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Comparative Study of Structural Aspects of Branched Oligosilanes

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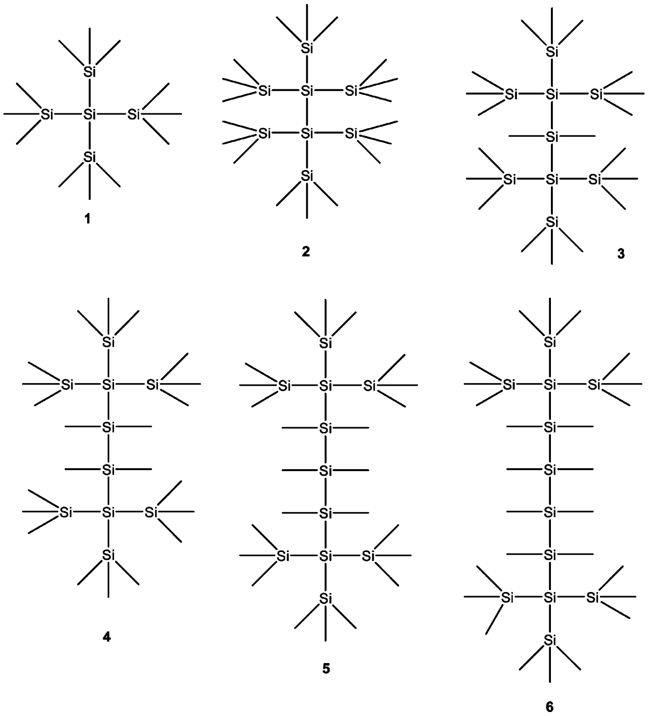
Some newly synthesized di-, tri-, penta-, and hexasilanes bearing trimethylsilyl groups together with some previously reported related compounds were analyzed using single-crystal X-ray crystallography. The structure analyses were compared to similar compounds already known. The influence of bulky tris(silyl)silyl groups on the Si−Si skeleton was studied.

1. Introduction

The space-filling tris(trimethylsilyl)silyl group with its good solubility in organic solvents is a popular ligand in main-group[1] and transition metal chemistry.[2] Some 40 years ago Gilman and co-workers[3] had introduced this substituent, which is nowadays called the “hypersilyl” group.[4] Since then, a great variety of molecules with this or spatially even more demanding silyl groups have been prepared such as hexa-*tert*-butyldisilane.[5] Synthetic efforts toward this direction were accompanied by numerous studies concerning the behavior and properties of polysilanes.[6] Bock et al. have studied hexakis(trimethylsilyl)disilane and elaborated on the elongated central silicon bond and especially on the cogwheel-like arrangement of the two hypersilyl groups. Carbon atoms of methyl groups on the two different shells approach each other as close as 3.51 Å.[7] As the van der Waals radius of a methyl group is thought be close to 2.0 Å,[8] the found distance falls short of the sum of two van der Waals radii.

Over the past few years our group has been involved in the synthesis of defined higher oligosilanes, especially those bearing tris(trimethylsilyl)silyl groups. Still the number of compounds with all-silicon scaffolds is small, mainly due to the lack of suitable methods for connecting fragments already containing silicon−silicon bonds. The development of oligosilyl potassium chemistry turned out to be a straightforward route to compounds bearing tris(trimethylsilyl)silyl groups linked to silicon atoms. As these compounds served as starting materials for our studies toward α,ω-oligosilyl dianions,[9] we also became interested in their structural features.

Scheme 1. Analyzed Linear Bis(hypersilyl) Compounds Starting with the Parent Tetrakis(trimethylsilyl)silane (1)



A search in the Cambridge Crystallographic Data Base for the structure element $(Si)_3Si{-}Si$ resulted

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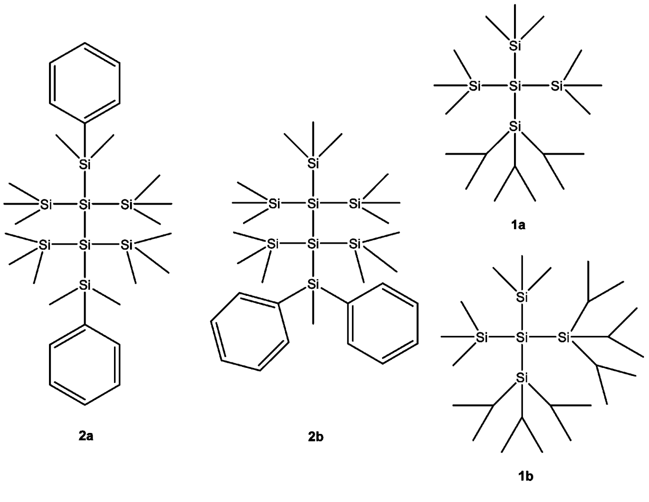
Table 1. Selected Si−Si Bond Distances (Å)

compound	$(\text{Me}_3\text{Si})_3\textbf{Si}-\textbf{Si}$	$(\text{Me}_3\textbf{Si})-\textbf{Si}$	$(\text{Me}_3\text{Si})_3\textbf{Si}\cdots\textbf{Si}(\text{SiMe}_3)_3$
1[11]		2.346(1)	
1a		2.385(2), 2.3668(12)	
1b		2.3948(17), 2.4015(14)	
2[12a]	2.403(2)	2.3738(9)	2.403(2)
2a	2.4166(9)	2.3846(9), 2.3947(10), 2.3835(11), 2.3855(10)	2.4166(9)
2b	2.4135(16)	2.3813(18), 2.3830(17), 2.374(2), 2.3761(18), 2.3909(19)	2.4135(16)
3	2.3851(8)	2.3833(11), 2.3520(10), 2.3684(10)	4.2457(1)
3a	2.3509(14)	2.3436(17), 2.3542(15), 2.3398(17), 2.3427(17)	3.9684(18)
4[18a]	2.372(1)	2.3467(9), 2.3550(9), 2.3604(8)	6.1885(32)
5	2.365(3), 2.361(3)	2.353(3), 2.349(3), 2.365(3), 2.339(3), 2.353(3), 2.367(3)	8.1005(23)
5a		2.3718(19), 2.3776(18), 2.380(2), 2.385(2)	8.2053(29)
6	2.3711(11)	2.3596(9), 2.3613(11), 2.3648(7)	9.9731(34)

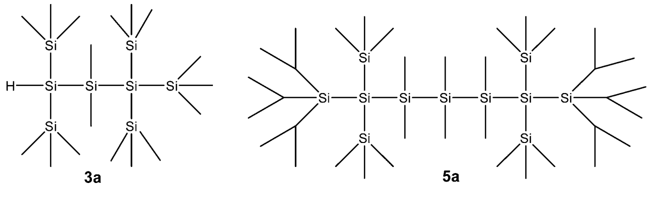
Table 2. Crystallographic Data for Compounds 3, 5, and 6

	3	**5**	**6**
empirical formula	$\text{Si}_9\text{C}_{20}\text{H}_{60}$	$\text{Si}_{11}\text{C}_{24}\text{H}_{72}$	$\text{Si}_{12}\text{C}_{26}\text{H}_{78}$
M_w	553.49	669.81	727.96
temperature [K]	293(2)	100(2)	223(2)
size [mm]	0.80 × 0.20 × 0.10	0.42 × 0.35 × 0.03	0.55 × 0.34 × 0.12
cryst syst	monoclinic	monoclinic	triclinic
space group	$C2/c$	$C2/c$	$P\bar{1}$
a [Å]	17.0693(2)	15.559(3)	9.1189(18)
b [Å]	9.3284(1)	9.866(2)	9.2621(19)
c [Å]	24.9319(4)	57.908(12)	16.395(3)
α [deg]	90	90	82.46(3)
β [deg]	107.8740(10)	96.23(3)	76.69(3)
γ [deg]	90	90	66.86(3)
V [Å^3]	3778.28	8836(3)	1237.8(4)
Z	4	8	1
ρ_calc [g cm^{-3}]	0.973	1.007	0.977
abs coeff [mm^{-1}]	0.324	0.338	0.329
F(000)	1224	2960	402
θ range [deg]	$1.72 < \theta < 25.00$	$0.71 < \theta < 23.00$	$2.39 < \theta < 26.00$
no. of reflns collected/unique	14 981/3314	25 829/6138	9460/4788
completeness to θ [%]	99.5	100	98.2
no. of data/restraints/params	3314/15/157	6138/0/340	4788/0/185
goodness of fit on F^2	1.13	1.19	1.05
final R indices [$I > 2\sigma(I)$]	R1 = 0.051, wR2 = 0.131	R1 = 0.095, wR2 = 0.158	R1 = 0.032, wR2 = 0.090
R indices (all data)	R1 = 0.060, wR2 = 0.137	R1 = 0.130, wR2 = 0.172	R1 = 0.035, wR2 = 0.093
largest diff peak/hole [e$^-$/Å^3]	0.26/−0.15	0.45/−0.44	0.27/−0.17

