

Synthesis and Structures of Simple (Silylmethyl)(methyl)ethers

Norbert W. Mitzel

Westfälische Wilhelms-Universität Münster, Institut für Anorganische und Analytische Chemie,
Wilhelm-Klemm-Str. 8, D-48149 Münster, Germany

Reprint requests to Prof. Dr. N. W. Mitzel. Fax (+49)251 83 36007. E-mail: Mitzel@uni-muenster.de

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The compound $\text{Cl}_3\text{SiCH}_2\text{OCH}_3$ was prepared by reacting $\text{ClCH}_2\text{OCH}_3$ with the $\text{Cl}_3\text{SiH}/\text{NEt}_3$ reagent. $\text{H}_3\text{SiCH}_2\text{OCH}_3$ and $\text{F}_3\text{SiCH}_2\text{OCH}_3$ were synthesized from $\text{Cl}_3\text{SiCH}_2\text{OCH}_3$ by reduction with LiAlH_4 and by fluorination with SbF_3 , respectively. The crystal structures of the low-melting compounds $\text{H}_3\text{SiCH}_2\text{OCH}_3$ and $\text{F}_3\text{SiCH}_2\text{OCH}_3$ were determined by X-ray diffraction of *in situ* grown crystals. Both compounds do not show any observable β -donor-acceptor interactions, but behave structurally like usual dialkylethers or silanes, as is obvious from the structural parameters in $\text{H}_3\text{SiCH}_2\text{OCH}_3$ ($\angle\text{SiCO}$ 108.4(3)–109.4(3) $^\circ$, $\angle\text{COC}$ 111.0(4)–111.6(4) $^\circ$) and in $\text{F}_3\text{SiCH}_2\text{OCH}_3$ ($\angle\text{SiCO}$ 107.1(1), $\angle\text{COC}$ 111.2(2) $^\circ$). Earlier postulates of $\text{Si}\cdots\text{O}$ interactions in compounds with SiCO units could thus not be confirmed on a structural basis.

Key words: Silicon, Crystal Structure, Hypercoordination

There are numerous reports that certain properties of compounds which contain a silicon atom or its higher congeners bonded to a donor atom through a methylene or similar bridge are often anomalous compared to those of the carbon analogues [1]. The deviating properties include magnetic susceptibility [2], dipole moments [3], basicity [4], various spectroscopic parameters [5] and structural parameters [6].

Structural deviations are quite pronounced for O-silylhydroxylamines with electronegative substituents bonded to the silicon atoms. Mediated by a short $\text{Si}\cdots\text{N}$ interaction of 1.963(1) Å, $\text{F}_3\text{SiONMe}_2$ forms a three-membered ring with a valence angle of 77.1(1) $^\circ$ at the oxygen atom in the crystal [7], where the surrounding is quite polar due to the high dipole moments of the molecules. These interactions are weaker for isolated molecules in the gas phase ($\text{Si}\cdots\text{N}$ 1.963(1) Å, $\angle\text{SiON}$ 94.3(9) $^\circ$), and of intermediate strength in non-polar but polarizable solvents such as benzene. Interactions of this type are also dependent on the nature of the substituents at silicon and their relative position towards the donor centre, *i. e.* the molecular conformation. Crystalline $\text{ClH}_2\text{SiONMe}_2$ also has a strong $\text{Si}\cdots\text{N}$ interaction and consists of solely the anti-conformer with the torsional angle ClSiON being 180 $^\circ$, *i. e.* the Cl atom in anti-position to the N centre [8]. In the gas phase the $\text{Si}\cdots\text{N}$ interaction is expectedly weaker in this conformer, but a gauche-

conformer is present in addition, which has almost equal energy, but a much less pronounced $\text{Si}\cdots\text{N}$ interaction, resulting in a SiON angle wider by 17 $^\circ$ than in the anti-conformer. In this conformer an H atom is anti relative to the N atom, and thus the situation is comparable to $\text{H}_3\text{SiONMe}_2$ ($\angle\text{SiON}$ 102.6 $^\circ$ in the solid) [9].

Such “ β -donor-interactions” were also found to be structure determining in silylhydrazines, but by contrast the aminomethylsilane $\text{H}_3\text{SiCH}_2\text{NMe}_2$ did not show similar interactions though calculations for $\text{FH}_2\text{SiCH}_2\text{NMe}_2$ have predicted their presence in electronegatively substituted systems [10]. Structural investigations of such systems with donor atoms other than nitrogen are still scarce.

