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Synthesis of the Multifunctional (Chloromethyl)silanes $Cl_2Si(CH_2Cl)_2$, $(MeO)_2Si(CH_2Cl)_2$, $RSi(CH_2Cl)_3$ (R = 2,4,6-Trimethoxyphenyl), $ClSi(CH_2Cl)_3$, $MeOSi(CH_2Cl)_3$, $Si(CH_2Cl)_4$, and $ClCH_2CH_2Si(CH_2Cl)_3$[§]

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A series of multifunctional (chloromethyl)silanes have been synthesized: $Cl_2Si(CH_2Cl)_2$ (**1**), $(MeO)_2Si(CH_2Cl)_2$ (**2**), tris(chloromethyl)(2,4,6-trimethoxyphenyl)silane (**3**), $ClSi(CH_2Cl)_3$ (**4**), $MeOSi(CH_2Cl)_3$ (**5**), $Si(CH_2Cl)_4$ (**6**), and $ClCH_2CH_2Si(CH_2Cl)_3$ (**7**). The synthesis of these compounds is based on coupling reactions between (chloromethyl)lithium, generated in situ from bromochloromethane and *n*-butyllithium in tetrahydrofuran, and chlorosilanes. Compounds **1**−**7** were characterized by NMR studies (^{1}H, ^{13}C, ^{29}Si) and elemental analyses, and **3** and **6** were additionally studied by single-crystal X-ray diffraction. Silanes with more than one $SiCH_2Cl$ moiety and compounds of this type with additional *Si*-functional groups are of great interest for synthetic organosilicon chemistry.

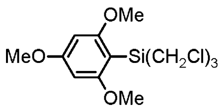
Introduction

(Chloromethyl)silanes are versatile starting materials for the synthesis of organofunctional silanes.[1] The coupling reaction between chlorosilanes and (chloromethyl)lithium, generated in situ from bromochloromethane and *n*-butyllithium in tetrahydrofuran, has been demonstrated to be an excellent preparative method for the synthesis of (chloromethyl)silanes.[2,3] We have used this method for the preparation of bis(chloromethyl)silanes $R_2Si(CH_2Cl)_2$, tris(chloromethyl)silanes $RSi(CH_2Cl)_3$, and tetrakis(chloromethyl)silane. Silanes with more than one $SiCH_2Cl$ moiety and compounds of this type with additional *Si*-functional groups are of great interest for synthetic organosilicon chemistry. There is a need for convenient and reliable preparative methods for the synthesis of such compounds, for instance for the development of new silicon-based drugs that contain more than one *Si*-bound organofunctional group.[4]

Investigations prior to this work have shown that neither the photochlorination of methylsilanes[5] nor the reaction of chlorosilanes with diazomethane[6,7] is a convenient method for the preparation of such compounds, since both methods suffer from their lack of selectivity and broad applicability to a wide range of chloro(organyl)silanes. In addition, the diazomethane method is problematic due to its dangerous handling and the toxicity of this reagent.

We report here the synthesis and characterization of the (chloromethyl)silanes **1**−**7**, including the crystal structure analyses of **3** and **6**. The synthesis of **1**−**7** is based on coupling reactions between (chloromethyl)lithium, generated in situ, and chlorosilanes. Preliminary results of these studies have already been reported elsewhere.[8]

$R_2Si(CH_2Cl)_2$
1: R = Cl
2: R = OMe



3

$RSi(CH_2Cl)_3$
4: R = Cl
5: R = OMe

$Si(CH_2Cl)_4$
6

$ClCH_2CH_2Si(CH_2Cl)_3$
7

[§] Dedicated to Professor Nils Wiberg on the occasion of his 70th birthday.

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

(3) Handmann, V. I.; Bertermann, R.; Burschka, C.; Tacke, R. *J. Organomet. Chem.* **2000**, *613*, 19−25.

(4) Recent review on silicon-based drugs: Bains, W.; Tacke, R. *Curr. Opin. Drug Discovery Dev.* **2003**, *6*, 526−543.

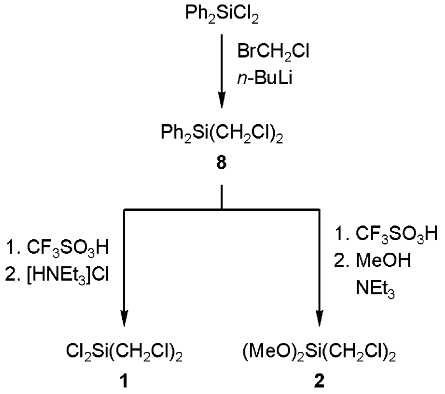
(5) The photochlorination of Me_3SiCl preferably results in an exhaustive chlorination of one methyl group rather than in monochlorination of all three methyl groups; that is, no $ClSi(CH_2Cl)_3$ (**4**) could be isolated: Speier, J. L. *J. Am. Chem. Soc.* **1951**, *73*, 824−826.