Scheme 2. Derivatives of the Compounds 1 and 2



Scheme 3. Derivatives of the Compounds 3 and 5



in 50 structures, and herein just 27 contained the $(\text{Me}_3\text{Si})_3\text{Si}-\text{Si}$ element. In this account we intend to report on new crystal structures of the type $[(\text{Me}_3\text{Si})_3\text{Si}](\text{SiMe}_2)_n[\text{Si}(\text{SiMe}_3)_3]$ [$n = 1$ (**3**), $n = 3$ (**5**), and $n = 4$ (**6**)] and to compare them to the already published structures with $n = 0$ and 2. The *intra*molecular steric overcrowding in this series is diminished stepwise by adding dimethylsilylene (SiMe_2) spacers. In another approach we have varied the spatial demand of the hypersilyl group by replacing trimethylsilyl groups, in some compounds of the series, by triisopropylsilyl groups (**1a**, **1b**, and **5a**) or a hydrogen atom (**3a)** or by the introduction of phenyl groups (**2a** and **2b**).

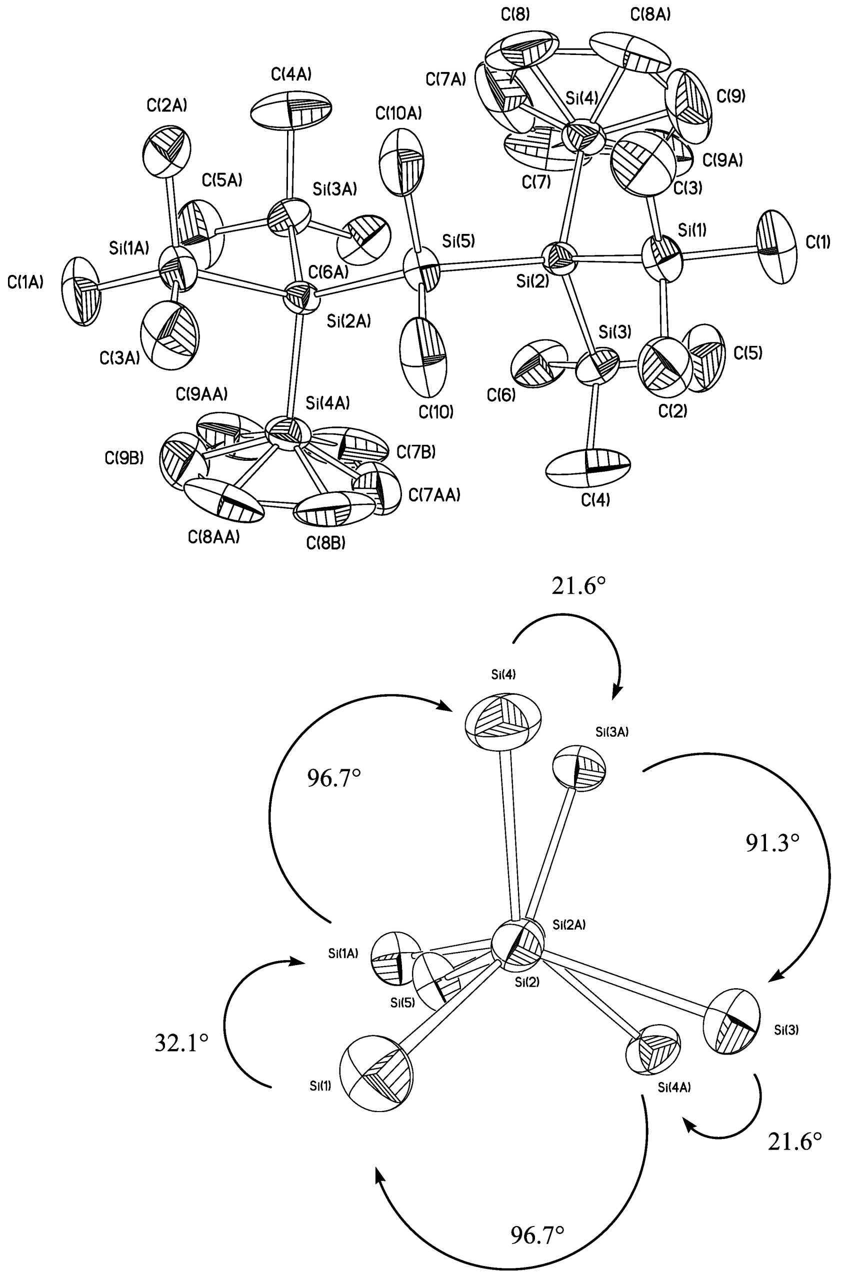


Figure 1. (Top) Molecular structure and numbering of **3**. (Bottom) Newman projection of **3** along the Si2−Si2A axis.

2. Results and Discussion

The crystal structure of the parent compound in our series, tetrakis(trimethylsilyl)silane (**1**), was determined recently by synchrotron radiation. It was found to crystallize at room temperature orientationally disordered in the cubic space group *Fm*-3*m*. After cooling to 200 K **1** underwent a phase transition to a fully ordered structure in the cubic space group $P2_13$.[10] Previously, a structure was reported containing uncoordinated THF in the unit cell which crystallized in the tetragonal space group *P*4/*ncc*.[11] Hexakis(trimethylsilyldisilane) (**2**) crystallizes in the lower trigonal space group *R*-3*c*.[7,12] Half of a molecule is in the asymmetric unit, and the central Si−Si bond is located on a 3-fold axis. This central Si−Si bond in **2** is elongated (2.40 Å) compared to the peripheral Si−Si bonds (Table 1). Despite this prolongation the shortest *intra*molecular contact between methyl groups (3.52 Å) was considerably shorter than the typical sum of van der Waals radii of methyl groups.[13] The same counts for *inter*molecular contacts, where the shortest distance between the carbon atoms of methyl groups was found to be 3.89 Å. As a consequence of the sterical overcrowding, deviations from the ideal tetrahedral bond angles were found frequently (angles between 114° and 105°).

1,1,1,3,3,3-Hexakis(trimethylsilyl)-2,2-dimethyltrisilane (**3**) crystallizes in the monoclinic space group *C*2/*c*

