4548 *Organometallics* **2010,** *29,* 4548–4554
DOI: 10.1021/om100721t

ORGANOMETALLICS
Article

Synthesis and Characterization of {[Tris(trimethylsilyl)silyl]methyl}silanes of the Formula Type $Me_{4-n}Si[CH_2Si(SiMe_3)_3]_n$ (n = 1−3) and Derivatives

André Berkefeld, Dennis Troegel, Christian Burschka, and Reinhold Tacke*

Universität Würzburg, Institut für Anorganische Chemie, Am Hubland, D-97074 Würzburg, Germany

Received July 23, 2010

In context with systematic studies on multifunctional tetraorganylsilanes of the formula type $R_{4-n}Si(CH_2X)_n$ (R = organyl, X = functional group, n = 2−4), a series of new (silylmethyl)silanes of the formula types $Me_{4-n}Si[CH_2Si(SiMe_3)_3]_n$ [n = 1 (**5**), n = 2 (**6**), n = 3 (**7**)] and $Me_{3-n}(TMOP)Si[CH_2Si(SiMe_3)_3]_n$ [TMOP = 2,4,6-trimethoxyphenyl, n = 1 (**9**), n = 2 (**10**)] was synthesized by treatment of the corresponding (chloromethyl)silanes with [tris(trimethylsilyl)silyl]potassium−18-crown-6 (**12**). Reaction of tetrakis(chloromethyl)silane (**4**) with **12**, however, yielded the unexpected disilacyclobutane derivative 1,1-bis(trimethylsilyl)-3,3-bis{[tris(trimethylsilyl)silyl]methyl}-1,3-disilacyclobutane (**11**). Compounds **5**−**7** and **9**−**11** were characterized by elemental analyses (C, H) and NMR spectroscopic studies in solution (^{1}H, ^{13}C, ^{29}Si). In addition, compounds **6**, **7**, and **9**−**11** were structurally characterized by single-crystal X-ray diffraction (**7** was studied as the solvate **7**·0.46Et_2O).

Introduction

Multifunctional tetraorganylsilanes of the formula type $R_{4-n}Si(CH_2X)_n$ (R = organyl group, X = functional group, n = 2−4) are versatile building blocks in organosilicon chemistry and are also useful for diverse practical applications. For example, (i) (nitratomethyl)silanes [$R_{4-n}Si(CH_2ONO_2)_n$] have been demonstrated to be highly potent explosives,[1] (ii) (mercaptomethyl)silanes [$R_{4-n}Si(CH_2SH)_n$] have been used as multidentate ligands in iron complexes,[2] and (iii) tris(mercaptomethyl)silanes [$RSi(CH_2SH)_3$] have been applied as tripodal adsorbate molecules for the fabrication of self-assembled monolayers on Au(111).[3] The corresponding multifunctional (chloromethyl)silanes [$R_{4-n}Si(CH_2Cl)_n$] are the most versatile starting materials in this chemistry and can be prepared by treatment of the respective chlorosilanes [$R_{4-n}SiCl_n$] with (chloromethyl)lithium, generated *in situ* from bromochloromethane and *n*-butyllithium in tetrahydrofuran.[2−5] In continuation of our systematic studies on multifunctional tetraorganylsilanes of the type $R_{4-n}Si(CH_2X)_n$[1−3,5,6] and inspired by studies of Marschner et al.,[7] we have been interested in the reactivity of (chloromethyl)silanes of the type $R_{4-n}Si(CH_2Cl)_n$ against silyl anions and have attempted to synthesize {[tris(trimethylsilyl)silyl]methyl}silanes of the type $Me_{4-n}Si[CH_2Si(SiMe_3)_3]_n$ (n = 1−4), compounds **5**−**8**,[7] starting from the corresponding (chloromethyl)silanes **1**−**4**. Owing to their reactive Si−Si bonds, the target compounds **5**−**8** are expected to be versatile starting materials for the synthesis of a variety of further multifunctional tetraorganylsilanes. In addition, we attempted to synthesize the related silanes **9** and **10**, which are derivatives of **1** and **2**, respectively, that contain a silicon-bound 2,4,6-trimethoxyphenyl (TMOP) group instead of a methyl substituent. As the TMOP moiety is a protection group for silicon,[5a,6b,8] the {[tris(trimethylsilyl)silyl]methyl}silanes **9** and **10** should allow for additional functionalization at the central silicon atom. We report here on the syntheses of compounds **5**−**7** and **9**−**11**. The synthesis of **8** failed; instead the 1,3-disilacyclobutane

---

*To whom correspondence should be addressed. Phone: +49-931-31-85250. Fax: +49-931-31-84609. E-mail: r.tacke@uni-wuerzburg.de.

(1) (a) Klapötke, T. M.; Krumm, B.; Ilg, R.; Troegel, D.; Tacke, R. *J. Am. Chem. Soc.* **2007**, *129*, 6908–6915. (b) Evangelisti, C.; Klapötke, T. M.; Krumm, B.; Nieder, A.; Berger, R. J. F.; Hayes, S. A.; Mitzel, N. W.; Troegel, D.; Tacke, R. *Inorg. Chem.* **2010**, *49*, 4865–4880.

(2) (a) Apfel, U.-P.; Troegel, D.; Halpin, Y.; Tschierlei, S.; Uhlemann, U.; Görls, H.; Schmitt, M.; Popp, J.; Dunne, P.; Venkatesan, M.; Coey, M.; Rudolph, M.; Vos, J. G.; Tacke, R.; Weigand, W., *Inorg. Chem.* DOI: 10.1021/ic101399k. (b) Troegel, D. Dissertation, University of Würzburg, Würzburg, Germany, 2009.

(3) Weidner, T.; Ballav, N.; Siemeling, U.; Troegel, D.; Walter, T.; Tacke, R.; Castner, D. G.; Zharnikov, M. *J. Phys. Chem. C* **2009**, *113*, 19609–19617.

(4) (a) Kobayashi, T.; Pannell, K. H. *Organometallics* **1990**, *9*, 2201–2203. (b) Kobayashi, T.; Pannell, K. H. *Organometallics* **1991**, *10*, 1960–1964.

(5) (a) Daiss, J. O.; Barth, K. A.; Burschka, C.; Hey, P.; Ilg, R.; Klemm, K.; Richter, I.; Wagner, S. A.; Tacke, R. *Organometallics* **2004**, *23*, 5193–5197. (b) Troegel, D.; Lippert, W. P.; Möller, F.; Burschka, C.; Tacke, R. *J. Organomet. Chem.* **2010**, *695*, 1700–1707.

(6) (a) Ilg, R.; Troegel, D.; Burschka, C.; Tacke, R. *Organometallics* **2006**, *25*, 548–551. (b) Troegel, D.; Walter, T.; Burschka, C.; Tacke, R. *Organometallics* **2009**, *28*, 2756–2761. (c) Troegel, D.; Möller, F.; Burschka, C.; Tacke, R. *Organometallics* **2009**, *28*, 5765–5770.

