Journal of Organometallic Chemistry, 427 (1992) 293–308
Elsevier Sequoia S.A., Lausanne
JOM 22440

The synthesis and properties of $(CH_2F)SiH_3$ and related monofluoromethylsilanes *

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(Received September 27, 1991)

Abstract

The reduction of $(CFCl_2)SiCl_3$ by $LiAlH_4$, Me_3SnH, and $(^nBu)_3SnH$ has been studied. The compound $(CH_2F)SiH_3$ (I) and all the compounds of the series $(CFCl_{2-m}H_m)SiCl_{3-n}H_n$, $m = 0$, 1 and $n = 0$–3 were detected and characterized by NMR spectroscopy. Conditions for the synthesis of I, $(CHFCl)SiH_3$ (IX) and $(CFCl_2)SiH_3$ (V) with acceptable yields have been optimized. These novel compounds were studied by ^1H, ^{19}F, ^{13}C and ^{29}Si NMR spectroscopy; their infrared and Raman spectra were recorded and assigned with the assistance of a normal coordinate analysis of I and its isotopomer $(CD_2F)SiD_3$. The thermolyses of I, IX and $(CHF_2)SiH_3$ (X) which start at about 120, 200 and 180°C, respectively, have been studied. Whereas I decomposes by a migration of F from C to Si, compound X undergoes elimination of the carbene CHF, insertion of which into SiH bonds ultimately gives CH_3Si derivatives.

Introduction

In spite of continuous efforts, only a very few fluoromethylsilicon compounds $(CF_nX_{3-n})Si\equiv$, X = H, Cl, Br, I, have been described up to now. In contrast to their $CH_3Si\equiv$ analogues they are both difficult to obtain, and are unstable because of ease of fluorocarbene elimination, with concomitant formation of SiF bonds. Most of the fluoromethyl derivatives are species containing a CF_3Si moiety, which became accessible mainly through the pioneering work of Ruppert [1]. Silanes bearing CHF_2 groups were selectively synthesized only recently, by CF_2 insertion into SiH bonds [2].

The monofluoro derivatives $(CH_2F)Si\equiv$ are still the least known of the fluoromethylsilanes, and the fluoro species were mostly excluded from systematic, particularly spectroscopic investigations of halomethylsilicon derivatives $(CH_2X)Si\equiv$. Thus attempts to convert $(CH_2Cl)SiH_3$ into $(CH_2F)SiH_3$ (I) by use of AgF failed, only H_3SiF being obtained [3], and attempted fluorination of Me_3SiCH_2Cl

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* Dedicated to Professor K.H. Büchel on the occasion of his 60th birthday.

with SbF_5 [4], Me_3SiCCl_3 with KF [5] or of $Me_3SiCHCl_2$ with KF in toluene [6] was found to result in breakdown of the haloalkylsilicon moiety. Unselective formation of a large series of $(CH_2F)Si$ compounds has been observed in low temperature fluorination of $SiMe_4$, and characterization of some of the species containing the $(CH_2F)Si$ group was achieved mainly by NMR spectroscopy [7]. The insertion of CHF into a SiH bond in the gas phase was first observed during the thermolysis of CF_3SiH_3 [8]. This is, in principle, a reasonably selective route to monofluoromethylsilane derivatives, but its extensive and large scale use would require a more convenient gas phase source of CHF than that provided by, for example, the thermolysis of difluoromethylsilane derivatives [2].

A convenient synthesis of I is a necessity if its chemical and spectroscopic properties and, in particular, its thermal and laser-induced decomposition are to be studied. To our knowledge Me_3SiCH_2F is the only fluoromethylsilane that has been fully characterized [9,10]. A variant of its recently reported synthesis

$$(CFCl_2)SiMe_3 + 2(^nBu)_3SnH \rightarrow (CH_2F)SiMe_3 + 2(^nBu)_3SnCl \qquad (1)$$

from a $(CFCl_2)Si$ derivative might be used to synthesize I from $CFCl_2SiCl_3$ [11] by selective and total H/Cl exchange. In this connection, we recall that reaction of CF_3SiCl_3 with $LiAlH_4$ leads to substitution at silicon, with preservation of the CF_3Si moiety [12]. We thus decided to study the reduction of $(CFCl_2)SiCl_3$ (II) in detail, and report below on several novel fluoromethylsilicon derivatives.

