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Syntheses, Structures, and Reactions of 2,2,3,3-Tetrakis(trifluoromethanesulfonato)tetrasilanes: Hexacoordination ([4 + 2] Coordination) of the Two Central Silicon Atoms

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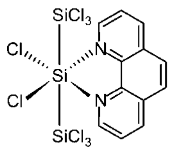
The 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes $RMe_2Si-Si(OTf)_2-Si(OTf)_2-SiMe_2R$ (OTf = OSO_2CF_3; **4a**, R = Me; **4b**, R = Et; **4c**, R = *t*-Bu), a series of novel 2,2,3,3-tetrafunctionalized tetrasilanes, were synthesized by reaction of the respective 2,2,3,3-tetraphenyltetrasilanes **3a**−**3c** with trifluoromethanesulfonic acid. The structural characterization of **4a**−**4c** by single-crystal X-ray diffraction revealed a distorted octahedral coordination (distorted tetrahedral coordination, with the capping of two of the tetrahedral faces by oxygen atoms opposite short Si−O bonds) of the two central silicon atoms due to Si•••O interactions with one oxygen atom of each of the two trifluoromethanesulfonato groups on the adjacent silicon atom. As demonstrated by the reaction of **4a** with methylmagnesium chloride, acetyl chloride, and 2-propanol, the title compounds can serve as versatile starting materials for the synthesis of other 2,2,3,3-functionalized tetrasilanes.

Introduction

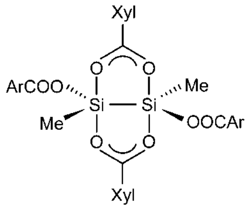
The chemistry of higher-coordinate silicon compounds has been studied extensively due to their interesting structural and chemical properties and because they may serve as useful materials for practical applications.[1] In particular, di- and oligosilanes containing higher-coordinate silicon atoms in the silicon backbone are of interest because they might have unique physical and chemical properties arising from altered Si−Si bond lengths, Si−Si−Si bond angles, conformations, and electronic structures of the silicon chain.[2] Although it is difficult to synthesize di- and oligosilanes with higher-coordinate silicon atoms (because Si−Si bond cleavage occurs more easily due to the activation of Si−Si bonds by hypercoordination of silicon),[3] some examples of this particular type of structure have been reported (e.g., compounds **A**,[4e] **B**,[6c] and **C**;[6a] Chart 1), including (i) di- and trisilanes with one penta- or hexacoordinate silicon atom,[4] (ii) tetrasilanes in which two pentacoordinate silicon atoms are directly connected to each other in position 2 and 3 of the silicon backbone,[5] (iii) disilanes in which penta- or heptacoordinate silicon atoms with μ_2-bridging ligands are directly connected to each other,[6] and (iv) tri-, tetra-, and pentasilanes with two pentacoordinate silicon atoms that are

Chart 1



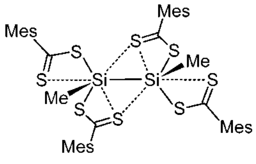
A

Hexacoordination



B

Pentacoordination



C

Heptacoordination

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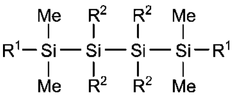
10.1021/om800332j CCC: $40.75

Chart 2



(OTf = OSO$_2$CF$_3$)

	R¹	R²
3a	Me	Ph
4a	Me	OTf
3b	Et	Ph
4b	Et	OTf
3c	*t*-Bu	Ph
4c	*t*-Bu	OTf

connected by one or two tetracoordinate silicon atoms.[7] However, the existence of oligosilanes in which hexacoordinate silicon atoms are directly connected to each other has not yet been established unequivocally.[8] In order to synthesize such compounds, we chose the trifluoromethanesulfonato group as a potential μ_2-bridging ligand. This particular substituent can be selectively introduced without Si−Si bond cleavage by reaction of the respective phenyl-substituted oligosilanes with trifluoromethanesulfonic acid.[9]

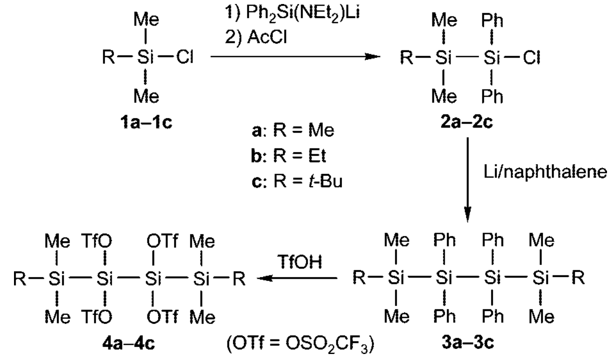
We present herein the synthesis of the novel 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes **4a**−**4c** by reaction of the corresponding 2,2,3,3-tetraphenyltetrasilanes **3a**−**3c** with trifluoromethanesulfonic acid (Chart 2). Compounds **4a**−**4c** were characterized by NMR spectroscopy in solution (^{1}H, ^{13}C, ^{19}F, ^{19}Si), elemental analyses (C, H), and single-crystal X-ray diffraction. Preliminary results of these studies have already been reported elsewhere.[10]

Results and Discussion

The title compounds, the 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes **4a**−**4c**, were synthesized according to Scheme 1. The preparation of the corresponding starting materials, the 2,2,3,3-tetraphenyltetrasilanes **3a**−**3c**, was accomplished by using a method reported by Tamao et al.[11] Thus, treatment of the chlorosilanes **1a**−**1c** with Ph$_2$Si(NEt$_2$)Li, followed by reaction with acetyl chloride, gave the corresponding chlorodisilanes **2a**−**2c**, which upon reductive coupling with lithium/naphthalene afforded **3a**−**3c**. Treatment of the 2,2,3,3-tetraphenyltetrasilanes **3a**−**3c** with an excess of trifluoromethanesulfonic acid in *n*-pentane gave the corresponding 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes **4a**−**4c**.