(7) Synthesis of $Me_3SiCH_2Si(SiMe_3)_3$: (a) Marschner, C.; Wallner, A. Unpublished results. (b) Wallner, A., Dissertation, TU Graz, Austria, 2006.

(8) (a) Daiss, J. O.; Penka, M.; Burschka, C.; Tacke, R. *Organometallics* **2004**, *23*, 4987–4994. (b) Popp, F.; Nätscher, J. B.; Daiss, J. O.; Burschka, C.; Tacke, R. *Organometallics* **2007**, *26*, 6014–6028. (c) Tacke, R.; Popp, F.; Müller, B.; Theis, B.; Burschka, C.; Hamacher, A.; Kassack, M. U.; Schepmann, D.; Wünsch, B.; Jurva, U.; Wellner, E. *ChemMedChem* **2008**, *3*, 152–164. (d) Tacke, R.; Nguyen, B.; Burschka, C.; Lippert, W. P.; Hamacher, A.; Urban, C.; Kassack, M. U. *Organometallics* **2010**, *29*, 1652–1660.

derivative **11** was obtained. Compounds **5**−**7** and **9**−**11** were characterized by elemental analyses, NMR studies in solution (^{1}H, ^{13}C, ^{29}Si), and crystal structure analyses (except for **5**).

$Me_{4-n}Si(CH_2Cl)_n$

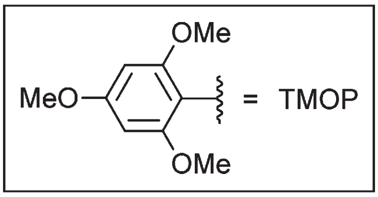
	1	**2**	**3**	**4**
n	1	2	3	4

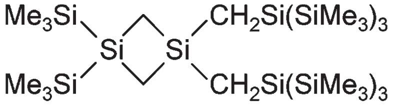
$Me_{4-n}Si[CH_2Si(SiMe_3)_3]_n$

	5	**6**	**7**	**8**
n	1	2	3	4

$Me_{3-n}(TMOP)Si[CH_2Si(SiMe_3)_3]_n$

	9	**10**
n	1	2





11

Results and Discussion

Synthesis. The {[tris(trimethylsilyl)silyl]methyl}silanes **5**−**7** were synthesized according to Scheme 1, starting from the corresponding (chloromethyl)silanes **1**−**3**. Thus, treatment of **1**−**3** with [tris(trimethylsilyl)silyl]potassium−18-crown-6 (**12**), generated from tetrakis(trimethylsilyl)silane[9] [$Si(SiMe_3)_4$ (**13**)] with potassium *tert*-butoxide in toluene in the presence of 1 molar equiv of 18-crown-6,[10,11] yielded the compounds **5**−**7** (yield: **5**, 82%; **6**, 72%; **7**, 86%). Treatment of tetrakis(chloromethyl)silane (**4**) with **12**, however, did not afford the expected tetrakis{[tris(trimethylsilyl)silyl]methyl}silane (**8**); instead the 1,3-disilacyclobutane derivative **11** was obtained (Scheme 1, 38% yield).

A potential mechanism for the formation of the 1,3-disilacyclobutane **11** is depicted in Scheme 2. Successive substitution of three of the four chlorine atoms of **4** leads to the intermediate **14**, which upon reaction with **12** affords the intermediate **15** and tetrakis(trimethylsilyl)silane (**13**), the formation of which could be established by GC/EI-MS studies of the reaction mixture. In the last step, the intermediate **15** undergoes an intramolecular cyclization (elimination of potassium chloride) to furnish the 1,3-disilacyclobutane **11**.

The {[tris(trimethylsilyl)silyl]methyl}silanes **9** and **10** were synthesized according to Scheme 3, starting from chloro(chloromethyl)dimethylsilane and trichloro(methyl)silane, respectively. Thus, treatment of $Me_2Si(CH_2Cl)Cl$ and $MeSiCl_3$ with 1 molar equiv of (2,4,6-trimethoxyphenyl)lithium afforded the corresponding (2,4,6-trimethoxyphenyl)silanes **16** (63% yield) and **17** (62% yield). Reaction of **17** with (chloromethyl)lithium, generated *in situ* from bromochloromethane and *n*-butyllithium in tetrahydrofuran, furnished the bis(chloromethyl)silane **18** (59% yield). Treatment of **16** and **18** with **12** finally afforded compounds **9** (76% yield) and **10** (77% yield), respectively.

Compounds **6**, **7**, and **9**−**11** were isolated as colorless crystalline solids, whereas **5** was obtained as a colorless liquid. The identities of all these compounds were established by elemental analyses (C, H) and NMR spectroscopic studies in solution (^{1}H, ^{13}C, ^{29}Si). In addition, compounds **6**, **7**, and **9**−**11** were characterized by crystal structure analyses.

Crystal Structure Analyses. Compounds **6**, **7**, and **9**−**11** were structurally characterized by single-crystal X-ray diffraction. Compound **7** was studied as the solvate $\mathbf{7}\cdot 0.46Et_2O$. The crystal data and the experimental parameters used for these studies are given in Table 1. The molecular structures of **7**, **10**, and **11** are depicted in Figures 1−3; selected bond lengths and angles are given in the respective figure legends (for further details concerning the crystal structure analyses, see the Supporting Information).

Most of the bond lengths and angles of **6**, **7**, and **9**−**11** (Figures 1−3, Supporting Information) are in the expected ranges and therefore do not need any further comments, except for following structural features. The Si−C−Si angles of the $SiCH_2Si(SiMe_3)_3$ moieties of the compounds studied [119.67(5)−127.27(8)°] deviate significantly from the ideal tetrahedral angle, probably due to the steric demand of the two bulky substituents bound to the methylene group. Additionally, the Si4−Si1−C10 angle of **10** [117.41(9)°] is also significantly widened [probably due to steric repulsion between the trimethylsilyl group (Si4) and the 2,4,6-trimethoxyphenyl moiety], leading to a decrease of the Si3−Si1−C10 angle [101.42(9)°]. Similar structural features were also observed for the related (2,4,6-trimethoxyphenyl)silane **9**. The Si−C−Si and C−Si−C angles of the 1,3-disilacyclobutane skeleton of **11** are in the range 88.46(4)−91.59(5)°; as a consequence, the angles C1−Si1−C4, C2−Si1−C3, C3−Si4−Si12, and C4−Si4−Si11 are significantly widened [116.23(5)−120.99(4)°].