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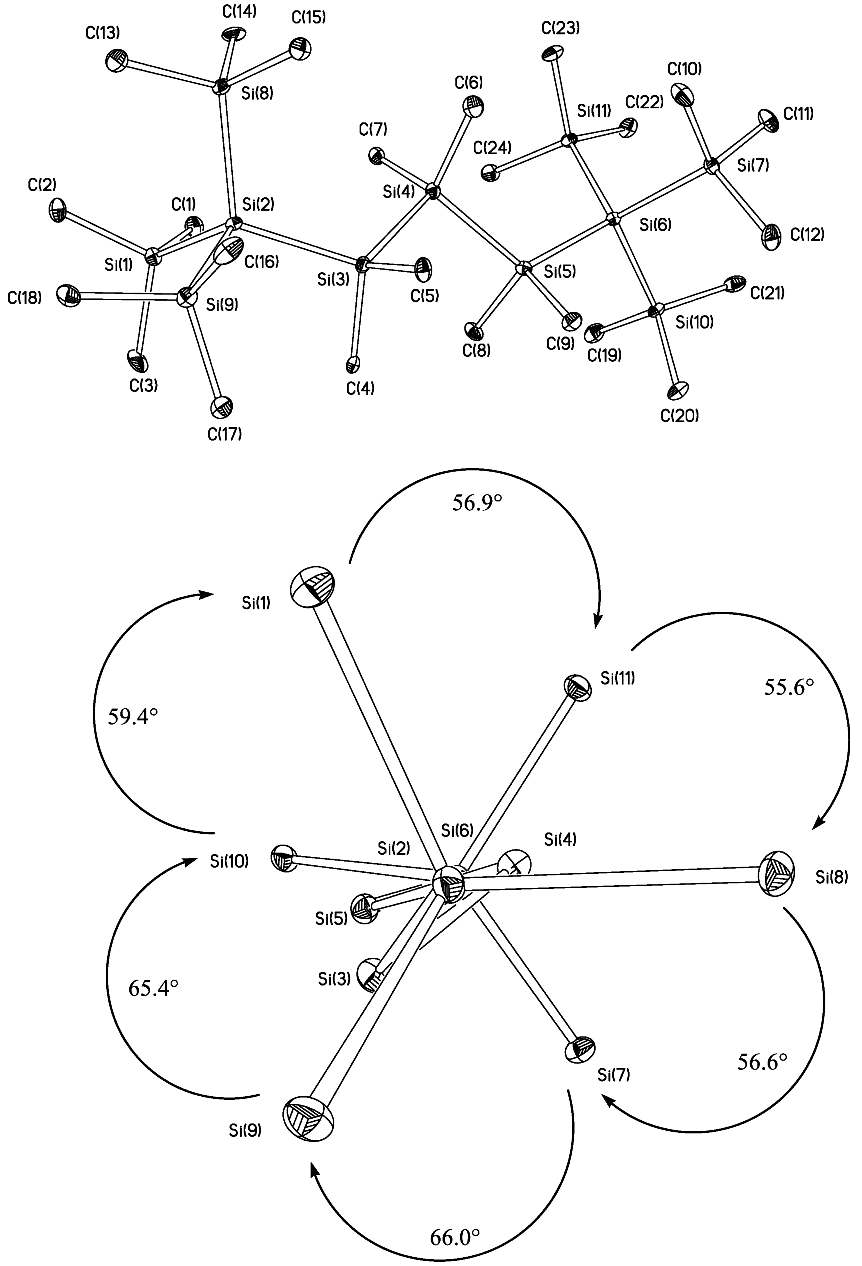

Figure 2. (Top) Molecular structure and numbering of **5**. (Bottom) Newman projection of **5** along the Si−Si skeleton; selected bond angles [deg] with estimated standard deviations: Si(8)−Si(2)−Si(1) 109.79(10), Si(8)−Si(2)−Si(9) 107.61(10), Si(1)−Si(2)−Si(9) 107.05(10), Si(8)−Si(2)−Si(3) 114.24(10), Si(1)−Si(2)−Si(3) 111.12(10), Si(9)−Si(2)−Si(3) 106.67(10), Si(2)−Si(3)−Si(4) 118.62(10), Si(5)−Si(4)−Si(3) 106.15(10), Si(4)−Si(5)−Si(6) 119.79(10), Si(11)−Si(6)−Si(7) 108.99(10), Si(11)−Si(6)−Si(5) 112.75(10), Si(7)−Si(6)−Si(5) 113.51(10), Si(11)−Si(6)−Si(10) 106.83(10), Si(7)−Si(6)−Si(10) 108.03(10), Si(5)−Si(6)−Si(10) 106.38(10).

(Table 2) with half a molecule in the asymmetric unit in which one trimethylsilyl group is disordered. There is half a molecule in the asymmetric unit, while the central Si atom resides on a symmetry center. The elongation of the central Si−Si bonds is almost minimized to normal values (Table 1). The shortest distance between methyl groups of the two hypersilyl groups is surprising. Despite the dimethylsilylene spacer separating the hemispherical hypersilyl shells, contacts are still shorter than the sum of the van der Waals radii also in this molecule (C4 −C7A 3.67 Å and C6A−C7 3.71 Å). This is remarkable, as the distance between the two central silicon atoms of the hypersilyl groups increases from 2.40 Å in **2** to 4.25 Å in **3**. The steric strain of the bulky (Me$_3$Si)$_3$Si substituents widens the Si2−Si5−Si2(A) bond angle at the central silicon atom to 125.8°. The tetrahedral configuration of the (Me$_3$Si)$_3$SiSi unit is distorted in such a way that at positions where the two hemispheres touch each other the trimethylsilyl groups (Si3 and Si4) bend back and the respective bond angles are widened from the ideal 109.5° to 116.0° (Si3−Si2−Si5) and 114.7° (Si4−Si2−Si5). The adjacent angles Si3−Si2−Si1, Si4−Si2−Si1, and Si1−Si2−Si5 are diminished to about 105.3°. Oehme et al. have studied compounds related to **3** containing a plain or substituted methylene group as spacer.[14] Their results are in good

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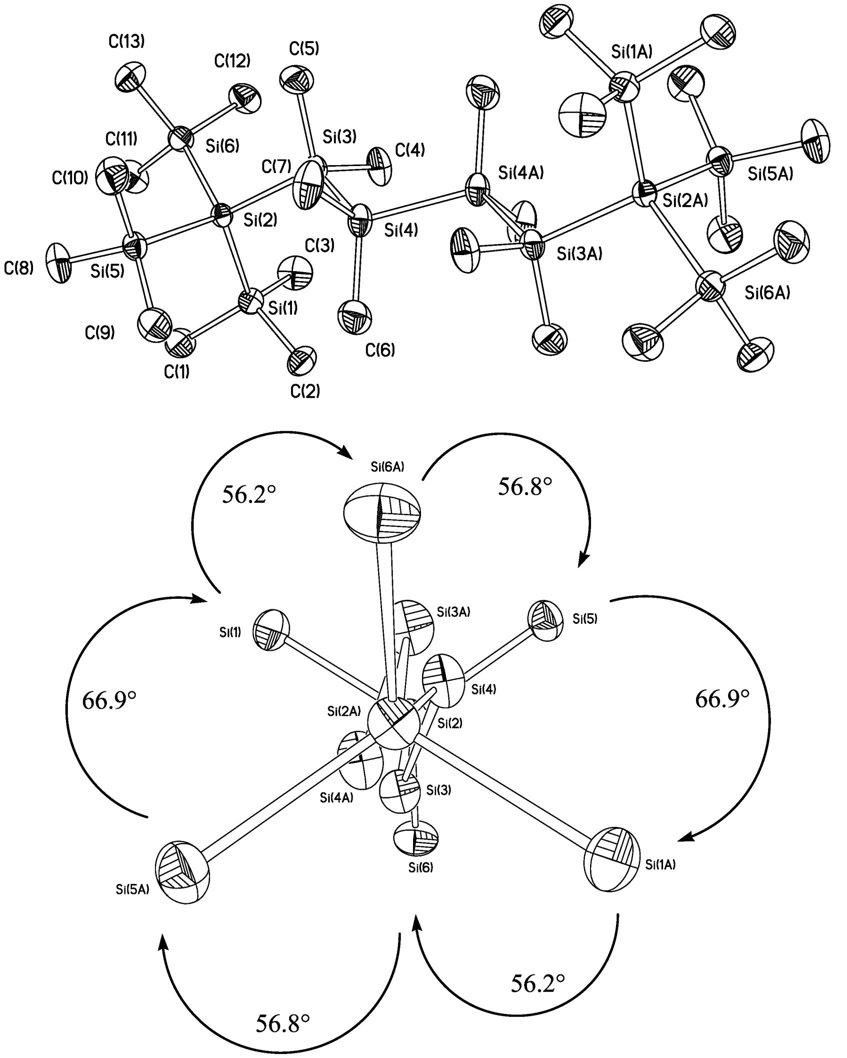

Figure 3. (Top) Molecular structure and numbering of **6**. (Bottom) Newman projection of **6** along the Si−Si skeleton; selected bond angles [deg] with estimated standard deviations: Si(1)−Si(2)−Si(5) 110.27(3), Si(1)−Si(2)−Si(6) 106.58(3), Si(5)−Si(2)−Si(6) 107.35(3), Si(1)−Si(2)−Si(3) 110.52(3), Si(5)−Si(2)−Si(3) 114.53(3), Si(6)−Si(2)−Si(3) 107.19(3), Si(4)−Si(3)−Si(2) 117.30(3), Si(4)#1−Si(4)−Si(3) 109.17(4).