(6) The yields of transformations of the type $R^1R^2R^3SiCl \rightarrow R^1R^2R^3SiCH_2Cl$ (R^1, R^2, R^3 = independently H, Cl, Me, Et) with the diazomethane method strongly depend on the $R^1R^2R^3Si$ groups: Seyferth, D.; Rochow, E. G. *J. Am. Chem. Soc.* **1955**, *77*, 907−908.

(7) Stepwise chloromethylation of $SiCl_4$ using the diazomethane method, $SiCl_4 \rightarrow Cl_3SiCH_2Cl \rightarrow Cl_2Si(CH_2Cl)_2$ (**1**) $\rightarrow ClSi(CH_2Cl)_3$ (**4**) (formation of $Si(CH_2Cl)_4$ (**6**) has not been reported): (a) Yakubovich, A. Y.; Makarov, S. P.; Ginsburg, V. A.; Gavrilov, G. I.; Merkulova, E. N. *Dokl. Akad. Nauk SSSR* **1950**, *72*, 69−72; *Chem. Abstr.* **1951**, *45*, 2856i. (b) Yakubovich, A. Y.; Ginsburg, V. A. *Zh. Obshch. Khim.* **1952**, *22*, 1783−1787; *Chem. Abstr.* **1953**, *47*, 9256e. (c) Anderson, W. K.; Kasliwal, R.; Houston, D. M.; Wang, Y.; Narayanan, V. L.; Haugwitz, R. D.; Plowman, J. *J. Med. Chem.* **1995**, *38*, 3789−3797.

10.1021/om040086v CCC: $27.50

Scheme 1



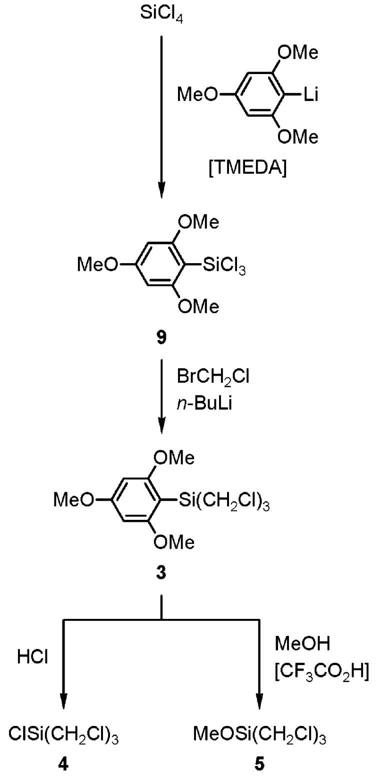
Results and Discussion

Syntheses. The bis(chloromethyl)silanes $Cl_2Si(CH_2Cl)_2$ (**1**) and $(MeO)_2Si(CH_2Cl)_2$ (**2**) were synthesized according to Scheme 1, starting from dichlorodiphenylsilane. Thus, treatment of Ph_2SiCl_2 with 2 molar equiv of the reagent system $BrCH_2Cl$/*n*-BuLi gave bis(chloromethyl)diphenylsilane[3] (**8**). Reaction of **8** with triflic acid, followed by treatment with triethylammonium chloride, gave **1** (yield 67%).[9] Reaction of **8** with triflic acid and subsequent methanolysis afforded **2** (yield 55%).

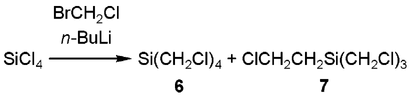
Tris(chloromethyl)(2,4,6-trimethoxyphenyl)silane (**3**) and the tris(chloromethyl)silanes $ClSi(CH_2Cl)_3$ (**4**) and $MeOSi(CH_2Cl)_3$ (**5**) were synthesized according to Scheme 2, starting from tetrachlorosilane. Thus, reaction of $SiCl_4$ with 1 molar equiv of (2,4,6-trimethoxyphenyl)lithium yielded trichloro(2,4,6-trimethoxyphenyl)silane (**9**) (yield 65%), which upon treatment with $BrCH_2Cl$/*n*-BuLi gave **3** (yield 39%). Treatment of **3** with an ethereal hydrogen chloride solution finally afforded **4** (yield 65%), whereas methanolysis of **3**, in the presence of trifluoroacetic acid, gave **5** (yield 69%).