Conclusions

Multifunctional tetraorganylsilanes are versatile building blocks for synthetic organosilicon chemistry and are also useful for diverse practical applications. In this study, we have evaluated the potential of multifunctional (chloromethyl)silanes of the formula types $Me_{4-n}Si(CH_2Cl)_n$ [n = 1−4 (**1**−**4**)]

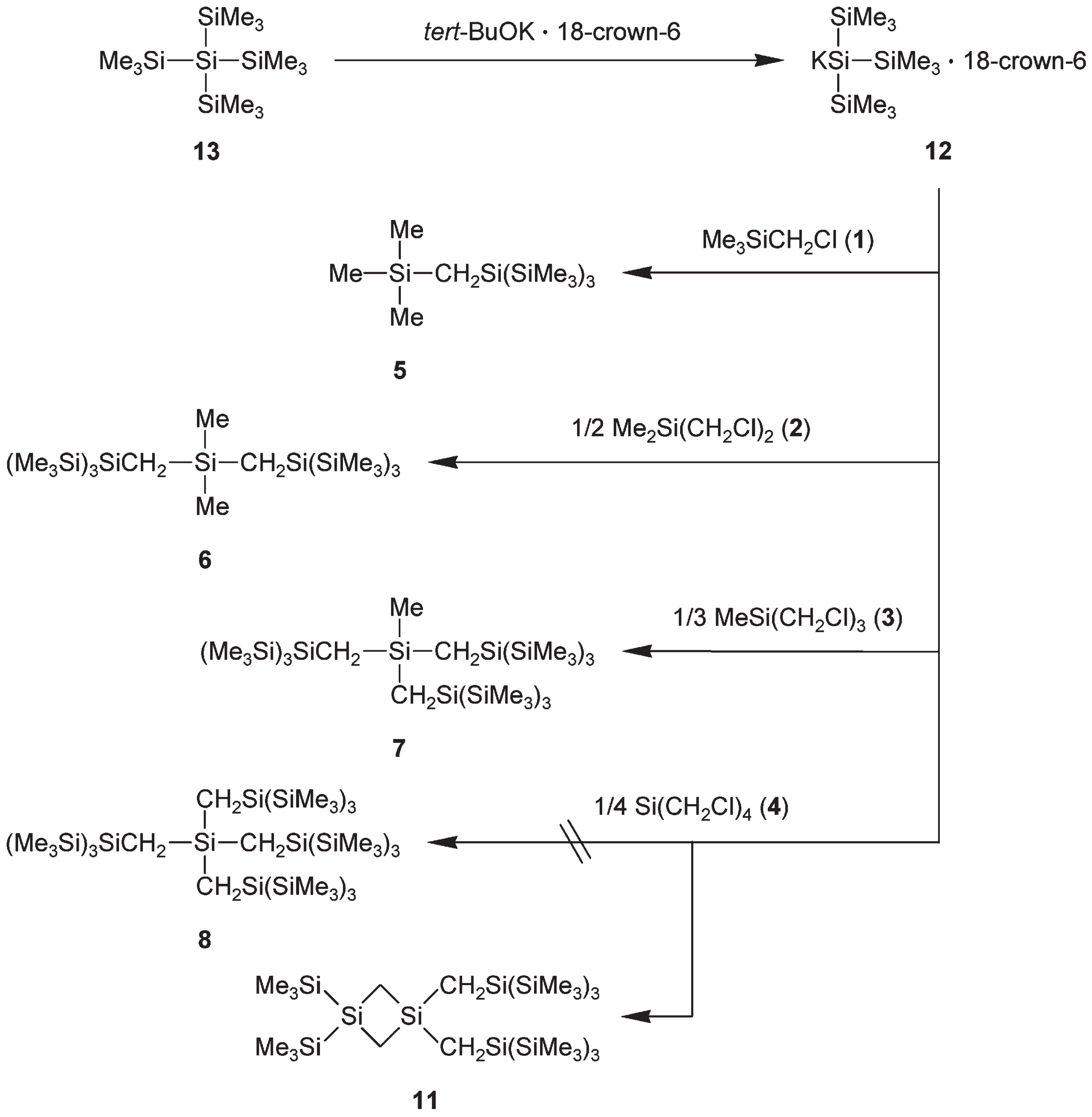
---

[9] Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1967**, *8*, 245–253.

[10] Synthesis and reactivity of $K[Si(SiMe_3)_3]$: (a) Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 221–226. (b) Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. *Organometallics* **2002**, *21*, 1023–1030. (c) Marschner, C. *Organometallics* **2006**, *25*, 2110–2125. (d) Niemeyer, M. *Inorg. Chem.* **2006**, *45*, 9085–9095.

[11] Synthesis and reactivity of $KSi(SiMe_3)_2(SiMe_2)_nSi(SiMe_3)_2K$ (n = 1−3): (a) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723–3731. (b) Zirngast, M.; Baumgartner, J.; Marschner, C. *Organometallics* **2008**, *27*, 6427–6478.

