Nanoscale Double-Core Oligosilane Dendrimers: Synthesis, Structure, and Electronic Properties

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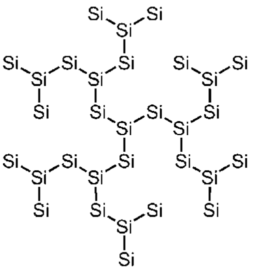
The novel nanoscale double-core oligosilane dendrimers of formula $\{[R(Me_3Si)_2SiMe_2Si]_2SiMeSiMe_2Si(SiMe_3)_2SiMe_2\}_2$ (**3a**, R = Me; **3b**, $SiMe_3$) have been prepared by a new synthetic approach, involving the reaction of $KSi(SiMe_3)_2SiMe_2SiMe_2Si(SiMe_3)_2K$ with $ClMe_2SiSiMe[SiMe_2Si(SiMe_3)_2R]_2$ (**2a**, R = Me; **2b**, R = $SiMe_3$). The X-ray studies reveal both molecules to have longest chains of 14 silicon atoms and totals of 28 (**3a**) and 32 (**3b**) silicon atoms.

Introduction

Three-dimensional silicon nanostructures including network polysilanes,[1] silicon nanocrystals and quantum dots[2] have been the focus of intensive research because of their unique photophysical properties such as intense absorption and luminescence. These properties strongly depend on size and shape (quantum confinement)[3] and also on the surface chemistry (oxide, hydrogen or alkyl termination), the latter in particular when the size of the particle approaches a few nanometers.[4] Controlling exactly these parameters appears to be difficult, mainly because of the lack of appropriate size selective synthetic methods, even though some progress has been made very recently.[5]

In this regard, well-defined oligosilane dendrimers[6,7] in the nanometer regime could be potentially useful molecular models to understand the photophysical properties of silicon nanostructures. They have a highly branched three-dimensional silicon backbone and their size, shape, and substitution pattern can be tuned by the appropriate choice of substituents introduced during the synthetic steps. There are now several single- and double-core oligosilane dendrimers. Among these structurally well-defined nanoscale dendrimers $MeSi\{SiMe_2SiMe[SiMe_2SiMe(SiMe_3)_2]_2\}_3$ (**I**) developed by Sekiguchi[8] and $MeSi[SiMe_2Si(SiMe_3)_2SiMe_2SiMe_2Si(SiMe_3)_3]_3$ (**II**) reported by Lambert[9] are the largest ones that have been synthesized so far. We report herein our first results on the synthesis, structure, and electronic properties of the hitherto largest nanoscale oligosilane dendrimers, one with longest chains of 14 silicon atoms and a total of 32 silicon atoms.



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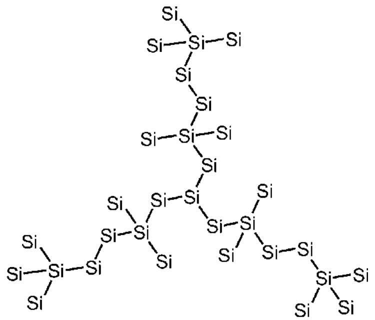

Si = $SiMe_n$; n = 1,2,3

II

Results and Discussion

For the synthesis of the nanoscale dendrimers **3a**,**b** we followed a convergent synthetic approach as outlined in Scheme 1. The chloro-substituted dendrons **2a**,**b** were prepared by reactions of 2 equiv of $KSi(SiMe_3)_2R$ with $MeSi(SiMe_2Cl)_3$. According to a procedure described by Marschner and coworkers,[10] the dipotassiumsilanide **1** was generated by the reaction of 2 equiv of $KOBu^t$ with $(Me_3Si)_3Si(SiMe_2)_2Si(SiMe_3)_3$ at ca. 60 °C in THF. Treatment of the latter solution with 2 equiv of **2a**,**b** at −78 °C furnished the double-core dendrimers **3a** (76%) and **3b** (70%), respectively, as air and thermally stable colorless solids.

The proposed structures of **3a,**b were determined by means of elemental analysis, X-ray crystallography, and multinuclear NMR spectroscopy. The results clearly reveal both dendrimers to have longest chains of 14 silcon atoms and a total of 28 (**3a**) and 32 (**3b**) silicon atoms. They may be described either as dimers of first-generation single-core dendrimers or as first-

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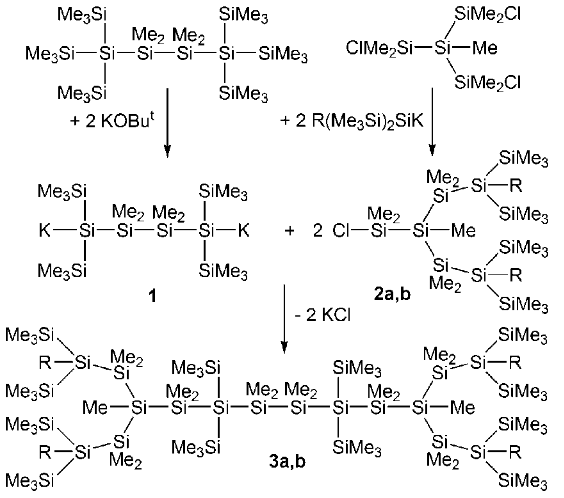
Scheme 1. Synthesis of 3a,b (a; R = Me, b; R = SiMe3)



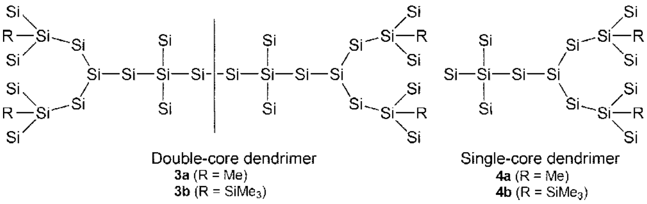
generation double-core dendrimers with two central silicon cores connected by a $SiMe_2Si(SiMe_3)_2(SiMe_2)_2Si(SiMe_3)_2SiMe_2$ spacer group (Scheme 2).