Here we report about the synthesis and structural characterisation of simple compounds with SiCO linkages with electronically very different substituent patterns at silicon: $\text{H}_3\text{SiCH}_2\text{OCH}_3$ and $\text{F}_3\text{SiCH}_2\text{OCH}_3$.

Results

The compound $\text{Cl}_3\text{SiCH}_2\text{OCH}_3$ was prepared previously by other authors [11] employing a Pd-catalysed reaction of Si_2Cl_6 with $\text{ClH}_2\text{COCH}_3$ [12], but also a Benkeser type reaction starting from (chloromethyl)methylether and trichlorosilane in the presence of triethylamine [13]. We obtained higher yields by applying cuprous chloride as a catalyst in the Benkeser reaction as suggested by Furuya and Sukawa [14].

	1	2	3	4	5	6	7	8
Si-C	1.877(5)	1.858(5)	1.871(5)	1.874(5)	1.874(4)	1.879(5)	1.880(5)	1.878(5)
C-O	1.418(5)	1.434(5)	1.397(5)	1.424(6)	1.434(6)	1.418(5)	1.419(6)	1.434(5)
O-C(H ₃)	1.418(8)	1.411(8)	1.439(7)	1.416(8)	1.408(8)	1.433(8)	1.434(7)	1.399(8)
Si-C-O	108.4(3)	109.4(3)	108.8(3)	108.6(3)	108.4(3)	108.9(3)	108.6(3)	108.7(3)
C-O-C	111.2(4)	111.3(4)	110.3(4)	111.6(4)	111.4(4)	111.0(4)	111.0(4)	111.4(4)

Table 1. Structural parameter values of the eight independent molecules of H₃SiCH₂OCH₃ as determined by low-temperature X-ray crystallography.

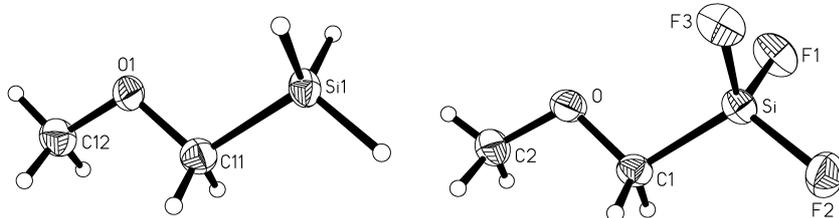
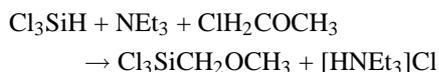
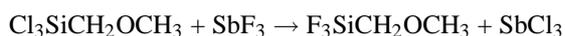
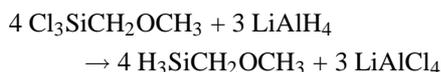


Fig. 1. Molecular structure of one of the eight crystallographically independent molecules of H₃SiCH₂OCH₃ (left) and of F₃SiCH₂OCH₃.



The hydrosilane H₃SiCH₂OCH₃ was obtained by reacting Cl₃SiCH₂OCH₃ with LiAlH₄, while F₃SiCH₂OCH₃ was prepared by complete fluorination of Cl₃SiCH₂OCH₃ with antimony trifluoride.



In addition to the characterisation already reported for Cl₃SiCH₂OCH₃ and H₃SiCH₂OCH₃ we measured ¹³C, ¹⁹F and ²⁹Si NMR spectra of these compounds.

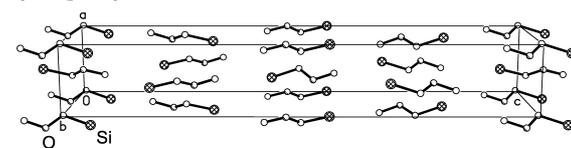
The silicon H and F substituents in H₃SiCH₂OCH₃ and F₃SiCH₂OCH₃ give one signal, which indicates that the silyl groups rotate freely about their SiC axes, *i.e.* no strong intermolecular Si...O interactions or dimerisation are observable. The ²⁹Si NMR chemical shifts are in the range established for carbosilanes with SiCl₃, SiH₃ and SiF₃ groups. The same applies to the magnitudes of the one-bond coupling constants ¹J(Si-H) in H₃SiCH₂OCH₃ (198.8 Hz) and ¹J(Si-F) in F₃SiCH₂OCH₃ (282 Hz). In the ²⁹Si NMR of F₃SiCH₂OCH₃ there is a marked broadening of the resonance, which is also found in the ¹H and ¹³C NMR spectra of this compound, but cooling of samples dissolved in D⁸-toluene did not lead to a splitting of these signals, which could indicate inter- or intramolecular aggregation.