Scheme 1

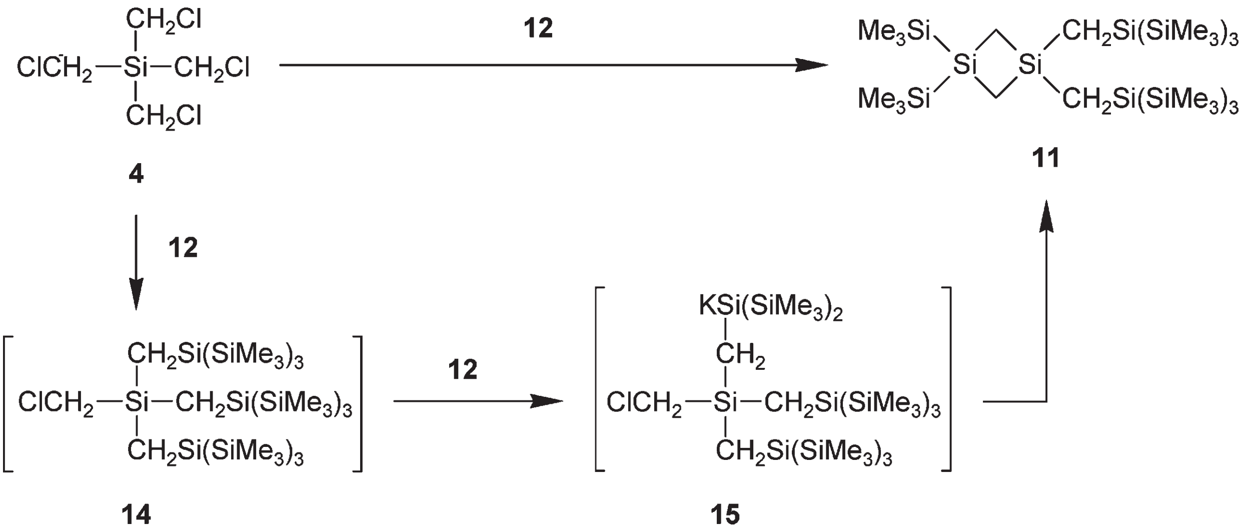


and $Me_{3-n}(TMOP)Si(CH_2Cl)_n$ [TMOP = 2,4,6-trimethoxyphenyl; n = 1 (**16**), 2 (**18**)] as starting materials for the preparation of a series of novel {[tris(trimethyl)silyl]methyl}silanes. We have succeeded in synthesizing compounds of the formula types $Me_{4-n}Si[CH_2Si(SiMe_3)_3]_n$ [n = 1−3 (**5**−**7**)] and $Me_{3-n}(TMOP)Si[CH_2Si(SiMe_3)_3]_n$ [n = 1 (**9**), 2 (**10**)] by treatment of the corresponding (chloromethyl)silanes with $(Me_3Si)_3SiK \cdot$ 18-crown-6. Unexpectedly, the analogous treatment of $Si(CH_2Cl)_4$ (**4**) with $(Me_3Si)_3SiK \cdot$ 18-crown-6 resulted in the formation of the 1,3-disilacyclobutane **11**, which contains two silicon-bound Me_3Si groups and $(Me_3Si)_3SiCH_2$ moieties. Compound **5**−**7**, **9**, and **10** with their reactive Si−Si bonds are expected to be versatile starting materials for the synthesis of a variety of further multifunctional tetraorganylsilanes, and compounds **9** and **10** with their silicon-bound 2,4,6-trimethoxyphenyl moiety (a protection group for silicon) should allow for additional functionalization at the central silicon atoms. Reactions at the Si−Si bonds of **11** should also allow transformations at both the peripheral silicon atoms and the silicon atom in the 1,3-disilacyclobutane ring system (in this context, see for example ref 10b). Future studies have to evaluate the synthetic potential of compounds **5**−**7** and **9**−**11**.

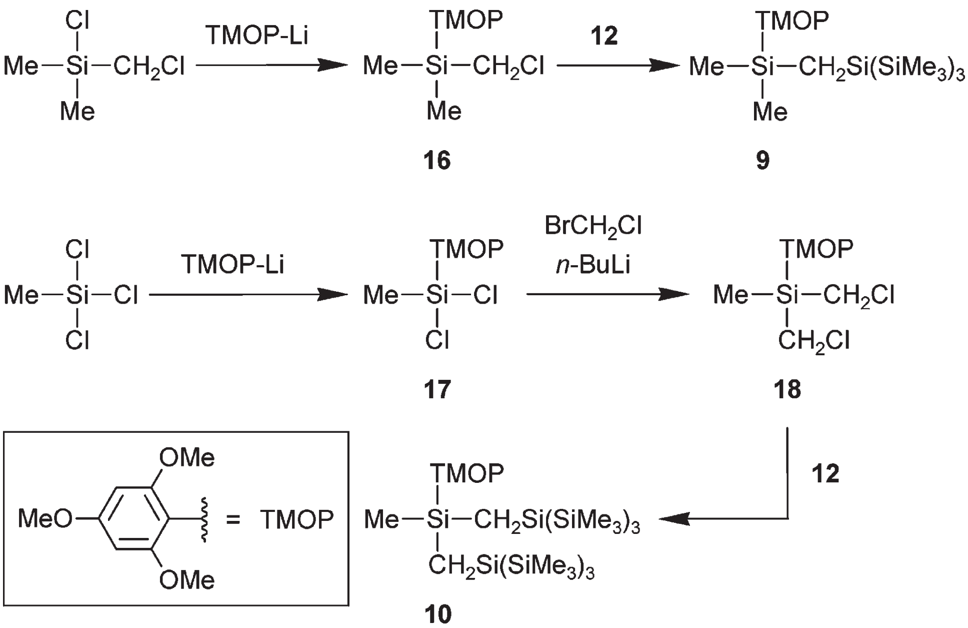
Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. The organic solvents used 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. The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded at 23 °C on a Bruker DRX-300 (^1H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz), a Bruker Avance 400 (^1H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz), or a Bruker Avance 500 NMR spectrometer (^1H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz). $CDCl_3$, CD_2Cl_2, or C_6D_6 were used as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^1H, δ 7.24; $CDCl_3$), internal $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), internal

Scheme 2



Scheme 3



$CHDCl_2$ (^1H, δ 5.32; CD_2Cl_2), internal CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), internal C_6HD_5 (^1H, δ 7.28; C_6D_6), internal C_6D_6 (^{13}C, δ 128.0; C_6D_6), or external TMS (^{29}Si, δ 0; $CDCl_3$, CD_2Cl_2, C_6D_6). Analysis and assignment of the ^1H NMR data were supported by ^1H,^1H COSY, ^{13}C,^1H HMQC, and ^{13}C,^1H HMBC experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135, ^{13}C,^1H HMQC, and ^{13}C,^1H HMBC experiments. Reverse-phase medium-pressure liquid chromatography (RP-MPLC) was performed as follows: pressure, 16 bar; column, 50 × 2.5 cm; RP-18 silica gel, YMC ODS-A, 15 μm; detector, Knauer Variable Wavelength Monitor. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in open glass capillaries.

(Chloromethyl)trimethylsilane (1). This compound was commercially available (Aldrich).

Bis(chloromethyl)dimethylsilane (2). This compound was commercially available (Aldrich).

Preparation of Tris(chloromethyl)methylsilane (3). This compound was synthesized according to ref 2.

Preparation of Tetrakis(chloromethyl)silane (4). This compound was synthesized according to ref 5a.

Preparation of Trimethyl{[tris(trimethylsilyl)silyl]methyl}silane (5). Potassium *tert*-butoxide (189 mg, 1.68 mmol) and 18-crown-6 (453 mg, 1.71 mmol) were added one after another to a stirred solution of **13** (500 mg, 1.56 mmol) in toluene (15 mL), and the resulting mixture was stirred at 20 °C for 2 h. Subsequently, compound **1** (191 mg, 1.56 mmol) was added dropwise to the stirred mixture at 20 °C within 10 min, and stirring was continued for a further 4 h. The solvent was removed under reduced pressure, diethyl ether (15 mL) and water (15 mL) were added to the residue, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the low-boiling components were removed by bulb-to-bulb distillation (80 °C/1 mbar). The resulting crude product was purified by column chromatography on RP-18 silica gel [5–20 μm, 10 g (LiChroprep, Merck); eluent, methanol/water (95:5 (v/v))] and subsequent RP-MPLC on RP-18 silica gel [eluent, methanol/water (95:5 (v/v); flow rate, 12 mL min^{-1}]. The solvent of the eluate was removed under reduced pressure and the residue dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **5** in 82% yield as a colorless liquid (428 mg, 1.28 mmol).