Compounds **4a** and **4b** were isolated as crystalline solids, whereas the bulk material of **4c** was obtained as an oily product that was contaminated with trifluoromethanesulfonic acid. All three 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes are extremely air- and moisture-sensitive and extremely difficult to handle. Nevertheless, the identities of **4a**−**4c** could be established by solution NMR studies (^{1}H, ^{13}C, ^{19}F, ^{19}Si; solvent, CDCl$_3$; 22 °C) and elemental analyses (C, H; except for compound **4c**, which was not analytically pure). In addition, in all cases single crystals could be grown, and **4a**−**4c** could be studied by crystal structure analyses. However, all attempts to further characterize **4a**−**4c** (e.g., determination of melting points and solid-state NMR studies) failed due to the extreme air- and moisture-sensitivity.

Scheme 1



Compounds **4a**−**4c** quickly decompose upon dissolution in tetrahydrofuran and diethyl ether. They are almost insoluble in nonpolar organic solvents, such as toluene and *n*-hexane, but soluble in di- and trichloromethane. The solution NMR studies were performed with CDCl$_3$ as the solvent. The ^{19}Si chemical shifts of the two central silicon atoms of **4a** (δ, −6.96 ppm), **4b** (δ, −6.62 ppm), and **4c** (δ, −8.17 ppm) are very similar, suggesting the environment of these atoms is similar in solution. However, as suitable comparative data are not available, no conclusions can be drawn from these chemical shifts in terms of potential intramolecular Si···O interactions as observed in the crystal (see below).

Compounds **4a**−**4c** were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for the crystal structure analyses are given in Table 1; selected interatomic distances and angles are listed in Table 2. The molecular structures of **4a**−**4c** in the crystal are shown in Figures 1–3.

The crystal structure analyses of **4a**−**4c** revealed a distorted octahedral coordination of the central silicon atoms Si2 and Si2* (Figures 1–4). Alternatively, the coordination of the two central silicon atoms could also be described in terms of a distorted tetrahedral coordination, with the capping of two of the tetrahedral faces by oxygen atoms opposite short Si−O bonds. Interestingly, one of the sulfonato oxygen atoms of each of the four trifluoromethanesulfonato groups is always located on the opposite side of an Si−O bond of the adjacent silicon atom (Figure 4), and the distances Si2···O2* (Si2*···O2) and Si2···O5* (Si2*···O5) are 2.7646(7)−2.8389(15) and 2.7149(10)−2.8464(7) Å, respectively (Table 2). These interatomic Si···O distances are considerably shorter than the sum of the van der Waals radii (3.6 Å), indicating intramolecular Si···O interactions in the crystal. As a consequence, the Si1−Si2−Si2* (Si1*−Si2*−Si2) bond angles of **4a**−**4c** are considerably increased (135.37(2)−136.18(3)°) compared to those found for the tetrasilane **3a** (Si−Si−Si, 112.1(1)−112.5(1)°)[12] or for the pentasilane chain of (Me$_3$Si)$_2$Si(OTf)−SiMe$_2$−Si(OTf)(SiMe$_3$)$_2$ (Si−Si−Si, 109.80(5)−118.90(5)°),[13] which is the only example of a crystal structure of a trifluoromethanesulfonato-substituted oligosilane described so far. Compared to the central Si−Si bond lengths of **3a** (2.362(3)−2.371(3) Å),[12] the Si2−Si2* distances

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Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 4a−4c

	4a	4b	4c
empirical formula	$C_{10}H_{18}F_{12}O_{12}S_4Si_4$	$C_{12}H_{22}F_{12}O_{12}S_4Si_4$	$C_{16}H_{30}F_{12}O_{12}S_4Si_4$
formula mass, g mol^{-1}	798.84	826.90	883.00
collection *T*, K	100(2)	193(2)	99(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	triclinic
space group (No.)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a, Å	9.30430(10)	10.7212(13)	9.6079(2)
b, Å	9.90300(10)	16.622(3)	10.0188(2)
c, Å	9.99230(10)	9.9668(15)	11.4265(3)
α, deg	115.9060(10)	90	96.9680(10)
β, deg	103.3100(10)	117.099(14)	112.9090(10)
γ, deg	106.9050(10)	90	114.3600(10)
V, Å^3	720.892(13)	1581.2(4)	869.32(3)
Z	1	2	1
D(calcd), g cm^{-3}	1.840	1.737	1.687
μ, mm^{-1}	0.625	0.573	0.527
F(000)	402	836	450
cryst dimens, mm	0.46 × 0.37 × 0.30	0.5 × 0.4 × 0.4	0.30 × 0.30 × 0.28
2θ ranges, deg	4.84−57.10	4.90−55.78	4.74−66.52
index ranges	$-11 \leq h \leq 12$,	$-14 \leq h \leq 14$,	$-14 \leq h \leq 14$,
	$-13 \leq k \leq 12$,	$-21 \leq k \leq 21$,	$-15 \leq k \leq 15$,
	$-13 \leq l \leq 13$	$-12 \leq l \leq 12$	$-17 \leq l \leq 17$
no. of collected reflns	21 943	19 079	49 724
no. of indep reflns	3565	3698	6592
R_{int}	0.0457	0.0373	0.0432
no. of reflns used	3565	3698	6592
no. of params	193	202	222
S^a	1.069	1.119	1.033
weight params *a/b*^{b}	0.0293/0.3880	0.0339/1.0158	0.0287/0.2725
$R1^c$ [$I > 2\sigma(I)$]	0.0250	0.0338	0.0222
$wR2^d$ (all data)	0.0690	0.0825	0.0637
max./min. residual electron density, e Å^{-3}	+0.561/−0.373	+0.378/−0.333	+0.473/−0.370