Particularly, ^{29}Si NMR spectroscopy provides useful information about the structure of the oligosilane dendrimers, because it permits us to distinguish between primary (P), secondary (S), tertiary (T), and quaternary (Q) silicon atoms on the basis of chemical shifts. Moreover, empirical rules have been proposed for the assignment of the silicon atoms in linear and branched oligosilanes,[6a,11] which consider the number of silicon atoms in α- and also in β-position on the chemical shift of a given silicon atom. In light of these rules, the chemical shifts of the eight silicon signals that have been found for **3b** in the ^{29}Si NMR spectrum (Figure 1) merit comment.

There are two quaternary silicon atoms; one with one β-silicon at −120.9 ppm and one with two β-silicons at −109.7 ppm, values that are both in good agreement with the expected shifts. The same applies for the chemical shifts of the three secondary and the two primary silicon atoms. The signal of the tertiary silicon core atom at −35.3 ppm, however, appears to be out of the expected range according to the rules proposed by Lambert et al. (ca. from −62 to −69 ppm).[6a] Also the signal of the tertiary silicon core in compound **3a** with −55.7 ppm is slightly downfield shifted. Although we have undertaken several ^{29}Si NMR experiments, including INEPT and DEPT pulse sequences, we could not find any other signals within the expected range of −60 to −80 ppm.

The recently reported single-core dendrimers $MeSi[SiMe_2Si(SiMe_3)_3]_3$ (**4b**)[12] and $MeSi[SiMe_2Si(SiMe_3)_2Me]_2[SiMe_2Si(SiMe_3)_3]$ (**4a**)[13] represent good model compounds for the assignment of silicon signals in the ^{29}Si NMR spectra, as they nicely reflect the substitution pattern of our double-core counterparts **3a** and **3b** (see Scheme 2). Thus, in the ^{29}Si NMR of **4a**, in which the tertiary silicon core atom is surrounded by three β- and seven γ-silicon atoms (symbol T^{3-7}), as much as in **3a**, the corresponding signal was found to be at a similar value (−59.9 ppm). Interestingly, there is a controversy in the literature with respect to the chemical shift of the central silicon core atom in **4b** reported independently by two groups. Whereas Lambert et al.[12a] reported the tertiary silicon core in **4b**, being connected to three β- and nine γ-silicon atoms (symbol T^{3-9}), to appear at −65.0 ppm in C_6D_6, Suzuki et al. [12b] found the latter signal to be at −37.0 ppm in $CDCl_3$, which differs markedly from the former one, but is much closer in chemical shift to the signal of our double-core analogue **3b**. By measuring **3a** again in C_6D_6 as solvent we found almost identical chemical shifts for the central silicon core and also the other silicon atoms as reported by Suzuki et al.[12b]

Scheme 2. Double and Single-Core Dendrimers 3a,b and 4a,b (all methyl groups are omitted for clarity)



The significant differences in chemical shifts, between **3a** and **3b** ($\Delta\delta$ = 20.4 ppm) and also between the model compounds **4a** and **4b** ($\Delta\delta$ = 22.8 ppm), which we think arise from the increased number of attached γ-silicon atoms from seven in **4a** to nine in **4b**, have also been observed in the chloro-substituted dendrimers $ClSi[SiMe_2Si(SiMe_3)_2Me]_3$ (δ_{SiCl} = 2.8 ppm, T^{3-6}) and $ClSi[SiMe_2Si(SiMe_3)_3]_3$ (δ_{SiCl} = 20.5 ppm, T^{3-9}).[14]

This view is further supported by a comparison of the chemical shifts of the silicon core and spacer atoms of single-core oligosilane dendrimers and some branched oligosilanes (Figure 2). The results are summarized in Table 1 and clearly reveal the signal of the tertiary silicon core ($T^{\beta-\gamma}$) to be progressively downfield shifted upon increasing the number of silicon atoms in γ-position from zero (T^{3-0}) to nine (T^{3-9}) with $\Delta\delta$ = 37.1 ppm. Interestingly, the signal of the silicon spacer atom ($S^{\beta-\gamma}$) is only slightly downfield shifted upon increasing the number of silicons in β-position, although these atoms should have a more pronounced effect on the chemical shift compared to the γ-silicon atoms.

According to this extended model, which considers the effect of surrounding α-, β-, and also γ-silicon atoms on the ^{29}Si NMR chemical shift, the data found for the double-core dendrimers **3a** and **3b** match perfectly to those of the corresponding single-core counterparts **4a** and **4b** (Table 1). However, caution must be given when applying these empirical rules because they do not consider effects such as steric interactions and the geometry of the silicon atom that obviously will affect the chemical shift of a given silicon atom in a molecule.

The results of the X-ray analysis of **3a**,**b** indicate steric strain in both molecules (Figures 3 and 4). As in the single-core oligosilane dendrimer **4a**,[13] the three Si−Si bonds emanating from the central core (Si4) in **3a** are elongated with a largest value of 2.391(1) Å for the Si3−Si4 bond. Also the Si1−Si2 [2.399(2) Å] distance within the central spacer group is markedly increased. The steric strain in the molecule is reduced by increasing the angles around the central core (Si4). In particular, the angle between the core and the spacer group Si2−Si3−Si4 is widened to a value of 122.56(6)°. Much stronger steric