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 6, 7·0.46Et$_2$O, 9, 10, and 11

	6	**7**·0.46Et$_2$O	**9**	**10**	**11**
empirical formula	$C_{22}H_{64}Si_9$	$C_{31}H_{90}Si_{13}\cdot 0.46C_4H_{10}O$	$C_{21}H_{46}O_3Si_5$	$C_{30}H_{72}O_3Si_9$	$C_{28}H_{80}Si_{12}$
formula mass, g mol^{-1}	581.54	862.13	487.03	733.69	754.00
collection T, K	193(2)	193(2)	173(2)	193(2)	100(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group (no.)	$P2_1/c$ (14)	$Pca2_1$ (29)	$P\bar{1}$ (2)	Pm (6)	$P2_1/n$ (14)
a, Å	16.138(2)	24.156(4)	9.8311(13)	10.017(2)	19.2212(15)
b, Å	13.614(2)	14.3086(17)	11.0157(13)	26.789(4)	26.902(2)
c, Å	18.046(2)	34.201(5)	15.9346(19)	10.0531(17)	19.2710(14)
α, deg	90	90	79.739(14)	90	90
β, deg	93.836(15)	90	84.820(15)	118.64(2)	95.416(4)
γ, deg	90	90	63.886(13)	90	90
V, Å^3	3955.9(10)	11821(3)	1524.6(3)	2367.8(7)	9920.2(13)
Z	4	8	2	2	8
D(calcd), g cm^{-3}	0.976	0.972	1.061	1.029	1.010
μ, mm^{-1}	0.312	0.304	0.252	0.277	0.330
F(000)	1288	3832	532	804	3328
cryst dimens, mm	0.5 × 0.5 × 0.5	0.5 × 0.5 × 0.5	0.4 × 0.4 × 0.1	0.5 × 0.4 × 0.3	0.30 × 0.22 × 0.132
θ range, deg	5.42−58.26	4.42−56.06	5.02−58.24	4.56−53.84	2.60−66.48
index ranges	$-22 \le h \le 22$, $-18 \le k \le 18$, $-24 \le l \le 24$	$-31 \le h \le 31$, $-18 \le k \le 18$, $-44 \le l \le 45$	$-13 \le h \le 13$, $-14 \le k \le 15$, $-21 \le l \le 21$	$-12 \le h \le 12$, $-33 \le k \le 33$, $-12 \le l \le 12$	$-29 \le h \le 29$, $-40 \le k \le 41$, $-28 \le l \le 29$
no. of collected reflns	58 711	150 836	17 727	24 080	223 384
no. of indep reflns	10 362	28 371	7820	10 099	37 929
R_{int}	0.0497	0.0642	0.0328	0.0549	0.0591
no. of reflns used	10 362	28 371	7820	10 099	37 929
no. of restraints	0	1	2	0	0
no. of params	300	873	276	440	769
S^a	1.035	1.036	1.069	1.060	1.061
weight params a/b^b	0.0596/0.2742	0.0724/0.6252	0.0681/0.1048	0.0797/0.8833	0.0329/2.7925
$R_1{}^c$ [$I > 2\sigma(I)$]	0.0356	0.0438	0.0387	0.0464	0.0334
$wR_2{}^d$ (all data)	0.0987	0.1126	0.1161	0.1314	0.0946
max./min. resid electron dens, e Å^{-3}	+0.372/−0.292	+0.532/−0.298	+0.459/−0.337	+0.595/−0.329	+0.540/−0.368

[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] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{0.5}$.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ −0.18 (s, 2 H, $\mathrm{SiC}H_2\mathrm{Si}$), 0.05 (s, 9 H, $\mathrm{CSiC}H_3$), 0.17 (s, 27 H, $\mathrm{SiSiC}H_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ −8.3 ($\mathrm{Si}C\mathrm{H_2Si}$), 1.3 ($\mathrm{SiSi}C\mathrm{H_3}$), 1.6 ($\mathrm{CSi}C\mathrm{H_3}$). ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ −85.1 ($\mathrm{CH_2}Si\mathrm{Si}$), −12.7 ($\mathrm{Si}Si\mathrm{CH_3}$), 2.0 ($\mathrm{C}Si\mathrm{C}$). Anal. Calcd for $C_{13}H_{38}Si_5$: C, 46.63; H, 11.44. Found: C, 45.19;[12] H, 11.43.

Preparation of Dimethylbis{[tris(trimethylsilyl)silyl]methyl}silane (6). This compound was synthesized analogously to **5** by using **13** (500 mg, 1.56 mmol), potassium *tert*-butoxide (189 mg, 1.68 mmol), 18-crown-6 (453 mg, 1.71 mmol), **2** (122 mg, 777 μmol), and toluene (15 mL). The crude product was purified by bulb-to-bulb distillation (120 °C/8 mbar) to remove the low-boiling components and was then crystallized from *n*-hexane (1 mL; slow cooling to −20 °C and crystallization over a period of 2 days). The product was isolated by removal of the mother liquor via a syringe and dried *in vacuo* (0.01 mbar, 20 °C, 2 h) to give **6** in 72% yield as a colorless crystalline solid (325 mg, 559 μmol); mp 125−127 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.05 (s, 4 H, $\mathrm{SiC}H_2\mathrm{Si}$), 0.09 (s, 6 H, $\mathrm{CSiC}H_3$), 0.13 (s, 54 H, $\mathrm{SiSiC}H_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ −6.5 ($\mathrm{Si}C\mathrm{H_2Si}$), 1.3 ($\mathrm{SiSi}C\mathrm{H_3}$), 2.6 ($\mathrm{CSi}C\mathrm{H_3}$). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ −84.7 ($\mathrm{CH_2}Si\mathrm{Si}$), −12.4 ($\mathrm{Si}Si\mathrm{CH_3}$), 4.4 ($\mathrm{C}Si\mathrm{C}$). Anal. Calcd for $C_{22}H_{64}Si_9$: C, 45.44; H, 11.09. Found: C, 43.81;[12] H, 10.91.

Preparation of Methyltris{[tris(trimethylsilyl)silyl]methyl}-silane (7). This compound was synthesized analogously to **5** by using **13** (500 mg, 1.56 mmol), potassium *tert*-butoxide (189 mg, 1.68 mmol), 18-crown-6 (453 mg, 1.71 mmol), **3** (100 mg, 522 μmol), and toluene (15 mL). The crude product was purified by bulb-to-bulb distillation (120 °C/8 mbar) to remove the low-boiling components and was then crystallized from diethyl ether (1 mL; slow cooling to −20 °C and crystallization over a period of 5 days). The product was isolated by removal of the mother liquor via a syringe and dried *in vacuo* (0.01 mbar, 20 °C, 2 h) to give **7** in 86% yield as a colorless crystalline solid (370 mg, 447 μmol); mp 180−181 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ −0.08 (s, 6 H, $\mathrm{SiC}H_2\mathrm{Si}$), 0.15 (s, 3 H, $\mathrm{CSiC}H_3$), 0.17 (s, 81 H, $\mathrm{SiSiC}H_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ −5.5 ($\mathrm{Si}C\mathrm{H_2Si}$), 1.3 ($\mathrm{SiSi}C\mathrm{H_3}$), 2.3 ($\mathrm{CSi}C\mathrm{H_3}$). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ −84.9 ($\mathrm{CH_2}Si\mathrm{Si}$), −12.7 ($\mathrm{Si}Si\mathrm{CH_3}$), 7.3 ($\mathrm{C}Si\mathrm{C}$). Anal. Calcd for $C_{31}H_{90}Si_{13}$: C, 44.96; H, 10.95. Found: C, 43.84;[12] H, 10.60.