Synthesis of fluoromethylsilanes

(Fluorodichloromethyl)-trichlorosilane, $(CFCl_2)SiCl_3$ (II) was first prepared by Josten and Ruppert [11] by the reaction of $CFCl_3$ with $HSiCl_3$ in the presence of Et_3N

$$HSiCl_3 + CFCl_3 \xrightarrow[-[Et_3NH]Cl]{+Et_3N} \underset{(II)}{(CFCl_2)SiCl_3} \qquad (2)$$

Attempts to synthesize II by nucleophilic fluorodichloromethylation of $SiCl_4$ with the reagent $CFCl_3/(Et_2N)_3P$ failed [11]. This observation is somewhat surprising because analogous reactions have been successfully employed to synthesize fluorodichloromethyl-methylchlorosilanes, $(CFCl_2)Si(CH_3)_nCl_{3-n}$ from $(CH_3)_nSiCl_{4-n}$ [11]. Furthermore $SiCl_4$ reacts with $CF_3Br/(Et_2N)_3P$ to yield CF_3SiCl_3 [12].

We have been able to reproduce the reported [11] synthesis of II; when NMe_3 was used as the base, the yield of II was slightly increased from 21% [11] to 25%. Although the ^{19}F NMR spectrum of our product was consistent with that previously reported its melting point was $+24 \pm 2$°C rather than the previously reported -10°C [11].

Traces of $(CFCl_2)SiHCl_2$ (III) were detected by ^1H and ^{19}F NMR spectroscopy in the volatile products (Table 1) but the quantities were too small to allow isolation of the pure material. We assume that III is a secondary product, formed by a H/Cl redistribution reaction of II with $HSiCl_3$. The NMR parameters were a useful guide for the identification of III also in the course of the reduction of II.

Reduction of II by hydride H^- may occur at three different sites:

(i) reduction of the $SiCl_3$ group to yield $(CFCl_2)SiH_{3-n}Cl_n$ species, such as III;
(ii) reduction of the $CFCl_2$ substituent, with preferential replacement of Cl;

Table 1

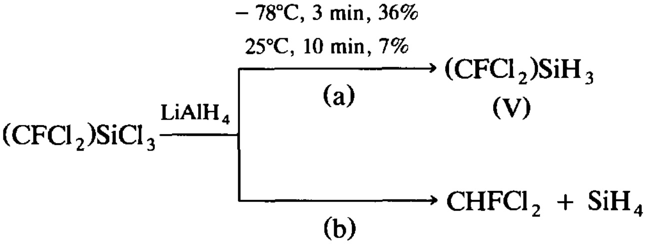
Distribution of products [a] and NMR [b] data for the reaction of $(CFCl_2)SiCl_3$ (II) with $(^nBu)_3SnH$, molar ratio 1:3.7, 15 min at room temperature

	II	III	IV	V	VI	VII	VIII	IX
Product (%)	0.1	9.0	22.5	5.3	6.7	37.2	12.8	6.4
$\delta(^1H)(CH)$	–	–	–	–	5.79d	5.77dd	5.87	5.92dq
$\delta(^1H)(SiH)$	–	5.32d	4.68d	4.01d	–	5.26dd	···	3.70dd
$\delta(^{19}F)$	−80.5	−81.4d	−78.1t	−69.5q	−170.1d	−173.3dd	−171.3 [c]	−163.5dq
$^2J(HF)$	–	–	–	–	45.7	46.1	46.2	47.8
$^3J(HF)$	–	3.7	6.2	6.7	–	3.2	8.5 [d]	10.0
$^3J(HH)$	–	–	–	–	–	2.2	2.2 [e]	2.2

[a] According to ^{19}F NMR spectrum. [b] In ppm, J in Hz. Measurements on neat sample, external standards TMS and $CFCl_3$. Shifts and coupling constants may differ from those quoted in Table 2. [c] ABMX spin system. [d] $1/2(^3J(FH_A)+^3J(FH_B))$. [e] $1/2(^3J(HH_A)+^3J(HH_B))$.