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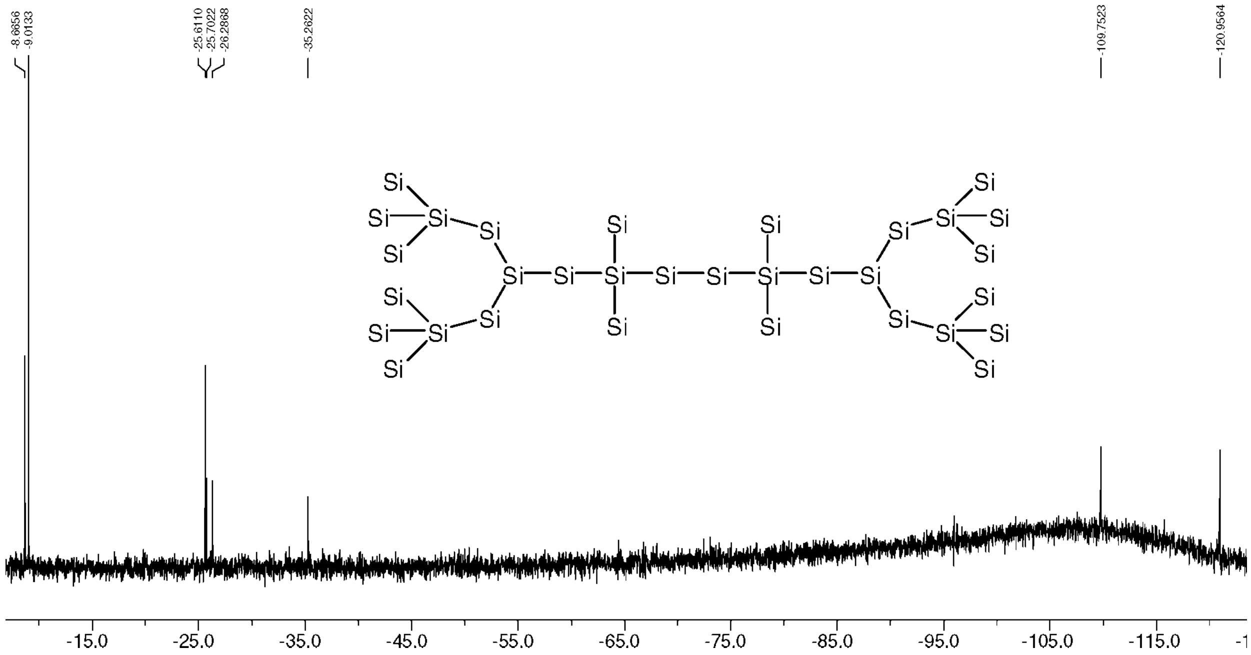

Figure 1. ^{29}Si NMR spectrum of **3b**.

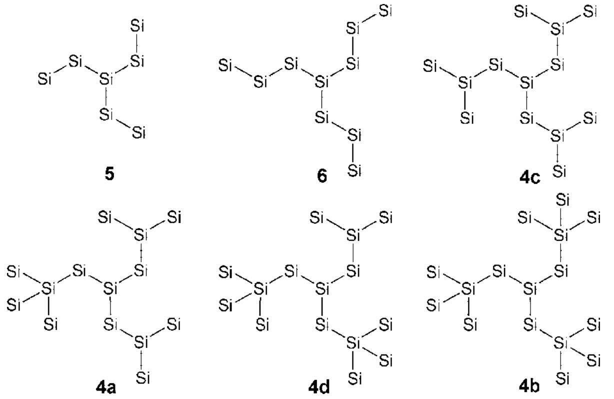

Figure 2. Formulas of the branched oligosilanes **5**, **6**, and **4a**−**d** (Si = SiMe$_n$; n = 1, 2, 3).

Table 1. ^{29}**Si NMR Chemical Shift of Silicon Branch, Spacer, and Cores of Selected Branched Oligosilanes**

compd	solvent	δ SiMe core	symbol $T^{\beta\text{-}\gamma}$	δ SiMe branch	symbol $T^{\beta\text{-}\gamma}$	δ SiMe$_2$ spacer	symbol $S^{\beta\text{-}\gamma}$
5[a]	$CDCl_3$	−74.2	T^{3-0}			−40.2	S^{2-2}
6	C_6D_6	−67.8	T^{3-3}			−35.4	S^{3-2}
4c[16]	C_6D_6	−66.0	T^{3-6}	−80.1	T^{1-2}	−29.8	S^{4-2}
4a[b]	C_6D_6	−59.9	T^{3-7}	−78.3	T^{1-2}	−29.3	S^{4-2}
						−25.1	S^{5-2}
3a	C_6D_6	−55.7	T^{3-7}	−78.2	T^{1-2}	−28.7	S^{4-2}
						−24.7	S^{5-2}
						−26.6	S^{4-4}
4d	C_6D_6	−50.8	T^{3-8}	−79.1	T^{1-2}	−29.3	S^{4-2}
						−25.2	S^{5-2}
4b	C_6D_6	−37.1	T^{3-9}			−25.6	S^{5-2}
3b	C_6D_6	−35.3	T^{3-9}			−25.6	S^{5-2}
						−25.7	S^{5-2}
						−26.3	S^{4-4}

[a] Data taken from ref 15. [b] Data taken from ref 13.

constraints were observed in **3b**; the largest distortion, 131.72(4)°, was found for the Si4−Si3−Si2 angle. The three bonds emanating from the central core atom (Si4) are also elongated: Si3−Si4 2.384(1) Å, Si5−Si4 2.392(1) Å, Si8−Si4 2.387 (1) Å.

A view along the hypothetical Si2−Si2 axes of **3a**,**b** (Figure 5) reveals the most striking difference to be the orientation of dendrimer wings with respect to each other. In **3a** both wings are spatially separated as indicated by an ortho arrangement [Si3−Si2−Si2−Si3, 100.0°] of the Si2−Si2 axis and the large dihedral angle Si1−Si2−Si3−Si4 (176°). In **3b** the conformational arrangement is described best to be gauche with a Si3−Si2−Si2−Si3 dihedral angle of ca. 45° and a relatively small dihedral angle Si1−Si2−Si3−Si4 (85°), which leads to face-to-face orientation of the dendrimer wings.

Space-filling models (Figure 6) show both molecules to be in the nanometer size regime even though shape and size differ considerably. In particular, dendrimer **3b**, with a total of 32 silicon atoms, is worth noting, because it is the largest well-defined oligosilane dendrimer so far observed. In addition, both dendrimer wings are in close proximity to one another, which leads to a more spherical shape (1.6 × 1.4 nm) of the molecule as compared to **3a**. As a result, close trimethylsilyl contacts were noted for the dendrimer wings with intramolecular distances C30−C24 [3.573 Å] and C10−C11 [3.813 Å] being slightly smaller than the sum of the van der Waals radii of two methyl groups, amounting to about 4.0 Å.[17]

It is widely accepted that the elongation of σ-conjugation along the silicon chain in permethylated oligosilanes arises mainly from all-anti conformers, while conformations with small dihedral angles (ω = 0–60°) do not contribute.[18] In our case, however, conformers with exclusively large dihedral angles such as all-anti or all-deviant segments exist only in several hexa- and pentasilane subunits, which in the tetradecasilane chains are interrupted by additional ortho (O) or gauche (G) conformers (Table 2).[19] Interestingly, the conformational arrangement of the longest tetradecasilane chains of **3a** defined by 11 SiSiSiSi dihedral angles differs markedly from that of **3b** in terms of

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(19) The conformations are classified as syn (S, 0°), gauche (G, 60°), ortho (O, 90°), eclipsed (E, 120°), deviant (D, 150°), and anti (A, 180°); see: Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *33*, 821.