agreement with the structural data obtained for **3**. The dihedral angles Me_3*Si*−*Si*−spacer−*Si*(A)−*Si*(A)Me_3 should be 60° in a perfectly staggered conformation. For **3** a strong deviation from these ideal values was found. Such behavior would be expected on the basis of recently discussed theory for rotational isomeric states of polysilanes or polymers. Following this theory energetic minima could be expected for *gauche*- (∼60°), *cisoid*- (∼40°), and *ortho*- (∼90°) conformers.[15] For compound **2**[11,12] the respective torsional angles 41.4°/78.2°, 43.4°/76.6°, and 46.3°/73.7° have been found for the different crystal structures. A compound analogous to **2**, with sterically more demanding tris(triethylsilyl)silyl groups,[16] exhibits this distortion to an even higher degree, with values of 36.4° and 83.6°. For the above-mentioned compound with a methylene spacer[14a] between two hypersilyl groups, values of between 35.8° and 38.0° for the *cisoid*- and between 79.7° and 86.2° for the *ortho*-dihedral angles have been reported. For the case of **3**, the respective numbers are 21.6°/32.1° and 91.3°/96.7° (Figure 1). Conformational minima around 90° for linear chains were found by calculations and X-ray structure determinations of branched oligosilanes.[17]

The crystal structure of the next polysilane compound **4** was determined to be triclinic ($P\bar{1}$), with an inversion center between the two dimethylsilylene spacer silicon atoms.[18] Here the steric strain along the spacer chain is largely diminished. The bond length between the central hypersilyl silicon atom and the adjacent dimethylsilylene (2.37 Å) only slightly differs from the other four Si−Si bonds (Table 1). The two hypersilyl shells are arranged in *anti*-fashion with respect to the central disilane. The related compound with two methylene groups instead of the two dimethylsilylenes was structurally studied and also exhibits the same *anti*-conformation of the hypersilyl groups attached to the ethylene spacer.[19]

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Table 3. Crystallographic Data for Compounds 2a, 2b, 1a, and 1b

	2a	**2b**	**1a**	**1b**	**3a**	**5a**
empirical formula	$Si_8C_{28}H_{58}$	$Si_8C_{28}H_{58}$	$Si_5C_{18}H_{48}$	$Si_5C_{24}H_{60}$	$Si_8C_{17}H_{52}$	$Si_{11}C_{36}H_{96}$
M_w	619.46	619.46	405.01	489.17	481.31	838.12
temperature [K]	150(2)	293(2)	150(2)	223(2)	293(2)	100(2)
size [mm]	0.32 × 0.25 × 0.04	0.30 × 0.20 × 0.06	0.36 × 0.24 × 0.20	0.48 × 0.30 × 0.28	0.35 × 0.15 × 0.10	0.47 × 0.38 × 0.22
cryst syst	triclinic	monoclinic	trigonal	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$R3$	$C2/c$	$C2/c$	$P2_1/c$
a [Å]	9.941(2)	10.307(2)	14.521(2)	35.635(7)	31.743(6)	19.479(4)
b [Å]	10.240(2)	18.699(4)	14.521(2)	11.090(2)	9.759(2)	9.1936(18)
c [Å]	19.172(4)	20.617(4)	10.749(2)	18.174(4)	23.294(9)	30.593(6)
α [deg]	89.66(3)	90	90	90	90	90
β [deg]	88.68(3)	90.18(3)	90	113.18(3)	111.56	98.84(3)
γ [deg]	80.88(3)	90	120	90	90	90
V [Å^3]	1926.4(7)	3973.6(14)	1962.9(6)	6602(2)	6711(2)	5413.4(19)
Z	2	4	3	8	8	4
ρ_{calc} [g cm^{-3}]	1.068	1.035	1.028	0.984	0.953	1.028
abs coeff [mm^{-1}]	0.295	0.286	0.273	0.226	0.323	0.287
F(000)	676	1352	678	2192	2128	1864
θ range [deg]	$1.06 < \theta < 24.71$	$1.47 < \theta < 23.26$	$2.49 < \theta < 25.29$	$1.94 < \theta < 24.00$	$1.38 < \theta < 23.31$	$1.06 < \theta < 24.50$
no. of reflns collected/unique	13 342/6473	16 996/5714	3299/1305	21 172/5189	14 636/4818	35 928/9004
completeness to θ [%]	98.5	99.9	99.6	99.9	99.6	99.8
no. of data/restraints/params	6473/0/341	5714/0/341	1305/1/75	5189/0/277	4818/0/247	9004/16/472
goodness of fit on F^2	1.04	1.03	1.02	1.11	0.97	1.07
final R indices [$I > 2\sigma(I)$]	R1 = 0.038, wR2 = 0.093	R1 = 0.062, wR2 = 0.141	R1 = 0.045, wR2 = 0.091	R1 = 0.063, wR2 = 0.133	R1 = 0.055, wR2 = 0.134	R1 = 0.0865, wR2 = 0.2097
R indices (all data)	R1 = 0.044, wR2 = 0.097	R1 = 0.107, wR2 = 0.157	R1 = 0.052, wR2 = 0.095	R1 = 0.089, wR2 = 0.143	R1 = 0.090, wR2 = 0.148	R1 = 0.102, wR2 = 0.221
largest diff peak/hole [e$^-$/ Å^3]	0.43/−0.21	0.48/−0.20	0.23/−0.19	0.30/−0.16	0.26/−0.15	1.27/−1.02

Compound **5**, with three dimethylsilylene units as spacer, crystallizes in the monoclinic space group $C2/c$. No unusually elongated Si−Si bonds can be found (Table 1). Through the trisilanyl spacer the closest distance between methyl groups of the two hypersilyl shells is now 6.66 Å (C1−C24). This is much closer than found for compound **4**, where these methyl groups are 7.76 Å apart. The distances between the methyl groups of the outer dimethylsilylene units and the attached hypersilyl groups are again shorter than the sum of van der Waals radii (C3−C4 3.87 Å, C16−C5 3.91 Å, C9−C20 3.87 Å, C19−C8 3.75 Å, and C4−C17 3.75 Å). The expansion of the chain bond angles at the two spacing dimethylsilylene groups and the distortion of the tetrahedral configuration of the $(Me_3Si)_3SiSi$ unit are similar to the situation of **3** (Figure 2). Xue et al. have synthesized a related compound with a 1,3-propylidene group as spacer instead of the 1,3-trisilyl unit.[19] They reported the smallest bond angle of the chain at the central bridging carbon (114.4°), whereas the angles between the outer bridging carbon atoms and the hypersilyl groups were 117.5° and 118.1°. These angles caused the methyl groups at Si3 and Si5 (C5−C9 3.81 Å, C4−C8 3.67 Å) to approach each other. In **5** the outer angles are similar (118.6° and 119.8°), but the inner one is only 106.2°. The dihedral angles Me_3Si−Si2···Si6−$SiMe_3$ are all between 56.6° and 66.0° and show a staggered conformation with respect to the hypersilyl groups (Figure 2).

The last molecule in this series is **6**, with four dimethylsilylene units as spacer, which crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of half a molecule with an inversion center in the middle of the central spacer chain bond. The shortest distance between methyl groups of the hypersilyl shells increases from 6.66 Å in **5** to 9.45 Å (C10−C2A). The situation regarding the bond angles and the dihedral angles is, in general, similar to **5** (Figure 3).

The exchange of two methyl groups in molecule **2** by two phenyl groups, one on Si1 and the other one on Si4, gives compound **2a**. This change lowers the Laue class symmetry of the crystal from trigonal to triclinic ($P\bar{1}$) (Table 3). Exchanging two methyl groups on Si1 by phenyl groups leads to the monoclinic space group $P2_1/n$ (**2b**). Both molecules (**2a**, **2b**) show an elongation of the central Si−Si bond, differing from molecule **2** by 0.01 Å. A similar observation has been made by Matsumoto et al.[16] for the above-mentioned hexakis(triethylsilyl)disilane. Due to the increased steric hindrance of the Et_3Si groups, central Si−Si bond lengths of 2.42 and 2.45 Å were observed. For the terminal Si−Si bonds distances of 2.38 and 2.40 Å were found for the two independent molecules in the cell. Relatively short *intra*molecular contacts between the methyl groups of the two hypersilyl shells were observed for **2b**, at 0.1 Å lower than for **2a** (**2a**: C8−C25 3.71 Å, C18−C27 3.90 Å, C23−C22 3.95 Å, C25−C22 3.75 Å; **2b**: C14−C17 3.63 Å, C1−C28 3.65 Å, C15−C21 3.79 Å). The dihedral angles in **2** are 42.0° and 77.0°; in **2a** they are 37.5°, 40.5°, and 42.7° and 76.6°, 79.1°, and 83.5°, respectively (Figure 4). In **2b** the *cisoid* angles are further diminished (35.5°, 39.0°, and 41.1°), and accordingly expanded (79.1°, 80.5°, and 84.8°) (Figure 5). Despite the change in the substitution pattern the dihedral angles of the Si skeleton of **2**, **2a**, and **2b** are similar. The shortest intermolecular distances between methyl carbons and those of the phenyl rings lie at about 3.9 Å for **2a** and about 3.7 Å for **2b**. Therefore, for both cases no pronounced π-stacking or π-CH interactions are present.