The solid state structures were determined using *in situ* techniques for the growth of suitable specimens for the single crystal X-ray diffraction experiments. The structure of one of the eight independent molecules of H₃SiCH₂OCH₃ is shown in Fig. 1 and geometrical val-

Table 2. Structural parameter values of F₃SiCH₂OCH₃ as determined by low-temperature X-ray crystallography.

Si-F(1)	1.572(2)	Si-F(2)	1.562(1)
Si-F(3)	1.563(2)	Si-C(1)	1.837(2)
O-C(1)	1.425(3)	O-C(2)	1.430(3)
F(1)-Si-F(2)	106.9(1)	F(1)-Si-F(3)	105.9(1)
F(2)-Si-F(3)	107.9(1)	F(1)-Si-C(1)	111.3(1)
F(2)-Si-C(1)	111.9(1)	F(3)-Si-C(1)	112.6(1)
C(1)-O-C(2)	111.2(2)	O-C(1)-Si	107.1(1)

H₃SiCH₂OCH₃



F₃SiCH₂OCH₃

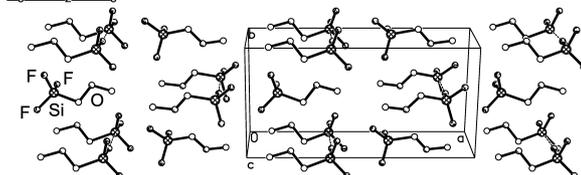


Fig. 2. Packing diagrams of H₃SiCH₂OCH₃ (upper part) and F₃SiCH₂OCH₃ (lower part). Hydrogen atoms are omitted for clarity.

ues are listed in Table 1. The molecular structure of F₃SiCH₂OCH₃ is also shown in Fig. 1 and structural parameters are provided in Table 2.

H₃SiCH₂OCH₃ crystallises in the triclinic space group *P*1 with eight crystallographically independent molecules in the cell. The cell dimensions are close to that of an orthorhombic cell. F₃SiCH₂OCH₃ crystallises in such an orthorhombic space group (*Pna*2₁), and the molecules are arranged in a manner related

	H ₃ SiCH ₂ OCH ₃		F ₃ SiCH ₂ OCH ₃		FH ₂ SiCH ₂ OCH ₃	
	anti	anti	gauche	anti	gauche-anti	gauche-gauche
Si-C	1.892	1.854	1.861	1.880	1.877	1.844
Si-F		1.590	1.596	1.621	1.617	1.618
		1.595	1.591			
		1.590	1.595			
C-O	1.420	1.416	1.426	1.421	1.418	1.429
O-C(H ₃)	1.412	1.414	1.417	1.412	1.412	1.412
Si-C-O	106.9	106.9	111.1	104.3	107.8	112.2
C-O-C	111.3	111.1	111.6	111.5	111.3	111.3
t(SiCOC)	180.0	180.0	89.8	180.0	181.9	71.7
t(FSiCO)				180.0	71.2	88.4
μ	1.77	3.84	2.82	2.27	2.99	3.18
E		0	6.4	0	1.0	4.0

Table 3. Structural parameter values of the different conformers of H₃SiCH₂OCH₃, F₃SiCH₂OCH₃ and FH₂SiCH₂OCH₃ as calculated ab initio at the MP2/6-311G(d,p) level of theory.

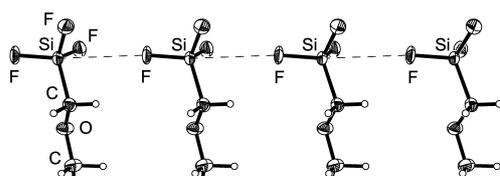


Fig. 3. Intermolecular aggregation with F...Si contacts in F₃SiCH₂OCH₃.

to that of H₃SiCH₂OCH₃ (see Fig. 2). The major difference is that within one layer of molecules of H₃SiCH₂OCH₃ all molecules have the same orientation (silicon always on the right side in Fig. 2), but a different orientation of the SiCO plane, whereas in F₃SiCH₂OCH₃ the F₃Si groups point towards one another, *i.e.* the direction of the molecules is alternating. Crystals of both structures have non-centrosymmetric space groups, but as can be seen from Fig. 2 the molecules are arranged in a way that the substantial molecular dipole moments almost cancel out.