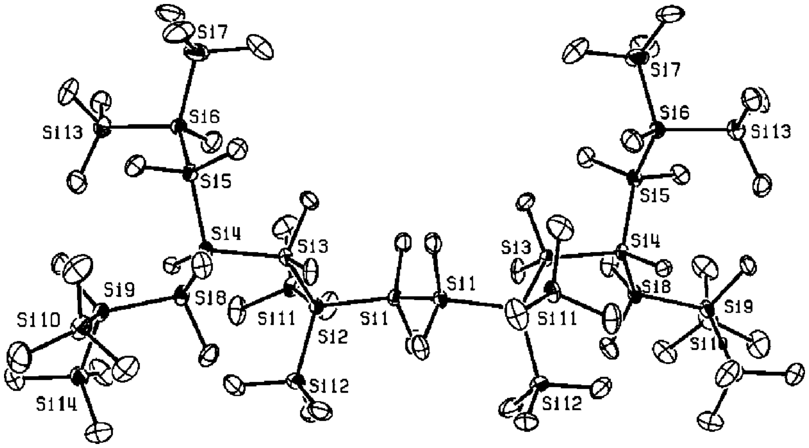

Figure 3. Molecular structure of **3a** in the crystal (ORTEP, 30% probability level, all hydrogen atoms are omitted for clarity). Selected bond lengths [Å] bond angles [deg] and torsion angles [deg]: Si1−Si1 2.381(2), Si1−Si2 2.399(2), Si3−Si4 2.391(1), Si(4)−Si(8) 2.380(1), Si(4)−Si(5) 2.381(1), Si2−Si3−Si4 122.56(6), Si1−Si1−Si2 119.37(8), Si9−Si8−Si4 116.68(6), Si6−Si5−Si4 114.57(6).

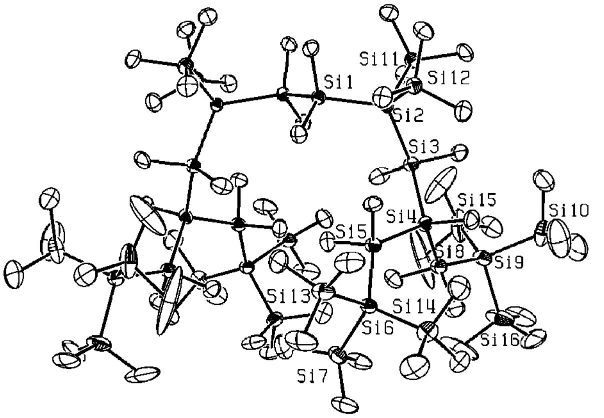

Figure 4. Molecular structure of **3b** in the crystal (ORTEP, 30% probability level, all hydrogen atoms are omitted for clarity). Of the disordered TMS groups around Si15 and Si16/17 only one orientation is shown. Selected bond lengths [Å], bond angles [deg], and dihedral angles [deg]: Si3−Si4 2.384(1), Si5−Si4 2.392(1), Si8−Si4 2.387(1), Si2−Si3 2.392(1), Si2−Si12 2.394(1), Si4−Si3−Si2 131.72(4), Si4−Si5−Si6 127.38(5), Si4−Si8−Si9 127.06(5), Si3−Si2−Si1 119.41(4), Si10−Si9−Si8 118.67(6), Si14−Si6−Si5 118.42(5).

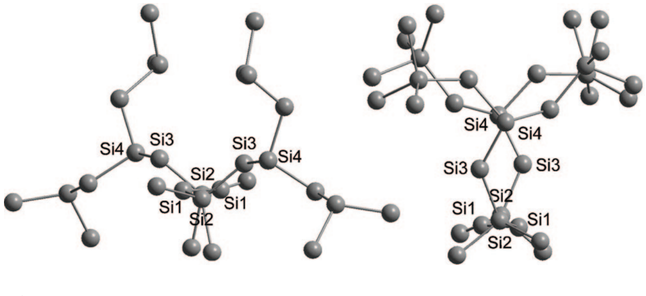

Figure 5. Left: molecular structure of **3a** (Si3−Si2−Si2−Si3 100°, Si1−Si2−Si3−Si4 176°); right: molecular structure of **3b** (Si3−Si2−Si2−Si3 45°, Si1−Si2−Si3−Si4 85°). All methyl groups are omitted for clarity.

the number of large dihedral angles such as deviant (D, ~150°) and anti (A, ~180°). In fact, dendrimer **3a** was found to have a DODAGDGADOD conformation, whereas **3b** exhibits a DGAOGDGOAGD conformation, which clearly reflects the predominance of deviant and anti segments in **3b** (Table 2). Note that the calculated average Si−Si distances of each of the tetradecasilane chains lie unremarkably within the relatively narrow range of 2.375–2.384 Å, suggesting only minimal influence of Si−Si bond stretching on the energy of the $\sigma-\sigma^*$ transition.[20] In the dendrimer wings of **3a**,**b** and in the single-core dendrimers **4a**,**b**, however, the heptasilane subunits have very similar conformations, again with a predominance of deviant and anti segments, but the range of the calculated average Si−Si distances in these chains is larger.

To study the influence of the conformational arrangement of **3a**,**b** on the electronic properties, UV spectroscopic measurements have been performed in solution and in the solid state as well. The spectra of **3a**,**b** together with those of the parent single-core dendrimers **4a**−**c** at 293 K are shown in Figures 7 and 8, and the data are summarized in Table 3. In the solid-state UV spectra (diffuse reflectance), the band gaps of the dendrimers become smaller in the order **4a** ≈ **4b** ≈ **4c** > **3b** > **3a**. The smaller band gap of **3a** relative to **3b** is in accordance with the results of our conformational analysis and again reveals that conformers mainly consisting of anti or deviant segments exhibit lower singlet excitation energies than those having more gauche and ortho defects in the longest chain. The fact that the band gaps of **3a**,**b** are significantly larger relative to **4a**−**c** is mainly attributable to the tremendous difference in size and silicon chain length.

