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Siloxanes and silylamines with fluoromethyl-methylsilicon groups: X-ray study of $[CH_2F(CH_3)SiO]_4$ [1]

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Abstract

CH_2FMe_2SiBr (II) was prepared by the reaction of CH_2FMe_2SiH with Br_2. The solvolysis of II with H_2O and NH_3 gave $(CH_2FMe_2Si)_2O$ (III) and $(CH_2FMe_2Si)_2NH$ (IV) respectively. After lithiation with n-BuLi and thereafter reaction with II, compound IV afforded the trisilylamine $(CH_2FMe_2Si)_3N$ (V). Hydrolysis of $CH_2FMeSiBr_2$ (I) with H_2O yielded a polysiloxane oil from which 10% of a crystalline material (VI) was isolated. This was shown by analyses, mass, NMR and IR spectra to be the cyclotetrasiloxane $(CH_2FMeSiO)_4$. The NMR spectra suggest random distribution of all possible stereoisomers. Single crystals of VI were examined by X-ray diffraction. An essentially planar Si_4O_4 ring was found, the SiOSi angles averaging $157.9(5)°$. Since the F atoms are extensively disordered, packing requirements at ambient temperature rather than the intrinsic conformational content of the crystal may be exerting the crystallographic inversion symmetry imposed on the ring.

Keywords: Silicon; Siloxanes; Silylamides; Fluoromethyl group

1. Introduction

α-fluoromethylsilicon derivatives $CH_{3-n}F_nSiRR'R''$ differ pronouncedly from their non-fluorinated organosilicon parents ($n = 0$). In general the few known α-fluoromethyl compounds have proven difficult to synthesize, and they decompose readily. While simple difluoro- ($n = 2$) and trifluoromethyl ($n = 3$) derivatives eliminate the respective carbenes CHF and CF_2 upon both thermolysis [1,2] and laser photolysis [3], monofluoromethyl silanes ($n = 1$) apparently prefer dyotropic F → H exchange with subsequent disproportionation by ligand scrambling, e.g.

$$CH_2FSiH_3 \rightarrow CH_3SiH_2F \rightarrow CH_3SiH_3 + CH_3SiHF_2$$
(1)
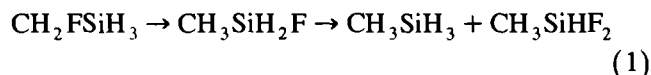
Migration of F from C to Si has been observed even at room temperature. When $CH_2FSiHClMe$ and

CH_2FSiBr_2Me, dissolved in C_6D_6, were stored for several weeks, complete transformation to $CH_2ClSiHF$-Me and $CH_2BrSiFBrMe$ was noted [4].

Since monofluoromethyl silanes show a resistance to carbene elimination, the corresponding halosilanes should be convertible to acceptably stable derivatives by standard organosilicon methods. Having developed a selective method for the synthesis of Si-functional CH_2FSi halides via the reduction of fluorodibromomethyl derivatives and having exploited its versatility [4], we now report on the reactions of monofluoromethyldibromosilane $CH_2F(CH_3)SiBr_2$ (I) with H_2O and of monofluoromethyl-dimethyl-bromosilane $CH_2F(CH_3)_2SiBr$ (II) with H_2O and NH_3. These standard reactions in organosilicon chemistry are expected to yield cyclo- and polysiloxanes in the case of I and a disiloxane and a disilazane in the case of II [5]. Bromo- rather than chlorosilanes were employed because they are easily available by treatment of the hydrides CH_2FSiH_2Me and $CH_2FSiHMe_2$ [4] with Br_2.

2. Syntheses

The starting materials I and CH_2FSiMe_2H were prepared as described previously [4]. Bromination of the

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[1] Dedicated to Professor Marianne Baudler on the occasion of her 75th birthday.

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latter with Br_2 in the absence of a solvent yielded 93% II. This was characterized by IR and multinuclear NMR spectroscopy, see Section 4.