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bp$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) of 4a−4c

	4a	4b	4c
Si1−Si2	2.3709(5)	2.3780(8)	2.3886(3)
Si2−Si2*	2.4195(7)	2.4280(10)	2.4461(4)
Si2−O1	1.7360(10)	1.7343(14)	1.7398(6)
Si2−O4	1.7346(9)	1.7284(13)	1.7287(6)
Si2···O2*	2.8350(10)	2.8389(15)	2.7646(7)
Si2···O5*	2.7149(10)	2.8442(15)	2.8464(7)
Si1−Si2−Si2*	135.37(2)	136.18(3)	135.383(15)
Si1−Si2−O1	104.41(3)	103.65(5)	101.92 (2)
Si1−Si2−O4	102.15(3)	101.79(5)	104.59(2)
Si2*−Si2−O1	105.53(4)	106.00(5)	105.03(2)
Si2*−Si2−O4	106.23(4)	106.08(5)	107.10(2)
Si1−Si2···O2*	80.03(2)	77.96(4)	82.267(15)
Si1−Si2···O5*	75.93(2)	78.80(4)	74.520(15)
Si2*−Si2···O2*	75.12(2)	74.80(4)	75.185(16)
Si2*−Si2···O5*	75.51(2)	74.91(4)	73.896(15)
O1−Si2−O4	96.89(5)	96.47(7)	96.09(3)
O1−Si2···O2*	171.42(4)	175.82(6)	172.83(3)
O1−Si2···O5*	83.40(4)	80.90(6)	83.68(3)
O4−Si2···O2*	74.86(4)	79.40(6)	77.13(3)
O4−Si2···O5*	178.06(4)	177.36(6)	179.00(2)
O2*···Si2···O5*	104.92(3)	103.24(5)	103.14(2)

of **4a**−**4c** (2.4195(7)−2.4451(4) Å) are only slightly increased. The dihedral angles Si1−Si2−Si2*−Si1* of **4a**−**4c** amount to 180°, giving a perfect trans conformation of the silicon backbone. In conclusion, the structures of the 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes **4a**−**4c** in the crystal are very similar. The most remarkable structural feature is the distorted octahedral coordination (distorted tetrahedral coordination, with the capping of two of the tetrahedral faces by oxygen atoms opposite short Si−O bonds) of the central silicon atoms Si2 and Si2*. Obviously, this hexacoordination ([4 + 2] coordination) represents a general structural feature of this particular class of compounds. It is not clear why the title compounds have this particular type of structure. One might speculate that the strongly electronegative triflate groups increase the Lewis-acidic character of the two central silicon atoms, resulting in hexacoordination ([4 + 2] coordination). However, this coordination mode might also be the result of minimum steric hindrance and minimum electronic repulsion, respectively,

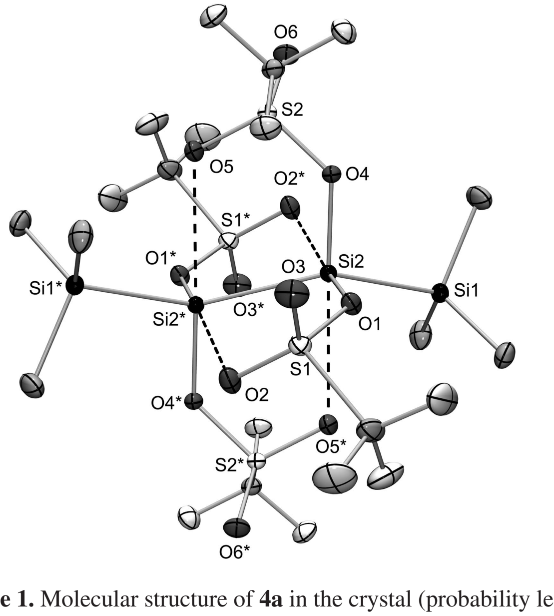


Figure 1. Molecular structure of **4a** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity.

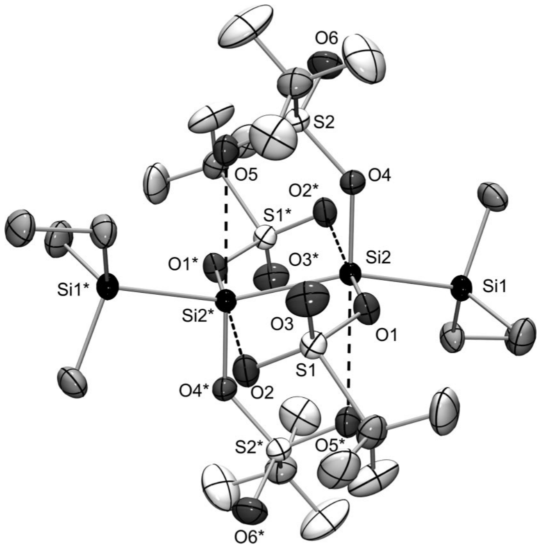


Figure 2. Molecular structure of **4b** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity.