The synthesis of **3** and the subsequent transformations **3** → **4** and **3** → **5** are quite remarkable (selective Si−C cleavage reactions of **3** with HCl or MeOH (catalyzed by CF_3COOH) under mild conditions), demonstrating that the *Si*-2,4,6-trimethoxyphenyl moiety can be used as a protecting group in synthetic organosilicon chemistry. Further applications of this protecting group have been published elsewhere.[10]

Scheme 2



Scheme 3



The silane $Si(CH_2Cl)_4$ (**6**) was synthesized according to Scheme 3 by treatment of tetrachlorosilane with 4 molar equiv of $BrCH_2Cl$/*n*-BuLi (yield 26%), and the silane **7** was obtained as a byproduct in this synthesis (27% yield, with respect to $SiCl_4$). It is likely that the formation of **7** is based on a coupling reaction of **6** with $BrCH_2Cl$/*n*-BuLi. Control experiments have demonstrated that treatment of **6** with $BrCH_2Cl$/*n*-BuLi, under the same conditions as described for the synthesis of **6**, results in the formation of **7**.

Compounds **1**, **2**, **4**, **5**, and **7** were isolated as colorless liquids, whereas **3**, **6**, and **9** were obtained as colorless crystalline solids. The identities of all these compounds were established by elemental analyses and NMR studies (^{1}H, ^{13}C, ^{29}Si), and **3** and **6** were additionally characterized by crystal structure analyses.

Crystal Structure Analyses. Compounds **3** and **6** were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for these studies are given in Table 1. The molecular structures of **3** and **6** are depicted in Figures 1 and 2; selected interatomic distances and bond angles are given in the respective figure captions.

Compound **3** crystallizes in the space group $P\bar{1}$. The molecular structure is characterized by short intramolecular distances between the silicon atom and the oxygen atoms in the *ortho*-methoxy groups. These Si···O distances amount to 2.8708(15) and 3.0679(14) Å, respectively, and are shorter than the sum of the van der Waals radii of silicon (2.1 Å) and oxygen (1.5 Å), but significantly longer than a typical covalent Si−O bond (1.64 Å)[11] of a tetracoordinate silicon compound. Very similar results have been reported for a series of other (2,4,6-trimethoxyphenyl)silanes.[12]

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[8] (a) Wagner, S. A.; Richter, I.; Barth, K.; Burschka, C. *13th International Symposium on Organosilicon Chemistry-35th Organosilicon Symposium*; Guanajuato, Mexico, August 25−31, 2002; Abstract P2-16. (b) Daiss, J. O.; Barth, K.; Burschka, C.; Hey, P.; Klemm, K.; Richter, I.; Tacke, R. *2nd European Organosilicon Days*; München, Germany, September 11−12, 2003; Abstract P131.

[9] Interestingly, attempts to prepare **1** in a one-step synthesis by treatment of Cl_3SiCH_2Cl with 1 molar equiv of $BrCH_2Cl$/*n*-BuLi resulted in the formation of a mixture of products, with $Si(CH_2Cl)_4$ (**6**) as the main product. The reaction conditions were the same as described for the transformation $SiCl_4$ → $Si(CH_2Cl)_4$ (**6**).

[10] Daiss, J. O.; Penka, M.; Burschka, C.; Tacke, R. *Organometallics*, in press.

[11] Rademacher, P. *Strukturen organischer Moleküle*; VCH Verlagsgesellschaft: Weinheim, Germany, 1987; p 56.

[12] Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *J. Organomet. Chem.* **1999**, *588*, 51−59.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 3 and 6