2.1. Reaction of II with H_2O and NH_3

The reaction of an etheral solution of II with an excess of H_2O gave a high yield of the disiloxane $[CH_2FMe_2Si]_2O$ (III). As in the case of Me_3SiCl formation of the silanol was not observed. III, a colourless liquid, b.p. 142–145°C, is less volatile than $(Me_3Si)_2O$, b.p. 100.8°C [5]. The disiloxane rather than the silanol structure follows from the IR spectra, which contains no $\nu(OH)$ stretching vibration; instead, a very strong absorption at 1085 cm^{-1}, assigned to ν_{as} (SiOSi) $(Me_3SiOSiMe_3$, 1068 cm^{-1} [6]), is most prominent in the spectrum. NMR spectra are in agreement with the proposed structure, although they would not convincingly rule out a silanol.

We have also studied the reaction of CH_2FSiH_2Cl with H_2O and Ag_2O at room temperature in order to synthesize $[H_2(CH_2F)Si]_2O$. However, both reactions led to total decomposition with evolution of H_2.

The reaction of II with NH_3 in excess was carried out as described for the disiloxane. Under the given conditions only the disilazane $(CH_2FMe_2Si)_2NH$ (IV) was formed. This was recovered from a $-40°C$ trap of a high vacuum system and purified by fractional condensation in vacuo; the yield was 70%.

A disilazane structure follows unambiguously from the IR spectrum of the product. The SiN(H)Si fragment gives rise to a strong doublet associated with the coupled ν_{as} (SiNSi) and δ (NH) vibrations at 940 and 1190 cm^{-1} (934 and 1177 cm^{-1} in $(Me_3Si)_2NH$) along with a sharp ν (NH) absorption at 3365 cm^{-1} (3375 cm^{-1} in $(Me_3Si)_2NH$) [6]. That the NH proton of IV was not observed in the ^1H NMR spectrum does not contradict a disilazane structure because SiN(H)Si protons usually give rise to very broad signals; such a signal may well be buried under those of the CH_2F group.

A typical feature of disilazanes is the acidity of the NH proton, of which advantage has been taken to introduce a third silyl substituent after metallation with sodium/styrene or LiR (R = Ph, n-Bu) [7]. Applying this strategy to IV to synthesize thereof $(CH_2FMe_2Si)_3N$ (V) would require that (i) the product was not too sterically crowded and (ii) the elimination of alkali metal fluoride was not of importance. Experience with CF_3SiCl_3 suggests a resistance of CF bonds towards organolithium reagents.

Metallation of IV with n-butyl lithium in hexane proceeded smoothly. Reaction of the N-lithio compound, which was not isolated, with II gave 51% of a colourless liquid, b.p. 70–73°C/0.05 mbar, that solidified to a waxy material whose appearance resembled

that of $(Me_3Si)_3N$. Further support for a trisilylamine constitution (V) follows from the IR spectrum in which NH vibrations are missing while the diagnostic vibration ν_{as} (NSi_3) at 915 cm^{-1} (917 cm^{-1} in $(Me_3Si)_3N$ [6]) is very intense. NMR and IR spectra of III–V are set out in Section 4.

2.2. Hydrolysis of I

Addition of water to an etheral solution of I at 0°C, followed by separation of the organic phase and evaporation of the solvent, yielded a viscous colourless oil. Its ^1H NMR spectrum indicated the presence of CH_3Si (0.22 ppm, 3H) and CH_2FSi (4.45 ppm, 2H, ^2J (HF) 47 Hz) groups. This is in agreement with the formation of polysiloxanes, possibly with some cyclosiloxanes present as well. From this oil around 10% could be isolated by sublimation as a colourless, apparently homogeneous material (VI) that formed long needles.

The elemental analyses are in agreement with a $[CH_2F(CH_3)SiO]n$ constitution. The IR spectrum displayed a strong and broad absorption at 1100 cm^{-1}, which may be assigned to ν_{as} (SiOSi) of a cyclotetrasiloxane (c.f. $(Me_2SiO)_4$, 1080 cm^{-1} [8]). The analogous absorption of $(Me_2SiO)_3$, 1020 cm^{-1} [8], occurs at substantially smaller wavenumber and makes a cyclotrisiloxane constitution for VI most unlikely.