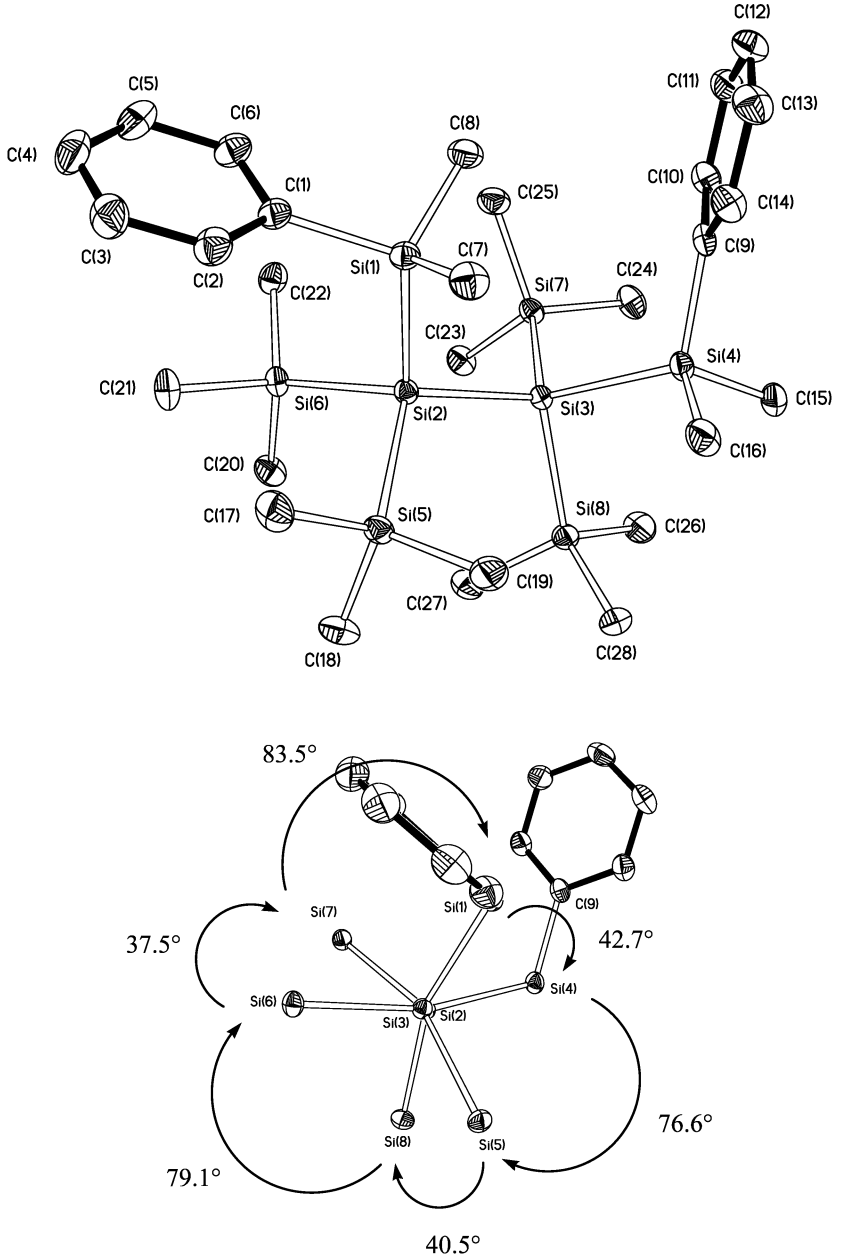

Figure 4. (Top) Molecular structure and numbering of **2a**. (Bottom) Newman projection of **2a** along the Si−Si skeleton; selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Si(4)−C(9) 1.888(2), Si(1)−C(1) 1.899(2), Si(6)−Si(2)−Si(5) 104.45(4), Si(6)−Si(2)−Si(1) 107.18(4), Si(5)−Si(2)−Si(1) 105.30(4), Si(6)−Si(2)−Si(3) 113.34(4), Si(5)−Si(2)−Si(3) 114.42(4), Si(1)−Si(2)−Si(3) 111.47(4), Si(8)−Si(3)−Si(4) 102.93(4), Si(8)−Si(3)−Si(7) 102.89(4), Si(4)−Si(3)−Si(7) 109.15(4), Si(8)−Si(3)−Si(2) 112.75(4), Si(4)−Si(3)−Si(2) 114.33(4), Si(7)−Si(3)−Si(2) 113.68(4).

Exchanging trimethylsilyl groups in compound **1** by either one triisopropyl group as in **1a** or two triisopropylsilyl groups as in **1b** lowers the symmetry from cubic (**1**) to trigonal (*R*3) (**1a**) and to monoclinic (*C*2/*c*) (**1b**). The distances of the Si−Si bonds are elongated from 2.34 Å in **1**[10] to 2.37−2.38 Å in **1a** and up to 2.39−2.44 Å in **1b** (Figures 6 and 7). The intermolecular C−C clearances for all three compounds are greater than 3.90 Å, and in this way they are in contrast to all the other presented examples. The shortest *intra*molecular C−C distance is 2.91 Å[10] for **1** and 3.35 Å (C3−C5) for **1a** and increases to 3.47 Å (C17−C12) for **1b**. The bond angles (Si−Si−Si) in **1** are 109.3° and 109.7°.[10] For **1a** the bond angles change to 105.6° for Me_3Si−Si−$SiMe_3$ and 113.1° for Me_3Si−Si−Si^iPr_3. The steric strain of the two Si^iPr_3 groups in **1b** increases the bond angle of Si^iPr_3−Si−Si^iPr_3 to 115.8° and reduces the Me_3Si−Si−$SiMe_3$ angle to 101.8°.

1,1,1,3,3-Pentakis(trimethylsilyl)-2,2-dimethyltrisilane (**3a**) crystallizes in the same space group as **3** (monoclinic, *C*2/*c*). The hydrogen (H90) on Si1 was found (Si1−H90 1.46 Å), while all other hydrogen atoms were calculated. Steric strain is released through the replacement of one trimethylsilyl group by a single hydrogen atom. The elongation of the central Si−Si bond is no longer present, while the intramolecular distances between the hypersilyl shell and the two remaining Me_3Si groups remain as close as in **3** [3.72 Å (C13−C10)]. The bond angle at the central silicon atom (Si2) is minimized from 125.8° in **3** to 114.8° in **3a**, while the other angles behave similarly to **3**. The dihedral angles Si−Si1−Si3−Si (Figure 8) are 42.6°, 45.5° up to 80.2°,