	3	**6**
empirical formula	$C_{12}H_{17}Cl_3O_3Si$	$C_4H_8Cl_4Si$
formula mass, g mol^{-1}	343.70	225.99
collection *T*, K	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073
cryst syst	triclinic	tetragonal
space group (no.)	$P\bar{1}$(2)	$P\bar{4}2_1c$ (114)
a, Å	7.8786(12)	8.4649(12)
b, Å	8.0041(11)	8.4649(12)
c, Å	12.4129(19)	6.6199(13)
α, deg	92.665(17)	90
β, deg	90.158(18)	90
γ, deg	93.517(17)	90
V, Å^3	780.4(2)	474.35(13)
Z	2	2
D(calcd), g cm^{-3}	1.463	1.582
μ, mm^{-1}	0.664	1.296
F(000)	356	228
cryst dimens, mm	0.3 × 0.3 × 0.1	0.5 × 0.2 × 0.1
2θ range, deg	5.18−54.00	7.82−55.98
index ranges	$-10 \le h \le 9$, $-10 \le k \le 9$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-8 \le k \le 11$, $-8 \le l \le 8$
no. of collected reflns	5891	2734
no. of indep reflns	3095	561
R_{int}	0.0226	0.0537
no. of reflns used	3095	561
no. of restraints	7	
no. of params	186	27
S^a	1.053	1.074
weight params *a*/*b*^{b}	0.0614/0.1586	0.0246/0.1794
$R1^c$ [$I > 2\sigma(I)$]	0.0353	0.0223
$wR2^d$ (all data)	0.1007	0.0581
absolute struct param		−0.07(15)
max./min. residual electron density, e Å^{-3}	+0.322/−0.332	+0.165/−0.293

[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] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Compound **6** crystallizes in the space group $P\bar{4}2_1c$. The asymmetric unit contains only one “quarter” of the $Si(CH_2Cl)_4$ molecule. The structure of **6** is not isostructural to that of its carbon analogue $C(CH_2Cl)_4$, which crystallizes in the space group $P2_1/n$.[13] On the basis of quantum-chemical calculations, the symmetry of **6** has recently been predicted to be S_4, containing four smaller and two larger C−Si−C bond angles,[14] which is confirmed by the crystal structure analysis of **6**.

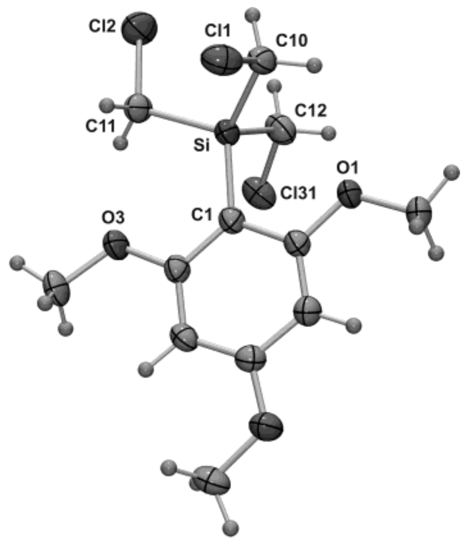

Figure 1. Molecular structure of **3** in the crystal (probability level of displacement ellipsoids 50%). Due to the presence of two different conformations of the Si−C12−Cl31(Cl32) group, the crystal structure of **3** is characterized by a disorder. The structure shown represents the dominating conformer (occupancy 65%). Selected interatomic distances (Å) and bond angles (deg): Si−C1 1.854(2), Si−C10 1.8750(19), Si−C11 1.8735(19), Si−C12 1.876(2), C10−Cl1 1.789(2), C11−Cl2 1.803(2), C12−Cl31 1.802(4), Si···O1 2.8708(15), Si···O3 3.0679(14), C1−Si−C10 113.46(9), C1−Si−C11 112.88(8), C1−Si−C12 110.51(10), C10−Si−C11 107.13(9), C10−Si−C12 104.40(9), C11−Si−C12 107.96(10), Si−C10−Cl1 111.08(10), Si−C11−Cl2 110.52(10), Si−C12−Cl31 111.42(14).

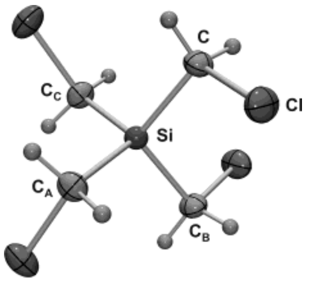

Figure 2. Molecular structure of **6** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si−C 1.8758(18), C−Cl 1.8035(19), C−Si−C_A 109.14(6), C−Si−C_B 110.14(12), Si−C−Cl 109.69(9). The silicon atom lies on a special position ($^1/_2$, $^1/_2$, $^1/_2$), and the molecule shows S_4 symmetry.