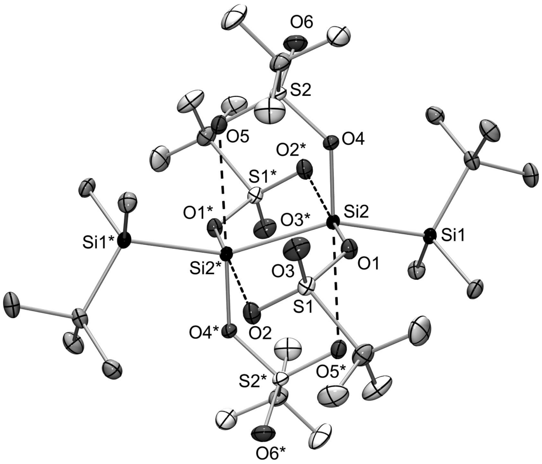


Figure 3. Molecular structure of **4c** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity.

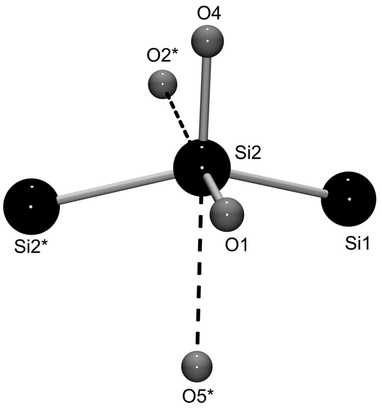
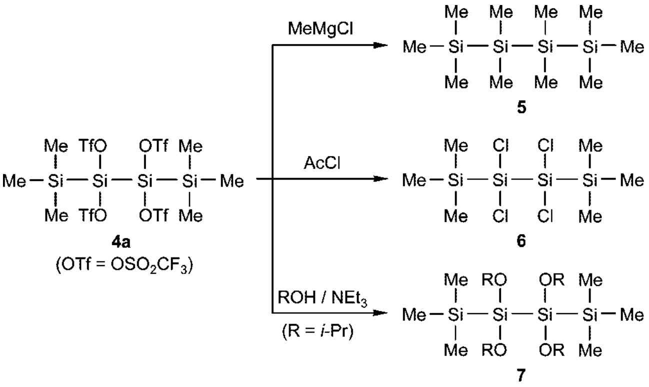


Figure 4. Coordination of the central silicon atom Si2 in compounds **4a**−**4c**.

rather than notable attractive forces. Further studies have to evaluate the real nature of these Si⋯O interactions.

Scheme 2



In order to evaluate the reactivity of the 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes, several reactions of **4a** were studied (Scheme 2). Treatment of **4a** with methylmagnesium chloride in *n*-pentane/diethyl ether gave decamethyltetrasilane (**5**) in 60% yield. Reaction of **4a** with acetyl chloride in *n*-pentane afforded the corresponding 2,2,3,3-tetrachlorotetrasilane **6** (68% yield). Treatment of **4a** with 2-propanol/triethylamine in *n*-pentane gave the corresponding 2,2,3,3-tetrakis(2-propoxy)tetrasilane **7** (95% yield). These results demonstrate that 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes may serve as starting materials for the synthesis of other 2,2,3,3-functionalized tetrasilanes, such as compounds **6** and **7**.

Conclusions

With the synthesis of the 2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilanes **4a**−**4c**, members of a novel class of 2,2,3,3-tetrafunctionalized tetrasilanes were made accessible on a preparative scale. Single-crystal X-ray diffraction studies of **4a**−**4c** revealed a distorted octahedral coordination ([4 + 2] coordination) of the two central silicon atoms of the tetrasilane backbone. One of the sulfonato oxygen atoms in each of the four trifluoromethanesulfonato groups of **4a**−**4c** is located on the opposite side of the Si−O bond of the adjacent silicon atom, with intramolecular Si⋯O distances of 2.715−2.846 Å. Compounds **4a**−**4c** represent the first oligosilanes in which hexacoordinate silicon atoms are directly connected to each other. Due to the presence of the four very reactive Si−OTf (OTf = OSO_2CF_3) groups, compounds **4a**−**4c** are extremely air- and moisture-sensitive and therefore very difficult to handle. However, as demonstrated by reactivity studies with **4a**, the four trifluoromethanesulfonato groups in the positions 2 and 3 of the tetrasilane backbone can be replaced by methyl, chloro, and alkoxy groups, respectively. Thus, compounds **4a**−**4c** not only are of interest due to their unique structural features but can also be regarded as useful starting materials for the synthesis of novel oligosilanes.

Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen immediately before use in all experiments. All the other organic solvents were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR-51 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi B-540 Melting Point apparatus using samples in sealed glass capillaries. The ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{19}Si, 59.6 MHz), Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{19}F, 376.5 MHz; ^{29}Si, 79.5 MHz), or Bruker

Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{19}Si, 99.4 MHz). CDCl$_3$ was used as the solvent. Chemical shifts (ppm) were determined relative to internal CHCl$_3$ (^{1}H, δ 7.24; CDCl$_3$), internal CDCl$_3$ (^{13}C, δ 77.0; CDCl$_3$), external CFCl$_3$ (^{19}F, δ 0; CDCl$_3$), or external TMS (^{29}Si, δ 0; CDCl$_3$). Assignment of the ^{13}C NMR data was supported by DEPT 135 and ^{13}C,^{1}H HMQC experiments.