The mass spectrum of VI is in agreement with a cyclotetramer rather than a cyclotrimer or a larger cyclooligomer. The fragmentation of VI is similar to that of $(Me_2SiO)_4$ [9], which is characterized by an M^+-CH_3 fragment as the parent ion, successive loss of $(CH_2)_2$ and retainment of the Si_4O_4 skeleton. In analogy VI eliminates in a primary step CH_2F rather than CH_3 to give the ion m/e 335 (1.5%, M^+-CH_2F) (relative intensity, assignment). Consecutive fragmentation involves loss of four CH_2 groups to yield the prominent ion m/e 279 (23%, $Si_4O_4F_3(CH_3)_3H^+$). This is associated with the peaks at m/e = 280, 281, and 282, and the relative intensities for these four peaks (100:23: 18: < 5) are in agreement with those of a calculated isotopic pattern (100:24:17:3). Finally, two more CH_2 units are lost to give the basis fragment m/e 251 (100%, $Si_4O_4F_3CH_6^+$).

3. Spectra and structure

3.1. NMR spectra of VI

We have studied the ^1H, ^{19}F and ^{13}C NMR spectra of VI in some detail. Although signal overlap in the ^1H and ^{13}C spectra foiled a complete assignment, they are in agreement with the ^{19}F spectra which provide qualitative and quantitative information on the stereochemistry of VI. Not taking into account possible distortion of the

Si_4O_4 ring from D_{4h} symmetry and assuming free rotation for the CH_3 and CH_2F groups, we have to consider the four possible stereoisomers **A–D** which are sketched in Table 1. The notation + and − refers to the relative positions of the NMR active nuclei (F, CH_2F, CH_3, CH_2F, CH_3) with respect to the Si_4O_4 plane. While the positions of these nuclei are fourfold degenerate in the stereoisomers **A–C**, the up–up–up–down isomer **D** possesses three non-equivalent nuclei in a ratio of 1 : 2 : 1.

For a random distribution of the different isomers six signals in a 2 : 2 : 1 : 1 : 1 : 1 ratio are expected for the monitored nuclei. Six signals in the correct intensity ratio are in fact observed for the F, CH_3 and CH_2F atoms although the resonance signals of the CH_2F and CH_3 atoms partly overlap in the ^{13}C and ^1H spectra respectively (Table 1). The ^{19}F signals near − 275 ppm (Fig. 1) are split into triplets by the two geminal hydrogens, with ^2J (HF) around 47.2 Hz. That the complex multiplet observed in the non-decoupled spectrum indeed consists of six triplets was proved by the proton decoupled spectrum (Fig. 1). Non-random distribution of the possible isomers was, however, deduced from the ^{29}Si NMR spectrum of γ-trifluoropropyl-methyl-cyclotetrasiloxane $[CF_3CH_2CH_2(CH_3)SiO]_4$ [10].

The NMR data of **VI** are collected in Table 1. Although the resonances are given in the order of increasing shifts, the two central resonances 3 and 4 are always twice as intense as the outer absorptions. Thus they belong to **B** and **D**, with the two nearest CH_2F groups on the same and the opposite side of the Si_4O_4

Table 1
NMR spectra of the stereoisomers of VI

	A	B	C	D
	+ +	− +	− +	+ +
	+ +	− +	+ −	+ −
Statistical weight	2	4	2	8
Equivalent nuclei	4	4	4	2 + 1 + 1
Relative intensity	8	16	8	16 + 8 + 8

NMR chemical shifts (ppm) and their relative intensities I of the geometric isomers **A–D** of **VI** in C_6D_6 solution [a]

Peak	$\delta(^{19}F)$ [b]	I	$\delta(CH_2F)$ [c]	I	$\delta(^{13}CH_3)$ [d]	I
1	− 274.70	1.0	4.14	1.1	− 3.12	1.0
2	− 274.88	1.0	4.18	1.0	− 3.18	1.2
3	− 274.96	2.1	4.20	2.2	− 3.24	2.0
4	− 275.09	2.0	4.22	2.1	− 3.30	2.1
5	− 275.17	1.0	4.23 [e]		− 3.35	1.2
6	− 275.27	0.8	4.24	1.1	− 3.43	1.1