Conclusions

We have succeeded in developing convenient and reliable preparative methods for the synthesis of a series of multifunctional (chloromethyl)silanes of the type $R_nSi(CH_2Cl)_{4-n}$ ($n = 0-2$), with R being an *Si*-functional group. Multifunctional (chloromethyl)silanes are of great interest for synthetic organosilicon chemistry. Tetrakis(chloromethyl)silane (**6**), with its four *C*-functional groups, is a particularly versatile starting material for the synthesis of a huge variety of tetrafunctionalized tetraorganylsilanes. For instance, we have recently succeeded in preparing the silanes $Si(CH_2OH)_4$ and $Si(CH_2SH)_4$, starting from **6**.[15] Currently, we are exploring the synthetic potential of **6** for the preparation of dendrimers.

Experimental Section

General Procedures. The transformations **8** → **1** and **8** → **2** were carried out under dry argon, whereas all the other syntheses were performed under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR 50 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi melting point B-540 apparatus using samples in open glass capillaries (except for **9**, for which sealed glass capillaries were used). The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker

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[14] Xu, Z.; Zhao, C.; Lin, Z. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2319−2323.

[15] Ilg, R.; Troegel, D.; Burschka, C.; Tacke, R., unpublished results.

DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz). $CDCl_3$, CD_2Cl_2, or C_6D_6 was used as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), $CHDCl_2$ (^{1}H, δ 5.32; CD_2Cl_2), CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), C_6HD_5 (^{1}H, δ 7.28; C_6D_6), 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). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments, and in the case of **3** assignment of the ^{1}H and ^{13}C NMR data was supported by ^{13}C,^{1}H correlation experiments. In the case of **7**, ^{13}C,^{1}H and ^{29}Si,^{1}H correlation experiments were performed. The GC/EI-MS studies were performed with a ThermoQuest MS-8060 gas chromatograph (Phenomenex Zebron ZB-1 capillary column, 15 m, i.d. 0.25 mm, film thickness 0.25 μm; injector, split (1:10), 220 °C; carrier gas, helium) and a ThermoQuest TRIO 1000 mass spectrometer (EI MS, 70 eV).

Preparation of Dichlorobis(chloromethyl)silane (1). Triflic acid (72.1 g, 480 mmol) was added dropwise at 20 °C within 45 min to a stirred solution of **8** (61.4 g, 218 mmol) in *n*-pentane (180 mL). After the addition was complete, the mixture was heated under reflux for 1 h and then cooled to 0 °C, followed by addition of triethylammonium chloride (66.1 g, 480 mmol) in small portions at 0 °C (vigorous reaction) within 10 min. The mixture was stirred at 0 °C for a further 5 min and then at 20 °C for another 16 h (formation of a two-phase system). The upper organic phase was separated, and the lower phase (mainly consisting of triethylammonium triflate) was washed with *n*-pentane (2 × 50 mL). The organic phase and the wash solutions were combined, the solvent was removed by distillation under atmospheric pressure, and the residue was distilled in vacuo (Vigreux column, 10 cm) to give **1** in 67% yield as a colorless liquid (28.9 g, 146 mmol); bp 91 °C/85 mbar. ^{1}H NMR (CD_2Cl_2): δ 3.32 (s, $SiCH_2Cl$). ^{13}C NMR (CD_2Cl_2): δ 28.0 ($SiCH_2Cl$). ^{29}Si NMR (CD_2Cl_2): δ 11.5. Anal. Calcd for $C_2H_4Cl_4Si$: C, 12.14; H, 2.04. Found: C, 12.5; H, 2.1.

Preparation of Bis(chloromethyl)dimethoxysilane (2). Triflic acid (41.0 g, 273 mmol) was added dropwise at 20 °C within 20 min to a stirred solution of **8** (34.9 g, 124 mmol) in *n*-pentane (100 mL) (slight warming), and the mixture was then heated under reflux for 1 h. The stirred mixture was cooled to 0 °C, and a mixture of methanol (8.70 g, 272 mmol) and triethylamine (27.7 g, 274 mmol) was added dropwise at 0 °C within 8 min (formation of a two-phase system), followed by warming to 20 °C within 30 min and stirring at 20 °C for a further 2 h. The upper organic phase was isolated, and the lower phase (mainly consisting of triethylammonium triflate) was washed with *n*-pentane (2 × 50 mL). The organic phase and the wash solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 20 cm) to give **2** in 55% yield as a colorless liquid (12.8 g, 67.7 mmol); bp 96 °C/49 mbar. ^{1}H NMR ($CDCl_3$): δ 2.95 (s, 4 H, $SiCH_2Cl$), 3.66 (s, 6 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 23.5 ($SiCH_2Cl$), 51.7 (OCH_3). ^{29}Si NMR ($CDCl_3$): δ −26.0. Anal. Calcd for $C_4H_{10}Cl_2O_2Si$: C, 25.40; H, 5.33. Found: C, 25.6; H, 5.0.