A number of significant deviations of atomic positions from higher symmetry do not allow the structure of H₃SiCH₂OCH₃ to be solved or refined in monoclinic or orthorhombic space groups, whereas a solution in *P*1 led to a stable refinement and to satisfactory structural parameters. The packing of the molecules is mediated through a number of weak interactions, and the shortest meaningful contacts in H₃SiCH₂OCH₃ are a Si...O contact of 3.70 Å, while in F₃SiCH₂OCH₃ Si...O contacts of 3.959 Å and Si...F contacts of 3.216 Å length are present. They lead to an aggregation of F₃SiCH₂OCH₃ molecules into endless Si-F...Si-F...Si-F chains as is illustrated in Fig. 3.

Expectedly, the structures of all eight molecules of H₃SiCH₂OCH₃ are similar. The Si-C distances are in the narrow range between 1.858(5) and 1.880(5) Å, which is in the region established for carbosilanes not electronegatively substituted at the silicon atoms.

By comparison, the Si-C bonds in F₃SiCH₂OCH₃ are shorter at 1.837(2) Å. The O-C bond lengths are all similar both in H₃SiCH₂OCH₃ and in F₃SiCH₂OCH₃.

The range of Si-C-O angles in H₃SiCH₂OCH₃ is from 108.4(3) to 109.4(3)°, and this is only slightly wider than in F₃SiCH₂OCH₃, where this angle is 107.1(1)°. This result shows, that there are no important attractive Si...O interactions comparable to Si...N interactions for instance in F₃SiONMe₂, which has a very different Si-O-N angle as compared to the hydrogen analogue H₃SiONMe₂ (25° wider!). The intramolecular Si...O distances are relatively large at 2.634 Å for F₃SiCH₂OCH₃ and at 2.686 Å for H₃SiCH₂OCH₃. There is no discussible lengthening of the Si-F bond in anti-position to the donor atom (oxygen), which was found to be the result of β-donor-bonding in F₃SiONMe₂. The longest Si-F bond in F₃SiCH₂OCH₃ is the gauche oriented Si-F(2) (1.572(2) Å), while the other two are 1.562(1) and 1.563(2) Å.

It should be noted that the structure of H₃SiCH₂OCH₃ has been determined earlier by microwave spectroscopy in the gas phase [15,16]. The geometrical parameters found for the free molecule do not deviate substantially from those found in the solid state, which again indicates the absence of relevant secondary bonding in this compound. The similarity can be illustrated by comparing two values: the gas phase SiCO angle is reported to be 108.7(4), while in the crystal this parameter varies between 108.4(3) to 109.4(3)°; the gas phase value for the COC angle is 112.2(6)°, and is found in the solid state between 110.3(4) and 111.6(4)°.

All molecules of H₃SiCH₂OCH₃ and F₃SiCH₂OCH₃ in the crystals adopt *anti*-conformations with respect to their Si-C-O-C skeleton. This made us interested in the dependence of structural parameters

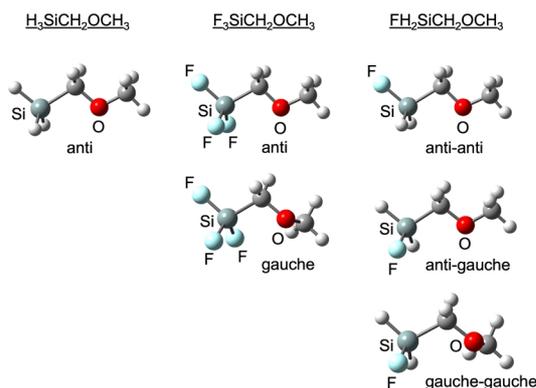


Fig. 4. Calculated molecular structures of the different stable conformers of $\text{H}_3\text{SiCH}_2\text{OCH}_3$, $\text{F}_3\text{SiCH}_2\text{OCH}_3$ and $\text{FH}_2\text{SiCH}_2\text{OCH}_3$ at the MP2/6-311G(d,p) level of theory.

and energies on the conformations of these molecules. Therefore we carried out ab initio calculations on the different conformations of $\text{H}_3\text{SiCH}_2\text{OCH}_3$ and $\text{F}_3\text{SiCH}_2\text{OCH}_3$, and additionally on $\text{FH}_2\text{SiCH}_2\text{OCH}_3$, which has further conformational degrees of freedom. The results of these MP2/6-311G(d,p) calculations are listed in Table 3 and the geometries of the stable conformers are shown in Fig. 4.