[a] NMR peaks in the order of increasing chemical shift. The accuracy of the quoted chemical shifts is (relative) precision. [b] External standard $CFCl_3$. $^2J(FCH)$ 47.18 ± 0.03 Hz. [c] External standard TMS; $\delta(CH_3)$ 0.15–0.18 ppm (five maxima, not resolved). [d] Internal standard C_6D_6 128.0 ppm, $\delta(^{13}CH_2F)$ 78.08 ppm, d, $^1J(CF) = 157.0$ Hz (five unresolved peaks) and one shoulder at $\delta(CH_2F)$ 78.0 ppm, d, $^1J(CF)$ 158.0 Hz [e] Shoulder.
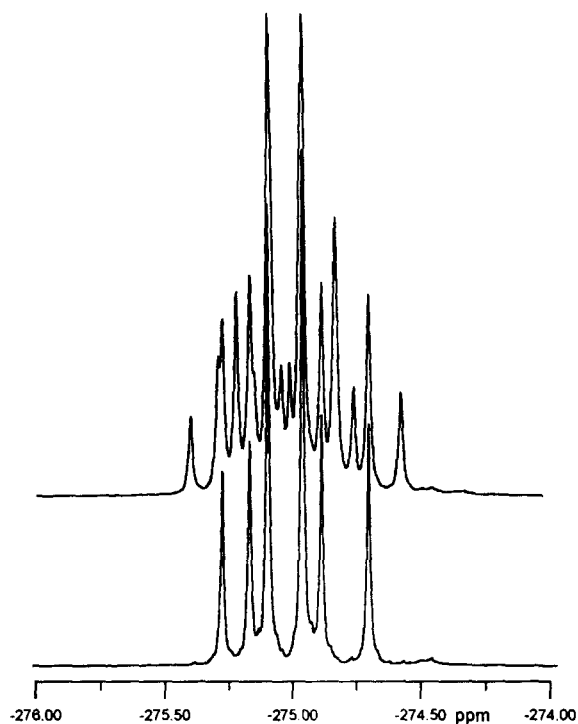

Fig. 1. The ^{19}F NMR spectrum of **VI** in methylene chloride without (above) and with (below) proton decoupling.

plane. No further assignment of the resonances seems to be possible at present.

3.2. Description of the crystal structure

The structural study of **VI** confirms its formulation as a tetrasiloxane. The principal difficulty encountered in this investigation was the identification of the partially occupied fluorine sites. Since significant amounts were found near all carbon atoms, the CH_2F and CH_3 groups are disordered in the crystal. The disorder is hardly random, the C(1) and C(3) atoms each bearing less than half as much fluorine as that attached to either the C(2) or C(4) atoms. While the crystal structure is most compliant with inversion-symmetric eight-membered rings, the observed scrambling of CH_2F and CH_3 groups opens the possibility for a small admixture of disordered, non-centrosymmetric stereoisomers. Nevertheless, it appears that either the centrosymmetric stereoisomers crystallize preferentially from methylene chloride solutions or they form the most attractive crystals—only a few specimens with well-developed faces having been grown. Staggered orientations with respect to the remaining valencies of the respective silicon atom were found for the C–F bonds with both antiperiplanar F–C–Si–O and F–C–Si–C fragments being well represented. The fluorine site occupation factors support the proposed constitution; that is, the occupancies sum to 1.00(4) and 1.10(5) for the fluorine atoms bonded to the
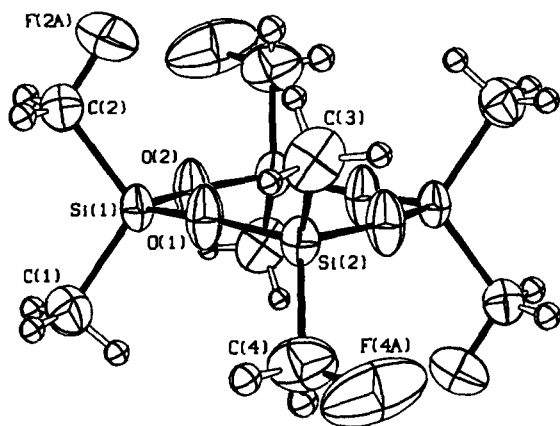
Fig. 2. Perspective drawing of VI with 20% probability thermal ellipsoids except for the hydrogen atoms. Only the two fluorine atoms of highest occupancy are shown.

methyl carbons of Si(1) and Si(2) respectively. No fluorine position is particularly favoured—the largest populations being found for the F(2A) (0.34(2)) and F(4A) (0.38(3)) atoms, which are shown in the ORTEP drawing of Fig. 2.