1-Chloro-2,2,2-trimethyl-1,1-diphenyldisilane (2a).[14] This compound was synthesized according to the general method reported in ref 11: Chloro(diethylamino)diphenylsilane (14.4 g, 49.7 mmol) was added at 0 °C to a stirred suspension of granular lithium (1.40 g, 202 mmol) in THF (70 mL) in a single portion, and the reaction mixture was stirred at 0 °C for 4 h. The resulting greenish solution was then added at 0 °C to chlorotrimethylsilane (5.95 g, 54.8 mmol) in a single portion, and the reaction mixture was stirred at 20 °C for 1 h. Thereafter, acetyl chloride (3.98 g, 50.7 mmol) was added at 0 °C in a single portion to the stirred reaction mixture, and the product was distilled directly out of the reaction mixture to afford **2a** in 69% yield (10.0 g, 34.4 mmol) as a colorless liquid; bp 140−143 °C/3 mbar. The spectroscopic data of the product were identical to those reported in ref 14.

1-Chloro-2-ethyl-2,2-dimethyl-1,1-diphenyldisilane (2b). This compound was synthesized according to the general method reported in ref 11: Chloro(diethylamino)diphenylsilane (5.92 g, 20.4 mmol) was added at 0 °C to a stirred suspension of granular lithium (543 mg, 78.2 mmol) in THF (25 mL) in a single portion, and the reaction mixture was stirred at 0 °C for 4 h. The resulting greenish solution was then added at 0 °C to a stirred solution of chloro(ethyl)dimethylsilane (2.51 g, 20.5 mmol) in THF (5 mL) in a single portion, and the reaction mixture was stirred at 20 °C for 1 h. Thereafter, acetyl chloride (1.66 g, 21.1 mmol) was added at 0 °C in a single portion to the reaction mixture, and the product was distilled directly out of the reaction mixture to afford **2b** in 70% yield (4.37 g, 14.3 mmol) as a colorless liquid; bp 136−140 °C/3 mbar. ^{1}H NMR (300.1 MHz): δ 0.24 (s, 6 H, Si(CH_3)$_2$), 0.71−0.80 (m, 2 H, SiCH_2CH$_3$), 0.90−0.97 (m, 3 H, SiCH$_2$CH_3), 7.35−7.45 (m, 6 H, H-3/H-4/H-5, C$_6$H$_5$), 7.57−7.63 (m, 4 H, H-2/H-6, C$_6$H$_5$). ^{13}C NMR (75.5 MHz): δ −4.44 (Si(CH$_3$)$_2$), 6.45 (SiCH$_2$CH$_3$), 7.71 (SiCH$_2$$CH_3$), 128.13 ($C$-3/$C$-5, C$_6H_5$), 130.03 ($C$-4, C$_6H_5$), 134.35 ($C$-2/$C$-6, C$_6H_5$), 134.98 ($C$-1, C$_6H_5$). ^{29}Si NMR (59.6 MHz): δ −13.18 (SiSiCl), 5.03 (SiSiCl). Anal. Calcd for C$_{16}$H$_{21}$ClSi$_2$: C, 63.02; H, 6.94. Found: C, 63.1; H, 6.9.

1-*tert*-Butyl-2-chloro-1,1-dimethyl-2,2-diphenyldisilane (2c).[15] This compound was synthesized according to the general method reported in ref 11: Chloro(diethylamino)diphenylsilane (10.7 g, 36.9 mmol) was added at 0 °C to a stirred suspension of granular lithium (970 mg, 140 mmol) in THF (25 mL) in a single portion, and the reaction mixture was stirred at 0 °C for 4 h. The resulting greenish solution was then added at 0 °C to a solution of *tert*-butylchlorodimethylsilane (5.49 g, 36.4 mmol) in THF (10 mL) in a single portion, and the reaction mixture was stirred at 20 °C for 17 h. Thereafter, acetyl chloride (2.98 g, 38.0 mmol) was added at 0 °C in a single portion to the reaction mixture, and the product was distilled directly out of the reaction mixture to afford **2c** in 83% yield (10.2 g, 30.6 mmol) as a colorless liquid; bp 150 °C/2 mbar. ^{1}H NMR (500.1 MHz): δ 0.25 (s, 6 H, Si(CH_3)$_2$), 0.88 (s, 9 H, C(CH_3)$_3$), 7.36−7.43 (m, 6 H, H-3/H-4/H-5, C$_6$H$_5$), 7.64−7.67 (m, 4 H, H-2/H-6, C$_6$H$_5$). ^{13}C NMR (125.8 MHz): δ −5.47 (Si(CH$_3$)$_2$), 18.33 (C(CH$_3$)$_3$), 27.52 (C(CH$_3$)$_3$), 128.07 (C-3/C-5, C$_6$H$_5$), 129.94 (C-4, C$_6$H$_5$), 134.46 (C-2/C-6, C$_6$H$_5$), 135.35 (C-1, C$_6$H$_5$). ^{29}Si NMR (99.4 MHz): δ −6.71 (SiSiCl), 4.50 (SiSiCl). Anal. Calcd for C$_{18}$H$_{25}$ClSi$_2$: C, 64.92; H, 7.57. Found: C, 65.0; H, 7.5.