Preparation of Tris(chloromethyl)(2,4,6-trimethoxyphenyl)silane (3). A 2.5 M solution of *n*-butyllithium in *n*-hexane (110 mL, 275 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 **9** (27.2 g, 90.2 mmol), bromochloromethane (52.8 g, 408 mmol), and THF (150 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 6 h and then warmed to −25 °C within 11 h. The cold (−25 °C) mixture was poured into a cold (0 °C), stirred two-phase mixture of half-saturated aqueous sodium hydrogen carbonate solution (200 mL, solution A) and ethyl acetate (100 mL). The resulting mixture was stirred at 0 °C for 5 min, and the organic phase was separated and washed with water (200 mL, solution B). The first aqueous wash solution (A) was extracted with ethyl acetate (100 mL), the resulting organic extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second and third extraction of the wash solutions A and B with fresh portions of ethyl acetate (2 × 100 mL) using the same protocol as described for the first extraction sequence. All organic extracts were combined and dried briefly over anhydrous sodium sulfate, followed by an additional thorough dynamic drying over anhydrous sodium sulfate using a standard chromatographic column densely packed with anhydrous sodium sulfate (column dimensions, 20 cm × 3.5 cm). The sodium sulfate was finally washed with ethyl acetate (3 × 300 mL), all organic solutions were combined, the solvent was removed under reduced pressure, and the oily residue (30 g) was purified by column chromatography on silica gel (column dimensions, 61 cm × 5.5 cm; silica gel (32−63 μm, ICN 02826), 640 g; eluent, *n*-hexane/diethyl ether/1,8-diazabicyclo[5.4.0]undec-7-ene (59:40:1 (v/v/v))). The relevant fractions (GC control) were combined, and the solvent was removed under reduced pressure to give 16 g of a colorless oily product, which was crystallized and then recrystallized twice from boiling *n*-hexane. A 200 mL portion was used for each crystallization step, and the crystallizations were carried out at 4 °C over a period of 1 day. The precipitate was isolated by filtration and washed with cold (0 °C) *n*-pentane (40 mL) after each crystallization step, and the product was finally dried in vacuo (0.001 mbar, 20 °C, 2 h) to give **3** in 39% yield (including workup of the combined mother liquors) as a colorless crystalline solid (12.1 g, 35.2 mmol); mp 88 °C. ^{1}H NMR (C_6D_6): δ 3.18 (s, 6 H, *o*-OCH_3), 3.40 (s, 3 H, *p*-OCH_3), 3.50 (s, 6 H, $SiCH_2Cl$), 5.97 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (C_6D_6): δ 26.8 ($SiCH_2Cl$), 54.72 (*p*-OCH_3), 54.75 (*o*-OCH_3), 90.9 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 95.9 (*C*-1, $C_6H_2(OCH_3)_3$), 165.4 (*C*-4, $C_6H_2(OCH_3)_3$), 167.3 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (C_6D_6): δ −7.0. Anal. Calcd for $C_{12}H_{17}Cl_3O_3Si$: C, 41.93; H, 4.99. Found: C, 41.9; H, 5.1.

Preparation of Chlorotris(chloromethyl)silane (4). A 2.0 M ethereal hydrogen chloride solution (24.0 mL, 48 mmol of HCl) was added dropwise at 0 °C within 2 min to a stirred suspension of **3** (14.4 g, 41.9 mmol) in diethyl ether (10 mL), and the resulting mixture was stirred at 0 °C for 1 min. After the cooling bath was removed, the temperature increased to 20 °C within ca. 5 min (concomitant dissolution of **3**), and the mixture was stirred at this temperature for a further 20 min (quantitative conversion **3** → **4** (GC control)). The solvent was removed under reduced pressure, the residue was distilled in vacuo (Vigreux column, 5 cm) to remove most of the 1,3,5-trimethoxybenzene formed, and the fraction boiling at 86−117 °C/1 mbar was collected (8.1 g) and then redistilled in vacuo (Vigreux column, 13 cm) to give **4** in 65% yield as a colorless liquid (5.77 g, 27.2 mmol); bp 85 °C/1 mbar. ^{1}H NMR (C_6D_6): δ 2.70 (s, $SiCH_2Cl$). ^{13}C NMR (C_6D_6): δ 24.8 ($SiCH_2Cl$). ^{29}Si NMR (C_6D_6): δ 10.5. Anal. Calcd for $C_3H_6Cl_4Si$: C, 17.00; H, 2.85. Found: C, 17.3; H, 3.0.