Preparation of Dimethyl(2,4,6-trimethoxyphenyl){[tris(trimethylsilyl)]methyl}silane (9). This compound was synthesized analogously to **5** by using **13** (500 mg, 1.56 mmol), potassium *tert*-butoxide (189 mg, 1.68 mmol), 18-crown-6 (453 mg, 1.71 mmol), **16** (428 mg, 1.56 mmol), and toluene (15 mL). The crude product was purified by bulb-to-bulb distillation (100 °C/3 mbar) to remove the low-boiling components and was then crystallized from *n*-pentane (1 mL; slow cooling to −20 °C and crystallization over a period of 2 days). The product was isolated by removal of the mother liquor via a syringe and dried *in vacuo* (0.01 mbar, 20 °C, 2 h) to give **9** in 76% yield as a colorless crystalline solid (577 mg, 1.18 mmol); mp 66−67 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 0.11 (s, 27 H, $\mathrm{SiSiC}H_3$), 0.20 (s, 2 H, $\mathrm{SiC}H_2\mathrm{Si}$), 0.30 (s, 6 H, $\mathrm{CSiC}H_3$), 3.71 (s, 6 H, *o*-$\mathrm{OC}H_3$, $C_6H_2(OCH_3)_3$), 3.79 (s, 3 H, *p*-$\mathrm{OC}H_3$, $C_6H_2(OCH_3)_3$), 6.05 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ −8.0 ($\mathrm{Si}C\mathrm{H_2Si}$), 1.3 ($\mathrm{SiSi}C\mathrm{H_3}$), 3.2 ($\mathrm{CSi}C\mathrm{H_3}$) 55.2 (*o*-$\mathrm{O}C\mathrm{H_3}$, $C_6H_2(OCH_3)_3$), 55.5 (*p*-$\mathrm{O}C\mathrm{H_3}$, $C_6H_2(OCH_3)_3$), 90.6 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 106.4 (*C*-1, $C_6H_2(OCH_3)_3$), 163.5 (*C*-4, $C_6H_2(OCH_3)_3$), 166.6 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ −85.3 ($\mathrm{CH_2}Si\mathrm{Si}$), −12.5 ($\mathrm{Si}Si\mathrm{CH_3}$), −4.6 ($\mathrm{C}Si\mathrm{C}$). Anal. Calcd for $C_{21}H_{46}O_3Si_5$: C, 51.79; H, 9.52. Found: C, 51.40; H, 9.32.

---

[12] The product isolated was NMR-spectroscopically pure. The deviation of the experimental carbon content from the calculated value might be explained by partial SiC formation in the course of the elemental analysis.

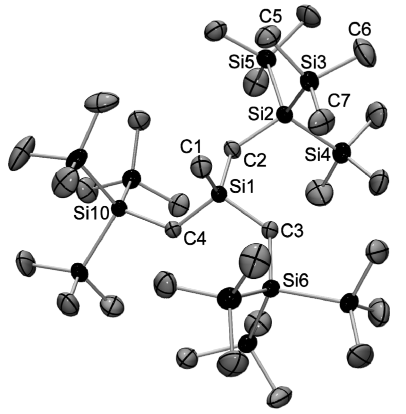


Figure 1. Molecular structure of one of the two crystallographically independent molecules of **7** in the crystal of **7**·0.46Et_2O (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−C1 1.878(3), Si1−C2 1.884(2), Si1−C3 1.879(2), Si1−C4 1.881(2), Si2−Si3 2.3562(10), Si2−Si4 2.3611(9), Si2−Si5 2.3616(9), Si2−C2 1.926(2), Si3−C5 1.881(3), Si3−C6 1.876(4), Si3−C7 1.883(4); Si1−C2−Si2 125.89(12), Si1−C3−Si6 125.54(13), Si1−C4−Si10 125.60(13), Si2−Si3−C5 111.62(13), Si2−Si3−C6 108.27(14), Si2−Si3−C7 113.58(13), Si3−Si2−Si4 111.00(4), Si3−Si2−Si5 109.23(4), Si3−Si2−C2 115.93(8), Si4−Si2−Si5 105.28(4), Si4−Si2−C2 111.18(8), Si5−Si2−C2 103.40(7), C1−Si1−C2 109.96(12), C1−Si1−C3 108.42(13), C1−Si1−C4 109.54(13), C2−Si1−C3 110.03(11), C2−Si1−C4 109.09(10), C3−Si1−C4 109.79(11), C5−Si3−C6 107.4(2), C5−Si3−C7 108.0(2), C6−Si3−C7 107.7(2).

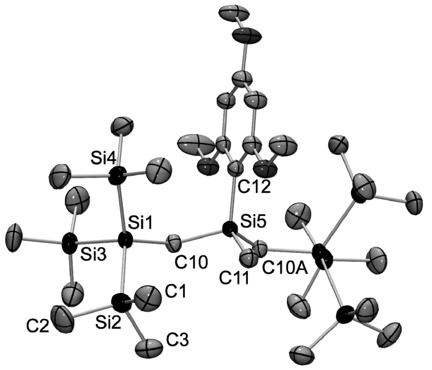


Figure 2. Molecular structure of one of the two crystallographically independent molecules of **10** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−Si2 2.3749(13), Si1−Si3 2.3534(12), Si1−Si4 2.3577(13), Si1−C10 1.923(3), Si2−C1 1.867(5), Si2−C2 1.878(5), Si2−C3 1.899(4), Si5−C10 1.875(3), Si5−C11 1.876(5), Si5−C12 1.920(4); Si1−Si2−C1 115.08(15), Si1−Si2−C2 110.41(17), Si1−Si2−C3 109.04(15), Si1−C10−Si5 126.13(16), Si2−Si1−Si3 107.56(5), Si2−Si1−Si4 111.00(5), Si2−Si1−C10 109.96(10), Si3−Si1−Si4 108.68(5), Si3−Si1−C10 101.42(9), Si4−Si1−C10 117.41(9), C1−Si2−C2 106.5(2), C1−Si2−C3 107.9(2), C2−Si2−C3 107.6(2), C10−Si5−C11 108.96(13), C10−Si5−C12 109.80(12), C10−Si5−C10A 104.71(18), C11−Si5−C12 114.2(2), C11−Si5−C10A 108.96(13), C12−Si5−C10A 109.80(12).