Rather similar trends are seen in solution; the absorption maxima of **3a**,**b** are intense but very broad owing to the high redundancy of Si−Si chains within these molecules. This results in a statistical distribution of flexible conformers, which contribute differently to the energy of the $\sigma-\sigma^*$ transition. Thus, **3b** exhibits a broad maximum at 269 nm ($\epsilon = 1.3 \times 10^5$), whereas the absorption maximum of **3a** is shifted to longer wavelength by ca. 5 nm ($\lambda_{\max} = 274$ nm, $\epsilon = 1.3 \times 10^5$).

It is worth noting that the extinction coefficients of the double-core dendrimers **3a**,**b** are more than twice as large as those of the single-core dendrimers **4a**,**b**, which again arises from size effects. The absorption maxima of **3a**,**b**, however, are only slightly red-shifted toward **4a**−**c** and are blue-shifted with respect to the linear permethylated dodecasilane, $Si_{12}Me_{26}$,[21] Sekiguchi's second-generation dendrimer MeSi{$SiMe_2SiMe$-[$SiMe_2SiMe(SiMe_3)_2]_2$}$_3$ (**I**) ($\lambda_{\max} = 279$ nm, $\epsilon = 9.6 \times 10^4$), and Lambert's compound MeSi[$SiMe_2Si(SiMe_3)_2SiMe_2SiMe_2Si$-$(SiMe_3)_3]_3$ (**II**) ($\lambda_{\max} = 285$ nm, $\epsilon = 1.2 \times 10^5$). These

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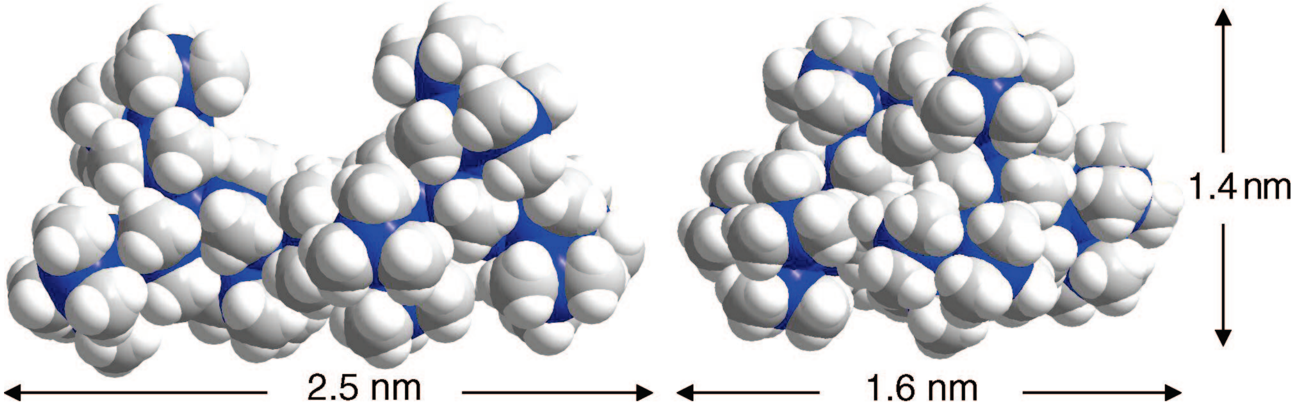

Figure 6. Space-filling models of the dendrimer **3a** (left), **3b** (right): blue, silicon; light gray, carbon; white, hydrogen.

Table 2. Conformations of Some Selected Tetradecasilane and Heptasilane Chains of 3a,b and 4a,b

compd	tetradecasilane chain	dihedral angle	symbol	av Si−Si distance
3a	7–6–5–4–3–2–1–1–2–3–4–5–6–7	154–89–147–175–50–164–50–175–147–89–154	DODAGDGADOD	2.375
	10–9–8–4–3–2–1–1–2–3–4–8–9–10	155–163–98–175–50–164–50–175–98–163–155	DDOAGDGAODD	2.377
3b	16–9–8–4–3–2–1–1–2–3–4–8–9–16	152–53–172–85–68–161–68–85–172–53–152	DGAOGDGOAGD	2.384
	13–6–5–4–3–2–1–1–2–3–4–5–6–13	153–180–46–85–68–161–68–85–46–180–153	DAGOGDGOGAD	2.382
compd	heptasilane chain	dihedral angle	symbol	av Si−Si distance
3a	7–6–5–4–8–9–10	154–153–81–155	DDOD	2.361
3b	16–9–8–4–5–6–13	152–177–57–153	DAGD	2.377
4a[a]	7–6–5–4–11–12–13	180–147–82–156	ADOD	2.374
4b[b]		157–173–64–157	DDOD	2.357
4b[c]		152–177–62–152	DAGD	2.393

[a] Taken from ref 13. [b] Taken from ref 12c. [c] Taken from ref 12b.

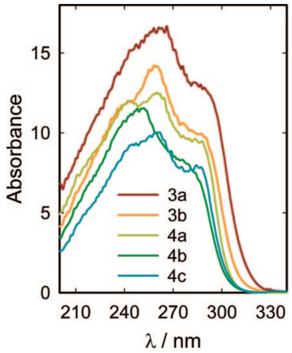

Figure 7. Solid-state UV spectra (diffuse reflectance) of **3a**,**b** and **4a**−**c**.