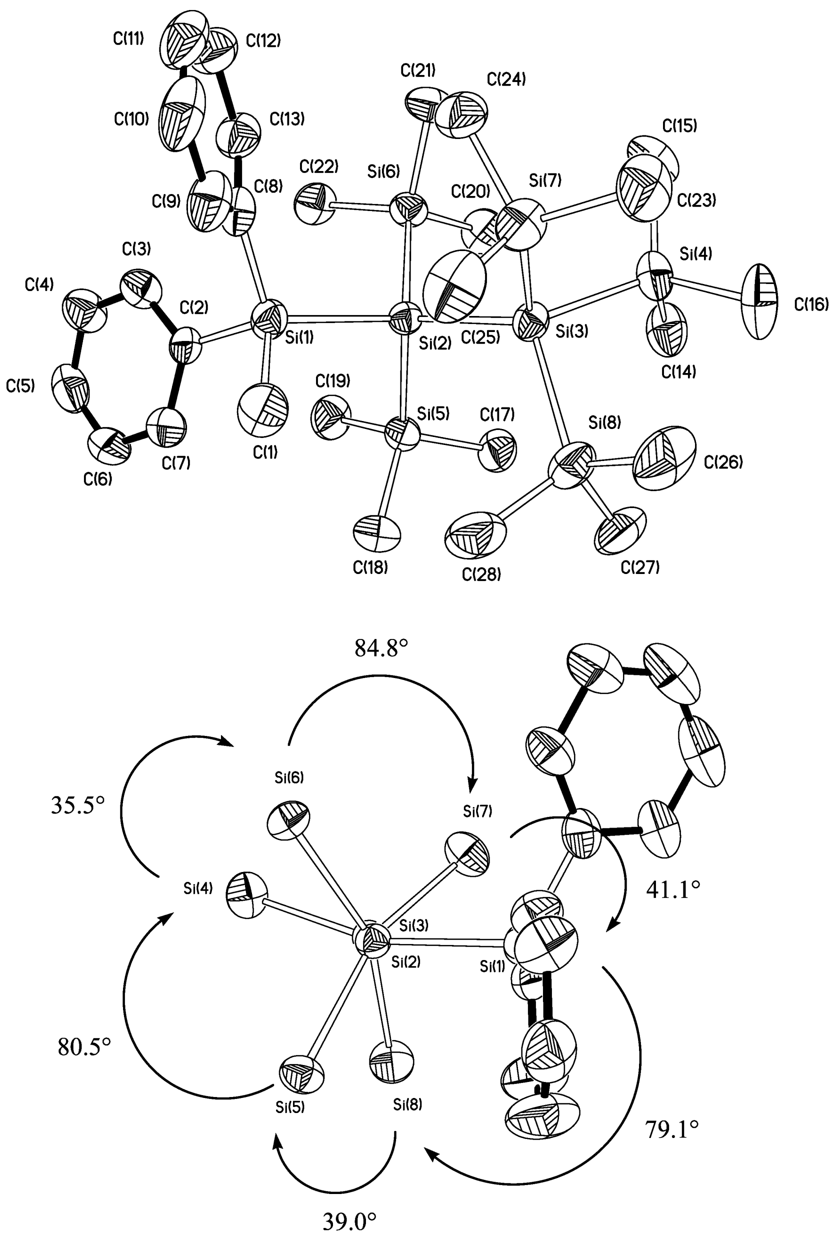

Figure 5. (Top) Molecular structure and numbering of **2b**. (Bottom) Newman projection of **2b** along the Si–Si skeleton; selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Si(1)–C(8) 1.873(5), Si(1)–C(2) 1.886(5), Si(6)–Si(2)–Si(5) 103.84(6), Si(6)–Si(2)–Si(1) 109.72(7), Si(5)–Si(2)–Si(1) 104.98(6), Si(6)–Si(2)–Si(3) 112.83(6), Si(5)–Si(2)–Si(3) 110.87(6), Si(1)–Si(2)–Si(3) 113.85(6), Si(8)–Si(3)–Si(7) 104.47(7), Si(8)–Si(3)–Si(4) 103.59(7), Si(7)–Si(3)–Si(4) 105.62(7), Si(8)–Si(3)–Si(2) 115.49(7), Si(7)–Si(3)–Si(2) 112.99(7), Si(4)–Si(3)–Si(2) 113.60(7).

82.1° and are more similar to **2** than to **3**. The shortest intermolecular distances are 3.83 Å (C5–C12′) and 3.97 Å (C9–C16′).

Compound **5a** crystallizes in a monoclinic space group ($P2_1/c$), and one triisopropylsilyl group (at Si7) is disordered. The increase in required space of the $^i\mathrm{Pr}_3\mathrm{Si}(\mathrm{Me}_3\mathrm{Si})_2\mathrm{Si}$ shells is reflected by an elongation of the inner Si–Si bonds; the two shells move further apart by 0.2 Å compared to **5** (Table 1). The closest distance between methyl groups of the two shells decreases by 1.4 Å from 6.66 Å in **5** to 5.26 Å (C17–C27) in **5a**. Within the space-filling shells the $^i\mathrm{Pr}_3\mathit{Si}\text{–}\mathit{Si}$ distances are increasing to 2.40 Å (Si6–Si7) and 2.39 Å (Si1–Si2). The dihedral angle Si–Si2–Si6–Si differs from 23.3°, 23.4°, and 41.8° to 88.0°, 91.2°, and 92.4° (Figure 9). The bond angles of the bridging SiMe_2 units are increased to 123.1° (Si2–Si3–Si4) and 118.5° (Si4–Si5–Si6) for the outer ones compared to the inner one, which displays a value of 108.8° (Si3–Si4–Si5).

Conclusion

In the series of compounds $[(\mathrm{Me}_3\mathrm{Si})_3\mathrm{Si}](\mathrm{SiMe}_2)_n[\mathrm{Si}(\mathrm{SiMe}_3)_3]$ ($n = 0-4$) the mutual interference of the two hypersilyl shells is reduced by increasing the number of dimethylsilylene spacers between them (**2**–**6**). The spatial separation of the two $(\mathrm{Me}_3\mathrm{Si})_3\mathrm{Si}$ units is increased by some 2 Å for each added dimethylsilylene spacer unit. The bond lengths within the $(\mathrm{Me}_3\mathrm{Si})_3\mathrm{Si}$ shells are not greatly affected by the number of dimethylsilylene spacers. The introduction of additional steric bulk on the hypersilyl shells was accomplished by replacing trimethylsilyl by triisopropylsilyl groups. This transformation influences the lengths of the Si–

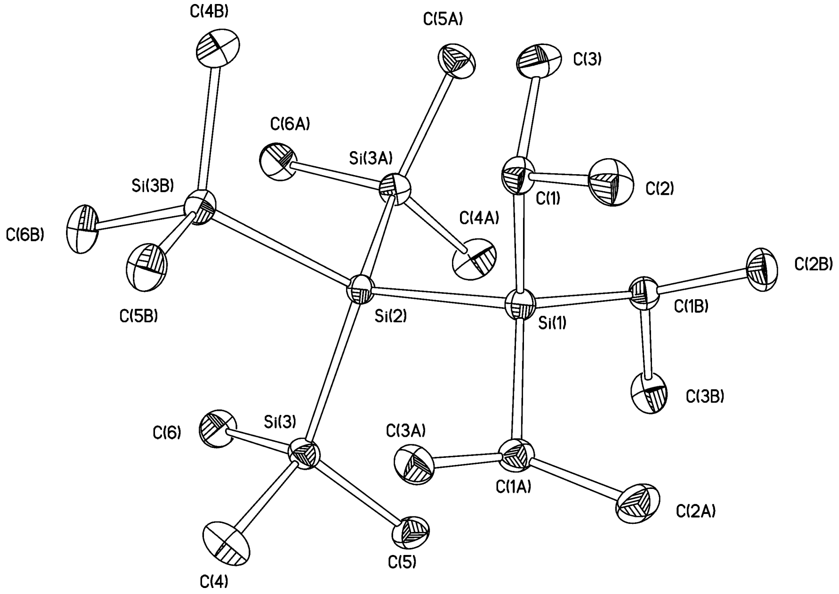

Figure 6. Molecular structure and numbering of **1a**. Selected bond angles [deg] with estimated standard deviations: Si(1)–Si(2) 2.385(2), Si(2)–Si(3A) = Si(2)–Si(3B) = Si(2)–Si(3) 2.3668(12), Si(3B)–Si(2)–Si(3A) = Si(3B)–Si(2)–Si(3) = Si(3A)–Si(2)–Si(3) 105.62(5), Si(3B)–Si(2)–Si(1) = Si(3A)–Si(2)–Si(1) = Si(3)–Si(2)–Si(1) 113.09(4).