Preparation of Tris(chloromethyl)methoxysilane (5). Trifluoroacetic acid (179 mg, 1.57 mmol) was added at 20 °C to a stirred suspension of **3** (10.2 g, 29.7 mmol) in methanol (30 mL), and the resulting mixture was stirred at this temperature for 22 h (dissolution of **3** and quantitative conversion **3** → **5** (GC control)). The solvent was removed under reduced pressure, the residue was distilled in vacuo (Vigreux column, 5 cm) to remove most of the 1,3,5-trimethoxybenzene formed, and the fraction boiling at 90−127 °C/1 mbar was collected (6.3 g) and then redistilled in vacuo (Vigreux column, 8 cm) to give **5** in 69% yield as a colorless liquid (4.24 g, 20.4 mmol); bp 94 °C/1 mbar. ^{1}H NMR (C_6D_6): δ 2.74 (s, 6 H, $SiCH_2Cl$), 3.38 (s, 3 H, OCH_3). ^{13}C NMR (C_6D_6): δ 23.9 ($SiCH_2Cl$), 52.3 (OCH_3). ^{29}Si NMR (C_6D_6): δ −4.9. Anal. Calcd for $C_4H_9Cl_3OSi$: C, 23.15; H, 4.37. Found: C, 23.2; H, 4.1.

Preparation of Tetrakis(chloromethyl)silane (6) and (2-Chloroethyl)tris(chloromethyl)silane (7). A 2.5 M solution of *n*-butyllithium in *n*-hexane (113 mL, 283 mmol of *n*-BuLi) was added dropwise at −68 °C (±3 °C, temperature measurement within the flask) within 4 h to a stirred mixture of tetrachlorosilane (11.5 g, 67.7 mmol), bromochloromethane (52.4 g, 405 mmol), and THF (150 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 −78 °C for 5 h and then warmed to 20 °C within 17 h. The solvent was removed under reduced pressure (formation of a precipitate), and the resulting slurry was subjected to column chromatography on silica gel to separate the products **6** and **7** (column dimensions, 50 cm × 5.5 cm; silica gel (32−63 μm, ICN 02826), 520 g; eluent, *n*-hexane). The relevant first fractions containing **6** (GC control) were combined, and the solvent was removed under reduced pressure to give 5.1 g of a colorless sticky solid, which was recrystallized from boiling *n*-heptane (10 mL; crystallization at 20 °C over a period of 6 h). The resulting precipitate was isolated by removal of the supernatant solution via a syringe, washed with *n*-heptane (4 mL), and dried in vacuo (0.001 mbar, 20 °C, 4 h) to give **6** in 26% yield as a colorless crystalline solid (4.02 g, 17.8 mmol); mp 71−72 °C. After further elution of the column with *n*-hexane (ca. 3 L), compound **7** was obtained. The relevant fractions (GC control) were combined, and the solvent was removed under reduced pressure to give **7** in 27% yield as an NMR-spectroscopically pure colorless liquid (4.40 g, 18.3 mmol).[16]

Data for 6. ^{1}H NMR (CDCl$_3$): δ 3.15 (s, SiCH_2Cl). ^{13}C NMR (CDCl$_3$): δ 22.7 (SiCH$_2$Cl). ^{29}Si NMR (CDCl$_3$): δ −0.7. Anal. Calcd for $C_4H_8Cl_4Si$: C, 21.26; H, 3.57. Found: C, 21.5; H, 3.5.

Data for 7. ^{1}H NMR (CDCl$_3$): δ 1.63 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, SiCH_2CH$_2$Cl), 3.09 (s, 6 H, SiCH_2Cl), 3.81 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, SiCH$_2$CH_2Cl). ^{13}C NMR (CDCl$_3$): δ 14.8 (SiCH$_2$CH$_2$Cl), 24.4 (SiCH$_2$Cl), 40.8 (SiCH$_2$$CH_2$Cl). ^{29}Si NMR (CDCl$_3$): δ 0.3. Anal. Calcd for $C_5H_{10}Cl_4Si$: C, 25.02; H, 4.20. Found: C, 25.0; H, 4.3.

Preparation of Bis(chloromethyl)diphenylsilane (8). This compound was synthesized according to ref 3.