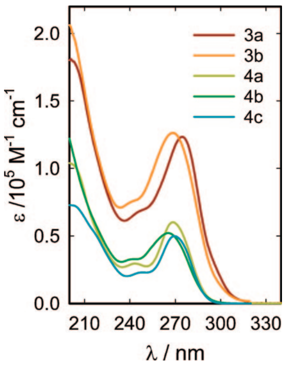

Figure 8. UV spectra of **3a**,**b** and **4a**−**c** (*n*-heptane solution).

observations are inconsistent with the fact that the energy of the absorption maximum decreases with increasing chain length of the oligosilane chain. The conformational analysis of the longest chains does not show any remarkable differences between these nanoscale dendrimers. Moreover, in all molecules,

Table 3. UV Spectroscopic Properties of 3a,b and 4a−c

compd	λ_{max} [nm] (solution)	ϵ [$M^{-1}cm^{-1}$] (solution)	band gap [nm] (solution)	band gap [nm] (solid state)
3a	274	1.2×10^5	~ 298	~ 315
3b	269	1.3×10^5	~ 297	~ 310
4a[a]	269	6.0×10^4	~ 290	~ 304
4b[a]	265	5.2×10^4	~ 290	~ 303
4c[a]	269	5.0×10^4	~ 291	~ 304

[a] Data taken from ref 13.

conformers with exclusively large dihedral angles such as all-anti or all-deviant segments exist only in some subunits, which are interrupted by ortho (O) or gauche (G) links. We assume particularly incorporated quaternary silicon atoms to be ineffective toward the delocalization of σ-electrons (σ-conjugation) along the longest oligosilane chains in **3a**,**b**. Theoretical and experimental investigations on smaller model compounds with respect to the latter are currently underway.

Interestingly, the broad absorption maxima of colloidal solutions of 1-heptene-capped silicon nanocrystals (size between 1 and 2 nm)[22] in *n*-hexane were found to be at ca. 250–260 nm, rather similar to the broad maxima of our dendrimers. When excited at ca. 300 nm, these nanocrystals exhibit a blue luminescence which is significantly red shifted upon increasing the energy of excitation. In our case, however, a rather weak dual luminescence in the visible (broad at 450–460 nm) and at 330 nm was observed for **3a**,**b** and also **4a–c** at room temperature (Figure 9).[23]

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(23) A similar weak dual luminescence at ca. 350 and 450 nm was observed for the single-core dendrimer **4c**, with a quantum yield of 0.014 at 77 K; see also ref 15.

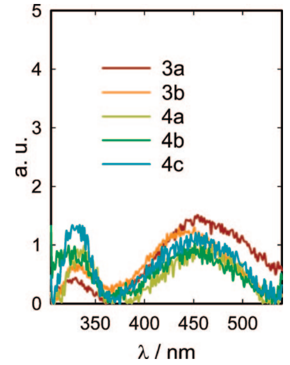

Figure 9. Room-temperature emission spectra of **3a**,**b** and **4a**−**c** (ca. 10^{-5} M *n*-heptane solutions).

Conclusion

We have developed a new synthetic approach to the hitherto largest double-core oligosilane dendrimers with longest chains of 14 silicon atoms. The structures of these compounds have been unambiguously identified by X-ray crystallography and by ^{29}Si NMR spectroscopy. Considering the marked influence of surrounding γ-silicon atoms on the chemical shift of a given silicon atom, we were able to assign all the silicon signals observed in the ^{29}Si NMR spectrum. These nanoscale molecules exhibit a weak dual luminescence and very broad and intense absorptions in the near UV, of which the latter arise from a variety of different conformers, according to the X-ray data.

Experimental Section

General Procedure. All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk and glovebox techniques. THF and *n*-pentane were distilled under argon from alkali metals prior to use. Acetonitrile was distilled under argon from CaH_2 and stored over activated molecular sieves. Benzene-d_6 was dried over activated molecular sieves and stored in the glovebox. The compounds $Si(SiMe_3)_4$,[24] $MeSi(SiMe_2Cl)_3$,[25] $Si(SiMe_3)_2Ph_2$,[26] $(Me_3Si)_3Si(SiMe_2)_2Si(SiMe_3)_3$,[10] and $ClMe_2SiMeSi[SiMe_2Si(SiMe_3)_2Me]_2$ (**2a**)[7c] were synthesized according to literature procedures. The potassium silanides $KSi(SiMe_3)_2Me$ and $KSi(SiMe_3)_3$ have been prepared according to a procedure described by Marschner.[27] The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained using Bruker AC 250 and ARX 300 spectrometers at 300 K if not otherwise stated. Microanalyses were carried out with a C/H/N/S- Thermoquest Flash EA 1112 analyzer by addition of V_2O_5 (**3a** and **3b**) and Pb_3O_4 for silicon-containing compounds. MS: Intectra AMD 402. UV/vis: Perkin-Elmer Lambda 2, quartz cells of 1.0 cm path length, and spectral grade *n*-heptane. The diffuse reflectance UV measurements were carried out with a Perkin-Elmer Lambda 20.

4-Chlorodimethylsilyl-1,1,1,3,3,4,5,5,7,7,7-undecamethyl-2,2,6,6-tetrakis(trimethylsilyl)heptasilane (2b). In a Schlenk flask with magnetic stirrer were placed rapidly $Si(SiMe_3)_4$ (3.21 g, 10 mmol) and Bu^{t}OK (1.12 g, 10 mmol). The flask was evacuated and refilled with argon three times, THF (ca. 20 mL) was added, and the yellow solution of $KSi(SiMe_3)_3$ formed within several hours was stirred overnight. The solvent was replaced by *n*-pentane, and the resulting solution was slowly added to a vigorously stirred *n*-pentane solution of $(ClMe_2Si)_3SiMe$ (1.94 g, 6 mmol) at −78 °C. After stirring for 30 min at −78 °C, the mixture was allowed to warm to room temperature within 2 h. Filtration of the resulting suspension and removal of the solvent from the filtrate gave a white solid, which was kept under vacuum (10^{-2} mbar, 180 °C) for several hours to remove volatile byproduct. The resulting residue was suspended in dry acetonitrile, filtered, and dried under vacuum to give the title compound as a white solid. Yield 4.26 g (95%). ^{1}H NMR (C_6D_6, 250 MHz): δ 0.67, 0.66, 0.64 (3s, $SiMe_2$, 3 × 6 H), 0.39 (s, SiMe, 3 H), 0.36 (s, $SiMe_3$, 54 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 6.9 ($SiMe_2Cl$), 4.6, 4.1 ($SiMe_2$), 4.0 ($SiMe_3$), −5.6 (SiMe) ppm. ^{29}Si NMR (C_6D_6, MHz): δ 30.4 ($SiMe_2Cl$), −9.2 ($SiMe_3$), −25.6 ($SiMe_2$), −63.6 (SiMe), −122.6 ($\underline{Si}Si_4$) ppm. Anal. Calc for $C_{25}H_{75}ClSi_{12}$ (748.34): C 40.12, H 10.10. Found: C 39.88, H 10.08.