Not all conformations represent minima on the potential hypersurface. For $\text{H}_3\text{SiCH}_2\text{OCH}_3$ only the experimentally observed *anti* conformer is stable and other start geometries converge into this conformation. For $\text{F}_3\text{SiCH}_2\text{OCH}_3$ both conformers, *anti* and *gauche* are minima, with the experimentally observed one, *anti*, being more stable by only 6.4 kJ mol^{-1} . For $\text{FH}_2\text{SiCH}_2\text{OCH}_3$ three conformations out of four are found to be stable minima: *anti-anti*, which represents the ground state, *gauche-anti* being only marginally higher in energy by 1.0 kJ mol^{-1} , and *gauche-gauche*, which is 4.0 kJ mol^{-1} higher in energy than the ground state. The *anti-gauche* conformer does not represent a minimum, which parallels the situation for $\text{H}_3\text{SiCH}_2\text{OCH}_3$.

The calculated parameters are very similar to those determined experimentally and the geometries of the conformers not observed experimentally deserve no further comments.

The results of the present investigations have shown, that there is no support on a structural basis, neither in the gas phase nor the solid state, for the postulate that intermolecular $\text{Si} \cdots \text{O}$ interactions between geminal Si and O atoms in SiCO linkages would be structure determining or be the reason for unusual physical properties of this class of compounds.

Experimental Section

All experiments have been carried out under rigorous inert gas conditions or at a vacuum line with greaseless valves (Young). NMR: Jeol JNM-LA400, MS: Varian MAT 311 A, IR: Midac Prospekt IR. Triethylamine and all solvents were dried and distilled before use.

$\text{Cl}_3\text{SiCH}_2\text{OCH}_3$: Over a period of 1 h a mixture of trichlorosilane (100 ml, 1 mol) and (chloromethyl)methyl-ether (68.3 ml, 0.9 mol) was slowly dropped into a mixture of triethylamine (125 ml, 0.9 mol) and copper(I) chloride (4.5 g) in 500 ml of diethyl ether at ambient temperature. During addition a precipitate was formed while the mixture refluxed. After the refluxing had stopped, the mixture was heated to reflux for 2 h, then cooled to ambient temperature and filtered. The residue was washed two times with 50 ml of diethyl ether. The ether phases were combined and the ether removed by distillation. The residue was distilled using a 10 cm Vigreux column to give 71 g of $\text{Cl}_3\text{SiCH}_2\text{OCH}_3$ (44% yield).

^1H NMR (400.05 MHz, C_6D_6 , 21 °C): $\delta = 2.95$ (s, CH_2), 3.04 (s, CH_3). – ^{13}C NMR (100.64 MHz, C_6D_6 , 21 °C): $\delta = 67.15$ (tq, $^1J_{\text{CH}} = 137.3 \text{ Hz}$, $^3J_{\text{CH}} = 5.6 \text{ Hz}$), 67.15 (tq, $^1J_{\text{CH}} = 141.9 \text{ Hz}$, $^3J_{\text{CH}} = 62.25 \text{ Hz}$). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.38 MHz, C_6D_6 , 21 °C): $\delta = -3.3$ (s). – MS (EI): $m/z = 179$ (M^+), 163, 147, 135 (100%), 113, 98, 63.

$\text{H}_3\text{SiCH}_2\text{OCH}_3$: LiAlH_4 (1.4 g, 0.037 mol) was added to di-*n*-butyl ether (60 ml) at 0 °C. A solution of $\text{Cl}_3\text{SiCH}_2\text{OCH}_3$ (8.2 g, 0.05 mol) in 20 ml of di-*n*-butyl ether was added dropwise at 0 °C. Cooling is essential to suppress side reactions (formation of CH_3SiH_3). The mixture was stirred for 0.5 h at this temperature and the volatile components including about 10 ml of di-*n*-butyl ether were transferred under vacuum to a cold trap. The contents of this trap were passed through a series of traps held at -40 , -96 and -196 °C. The -96 °C trap contained the product (2.3 g, 58% yield), while some SiH_4 was collected in the -196 °C trap.