The r.m.s. deviation of the ring atoms from planarity, 0.058 Å, is much less than that found for $[Me_2SiO]_4$ either in the solid state (0.21 Å) [11] or in the gas phase (0.371 Å) [12] but is similar to that reported for crystalline $[Cl_2SiO]_4$, 0.048 Å [13]. Inspection of the selected bond distances and angles given in Table 2 reveals small but significant deviations in the symmetry of the $[C_2SiO]_4$ framework in VI from D_{2h}. The average Si–O–Si bond angle in VI, 157.9(5)°, is much larger than that of $[Me_2SiO]_4$ in the solid state or gas phase—142.5 and 145(1)° respectively. While the average Si–O bond length in VI, 1.597(5) Å, appears short, corrections [14] for the librational motion of the C_2SiO_2 fragments increases this distance to 1.631(6) Å, which agrees well with those reported for $[Me_2SiO]_4$ in both the crystal (1.65(2) Å [11]) and in the vapour (1.622(3) Å [12]).

Table 2
Selected bond distances (Å) and angles (°) in VI

Si(1)–O(1)	1.599(3)	Si(1)–C(1)	1.827(6)
Si(1)–O(2)	1.602(3)	Si(1)–C(2)	1.856(6)
Si(2)–O(1)	1.597(3)	Si(2)–C(3)	1.854(7)
Si(2)–O(2')[a]	1.591(3)	Si(2)–C(4)	1.799(7)
O(1)–Si(1)–O(2)	110.9(2)	O(1)–Si(2)–O(2')	110.2(2)
O(1)–Si(1)–C(1)	109.8(3)	O(1)–Si(2)–C(3)	109.6(3)
O(1)–Si(1)–C(2)	105.9(3)	O(1)–Si(2)–C(4)	111.2(4)
O(2)–Si(1)–C(1)	110.1(3)	O(2')–Si(2)–C(3)	108.2(3)
O(2)–Si(1)–C(2)	109.5(3)	O(2')–Si(2)–C(4)	109.5(3)
C(1)–Si(1)–C(2)	110.5(3)	C(3)–Si(2)–C(4)	108.0(4)
Si(1)–O(1)–Si(2)	158.3(2)	Si(1)–O(2)–Si(2')	157.6(2)

[a] x', y', $z' = 1 - x$, $- y$, $- z$.

4. Experimental details

4.1. General and spectra

Reactions were carried out either in an atmosphere of dry nitrogen or using a standard vacuum line at a pressure of 10^{-2}–10^{-3} mbar. Solvents were dried and purified by standard methods prior to their use. CH_2FSiMe_2H, $CH_2FMeSiBr_2$ (I) and CH_2FSiH_2Cl were prepared according to Ref. [4], while other starting material was commercially available.

Spectra were recorded on the following instruments: NMR ^1H, ^{19}F, ^{13}C: Bruker AC 250 or AC 400 spectrometers at 250.0 and 400 MHz, 235.4 and 376.5 MHz, 62.8 and 100.5 MHz respectively. TMS (^1H and ^{13}C) and $CFCl_3$ (^{19}F) were used as internal standards. IR spectra were recorded on Perkin-Elmer 580 B and Bruker IFS 25 instruments on gaseous, liquid and solid samples. EI mass spectra were obtained employing a MAT 311 spectrometer, ionization energy 70 eV.