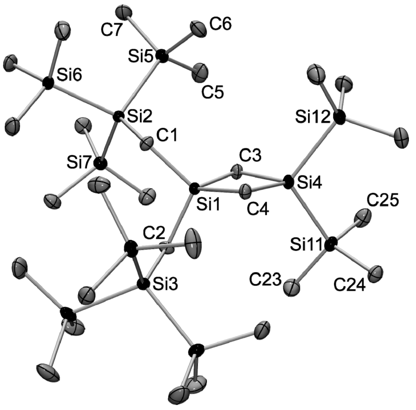


Figure 3. Molecular structure of one of the two crystallographically independent molecules of **11** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−C1 1.8713(10), Si1−C2 1.8700(10), Si1−C3 1.8991(11), Si1−C4 1.8968(10), Si2−Si5 2.3571(4), Si2−Si6 2.3560(4), Si2−Si7 2.3497(4), Si2−C1 1.9167(10), Si4−Si11 2.3540(4), Si4−Si12 2.3524(4), Si4−C3 1.9125(11), Si4−C4 1.9151(11), Si5−C5 1.8785(13), Si5−C6 1.8812(13), Si5−C7 1.8811(13), Si11−C23 1.8791(12), Si11−C24 1.8745(11), Si11−C25 1.8796(12); Si1−C1−Si2 120.67(5), Si1−C2−Si3 119.67(5), Si1−C3−Si4 88.47(4), Si1−C4−Si4 88.46(4), Si2−Si5−C5 114.79(5), Si2−Si5−C6 108.35(4), Si2−Si5−C7 110.15(4), Si4−Si11−C23 111.36(4), Si4−Si11−C24 114.64(4), Si4−Si11−C25 105.83(4), Si5−Si2−C1 111.58(4), Si6−Si2−C1 103.33(3), Si7−Si2−C1 118.88(3), Si11−Si4−Si12 109.542(17), Si11−Si4−C3 107.28(4), Si11−Si4−C4 120.99(4), Si12−Si4−C3 116.31(4), Si12−Si4−C4 111.21(3), C1−Si1−C2 108.69(5), C1−Si1−C3 112.46(5), C1−Si1−C4 117.67(5), C2−Si1−C3 116.23(5), C2−Si1−C4 109.67(5), C3−Si1−C4 91.59(5), C3−Si4−C4 90.62(5).

Preparation of Methyl(2,4,6-trimethoxyphenyl)bis{[tris(trimethylsilyl)silyl]methyl}silane (10). This compound was synthesized analogously to **5** by using **13** (500 mg, 1.56 mmol), potassium *tert*-butoxide (189 mg, 1.68 mmol), 18-crown-6 (453 mg, 1.71 mmol), **18** (219 mg, 708 μmol), and toluene (10 mL). Deviating from the synthesis of **5**, the reaction mixture was additionally stirred at 55 °C for 1 h. The crude product was purified by bulb-to-bulb distillation (120 °C/0.1 mbar) to remove the low-boiling components and was then crystallized from *n*-pentane (1 mL; slow cooling to −20 °C and crystallization over a period of 2 days). The product was isolated by removal of the mother liquor via a syringe and dried *in vacuo* (0.01 mbar, 20 °C, 2 h) to give **10** in 77% yield as a colorless crystalline solid (400 mg, 545 μmol); mp 162−164 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ −0.06 (δ_A) and 0.49 (δ_B) (SiCH_AH_BSi, 4 H, $^2J_{AB}$ = 13.6 Hz), 0.07 (s, 54 H, SiSiCH_3), 0.46 (s, 3 H, CSiCH_3), 3.64 (s, 3 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.74 (s, 3 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.78 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 5.99 (s, 1 H, *H*-3 or *H*-5, $C_6H_2(OCH_3)_3$), 6.03 (s, 1 H, *H*-3 or *H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ −5.7 (SiCH_2Si), 1.4 (SiSiCH_3), 4.9 (CSiCH_3), 54.5 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.2 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.6 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.46 (*C*-3 or *C*-5, $C_6H_2(OCH_3)_3$), 90.51 (*C*-3 or *C*-5, $C_6H_2(OCH_3)_3$), 106.0 (*C*-1, $C_6H_2(OCH_3)_3$), 163.6 (*C*-4, $C_6H_2(OCH_3)_3$), 166.5 (*C*-2 or *C*-6, $C_6H_2(OCH_3)_3$), 167.0 (*C*-2 or *C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ −85.1 (CH_2*Si*Si), −12.5 (Si*Si*CH_3), −2.0 (C*Si*C). Anal. Calcd for $C_{30}H_{72}O_3Si_9$: C, 49.11; H, 9.89. Found: C, 47.27;[12] H, 9.75.

Preparation of 1,1-Bis(trimethylsilyl)-3,3-bis{[tris(trimethylsilyl)silyl]methyl}-1,3-disilacyclobutane (11). This compound was synthesized analogously to **5** by using **13** (1.00 g, 3.12 mmol), potassium *tert*-butoxide (378 mg, 3.37 mmol), 18-crown-6 (906 mg, 3.43 mmol), **4** (176 mg, 779 μmol), and toluene (15 mL). Deviating from the synthesis of **5**, the reaction mixture was additionally stirred at 55 °C for 6 h. The crude product was purified by bulb-to-bulb distillation (160 °C/8 mbar) to remove the low-boiling components and was then crystallized from *n*-hexane (1 mL; slow cooling to −20 °C and crystallization over a period of 8 days). The product was isolated by removal of the mother liquor via a syringe and dried *in vacuo* (0.01 mbar, 20 °C, 2 h) to give **11** in 38% yield as a colorless crystalline solid (222 mg, 294 μmol); mp 167−168 °C. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ 0.19 (s, 18 H, Si-$(Si(CH_3)_3)_2$), 0.21 (s, 54 H, $Si(Si(CH_3)_3)_3$), 0.22 (s, 4 H, $SiCH_2Si$-$(Si(CH_3)_3)_3$), 0.32 (s, 4 H, $SiCH_2Si(Si(CH_3)_3)_2$). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ −4.1 ($SiCH_2Si(Si(CH_3)_3)_3$), −0.1 (Si(Si-$(CH_3)_3)_2$), 0.2 ($SiCH_2Si(Si(CH_3)_3)_2$), 2.2 ($Si(Si(CH_3)_3)_3$). ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ −85.0 ($Si(Si(CH_3)_3)_3$), −46.5 (*Si*-$(Si(CH_3)_3)_2$), −15.5 ($Si(Si(CH_3)_3)_2$), −12.7 ($Si(Si(CH_3)_3)_3$), 18.7 (SiC_4). Anal. Calcd for $C_{28}H_{80}Si_{12}$: C, 44.61; H, 10.69. Found: C, 43.28;[12] H, 10.71.

Tetrakis(trimethylsilyl)silane (13). This compound was commercially available (ABCR).