1,1,1,4,4,4-Hexamethyl-2,2,3,3-tetraphenyltetrasilane (3a).[16] A mixture of lithium (208 mg, 30.0 mmol)/naphthalene (3.46 g, 27.0 mmol) and THF (24 mL) was added dropwise at 0 °C within 5 min to a stirred solution of **2a** (7.54 g, 25.9 mmol) in THF (30 mL), and the reaction mixture was stirred at 0 °C for 30 min. The solvent was removed under reduced pressure, and diethyl ether (15 mL) and a saturated aqueous solution of NH$_4$Cl (30 mL) were added to the residue. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 15 mL), and the combined ethereal fractions were dried over anhydrous MgSO$_4$. After the solvent was removed under reduced pressure, the residue was washed with ethanol (3 × 50 mL), and **3a** was obtained in 80% yield (5.28 g, 10.3 mmol) as a colorless crystalline solid. The spectroscopic data of the product were identical to those reported in ref 16.

1,4-Diethyl-1,1,4,4-tetramethyl-2,2,3,3-tetraphenyltetrasilane (3b). A mixture of lithium (107 mg, 15.4 mmol)/naphthalene (1.80 g, 14.0 mmol) and THF (12.5 mL) was added dropwise at 0 °C within 2 min to a stirred solution of **2b** (4.04 g, 13.2 mmol) in THF (5 mL), and the reaction mixture was stirred at 20 °C for 1 h. The solvent was removed under reduced pressure, and diethyl ether (10 mL) and a saturated aqueous solution of NH$_4$Cl (30 mL) were added to the residue. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined ethereal fractions were dried over anhydrous MgSO$_4$. After the solvent was removed under reduced pressure, the residue was washed with ethanol (2 × 50 mL), and **3b** was obtained in 62% yield (2.20 g, 4.08 mmol) as a colorless crystalline solid; mp 230−231 °C. ^{1}H NMR (400.1 MHz): δ −0.11 (s, 12 H, Si(CH_3)$_2$), 0.38−0.44 (m, 4 H, SiCH_2CH$_3$), 0.66−0.71 (m, 6 H, SiCH$_2$CH_3), 7.20−7.32 (m, 12 H, H-3/H-4/H-5, C$_6$H$_5$), 7.40−7.45 (m, 8 H, H-2/H-6, C$_6$H$_5$). ^{13}C NMR (75.5 MHz): δ −3.21 (Si(CH$_3$)$_2$), 7.38 (SiCH$_2$CH$_3$), 7.49 (SiCH$_2$$CH_3$), 127.66 ($C$-3/$C$-5, C$_6H_5$), 128.34 ($C$-4, C$_6H_5$), 135.81 ($C$-1, C$_6H_5$), 136.75 ($C$-2/$C$-6, C$_6H_5$). ^{29}Si NMR (59.6 MHz): δ −37.06 (CH$_3$SiSi), −11.15 (CH$_3$$Si$Si). Anal. Calcd for C$_{32}H_{42}Si_4$: C, 71.30; H, 7.85. Found: C, 71.3; H, 7.9.

1,4-Di-*tert*-butyl-1,1,4,4-tetramethyl-2,2,3,3-tetraphenyltetrasilane (3c).[17] This compound was synthesized similarly to **3a**: A mixture of lithium (37.0 mg, 5.33 mmol)/naphthalene (585 mg, 4.56 mmol) and THF (4.5 mL) was added dropwise at 0 °C within 1 min to a stirred solution of **2c** (1.43 g, 4.29 mmol) in THF (5 mL), and the reaction mixture was stirred at 20 °C for 1 h. The solvent was removed under reduced pressure, and diethyl ether (10 mL) and a saturated aqueous solution of NH$_4$Cl (30 mL) were added to the residue. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined ethereal fractions were dried over anhydrous MgSO$_4$. After the solvent was removed under reduced pressure, the residue was washed with ethanol (2 × 50 mL), and **3c** was obtained in 71% yield as a colorless crystalline solid (904 mg, 1.52 mmol); mp 233−233.5 °C. ^{1}H NMR (300.1 MHz): δ −0.11 (s, 12 H, Si(CH_3)$_2$), 0.50 (s, 18 H, C(CH_3)$_3$), 7.18−7.32 (m, 12 H, H-3/H-4/H-5, C$_6$H$_5$), 7.51−7.59 (m, 8 H, H-2/H-6, C$_6$H$_5$). ^{13}C NMR (125.8 MHz): δ −3.48 (Si(CH$_3$)$_2$), 19.73 (C(CH$_3$)$_3$), 27.90 (C(CH$_3$)$_3$), 127.46 (C-3/C-5, C$_6$H$_5$), 128.39 (C-4, C$_6$H$_5$), 135.83 (C-1, C$_6$H$_5$), 137.21 (C-2/C-6, C$_6$H$_5$). ^{29}Si NMR (99.4 MHz): δ −36.65 (CH$_3$SiSi), −4.09 (CH$_3$$Si$Si). Anal. Calcd for C$_{36}H_{50}Si_4$: C, 72.66; H, 8.47. Found: C, 72.4; H, 8.2.

1,1,1,4,4,4-Hexamethyl-2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilane (4a). Trifluoromethanesulfonic acid (353 mg, 2.35 mmol) was added at 20 °C to a stirred suspension of **3a** (203 mg, 397 μmol) in *n*-pentane (5 mL) in a single portion. The solid disappeared

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[14] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139–153.

[15] Although compound **2c** has already been synthesized using the method reported in ref 11, the physical data of **2c** and experimental details of the synthesis have not been described: Suginome, M.; Iwanami, T.; Ohmori, Y.; Matsumoto, A.; Ito, Y. *Chem. Eur. J.* **2005**, *11*, 2954–2965.