(iii) reductive cleavage of the C–Si bond with formation of $CHFCl_2$ and SiH_4, along with concomitant complete reduction by process (i).

Whereas $LiAlH_4$ reacts with CF_3SiCl_3 to yield CF_3SiH_3 almost quantitatively [12], it reacts with II at room temperature predominantly by process (iii) involving cleavage of the SiC bond (eq. 3b), only 7% of the desired $(CFCl_2)SiH_3$ (V) being obtained (eq. 3a). When the reaction (eq. 3) was carried out in di-n-butyl ether at −78°C, the novel compound V was obtained in a yield of 36%, decomposition according to (eq. 3b) being negligible.



(3)

At and above room temperature Me_3SnH is a more selective reducing agent, only V and $CHFClSiH_3$ (IX) being formed, in a ratio which depends on the reaction time (eq. 4).

$$CFCl_2SiCl_3 \xrightarrow[-Me_3SnCl]{Me_3SnH,\ 50°C,\ 2\text{–}24\ h} \underset{(V)}{CFCl_2SiH_3} + \underset{(IX)}{CHFClSiH_3} \qquad (4)$$

Attempts to replace all the Cl atoms of II under more vigorous conditions, *i.e.* by treatment with Me_3SnH for 3 days at 80°C, resulted in extensive decomposition, no I being obtained.

A smooth and stepwise replacement of Cl by H was achieved with $(^nBu)_3SnH$. Treatment of II with $(^nBu)_3SnH$ in a 1:3.7 molar ratio for 15 min at room temperature yielded a mixture containing, as indicated by their NMR spectra, all eight components of the two series $(CFCl_2)SiH_nCl_{3-n}$

$n = 0$ (II), 1 (III), 2 (IV), 3 (V)

and $(CHFCl)SiH_nCl_{3-n}$
$n = 0$ (VI), 1 (VII), 2 (VIII) and 3 (IX),

in the proportions specified in Table 1. Although it was observed that Si–Cl groups are generally more easily reduced than C–Cl units, there seems to be a complex interdependence. Heating II with $(^nBu)_3SnH$ in a 1 : 10 molar ratio to 80°C for 3 days yielded, after isothermal distillation at −60°C, 26.2% I and 28.3% IX as major components. The deuterated species $(CD_2F)SiD_3$ was obtained analogously in a yield of 39% by use of $(^nBu)_3SnD$. Use of reaction time exceeding 3 days led to an increase in the amount of decomposition products rather than in the yield of V and IX. Alternatively, I and IX can be isolated in yields of 40% each by fractional condensation *in vacuo*, but their NMR spectra reveal that these fractions also contain about 2% of CH_3SiH_3 and $(CH_2Cl)SiH_3$, respectively.

Physical and chemical properties

The temperature dependence of the vapour pressure of I, V and IX was determined and fitted to the equation:

$$\ln p(\text{mbar}) = -A/T(\text{K}) + B \tag{5}$$

I: $A = 2655.3$, $B = 17.227$ ($176.7 \leq T \leq 246.3$ K), $\Delta H = 22.08$ kJ mol^{-1},
$\Delta S = 85.7$ J mol^{-1} K^{-1}, extrapolated b.p. −15.5°C.
V: $A = 3108.7$, $B = 16.891$ ($195.1 \leq T \leq 293.0$ K), $\Delta H = 25.80$ kJ mol^{-1},
$\Delta S = 82.9$ J mol^{-1} K^{-1}, extrapolated b.p. 38.6°C.
IX: $A = 3655.5$, $B = 19.335$ ($205.9 \leq T \leq 283.4$ K), $\Delta H = 30.39$ kJ mol^{-1},
$\Delta S = 103.2$ J mol^{-1} K^{-1}, extrapolated b.p. 21.3°C.