Preparation of Trichloro(2,4,6-trimethoxyphenyl)silane (9). A suspension of 1,3,5-trimethoxybenzene (100 g, 595 mmol) in a mixture of *n*-hexane (350 mL) and *N,N,N′,N′*-tetramethylethane-1,2-diamine (TMEDA; 71.4 g, 614 mmol) was heated to ca. 50 °C to dissolve the 1,3,5-trimethoxybenzene. After the heat source was removed, a 2.5 M solution of *n*-butyllithium in *n*-hexane (244 mL, 610 mmol of *n*-BuLi) was added dropwise within 20 min to the vigorously stirred mixture. During the addition, the heat of reaction caused the mixture to boil under reflux, and a white precipitate was formed. After the addition was complete, the mixture was stirred vigorously (to prevent agglomeration) at 20 °C for 3 days (formation of (2,4,6-trimethoxyphenyl)lithium), and the resulting suspension was then added via a dropping funnel at 0 °C within 30 min to a vigorously stirred solution of tetrachlorosilane (101 g, 594 mmol) in *n*-hexane (200 mL). The mixture was stirred at 0 °C for a further 15 min and then at 20 °C for 16 h. Diethyl ether (700 mL) was added, the resulting mixture was stirred at 20 °C for a further 1 h, the precipitate was separated by filtration and washed with diethyl ether (3 × 100 mL), and the filtrate and the wash solutions were combined. The solvent was removed under reduced pressure, the residue was dissolved in boiling *n*-heptane (1 L), and the resulting solution was filtered hot. The filtrate was cooled to 20 °C within 3 h and then kept undisturbed at this temperature for 16 h, and the resulting precipitate was isolated by filtration and recrystallized from boiling *n*-heptane (700 mL; including hot filtration, cooling to 20 °C within 3 h, and undisturbed storage at 20 °C for 16 h). The product was isolated by filtration and dried in vacuo (0.001 mbar, 20 °C, 5 h) to give **9** in 65% yield as a colorless crystalline solid (116 g, 385 mmol); mp 102 °C. ^{1}H NMR (C$_6$D$_6$): δ 3.30 (s, 6 H, *o*-OCH_3), 3.33 (s, 3 H, *p*-OCH_3), 5.89 (s, 2 H, *H*-3/*H*-5, C$_6$H$_2$-(OCH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$): δ 54.8 (*p*-OCH$_3$), 55.1 (*o*-OCH$_3$), 91.0 (*C*-3/*C*-5, C$_6$H$_2$(OCH$_3$)$_3$), 98.9 (*C*-1, C$_6$H$_2$(OCH$_3$)$_3$), 166.7 (*C*-4, C$_6$H$_2$(OCH$_3$)$_3$), 166.8 (*C*-2/*C*-6, C$_6$H$_2$(OCH$_3$)$_3$). ^{29}Si NMR (C$_6$D$_6$): δ −6.7. Anal. Calcd for $C_9H_{11}Cl_3O_3Si$: C, 35.84; H, 3.68. Found: C, 36.0; H, 3.7.

Treatment of 6 with (Chloromethyl)lithium. A 2.5 M solution of *n*-butyllithium in *n*-hexane (177 μL, 443 μmol of *n*-BuLi) was added dropwise via a syringe at −68 °C (±3 °C, temperature measurement within the flask) within 1 min to a stirred mixture of **6** (100 mg, 442 μmol), bromochloromethane (63 mg, 487 μmol), and THF (5 mL). After the addition was complete, the mixture was stirred at −78 °C for 5 h and then warmed to 20 °C within 17 h. Subsequent GC/EI-MS analysis of the reaction mixture revealed a ca. 1:1 mixture of unreacted **6** and the product **7** (comparison with GC/EI-MS data of authentic samples of **6** and **7**).

Crystal Structure Analyses. Suitable single crystals of **3** and **6** were obtained directly from the preparation of these compounds (see above). 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 (Stoe IPDS; graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)). The structures were solved by direct methods.[17] All non-hydrogen atoms were refined anisotropically.[18] 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-247446 (**3**) and CCDC-247447 (**6**). 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).

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] According to GC studies, the purity of the product was ca. 95%. Attempts to increase the purity by distillation in vacuo failed. An analytically pure sample of **7** was obtained by medium-pressure liquid chromatography (stationary phase, LiChroprep RP18 (Merck); eluent, acetonitrile) and subsequent bulb-to-bulb-distillation (Kugelrohr apparatus, 110−120 °C/0.04 mbar).

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