s, 9 H), 0.33 (s, 18 H), 0.32 (s, 18 H), 0.25 (s, 18 H), 0.22 ppm (s, 18 H); ^{29}Si NMR (toluene): $\delta = -14.7$ and -14.9 (diastereotopic silicon atoms), $-26.2, -28.4, -61.6, -63.4, -78.5$ ppm; elemental analysis (%) found/calcd for $C_{124}H_{216}Si_{31}$: C 56.81, H 8.57; found: C 57.78, H 8.45.

Permethyl-4,6,10-trioxa-1,2,3,5,7,8,9-heptasilatricyclo[3.3.1.1^{3,7}]decane (4): Compound **1a** (2.50 g, 3.03 mmol) was dissolved in *n*-heptane (120 mL) and the solution was cooled to 0 °C. Then a solution of H_2O (18.20 mmol, 0.33 g) and imidazole (1.35 g, 19.83 mmol) in THF (40 mL) was added dropwise over 2 h. A voluminous precipitate of imidazole hydrobromide formed after some time. After completion, the reaction mixture was allowed to warm to room temperature, and Na_2SO_4 (20 g) was added to remove any excess of water by stirring for about 12 h. The precipitate was removed by filtration, and the solvent removed completely by evaporation in vacuum. The oily residue was recrystallized from *n*-pentane. colorless crystals of **4** (0.94 g, 78 %) were obtained at −70 °C. Elemental analysis (%) calcd for $C_{10}H_{30}Si_7O_3$ (394.95): C 30.41, H 7.66; found C 30.31, H 7.63. GC-MS: *m*/*z*: 395 $[M]^+$, 379 $[M^+{-}Me]$, 349 $[Si_7Me_8O_2]^+$, 335 $[Si_6Me_9O_2]^+$, 319 $[Si_6Me_9O]^+$, 305 $[Si_5Me_7O_2]^+$, 275 $[Si_5Me_8O]^+$, 233 $[Si_4Me_7O]^+$, 217 $[Si_4Me_7]^+$, 202 $[Si_4Me_6]^+$, 189 $[Si_4Me_5]^+$, 175 $[Si_3Me_5O]^+$, 159 $[Si_3Me_5]^+$, 133 $[Si_2Me_3O_2]^+$, 117 $[Si_2Me_3O]^+$, 101 $[Si_2Me_3]^+$, 73 $[SiMe_3]^+$

Permethyl-4,6,10-trithia-1,2,3,5,7,8,9-heptasilatricyclo[3.3.1.1^{3,7}]decane (5): A solution of **1a** (2.00 g, 2.42 mmol) and imidazole (1.08 g, 15.87 mmol) in *n*-heptane (100 mL) and THF (30 mL) was cooled to 0 °C. A steady stream of H_2S, which had been dried over P_4O_{10}, was passed through the solution. Immediately, a precipitate of imidazole hydrobromide formed. The reaction was continued for about 2 h, during which about 6 g of H_2S were passed through the solution. The reaction mixture was then allowed to warm to room temperature and stirred for another 3 h. The precipitate was separated by filtration, and the solvent (heptane/THF) removed in vacuum. The solid residue was recrystallized from *n*-pentane to give **5** (0.81 g, 75 %) as colorless crystals. Elemental analysis (%) found/calcd for $C_{10}H_{30}Si_7S_3$ (443.13): C 27.10, H 6.82; found: C 27.15, H 6.76. GC-MS: *m*/*z*: 443 $[M]^+$, 427 $[M{-}Me]^+$, 383 $[Si_7Me_{10}S_2]^+$, 369 $[Si_6Me_9S_2]^+$, 337 $[Si_6Me_7S_2]^+$, 277 $[Si_5Me_7S]^+$, 249 $[Si_4Me_7S]^+$, 219 $[Si_4Me_5S]^+$, 159 $[Si_3Me_5]^+$, 131 $[Si_2Me_4]^+$, 73 $[SiMe_3]^+$.