[16] Tamao, K.; Kawachi, A. *Organometallics* **1995**, *14*, 3108–3111.

[17] Although compound **3c** has already been used as a starting material, the physical data of **3c** have not been reported: Matsumoto, H.; Higuchi, K.; Hoshino, Y.; Koike, H.; Naoi, Y.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1083–1084. Compound **3c** was synthesized similarly to compound **3a**.

immediately to give a yellowish, clear solution. After the reaction mixture was stirred at 20 °C for 10 min, a crystalline solid precipitated. The resulting suspension was stirred at 20 °C for 1 h, the solution was removed with a syringe, and the precipitate was washed with cold (0 °C) *n*-pentane (2 × 3 mL) and then dried in vacuo at 0 °C to give **4a** in 92% yield (292 mg, 366 μmol) as a colorless crystalline solid. ^{1}H NMR (400.1 MHz): δ 0.42 (s, 18 H, $\mathrm{Si(C}H_3)_3$). ^{13}C NMR (100.6 MHz): δ −1.60 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 118.09 (q, $^1J_{\mathrm{CF}} = 319$ Hz, $C\mathrm{F_3}$). ^{19}F NMR (376.5 MHz): δ −74.78 ($\mathrm{C}F_3$). ^{29}Si NMR (59.6 MHz): δ −6.96 ($\mathrm{CH_3Si}Si$), 4.46 ($\mathrm{CH_3}Si\mathrm{Si}$). Anal. Calcd for $\mathrm{C_{10}H_{18}F_{12}O_{12}S_4Si_4}$: C, 15.04; H, 2.27. Found: C, 14.7; H, 2.6.

1,4-Diethyl-1,1,4,4-tetramethyl-2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilane (4b). Trifluoromethanesulfonic acid (258 mg, 1.72 mmol) was added at 0 °C to a stirred solution of **3b** (150 mg, 278 μmol) in *n*-pentane (5 mL) in a single portion. After the reaction mixture was stirred at 0 °C for 5 min, an orange oil began to precipitate. The reaction mixture was stirred at 0 °C for a further 1 h, the solvent was removed with a syringe, and the remaining orange oil was dried in vacuo at 0 °C for 5 min. The oil was then dissolved in dichloromethane (3 mL)/toluene (3 mL), and the product was crystallized from this solution within 2 weeks at −20 °C to give **4b** in 73% yield as a colorless crystalline solid (168 mg, 203 μmol). ^{1}H NMR (300.1 MHz): δ 0.39 (s, 12 H, $\mathrm{Si(C}H_3)_2$), 0.85−0.94 (m, 4 H, $\mathrm{SiC}H_2\mathrm{CH_3}$), 0.98−1.05 (m, 6 H, $\mathrm{SiCH_2C}H_3$). ^{13}C NMR (75.5 MHz): δ −4.12 ($\mathrm{Si(}C\mathrm{H_3)_2}$), 6.45 ($\mathrm{Si}C\mathrm{H_2CH_3}$), 6.80 ($\mathrm{SiCH_2}C\mathrm{H_3}$), 118.10 (q, $^1J_{\mathrm{CF}} = 320$ Hz, $C\mathrm{F_3}$). ^{19}F NMR (376.5 MHz): δ −74.79 ($\mathrm{C}F_3$). ^{29}Si NMR (59.6 MHz): δ −6.62 ($\mathrm{CH_3Si}Si$), 7.33 ($\mathrm{CH_3}Si\mathrm{Si}$). Anal. Calcd for $\mathrm{C_{12}H_{22}F_{12}O_{12}S_4Si_4}$: C, 17.43; H, 2.68. Found: C, 17.2; H, 2.7.

1,4-Di-*tert*-butyl-1,1,4,4-tetramethyl-2,2,3,3-tetrakis(trifluoromethanesulfonato)tetrasilane (4c). Trifluoromethanesulfonic acid (206 mg, 1.37 mmol) was added at 20 °C to a stirred suspension of **3c** (90.0 mg, 151 μmol) in *n*-pentane (3 mL) in a single portion. The solid disappeared immediately to give a yellowish, clear solution. After the reaction mixture was stirred at 20 °C for 5 min, an orange oil began to precipitate. After the reaction mixture was stirred at 20 °C for 24 h, the solution was removed with a syringe, and the remaining orange oil was dried in vacuo at 0 °C for 5 min to give an oily product consisting of **4c** and trifluoromethanesulfonic acid (molar ratio ca. 1:5).[18] ^{1}H NMR (500.1 MHz$_3$): δ 0.41 (s, 12 H, $\mathrm{Si(C}H_3)_2$), 1.02 (s, 18 H, $\mathrm{C(C}H_3)_3$), 9.76 (s, 1 H, $\mathrm{TfO}H$). ^{13}C NMR (125.8 MHz): δ −5.17 ($\mathrm{Si(}C\mathrm{H_3)_2}$), 20.53 ($C\mathrm{(CH_3)_3}$), 26.55 ($\mathrm{C(}C\mathrm{H_3)_3}$), 118.08 (q, $^1J_{\mathrm{CF}} = 319$ Hz, $C\mathrm{F_3}$), 118.26 (q, $^1J_{\mathrm{CF}} = 319$ Hz, TfOH). ^{19}F NMR (376.5 MHz): δ −74.69 ($\mathrm{C}F_3$), −76.19 (TfOH). ^{29}Si NMR (99.4 MHz): δ −8.17 ($\mathrm{CH_3Si}Si$), 16.18 ($\mathrm{CH_3}Si\mathrm{Si}$).