General Procedure for the Synthesis of the Double-Core Dendrimers 3a,b. A THF solution of $K(Me_3Si)_2Si(SiMe_2)_2Si(SiMe_3)_2K$ was generated by reacting $(Me_3Si)_3Si(SiMe_2)_2Si(SiMe_3)_3$ with 2 equiv of Bu^{t}OK in THF for ca. 12 h at 60–65 °C. This solution was cooled to −78 °C, and 2 equiv of **2a** or **2b** dissolved in *n*-pentane was added. After stirring for 2 h at −78 °C, the reaction mixture was allowed to warm to room temperature. Water was added to the resulting suspension, the organic layer was separated, and the aqueous layer was extracted twice with pentane. The combined organic extracts were dried over $MgSO_4$, filtered, concentrated, and kept overnight under vacuum (10^{-2} mbar, 170 °C) to remove volatile byproduct. The solid residues were suspended in acetone, filtered, and dried under vacuum to afford the title compounds as white solids. Recrystallization from ethyl acetate gave analytically pure samples.

1,1,1,2,3,3,4,5,5,7,7,8,8,10,10,11,12,12,13,14,14,14-Docosamethyl-2,6,6,9,9,13-hexakis(trimethylsilyl)-4,11-bis[1′,1′,2′,3′,3′,3′hexamethyl-2′-trimethylsilyltrisilanyl]tetradecasilane (3a). $(Me_3Si)_3Si(SiMe_2)_2Si(SiMe_3)_3$ (0.4 g, 0.65 mmol), Bu^{t}OK (0.15 g, 1.34 mmol), and **2a** (0.87 g, 1.38 mmol). Yield 0.77 g (76%). Mp 179 °C. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.80, 0.77, 0.66, 0.63, (4s, $SiMe_2$, 4 × 12 H), 0.44 (s, SiMe, 12 H), 0.76 (s, SiMe, 6 H), 0.48 (s, $SiMe_3$, 36 H), 0.31, 0.30 (2s, $SiMe_3$, 2 × 36 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz):δ 6.0, 3.5, 3.1, 2.9 ($SiMe_2$), 5.1 $[Si(SiMe_3)_2]$, 1.4 [two signals for $Si(Si\underline{Me_3})_2Me$], −4.0 (SiMe), −9.1 $[Si(SiMe_3)_2\underline{Me}]$ ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz, 313 K): δ −9.1, −11.0, −11.2 ($SiMe_3$), −24.7, −26.6, −28.7 ($SiMe_2$), −55.7, −78.2 (SiMe), −109.7 ($\underline{Si}Si_4$) ppm. Anal. Calc for $C_{58}H_{174}Si_{28}$ (1658.41): C 42.01, H 10.58. Found: C 41.68, H 10.63.

1,1,1,3,3,4,5,5,7,7,8,8,10,10,11,12,12,14,14,14-Eicosamethyl-2,2,6,6,9,9,13,13-octakis(trimethylsilyl)-4,11-bis[1′,1′,3′,3′,3′-pentamethyl-2′,2′-bis(trimethylsilyl)trisilanyl]tetradecasilane (3b). $(Me_3Si)_3Si(SiMe_2)_2Si(SiMe_3)_3$ (0.384 g, 0.63 mmol), Bu^{t}OK (0.143 g, 1.28 mmol), and **2b** (0.97 g, 1.29 mmol). Yield 0.83 g (70%). Mp 227 °C. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.88, 0.83, 0.80, 0.79 (4s, $SiMe_2$, 4 × 12 H), 0.83 (s, SiMe, 6 H), 0.50 (s, $SiMe_3$, 36 H), 0.41 (s, $SiMe_3$, 108 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 6.9, 6.2, 6.0, 3.6 ($SiMe_2$), 5.3 $[Si(SiMe_3)_2]$, 4.4 $[Si(SiMe_3)_3]$, −3.8 (SiMe) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −8.7, −9.0 ($SiMe_3$), −25.6, −25.7, −26.3 ($SiMe_2$), −35.3 (SiMe), −109.7, −120.9 ($\underline{Si}Si_4$) ppm. Anal. Calc for $C_{66}H_{198}Si_{32}$ (1891.03): C 41.92, H 10.55. Found: C 41.51, H 10.51.

1,1,1,2,2,3,3,4,5,5,6,6,7,7,7-Pentadecamethyl-4-[1′,1′,2′,2′,3′,3′,3′-heptamethyltrisilanyl]heptasilane (5). In a Schlenk flask with magnetic stirrer were placed rapidly Bu^{t}OK (1.705 g, 15.2 mmol) and $Ph_2Si(SiMe_3)_2$ (5 g, 15.2 mmol). The flask was evacuated and refilled with argon three times, THF was added, and the colored solution immediately formed was stirred overnight. After replacing the solvent by pentane, the resulting solution was cooled to −78°C, $MeSi(SiMe_2Cl)_3$ (1.49 g, 4.61 mmol) dissolved in pentane was added, and stirring was continued for additional 30 min at −78 °C. Subsequently, the reaction mixture was allowed to warm to room temperature, water was added, the organic layer was separated, and the aqueous layer was extracted twice with pentane. The combined organic extracts were dried over $MgSO_4$ and filtered,

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the solvent was evaporated, and the residue was dried under vacuum (0.01 mbar, 100 °C). The solid crude product was recrystallized from acetone to give 3.12 g (69%) of $MeSi[SiMe_2Si(SiMe_3)Ph_2]_3$. ^1H NMR (C_6D_6, 250 MHz): δ 7.67–7.64, 7.22–7.14 (m, phenyl, 30 H), 0.41 (s, SiMe, 3 H), 0.23 (s, $SiMe_2$, 18 H), 0.13 (s, $SiMe_3$, 27 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 136.6, 136.1, 128.8, 128.2 (C arom.), 0.0 ($SiMe_3$), −0.1 ($SiMe_2$), −6.0 (SiMe). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −35.8 ($SiMe_2$), −32.9 (SiPh), −13.8 ($SiMe_3$) −57.9 (SiMe). Anal. Calc for $C_{52}H_{78}Si_{10}$ (984.04): C, 63.47; H, 7.99. Found: C, 63.14; H, 7.92.