The starting material II is easily hydrolyzed. In contrast to IX and SiH_4, I is neither pyrophoric when exposed to air nor sensitive to moisture. In agreement with previously reported [2] observations on $(CHF_2)SiH_2Cl$, any material containing CHF and SiCl moieties is dangerously shock-sensitive at room temperature; such incompletely reduced products should be handled with extreme care. All the other compounds are stable at room temperature when sealed in glass containers.

Thermolysis

In extensions of earlier thermolysis studies on CF_3SiH_3 [8] and CH_3SiH_3 [13] we have investigated the thermal decomposition of I, IX and $(CHF_2)SiH_3$ (X).

In the gas phase the decomposition of I becomes significant above 120°C; thus 96% of I decomposed within 7 days at 145°C according to

$$(CH_2F)SiH_3 \xrightarrow{\Delta} CH_3SiH_2F \tag{6}$$

About 14% of the CH_3SiH_2F formed undergoes a ligand exchange to form CH_3SiH_3 and CH_3SiHF_2. We assume that the decomposition of I has a dyotopic mechanism rather than following a carbene elimination/insertion pathway.

Difluoromethylsilane (X) is thermally more stable, decomposition being slow at 180°C, but almost complete after 7 days at 220°C at pressures exceeding 10 bar. The major decomposition products were fluorosilanes, difluoromethylsilanes, and, predominantly, methylfluorosilanes $MeSiH_{3-n}F_n$ (see Experimental section). Traces of additional compounds, assumed to be methyl-difluoromethylsilanes

$(CHF_2)SiH_nMe_{3-n}$ were detected, but no monofluoromethylsilane derivatives, even though these are likely to be the first intermediates in a carbene elimination/insertion process.

$$(CHF_2)SiH_3 \xrightarrow{\Delta} [CHF + SiH_3F] \rightarrow (CH_2F)SiH_2F \rightarrow \rightarrow \qquad (7)$$

Failure to detect monofluoromethyl intermediates is not surprising since their decomposition via the process in eq. (6) is rapid even at lower temperatures.

In order to confirm the occurrence of elimination of CHF and exclude formation of CF_2 as the first step of the thermal decomposition, we co-thermolyzed X with an excess of cyclohexene, which is an efficient carbene trap. We found a total of about 45% 7-fluorobicyclo[4.1.0]heptane in an *endo/exo* ratio of 3:4. Furthermore, about 20% of methylsilanes were formed (see Experimental section). These products confirm the intermediacy of CHF and favour a decomposition pathway depicted in eq. 7.

The thermolysis of $(CHFCl)SiH_3$ (IX) was almost complete after 3 days at 230–240°C. Numerous decomposition products were identified, the ^1H NMR spectrum of their mixture being very complex. Most constituents could be identified, and major components, listed in the order of decreasing abundance, were $MeSiHF_2$, MeSiHFCl, $MeSiCl_3$, $MeSiHCl_2$, Me_2SiFCl, Me_2SiCl_2, $MeSiH_2Cl$ and Me_2SiHCl. (For minor constituents and quantitative data see the Experimental section.) A significant observation was that all the CHFCl groups were transformed to CH_3 moieties, and the decomposition pathway is related to that of **X**. Of the possible elimination of the carbenes CHF, CHCl, and CFCl in the first step, obviously that of CHCl is preferred, and this carbene then inserts into a SiH bond. This is confirmed by the absence of any significant quantities of fluoromethylsilanes among the decomposition products (evidence for traces of $(CH_2F)SiCl_3$ being ambiguous) and the absence of 7-fluorobicyclo[4.1.0]heptane in the co-thermolysis products from IX and cyclohexene.