^1H NMR (400.05 MHz, C_6D_6 , 21 °C): δ 3.53 (t, $^3J_{\text{HH}} = 7.0 \text{ Hz}$, SiH_3), 3.26 (q, $^3J_{\text{HH}} = 7.0 \text{ Hz}$, SiH_3), 3.06 (s). – ^{13}C NMR (100.64 MHz, C_6D_6 , 21 °C): $\delta = 58.34$ (tm, $^1J_{\text{CH}} = 133.7 \text{ Hz}$, CH_2), 62.37 (qt, $^1J_{\text{CH}} = 140.2 \text{ Hz}$, $^3J_{\text{CH}} = 3.4 \text{ Hz}$). – ^{29}Si NMR (79.38 MHz, C_6D_6 , 21 °C): $\delta = -66.1$ (qt, $^1J_{\text{SiH}} = 198.8 \text{ Hz}$, $^3J_{\text{SiH}} = 4.3 \text{ Hz}$).

$\text{F}_3\text{SiCH}_2\text{OCH}_3$: Antimony trifluoride (11.5 g, 0.064 mol) was placed in a 100 ml-vessel and cooled to -78 °C. $\text{Cl}_3\text{SiCH}_2\text{OCH}_3$ (11.5 g, 0.064 mol) was added dropwise, with no reaction taking place. The mixture was slowly warmed in a bath and at about -40 ° bath temperature a vigorous reaction started and the mixture became black. The mixture was kept for 1 h at 0 °C and for 1 h at ambient temperature. The volatiles were condensed into a cold trap and subsequently passed through a series of traps held at -30 ,

−96 and −196 °C. The product was contained in the −96 °C trap (5.7 g, 69% yield), while some SiF₄ was received in the 196 °C trap.

¹H NMR (400.05 MHz, C₆D₆, 21 °C): δ = 2.95 (s, broad), 2.99 (s, broad). −¹³C NMR (100.64 MHz, C₆D₆, 21 °C): δ = 55.31 (t, broad, ¹J_{CH} = 137 Hz), 62.44 (qt, ¹J_{CH} = 141.7 Hz, ³J_{SiH} = 3.3 Hz, CH₃). −¹⁷O NMR (54.26 MHz, C₆D₆, 21 °C): δ = −53. −¹⁹F NMR (376.54 MHz, C₆D₆, 21 °C): δ = 65.26. −²⁹Si NMR (79.38 MHz, C₆D₆, 21 °C): δ = −69.4 (q, broad, ¹J_{SiF} = 282 Hz). − IR (ν, cm^{−1}) 2976 s, 2950 m, 2876 s, 2791 w, 1476 w, 1447 w, 1391 w, 1362 w, 1142 ss, 1080 w, 1030 m, 945 w, 808 ss.

Crystal structure determination of H₃SiCH₂OCH₃ and F₃SiCH₂OCH₃. Single crystals of H₃SiCH₂OCH₃ and F₃SiCH₂OCH₃ were grown *in situ* on the diffractometer by slowly cooling the melt in a sealed capillary below the melting point after generating a suitable seed crystal. Data collection was undertaken with a Nonius Turbo-CAD4 diffractometer.

Crystal data H₃SiCH₂OCH₃, C₂H₈OSi, *M_r* = 76.17, crystal system triclinic, space group *P*1, *Z* = 8, *a* = 4.524(1), *b* = 7.339(1), *c* = 29.207(5) Å, α = 89.98(1), β = 90.02(2), γ = 89.93(2)°, *V* = 969.7(3) Å³ at 123(2) K, μ = 0.306 mm^{−1}.

2θ_{max.} = 54°, ω-scan, 4028 scattering intensities collected of which all were unique, 390 parameters, *R*₁ = 0.0346 for 3170 reflections with *F*_o > 4σ(*F*_o) and *wR*₂ = 0.0979 for all 4028 data. Crystal data F₃SiCH₂OCH₃, C₂H₅OF₃Si, *M_r* = 130.15, crystal system orthorhombic, space group *Pna*2₁, *Z* = 4, *a* = 14.755(6), *b* = 7.461(4), *c* = 4.778(3) Å, *V* = 526.0(5) Å³ at 123(2) K, μ = 0.398 mm^{−1}. 2θ_{max.} = 54°, ω-scan, 2818 scattering intensities collected of which 782 were unique, 84 parameters, *R*₁ = 0.0388 for 760 reflections with *F*_o > 4σ(*F*_o) and *wR*₂ = 0.0979 for all 782 data.

Structure solutions and refinements were undertaken with the program SHELXTL 5.01 [17]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-204076 (H₃SiCH₂OCH₃) and CCDC-204075 (F₃SiCH₂OCH₃). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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