4.2. Fluoromethyl-dimethylbromosilane (II)

At −196°C 3 mmol portions of Br_2 were distilled onto 3.43 g (37.2 mmol) of CH_2FSiMe_2H contained in a 500 ml flask and the mixture brought to room temperature with stirring. After 4.42 g (27.7 mmol) Br_2 had been consumed, 4.42 g (25.8 mmol, 93%) II was separated from HBr and the excess of CH_2FSiMe_2H by fractionation through a −75°C trap in which II was recovered. IR, gas: 2977 s, 2954 m, 2919 m (ν(CH)), 2842 w, 1422 m ($\delta_{as}(CH_3)$), 1260 vs ($\delta_s(CH_3)$), 994 vs (ν(CF)), 426 s (ν(SiBr)). NMR (neat liquid): $\delta(CH_3)$ 0.73, s, $\delta(CH_2F)$ 4.60, d; $\delta(F)$ −262.0, t, $^2J(HCF)$ 48.0 Hz.

4.3. 1,3-bis(fluoromethyl-dimethyl)-disiloxane (III)

To a stirred solution of 4.42 g (25.8 mmol) II in 50 ml Et_2O, 5 ml H_2O was added within 2 min and stirring continued for 5 min. The organic layer was separated, dried with $CaCl_2$, Et_2O distilled off, the crude product transferred into a vaccum line and III collected in a −15°C trap as a colourless liquid, b.p. 142–145°C, yield 64%. IR, film: 2968 s, 2932 m, 2909 m (ν(CH)), 1434 m, 1417 m ($\delta_{as}(CH_3)$), 1263 vs ($\delta_s(CH_3)$), 1085 vs (ν_{as}(SiOSi)), 1000 s (ν(CF)). NMR (neat liquid): $\delta(CH_3)$ 0.12, s, $\delta(CH_2F)$ 4.12, d; $\delta(F)$ −271.2, t, $^2J(HCF)$ 48.0 Hz.

4.4. 1,3-bis(fluoromethyl-dimethyl)-disilazane (IV)

NH_3 (1.06 g, 6.25 mmol) was condensed onto a solution of 5.25 g II in 20 ml Et_2O at −196°C in a 500 ml flask, the mixture warmed to room temperature and stirring continued for 1 h. Volatile products were evapo-

rated into a vacuum line and 2.11 g (10.7 mmol, 70%) IV collected in a − 40°C trap. IR, film: 3365 s(ν(NH)), 2965 s, 2940 s, 2910 s (ν(CH)), 1430 m, 1415 m (δ_{as}(CH$_3$)), 1260 vs (δ_s(CH$_3$)), 1190 s (δ(NH)), 980 s (ν(CF)), 940 vs (ν_{as}(Si$_2$N)). NMR (in C$_6$D$_6$): δ(CH$_3$) 0.07, s, δ(CH$_2$F) 4.20, d; δ(F) − 268.6, t, ^2J(HCF) 47.4 Hz.

4.5. Tris(fluoromethyl-dimethylsilyl)-amine (V)

After slow addition of *n*-butyl lithium (6.7 ml of a 1.6 N solution in hexane) to 2.11 g (10.7 mmol) of IV dissolved in 20 ml hexane, the mixture was stirred for 1 h, cooled to − 196°C, and 2.21 g (12.9 mmol) of II condensed into the flask. After warming to room temperature and stirring for 2 h, 10 ml H$_2$O was added to dissolve LiBr. The organic phase was separated, dried and distilled. Yield 1.56 g (5.42 mmol, 51%) V, b.p. 70–73°C/0.05 mbar. IR, film: 2969 s, 2960 s, 2910 s (ν(CH)), 1420 m (δ_{as}(CH$_3$)), 1260 vs (δ_s(CH$_3$)), 980 s (ν(CF)), 915 vs (ν_{as}(Si$_3$N)). NMR (in acetone-d$_6$): δ(CH$_3$) 0.12, s, δ(CH$_2$F) 4.27 d; δ(F) − 262.5, t, ^2J(HCF) 48.6 Hz.