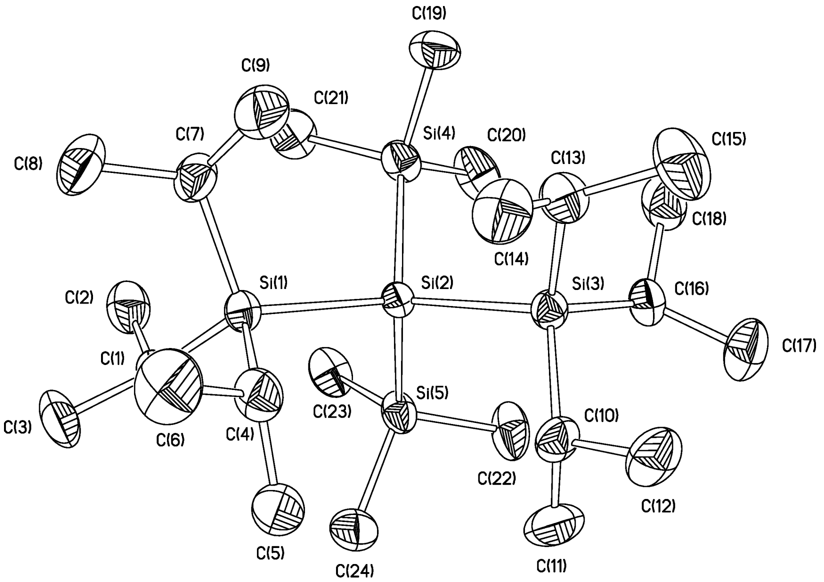

Figure 7. Molecular structure and numbering of **1b**. Selected bond angles [deg] with estimated standard deviations: Si(1)–Si(2) 2.4228(13), Si(2)–Si(4) 2.3948(17), Si(2)–Si(5) 2.4015(14), Si(2)–Si(3) 2.4402(13), Si(4)–Si(2)–Si(5) 101.81(5), Si(4)–Si(2)–Si(1) 109.86(5), Si(5)–Si(2)–Si(1) 108.85(5), Si(4)–Si(2)–Si(3) 108.92(5), Si(5)–Si(2)–Si(3) 110.73(5), Si(1)–Si(2)–Si(3) 115.75(5).

Si bonds dramatically both along the Si-skeleton and within the $(Me_3Si)_2(^iPr_3Si)Si$ unit (**1a**, **1b**, and **5a**). Releasing the steric strain of one shell through the exchange of a trimethylsilyl group by a hydrogen atom sets the length of the central Si–Si bond to normal values. The hypersilyl shell and the smaller $(Me_3Si)_2HSi$ shell use the additional space by decreasing the distance between the shells by some 0.28 Å (**3a**).

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents besides $CDCl_3$ were dried over sodium/potassium alloy under nitrogen and were freshly distilled prior to use. Potassium *tert*-butyl alcoholate was purchased from Merck. All other chemicals were bought from different suppliers and were used without further purification. 1,3-Dichlorohexamethyltrisilane,[20] 1,4-dichlorooctamethyltetrasilane,[20] tris(trimethylsilyl)silylpotassium,[21] pentakis(trimethylsilyl)-disilanylpotassium,[21] 1,1,3,3,3-pentakis(trimethylsilyl)-2,2-dimethyltrisilanylpotassium,[9] and triisopropylsilylbis(trimethylsilyl)silylpotassium[22] as well as compounds **3**,[21] **5**,[9] **1a**,[22] **1b**,[22] and **2a**[23] have been prepared according to literature procedures.

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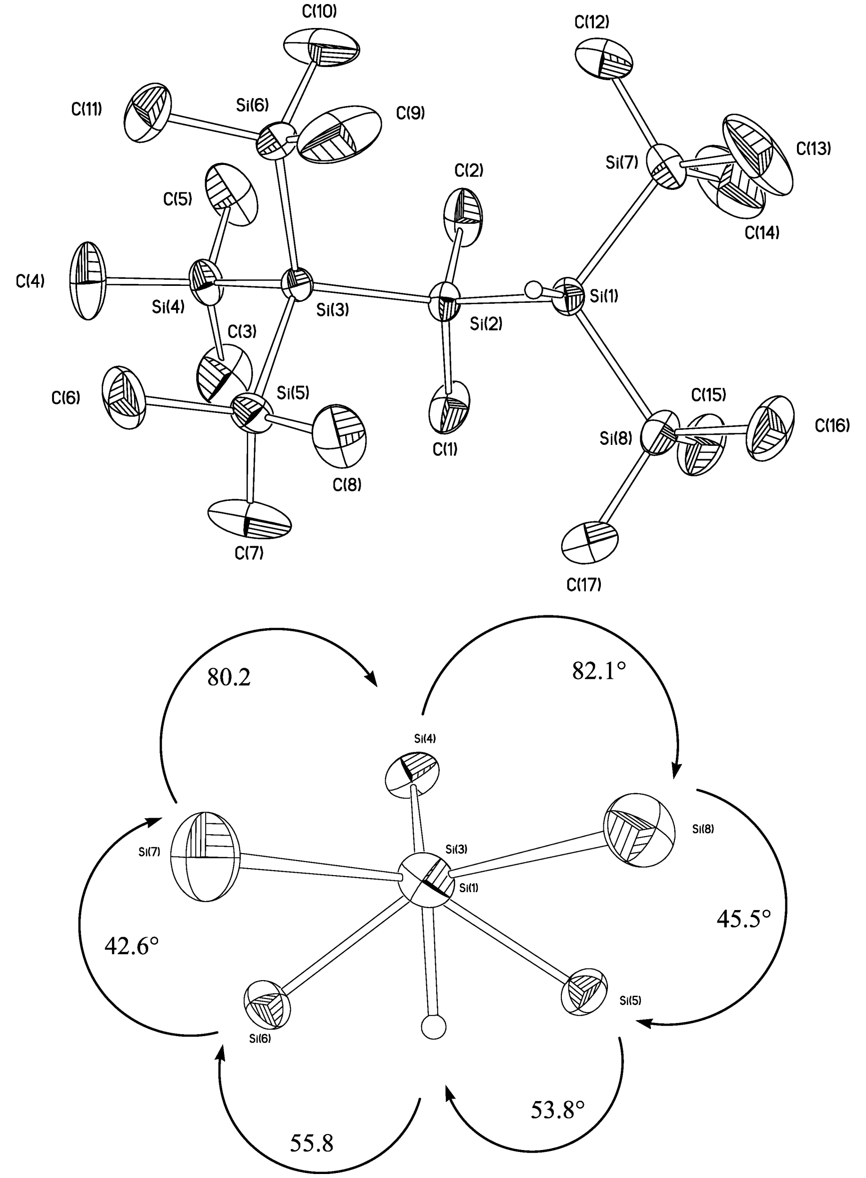

Figure 8. (Top) Molecular structure and numbering of **3a**. (Bottom) Newman projection of **3a** along the Si−Si skeleton. Selected bond angles [deg] with estimated standard deviations: Si(8)−Si(1)−Si(7) 108.73(6), Si(8)−Si(1)−Si(2) 112.95(6), Si(7)−Si(1)−Si(2) 115.73(7), Si(3)−Si(2)−Si(1) 114.78(5), Si(5)−Si(3)−Si(6) 109.37(6), Si(5)−Si(3)−Si(2) 110.71(6), Si(6)−Si(3)−Si(2) 111.62(6), Si(5)−Si(3)−Si(4) 108.53(6), Si(6)−Si(3)−Si(4) 108.31(6), Si(2)−Si(3)−Si(4) 108.22(6).

^{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 either dissolved in a deuterated solvent or 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.[24] Elementary analysis was carried out using a Heraeus Vario Elementar.

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 (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[25] and SADABS[26] (except **3**), respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).[27,28] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located at calculated positions to correspond to standard bond lengths and angles. The PARST program[29] was used to obtain the intramolecular distances summarized in Table 1. All structural diagrams were drawn at 30% probability thermal displacement ellipsoids, and all hydrogen atoms were omitted for clarity. Unfortunately the obtained crystal quality of some of the investigated substances was poor. This fact is reflected by high R and low θ values.

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[28] Crystallographic data (excluding structure factors) for the structures of compounds **3**, **5**, **6**, **1a**, **1b**, **2a**, **2b**, **3a**, and **5a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-244010 for **3**, 244009 for **5**, 244013 for **6**, 244015 for **1a**, 244014 for **1b**, 244012 for **2a**, 244016 for **2b**, 244011 for **3a**, and 244008 for **5a**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk].