Preparation of (Chloromethyl)dimethyl(2,4,6-trimethoxyphenyl)silane (16). A 2.5 M solution of *n*-butyllithium in hexanes (98.0 mL, 245 mmol of *n*-BuLi) was added dropwise at 20 °C within 30 min to a stirred suspension of 1,3,5-trimethoxybenzene (40.0 g, 238 mmol) in a mixture of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (28.2 g, 243 mmol) and *n*-hexane (250 mL), and stirring was continued for a further 5 h at 20 °C. The resulting suspension was then added via a dropping funnel at 0 °C within 30 min to a vigorously stirred solution of chloro(chloromethyl)dimethylsilane (32.3 g, 226 mmol) in diethyl ether (200 mL), followed by stirring for 17 h. Water (300 mL) was added to the reaction mixture, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 200 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (190 °C/1 mbar) to give **16** in 63% yield as a colorless crystalline solid (46.3 g, 168 mmol); mp 32−33 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 0.35 (s, 6 H, $SiCH_3$), 3.15 (s, 2 H, $SiCH_2Cl$), 3.74 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.81 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.08 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ −2.2 ($SiCH_3$), 33.8 ($SiCH_2Cl$), 55.5 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.6 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.6 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 102.5 (*C*-1, $C_6H_2(OCH_3)_3$), 164.2 (*C*-4, $C_6H_2(OCH_3)_3$), 166.7 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): δ −5.6. Anal. Calcd for $C_{12}H_{19}ClO_3Si$: C, 52.45; H, 6.97. Found: C, 52.66; H, 6.97.

Preparation of Dichloro(methyl)(2,4,6-trimethoxyphenyl)silane (17). A 2.5 M solution of *n*-butyllithium in hexanes (10.3 mL, 25.8 mmol of *n*-BuLi) was added dropwise at 20 °C within 10 min to a stirred suspension of 1,3,5-trimethoxybenzene (4.20 g, 25.0 mmol) in a mixture of TMEDA (2.96 g, 25.5 mmol) and *n*-hexane (30 mL). The resulting suspension was stirred at 20 °C for 17 h and was then added at 0 °C within 30 min to a stirred solution of trichloro(methyl)silane (3.55 g, 23.7 mmol) in *n*-hexane (30 mL). The mixture was stirred at 0 °C for 2 h and then at 20 °C for a further 17 h. Diethyl ether (20 mL) was added, and the resulting mixture was stirred for 1 h at 20 °C. The precipitate was separated by filtration and washed with diethyl ether (3 × 10 mL), and the filtrate and the wash solutions were combined. The solvent was removed under reduced pressure, the residue was dissolved in boiling *n*-hexane (20 mL), and the resulting hot solution was filtered. The filtrate was cooled to 20 °C within 30 min and then kept undisturbed at this temperature for 2 h, and the resulting precipitate was isolated by filtration to give **17** in 62% yield as a colorless crystalline solid (4.10 g, 14.6 mmol). ^{1}H NMR (300.1 MHz, C_6D_6): δ 1.27 (s, 3 H, $SiCH_3$), 3.30 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.37 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 5.97 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 11.3 ($SiCH_3$), 55.3 (*o*-OCH_3, $C_6H_2(OCH_3)_3$) 55.5 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 91.3 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 93.9 (*C*-1, C_6H_2-$(OCH_3)_3$), 166.3 (*C*-4, $C_6H_2(OCH_3)_3$), 167.2 (*C*-2/*C*-6, C_6H_2-$(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 14.9. Anal. Calcd for $C_{10}H_{14}Cl_2O_3Si$: C, 42.71; H, 5.02. Found: C, 42.72; H, 5.02.

Preparation of Bis(chloromethyl)methyl(2,4,6-trimethoxyphenyl)silane (18). A 2.5 M solution of *n*-butyllithium in hexanes (3.84 mL, 9.60 mmol of *n*-BuLi) was added dropwise at −70 °C (±3 °C, temperature measurement within the flask) within 4 h to a stirred mixture of **17** (1.35 g, 4.80 mmol), bromochloromethane (1.86 g, 14.4 mmol), and THF (100 mL) (the *n*-butyllithium solution was added via a special horizontally elongated side neck of the three-necked flask, which itself was immersed in the cooling bath to ensure precooling of the *n*-butyllithium solution before making contact with the reaction mixture). After the addition was complete, the mixture was stirred at −70 °C for 2 h and was then allowed to warm to 20 °C within 17 h. The solvent was removed under reduced pressure, and diethyl ether (50 mL) and half-saturated aqueous sodium hydrogen carbonate solution (50 mL) were added sequentially to the residue. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 25 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel [40−63 μm, 150 g (Merck); eluent, *n*-hexane/ethyl acetate/triethylamine (12:7:1 (v/v/v))]. The resulting product was dissolved in a boiling mixture of *n*-hexane (9.7 mL) and triethylamine (0.3 mL), and the resulting solution was cooled to 20 °C within 30 min and then kept undisturbed at this temperature for 3 days. The resulting precipitate was isolated by filtration and dried *in vacuo* (0.001 mbar, 20 °C, 2 h) to give **18** in 59% yield as a colorless crystalline solid (872 mg, 2.82 mmol); mp 42−43 °C. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.74 (s, 3 H, $SiCH_3$), 3.22 (s, 6 H, *o*-OCH_3, C_6H_2-$(OCH_3)_3$), 3.42 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 3.46 (δ_A) and 3.56 (δ_B) ($SiCH_AH_BCl$, 2 H, $^2J_{AB} = 13.4$ Hz), 6.02 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ −4.6 ($SiCH_3$), 29.6 ($SiCH_2Cl$), 54.7 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 54.8 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 99.3 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 162.3 (*C*-1, C_6H_2-$(OCH_3)_3$), 164.8 (*C*-4, $C_6H_2(OCH_3)_3$), 167.0 (*C*-2/*C*-6, C_6H_2-$(OCH_3)_3$). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 14.9. Anal. Calcd for $C_{12}H_{18}Cl_2O_3Si$: C, 46.60; H, 5.87. Found: C, 46.38; H, 5.82.

Crystal Structure Analyses. Suitable single crystals of **6**, **7**$\cdot 0.46Et_2O$, **9**, **10**, and **11** were obtained by crystallization from *n*-hexane (**6**, **11**), diethyl ether (**7**$\cdot 0.46Et_2O$), or *n*-pentane (**9**, **10**) at −20 °C. The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (**6**, **7**$\cdot 0.46Et_2O$, **9**, and **10**: Stoe IPDS, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); **11**: Bruker Nonius KAPPA APEX II CCD system with Montel mirror, Mo Kα radiation (λ = 0.71073 Å)). The structures were solved by direct methods (SHELXS-97).[13] Except for the solvent in the structure of **7**, all non-hydrogen atoms were refined anisotropically (SHELXL-97).[13] 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-790857 (**6**), CCDC-790858 (**7**$\cdot 0.46Et_2O$), CCDC-790859 (**9**), CCDC-790860 (**10**), and CCDC-790861 (**11**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223/336033; e-mail, deposit@ccdc.cam.ac.uk).

Acknowledgment. We thank Professor C. Marschner, Technical University of Graz, Austria, for his advice in context with the preparation of $(Me_3Si)_3SiK \cdot 18$-crown-6 and $Me_3SiCH_2Si(SiMe_3)_3$.

Supporting Information Available: Crystallographic data for **6**, **7**$\cdot 0.46Et_2O$, **9**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(13) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.