4.6. Hydrolysis of CH$_2$F(CH$_3$)$_2$SiBr (I): cyclo-1,3,5,7-tetrakis(fluormethyl-methyl)-tetrasiloxane (VI)

At 0°C 10 ml H$_2$O was added within 30 min to a vigorously stirred solution of 6.31 g (26.7 mmol) I in 100 ml Et$_2$O. Thereafter the mixture was refluxed for 60 min, the organic phase separated, washed with water and dried with CaCl$_2$. The solvent was distilled off and 2.1 g crude material was obtained. Its distillation afforded 0.2 g VI as a colourless oil, b.p. 57–60°C/0.01 mbar, which partly formed needle-like crystals. IR, KBr pellet: 2972 m, 2911 m (ν(CH)), 1433 w (δ_{as}(CH$_3$)), 1268 s (δ_s(CH$_3$)), 1100 vs (ν_{as}(SiOSi)), 982 s (ν(CF)). For NMR see Table 1. Anal. Found: C, 26.19; H, 5.56; F, 20.7. C$_8$H$_{20}$F$_4$O$_4$Si$_4$ Calc.: C, 26.11; H, 5.49; F, 20.6%.

4.7. X-ray structural determination of VI

A crystal of dimensions 0.10 × 0.26 × 0.37 mm^3 was grown by slow evaporation of a solution of VI in methylene chloride and sealed in a glass capillary under argon. Celln constants and intensity data were determined at room temperature with an Enraf-Nonius CAD-4 diffractometer employing Ni filtered Cu Kα radiation (λ 1.54178 Å). The crystal belonged to the monoclinic space group $P2_1/n$ with $a = 8.7439(6)$, $b = 6.5854(3)$, $c = 16.1428(8)$ Å, $\beta = 98.744(5)°$, $Z = 2$ and $D_c = 1.332$ g cm^{-3}. A hemisphere of data ($l \geq 0$, $5° \leq 2\theta \leq 150°$) was measured with the $2\theta-\omega$ scan technique. The intensities were corrected analytically for absorption ($\mu = 35.0$ cm^{-1}, transmission 0.436–0.736) and merged

to yield 1845 unique reflections, of which 1339 were deemed observed ($F_o \geq 4\sigma(F_o)$).

A Patterson search and tangent phase expansion technique as implemented by the program SHELXS-86 [15] was used to obtain positions of the Si, O and C atoms. Following an anisotropic refinement of these atoms, the low electron density (less than 1.11 e Å^{-3}) in a difference Fourier synthesis indicated that the two F atoms were disordered over nine sites—namely two bonded to C(1), three to C(2), one to C(3) and three to C(4). A variety of models was developed to describe the disorder, and the ultimate choice consisted of eclipsed H$_3$ and F$_3$ triangles, so defined that C–H 0.95 Å, H–C–H 109.5°, C–F 1.25 Å and F–C–F 104.0°. The groups were so oriented that their threefold axes coincided with an Si–C vector and that a C–F bond was directed towards a local maximum in the difference electron density. This was examined at the twelve F sites generated with the model, and thus initial occupancies were estimated for the nine F and 12 H atoms. The four rigid groups were introduced with the C atoms being the pivots. With the F atoms anisotropic, the isotropic Us of the H atoms tied to U(1,1) of the pivot C atom, variable fractional F and H occupancies and an extinction correction, refinement of the 149 parameters with the program SHELX-76 [16] converged with $R = 0.062$ and $R_w = 0.078$. The final difference Fourier synthesis (0.28 to − 0.27 eÅ^{-3}) contained only spurious peaks. Coordinates of the non-hydrogen atoms are listed in Table 3, the F atoms being labelled after the C atoms to which they are bonded [17].

Table 3
Positional and equivalent isotropic temperature factors [a] for the non-hydrogen atoms [b] of [(CH$_2$F)(CH$_3$)SiO]$_4$