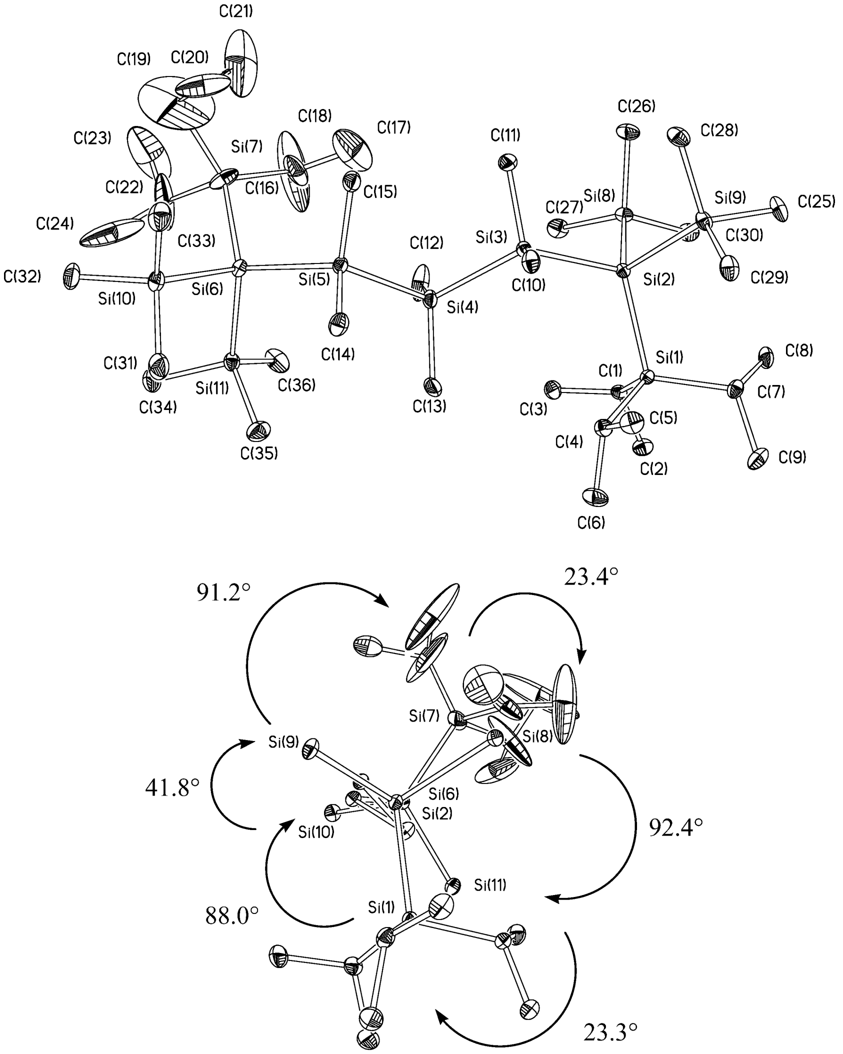

Figure 9. (Top) Molecular structure and numbering of **5a**. (Bottom) Newman projection of **5a** along the Si−Si skeleton. Selected bond angles [deg] with estimated standard deviations: Si(8)−Si(2)−Si(9) 104.22(7), Si(8)−Si(2)−Si(1) 112.35(7), Si(9)−Si(2)−Si(1) 110.58(7), Si(8)−Si(2)−Si(3) 107.70(7), Si(9)−Si(2)−Si(3) 104.91(7), Si(1)−Si(2)−Si(3) 116.17(7), Si(4)−Si(3)−Si(2) 123.05(7), Si(3)−Si(4)−Si(5) 108.81(7), Si(4)−Si(5)−Si(6) 118.48(8), Si(10)−Si(6)−Si(11) 102.19(8), Si(10)−Si(6)−Si(5) 105.07(7), Si(11)−Si(6)−Si(5) 109.50(7), Si(10)−Si(6)−Si(7) 112.69(8), Si(11)−Si(6)−Si(7) 114.23(9), Si(5)−Si(6)−Si(7) 112.33(9).

1,1,1,6,6,6-Hexakis(trimethylsilyl)-2,2,3,3,4,4,5,5-octa(dimethyl)hexasilane (6).[30] 1,4-Dichlorooctamethyltetrasilane (35 mmol) was dissolved in toluene (60 mL) and cooled to −70 °C. A solution of tris(trimethylsilyl)silylpotassium (70 mmol) in toluene (20 mL) was added dropwise over a period of 30 min. The reaction mixture was allowed to warm to rt, and stirring was continued for 2 h. After complete conversion the solution was poured into aqueous H_2SO_4 (1 M solution, 100 mL) and ice. The layers were separated, the aqueous phase was extracted several times with diethyl ether, the combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was recrystallized with ether/acetone (1:1), and white crystals (mp 272−274 °C) were obtained (84%). ^{29}Si NMR (pentane, D_2O, δ ppm): −9.8; −31.4; −35.8; −128.8. ^{13}C (C_6D_6, δ ppm): 3.4; 1.0; −2.5. ^{1}H (C_6D_6, δ ppm): 0.00 (s, 54H); 0.11 (s, 12H); 0.18 (s, 12H). Anal. Calcd for $Si_{12}C_{26}H_{78}$: C, 42.90; H, 10.80. Found: C, 42.74; H, 10.99.

Methyldiphenylsilylpentakis(trimethylsilyl)disilane (2b). Pentakis(trimethylsilyl)disilanylpotassium was reacted with chloromethyldiphenylsilane as described in the literature for the monosilane derivatives[21] (mp 118−122 °C). ^{29}Si NMR (ethanol, D_2O, δ ppm): −8.2; −8.5; −13.5, −123.3; −126.2. ^{13}C ($CDCl_3$, δ ppm): 139.8; 135.8; 128.9; 127.6; 4.8; 4.7; 2.0. ^{1}H ($CDCl_3$, δ ppm): 7.63 (m, 4H); 7.28 (m, 6H); 0.22 (s, 18H); 0.20 (s, 3H); 0.17 (s, 27H). Anal. Calcd for $Si_8C_{28}H_{58}$: C, 54.29; H, 9.44. Found: C, 53.82; H, 9.32.

1,1,1,3,3-Pentakis(trimethylsilyl)-2,2-dimethyltrisilane (3a). 1,1,3,3,3-Pentakis(trimethylsilyl)-2,2-dimethytrisilanyl potassium (0.50 g, 0.96 mmol) in 5 mL of THF was slowly added to an ice-cold mixture of 10 mL of H_2SO_4 (0.1 N) and 10 mL of ether. The mixture was allowed to come to rt. Then the layers were separated, the aequeous layer was extracted three times with ether, and the combined organic fractions were dried over Na_2SO_4. After removing the solvent white crystals of **3a** (0.43 g, 95%, mp 118−122 °C) were obtained. ^{29}Si NMR (pentane, D_2O, δ ppm): −9.3; −10.4; −33.0; −108.8 ($^{1}J_{\text{Si-H}}$ = 160.3 Hz); −126.5. ^{13}C (C_6D_6, δ ppm): 3.4; 2.8; 1.9. ^{1}H (C_6D_6, δ ppm): 2.84 (s, 1H); 0.55 (s, 6H); 0.34 (s, 27H), 0.31 (s, 18H). Anal. Calcd for $Si_8C_{17}H_{52}$: C, 42.42; H, 10.89. Found: C, 42.17; H, 10.98.

1,5-Bis(triisopropylsilyl)-1,1,5,5,-tetrakis(trimethylsilyl)-2,2,3,3,4,4-hexamethylpentasilane (5a). (Triisopropylsilyl)bis(trimethylsilyl)silylpotassium (20 mmol, 7.42 g) in 40

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mL of toluene was added dropwise at −70 °C to a solution of 1,3-dichlorohexamethyltrisilane (10 mmol, 2.45 g) in 80 mL of toluene. The stirring was continued for 24 h at rt before it was worked up according to the procedure described for **6**. The residue was recrystallized from acetone, and white crystals (mp 212−213 °C) were obtained (70%). ^{29}Si NMR (CDCl$_3$, δ ppm): 14.0; −9.3; −27.7; −31.5; −122.5. ^{13}C (CDCl$_3$, δ ppm): 20.8; 15.3; 5.1; 2.9; −1.5. ^{1}H (CDCl$_3$, δ ppm): 1.29 (m, 6H); 1.20 (d, 36H, J = 6.6 Hz); 0.46 (s, 12H), 0.37 (s, 6H); 0.32 (s, 36H). Anal. Calcd for $Si_{11}C_{36}H_{96}$: C, 51.59; H, 11.55. Found: C, 51.43; H, 11.29.

Acknowledgment. This study was carried out within the START project Chiral polysilanes (Y120) funded by the Austrian Ministry of Education, Science and Culture, and administered by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung. We want to thank Drs. Richard Fröhlich, Roland Fischer, and Christian Mechtler for synthetic help and Mr. Alan Crozier for proofreading the manuscript.

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