Then freshly distilled TfOH (0.4 mL, 4.56 mmol) was added to a stirred solution of $MeSi[SiMe_2Si(SiMe_3)Ph_2]_3$ (0.675 g, 0.69 mmol) in pentane (10 mL) at room temperature, and stirring was continued for 2 days. After replacing the solvent by diethyl ether, an ethereal solution of MeLi (1.6 M, 3.3 mL) was added, and stirring was continued for additional 2 days. After adding water to the stirred solution, the organic layer was separated and the aqueous layer was extracted twice with pentane. The combined organic extracts were dried over $MgSO_4$, filtered, concentrated, and dried under vacuum. Column chromatography on silica gel (*n*-heptane) followed by Kugelrohr distillation (0.01 mbar, 180–190 °C) afforded the title compound **5** as a white solid. Yield 0.37 g (88%). Mp 47 °C. ^1H NMR (C_6D_6, 250 MHz): δ 0.46 (s, SiMe, 3 H), 0.44, 0.32 (2s, $SiMe_2$, 2 × 18 H), 0.20 (s, $SiMe_3$, 27 H). ^{13}C NMR (C_6D_6, 75.5 MHz): δ −0.9, −4.6 ($SiMe_2$), −0.9 ($SiMe_3$), −7.6 (SiMe). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −14.4 ($SiMe_3$), −35.4, −41.8 ($SiMe_2$), −67.8 (SiMe). Anal. Calc for $C_{22}H_{66}Si_{10}$ (611.12): C, 43.20; H, 10.88. Found: C, 42.79; H, 10.89.

1,1,1,3,3,4,5,5,7,7,7-Undecamethyl-2,2,6,6-tetrakis(trimethylsilyl)-4-[2′-trimethylsilyl-1′,1′,2′,3′,3′,3′-hexamethyltrisilanyl]heptasilane (4d). A solution of **2b** (1.0 g, 1.34 mmol) in *n*-pentane (10 mL) was transferred via a cannula to a stirred *n*-pentane solution of $KSi(SiMe_3)_2Me$ [derived from $Si(SiMe_3)_3Me$ (0.433 g, 1.65 mmol) and Bu^tOK (0.185 g, 1.65 mmol) in THF] at −78 °C. After it had been stirred for 30 min at −78 °C, the reaction mixture was allowed to warm to room temperature. After adding water to the stirred suspension, the organic layer was separated and the aqueous layer was extracted twice with pentane. The combined organic extracts were dried over $MgSO_4$ and filtered, and the solvent was evaporated. Recrystallization of the residue from acetone afforded 0.83 g (69%) of the title compound. Mp 162 °C. ^1H NMR (C_6D_6, 250 MHz): δ 0.74 (s, SiMe, 3 H), 0.73, 0.71, 0.63 (3s, $SiMe_2$, 3 × 6 H), 0.42 (s, SiMe, 3 H), 0.39 (s, $Si(SiMe_3)_3$, 54 H), 0.30 (s, $Si(SiMe_3)_2$, 18 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 5.5, 5.3, 3.1 ($SiMe_2$), 4.4, 1.4 ($SiMe_3$), −3.9, −8.9 (SiMe) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −9.1, −11.1 ($SiMe_3$), −25.2, −29.3, ($SiMe_2$), −50.8, −78.3 (SiMe), −121.8 ($\underline{Si}Si_4$) ppm. Anal. Calc for $C_{32}H_{96}Si_{15}$ (902.387): C 42.59, H 10.72. Found: C 42.31, H 10.68.

Crystal Data. For both materials crystallization was difficult and many crystals were checked for good diffraction quality. The best obtained data are given below, even though internal *R*-values are still high.

3a: CCDC 642473: The crystal was fixed with a perfluoropolyether on a tip of a thin glass rod. Intensity data of this crystal were collected on a Bruker X8 APEX-diffractometer with CCD camera at 173(2) K, Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. Formula: $C_{58}H_{174}Si_{28}$, M = 1658.41 g/mol, colorless block, crystal dimensions 0.21 × 0.18 × 0.04 mm, monoclinic, space group *C*2/*c*, Z = 4, a = 24.622(2), b = 14.719(2), c = 32.450(3) Å, β = 111.040(6)°, V = 10977(2) Å^3, ρ_{calc} = 1.004 g·cm^{-3}, μ = 0.345 mm^{-1}, 90 565 measured reflections, 14 297 independent reflections (R_{int} = 0.1094), 388 parameters, R1(F) = 0.0650 for 5984 reflections with $I > 2\sigma(I)$ and wR2(F^2) = 0.1819 for all data, residual electron density highest peak 1.774 (1.3 Å apart from Si13) and deepest hole −0.534 e$^-$/Å^3.

3b: CCDC 642472: The crystal was fixed with a perfluoropolyether on a tip of a thin glass rod. Intensity data of this crystal were collected on a Bruker X8 APEX-diffractometer with CCD camera at 213(2) K, Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. Formula: $C_{66}H_{198}Si_{32}$, M = 1891.12 g/mol, colorless block, crystal dimensions 0.30 × 0.26 × 0.19 mm, monoclinic, space group *C*2/*c*, Z = 4, a = 26.6853(6), b = 14.9164(3), c = 32.2051(8) Å, β = 100.476(1)°, V = 12605.5(5) Å^3, ρ_{calc} = 0.996 g·cm^{-3}, μ = 0.343 mm^{-1}, 43 733 measured reflections, 12 198 independent reflections (R_{int} = 0.0560), 501 parameters, R1(F) = 0.0814 for 7384 reflections with $I > 2\sigma(I)$ and wR2(F^2) = 0.2364 for all data, residual electron density highest peak 1.604 (1.0 Å apart from Si5) and deepest hole −0.843 e$^-$/Å^3. Two of the outbound TMS groups show some disorder. The methyl groups around Si15 are refined as two sets rotated around the Si15−Si9 bond with a 30%–70% distribution. Another TMS group connected to Si9 is disordered on two sites (Si16 and Si17) with an occupation of 76% of the Si16-centered TMS group (and 24% Si17). For the refinement of these disordered groups, bond length constraints were used to keep the geometry tetrahedral.

Supporting Information Available: Crystallographic data for **3a** and **3b** (including CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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