Reaction of 4a with Methylmagnesium Chloride. A suspension of **4a** in *n*-pentane was obtained by treatment of **3a** (296 mg, 579 μmol) with trifluoromethanesulfonic acid (516 mg, 3.44 mmol) in *n*-pentane (5 mL) at 20 °C. Without isolation and further purification, this compound was used in the next reaction step. A 3.0 M solution of methylmagnesium chloride in diethyl ether (1.20 mL, 3.60 mmol of MeMgCl) was added at 0 °C to the stirred suspension of **4a** in a single portion. After the reaction mixture was stirred at 20 °C for 30 min, *n*-hexane was added, the precipitate was removed by filtration, and the solvent of the filtrate was removed under reduced pressure to give decamethyltetrasilane (**5**) in 60% yield as a colorless liquid (91.0 mg, 346 μmol). The spectroscopic data of the product were identical to those reported in ref 19.

Reaction of 4a with Acetyl Chloride. A suspension of **4a** in *n*-pentane was obtained by treatment of **3a** (938 mg, 1.84 mmol) with trifluoromethanesulfonic acid (1.65 g, 11.0 mmol) in *n*-pentane (10 mL) at 20 °C. Without isolation and further purification, this compound was used in the next reaction step. Acetyl chloride (862 mg, 11.0 mmol) was added to the stirred suspension of **4a** at 20 °C in a single portion. After the reaction mixture was stirred at 20 °C for 30 min, the resulting orange oil was removed by decantation, and the reaction solution was concentrated under reduced pressure. The residue was distilled in vacuo to afford 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexamethyltetrasilane[12] (**6**) in 68% yield as a colorless liquid (434 mg, 1.26 mmol); bp 75−78 °C/1 mbar. ^{1}H NMR (300.1 MHz): δ 0.36 (s, 18 H, $\mathrm{Si(C}H_3)_3$). ^{13}C NMR (75.5 MHz): δ −2.64 ($\mathrm{Si(}C\mathrm{H_3)_3}$). ^{29}Si NMR (59.6 MHz): δ −6.37 ($\mathrm{CH_3}Si\mathrm{Si}$), 19.48 ($\mathrm{CH_3Si}Si$). Anal. Calcd for $\mathrm{C_6H_{18}Cl_4Si_4}$: C, 20.93; H, 5.27. Found: C, 21.0; H, 5.3.

Reaction of 4a with 2-Propanol/Triethylamine. A stirred suspension of **4a** in *n*-pentane was obtained by treatment of **3a** (410 mg, 802 μmol) with trifluoromethanesulfonic acid (722 mg, 4.81 mmol) in *n*-pentane (7 mL) at 20 °C. Without isolation and further purification, this compound was used in the next reaction step. 2-Propanol (289 mg, 4.81 mmol) and triethylamine (482 mg, 4.76 mmol) were added to the stirred suspension of **4a** at 0 °C in a single portion. After the reaction mixture was stirred at 20 °C for 30 min, *n*-hexane (5 mL) was added, the precipitate was removed by filtration, and the solvent of the filtrate was removed under reduced pressure to give 1,1,1,4,4,4-hexamethyl-2,2,3,3-tetrakis(2-propoxy)tetrasilane (**7**) in 95% yield as a colorless solid (334 mg, 761 μmol). ^{1}H NMR (300.1 MHz): δ 0.14 (s, 18 H, $\mathrm{Si(C}H_3)_3$), 1.15 and 1.17 (d, $^3J_{\mathrm{HH}} = 6.0$ Hz, 24 H, $\mathrm{OCH(C}H_3)_2$), 4.08 (sep, $^3J_{\mathrm{HH}} = 6.0$ Hz, 4 H, $\mathrm{OC}H\mathrm{(CH_3)_2}$). ^{13}C NMR (75.5 MHz): δ −0.79 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 26.10 and 26.15 ($\mathrm{OCH(}C\mathrm{H_3)_2}$), 67.51 ($\mathrm{O}C\mathrm{H(CH_3)_2}$). ^{29}Si NMR (59.6 MHz): δ −22.49 ($\mathrm{CH_3}Si\mathrm{Si}$), −3.94 ($\mathrm{CH_3Si}Si$). Anal. Calcd for $\mathrm{C_{18}H_{46}O_4Si_4}$: C, 49.26; H, 10.56. Found: C, 49.5; H. 10.7.

Crystal Structure Analyses. Suitable single crystals of **4a**−**4c** were obtained by crystallization at −20 °C from dichloromethane/*n*-pentane (**4a**) or from dichloromethane/toluene (**4b** and **4c**). The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (**4b**: Stoe IPDS, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); **4a**, **4c**: Bruker-Nonius Kappa-APEXII CCD system with Goebel mirror, Mo Kα radiation (λ = 0.71073Å)). The structures were solved by direct methods.[20] All non-hydrogen atoms were refined anisotropically.[21] A riding model was employed in the refinement of the hydrogen atoms.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-693002 (**4a**), CCDC-693003 (**4b**), and CCDC-693004 (**4c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, (+44)1223/336033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Although compound **4c** could be obtained as a colorless crystalline solid from dichloromethane/toluene at −20 °C, it was not possible to determine its yield exactly because **4c** quickly decomposed during the operation of removing the solvents and trifluoromethanesulfonic acid in vacuo.

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