Atom	x	y	z	U
Si(1)	0.3985(1)	0.1530(2)	0.10089(6)	0.0850(5)
Si(2)	0.7330(1)	0.0169(2)	0.07693(7)	0.0882(5)
O(1)	0.5793(3)	0.1188(6)	0.1002(2)	0.125(2)
O(2)	0.2991(4)	0.0760(7)	0.0151(2)	0.129(2)
C(1)	0.3387(9)	0.019(1)	0.1898(4)	0.125(3)
F(1A)	0.4063(9)	0.051(1)	0.2626(4)	0.19(2)
F(1B)	0.1985(9)	0.019(1)	0.1972(4)	0.35(3)
C(2)	0.373(1)	0.4310(9)	0.1115(4)	0.128(3)
F(2A)	0.423(1)	0.5294(9)	0.0551(4)	0.20(1)
F(2B)	0.236(1)	0.4889(9)	0.1072(4)	0.20(2)
F(2C)	0.440(1)	0.5088(9)	0.1778(4)	0.16(1)
C(3)	0.8865(8)	0.212(1)	0.0796(6)	0.156(3)
F(3A)	0.9406(8)	0.264(1)	0.1527(6)	0.30(2)
C(4)	0.803(1)	− 0.179(2)	0.1505(5)	0.179(5)
F(4A)	0.931(1)	− 0.258(2)	0.1430(5)	0.32(2)
F(4B)	0.819(1)	− 0.126(2)	0.2256(5)	0.28(2)
F(4C)	0.713(1)	− 0.327(2)	0.1467(5)	0.58(3)

[a] $U = \frac{1}{3}\Sigma_i \, \Sigma_j \, \bar{a}_i \cdot \bar{a}_j a_i^* a_j^* U_{ij}$.

[b] The occupancies of the fluorine atoms in the above-given order are 0.12(1), 0.20(3), 0.34(2), 0.14(2), 0.20(2), 0.26(2), 0.38(3), 0.24(2) and 0.21(3).

References

[1] H. Bürger and P. Moritz, J. Organomet. Chem, 427 (1992) 293.

[2] H. Beckers and H. Bürger, J. Organomet. Chem. 385 (1990) 207.

[3] J. Pola, Z. Bastl, J. Tláskal, H. Beckers, H. Bürger and P. Moritz, Organometallics, 12 (1993) 171.

[4] H. Bürger and P. Moritz, Organometallics, 12 (1993) 4930.

[5] E.G. Rochow, in Comprehensive Inorganic Chemistry, Vol. 1, Pergamon, Oxford, 1973.

[6] H. Bürger, Organomet. Chem. Rev. A, 3 (1968) 425; H. Kriegsmann, Z. Elektrochem, 61 (1957) 1088.

[7] J. Goubeau and J. Jiménez-Barberá, Z. Anorg. Allg. Chem, 303 (1960) 217; U. Wannagat and H. Niederprüm, Angew. Chem. 71 (1959) 574.
H. Beckers, H. Bürger, P. Bursch and I. Ruppert, J. Organomet. Chem, 316 (1986) 41.

[8] E. Maslowsky, Jr., Vibrational Spectra of Organometallic compounds, Wiley, New York, 1977.

[9] V.Yu. Orlov, Zh. Obsh. Khim, 37 (1967) 2300; A.V. Polivanov, A.A. Bernadskii, V.N. Bochkarev, V.I Zhun' and V.D. Sheludyakov, Zh. Obsh. Khim, 50 (1980) 614.

[10] V.A. Pestunovich, M.F. Larin, M.G. Voronkov, G. Engelhardt, H. Jancke, V.P. Mileshkevich and Yu. A. Yuzhelevskii, Zh. Strukt. Khim, 18 (1977) 578.

[11] H. Steinfink, B. Post and I. Fankuchen, Acta Crystallogr, 8 (1955) 420.

[12] H. Oberhammer, W. Zeil and G. Fogarasi, J. Mol. Struct, 18 (1973) 309.

[13] U. Wannagat, G. Bogedain, A. Schervan, H.C. Marsmann, D.J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke, C. Krüger and K.-H. Claus, Z. Naturforsch, 46b (1991) 931.

[14] V. Shomaker and K.N. Trueblood, Acta Crystallogr., B24 (1968) 63.

[15] G.M. Sheldrick, SHELXS-86: program for crystal structure solutions, University of Göttingen, 1986.

[16] G.M. Sheldrick, SHELX-76: program for crystal structure determination, University of Cambridge, 1976.

[17] Additional crystallographic details may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, by quoting the deposit number CSD404395, the names of the authors and the literature reference.