1,2,2,3,3,5,5,7,8,9-Decamethyl-4,6,10-triaza-1,2,3,5,7,8,9-heptasilatricyclo[3.3.1.1^{3,7}]decane (6a): A steady stream of NH_3 was passed for about 1 h through a solution of **1a** (3.00 g, 3.63 mmol) in *n*-heptane (250 mL) cooled to ice temperature. Immediately a solid precipitate of NH_4Br formed. The reaction mixture was allowed to warm to room temperature and stirred for a further hour. The precipitate was then separated by filtration, and the solvent removed by evaporation in vacuum. The solid residue was recrystallized from *n*-pentane (−70 °C) to give **6a** (1.38 g, 97 %) as colorless needles. Elemental analysis (%) found/calcd for $C_{10}H_{33}Si_7N_3$ (392.00): C 30.64, H 8.49, N 10.57; found: C 30.58, H 8.51, N 10.72; GC-MS: *m*/*z*: 392 $[M]^+$, 376 $[M{-}Me]^+$, 346 $[Si_7Me_7N_3]^+$, 332 $[Si_6Me_9N_2H_2]^+$, 318 $[Si_6Me_9NH]^+$, 274 $[Si_5Me_8NH]^+$, 258 $[Si_5Me_6N_2H_2]^+$, 245 $[Si_4Me_7N_2]^+$, 231 $[Si_4Me_7N]^+$, 201 $[Si_4Me_6]^+$, 188 $[Si_3Me_7]^+$, 173 $[Si_3Me_5N]^+$, 158 $[Si_3Me_4N]^+$, 130 $[Si_2Me_4N]^+$, 116 $[Si_2Me_4]^+$, 101 $[Si_2Me_3]^+$, 73 $[SiMe_3]^+$

$]^+$**Permethyl-4,6,10-triaza-1,2,3,5,7,8,9-heptasilatricyclo[3.3.1.1^{3,7}]decane (6b)**: At 0 °C a steady stream of NH_2Me was passed through a solution of **1a** (2.50 g, 3.03 mmol) in *n*-heptane (150 mL). Immediately, a white precipitate of $MeNH_3Br$ formed. The reaction was continued for 3 h until about 2.6 g (4 mL) of methylamine had been consumed. After stirring for 2 h at room temperature, the volume of the reaction mixture was reduced to about 70 mL by evaporation of *n*-heptane in vacuum. Then the precipitate was separated by filtration, and the residual *n*-heptane again removed by evaporation. The oily residue was recrystallized from *n*-pentane at −70 °C to give **6b** (0.2 g, 15 %) as colorless needles. The ^{29}Si NMR spectrum of the mother liquor indicated that a considerable portion of **1a** gives chainlike products under these reaction conditions. No attempts were made to optimize these conditions. Elemental analysis (%) calcd for $C_{13}H_{39}Si_7N_3$ (434.08): C 35.97, H 9.06, N 9.72; found: C 36.01, H 9.03, N 9.68; GC-MS: *m*/*z*: 434 $[M]^+$, 374 $[Si_6Me_{11}N_3]^+$, 360 $[Si_6Me_{10}N_3]^+$, 316 $[Si_6Me_{10}N_2]^+$, 289 $[Si_5Me_{11}N]^+$, 230 $[Si_4Me_6N_2]^+$, 188 $[Si_3Me_6N]^+$, 158 $[Si_3Me_5]^+$, 116 $[Si_2Me_4]^+$, 101 $[Si_2Me_3]^+$, 73 $[SiMe_3]^+$

3,4,5-Tri-*tert*-butyl-1,2,2,6,6,7,7-heptamethyltheptasilatricyclo[2.2.1.0^{2,6}]-heptane (7): A solution of Li naphthalenide in THF was prepared from Li (0.185 g, 26.653 mmol) and naphthalene (3.6 g, 28.1 mmol) according to the literature procedure[41] and added dropwise to a solution of **1b** (4.2 g, 4.41 mmol) in THF (350 mL). A temperature of −70 °C was maintained throughout the procedure, which took about 5 h. Then the reaction mixture was allowed to warm to room temperature, whereby it changed from reddish-brown to yellow. Chlorotrimethylsilane (0.2 mL) was added to quench any silyl anions, and the solvent was removed completely by evaporation in vacuum. The yellowish crystalline residue was dissolved in *n*-pentane, and all insoluble material (LiBr) was separated by decantation. The ^{29}Si NMR spectrum of the solution consists of just three lines indicating nearly quantitative formation of **7**. All attempts to crystallize **7** from the solution failed (see above).

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