Spectra

NMR spectra

The ^1H, ^{13}C, ^{19}F and ^{29}Si NMR data for I, II, V and IX obtained with pure material are listed in Table 2. NMR data obtained from complex mixtures to enable identification of the constituents are given in the Experimental section. The multinuclear NMR spectra of I are illustrated in Fig. 1. The ^{19}F chemical shift of I is sensitive to deuteration, $\delta\delta(^{19}F)$ being -0.15 ppm per D atom bonded to Si and -0.58 ppm per D atom bonded to C.

The ^{19}F NMR signals of the (chlorofluoromethyl)silanes II, V and IX reveal a significant $^{35}Cl/^{37}Cl$ isotopic shift, which is illustrated in Fig. 2. An isotopic shift, $\delta\delta(^{19}F)$ -5.6×10^{-3} ppm, per ^{35}Cl replaced by ^{37}Cl, has been reported for $CFCl_3$ at 305 K [14].

While three singlets, relative intensity 9:6:1, with $\delta\delta(^{19}F)$ -7.5×10^{-3} ppm per geminal ^{35}Cl replaced by ^{37}Cl, are observed for II, three quartets, intensity ratio 9:6:1, $\delta\delta(^{19}F)$ -8.5×10^{-3}, and two doublets of quartets, intensity ratio 3:1, $\delta\delta(^{19}F)$ -8×10^{-3} ppm, were resolved for V and IX, respectively.

Table 2

NMR data for (monofluoromethyl)silanes [a]

	$(CFCl_2)SiCL_3$ [b] (II)	$(CFCl_2)SiH_3$ (V)	$(CHFCl)SiH_3$ (IX)	$(CH_2F)SiH_3$ (I)
^1H NMR [c]				
$\delta(CH)$			5.72	4.28
$\delta(SiH)$		3.95	3.64	3.55
$^2J(HCF)$			45.6	46.7
$^3J(HF)$		6.8	10.3	14.4
$^3J(HH)$			2.2	3.4
^{19}F NMR [d]				
$\delta(F)$	-80.6	-69.3	-163.4	-263.7
^{13}C NMR [e]				
$\delta(C)$	114.5	116.6	95.3	73.4
$^1J(H^{13}C)$			168.8	142.8
$^1J(F^{13}C)$	316.4	317.7	249.7	167.3
$^2J(HSi^{13}C)$		7.6	6.3	5.2
^{29}Si NMR [f]				
$\delta(Si)$	-13.7	-40.4	-54.0	-65.5
$^1J(H^{29}Si)$		224.9	214.3	202.9
$^2J(HC^{29}Si)$			4.6	2.4
$^2J(FC^{29}Si)$	53.9	34.6	30.3	24.6

[a] Chemical shifts δ in ppm, absolute values of coupling constants J in Hz. [b] Ref. 11:, $\delta(F)$ -81.5 ppm, $^2J(FC^{29}Si)$ 53.4 Hz, $\delta(^{29}Si)$ -13.7 ppm. [c] Solvent and internal standard C_6D_6. $\delta(C_6D_5H) = 7.27$ ppm. [d] In C_6D_6. External standard $CFCl_3$. [e] Solvent and internal standard C_6D_6, $\delta(C) = 128.0$ ppm. [f] In C_6D_6. External standard TMS.

On the whole, the NMR spectra, and in particular the coupling patterns, provide a powerful tool for establishing the constitution of the reported novel molecules. They are of great value for the identification of species in complex mixtures such as those obtained in the thermolysis experiments. Both chemical shifts and coupling constants are very sensitive to minor changes in the molecule (Table 2). As the hitherto missing link (I) in the series $(CH_nF_{3-n})SiH_3$, $n = 0$–3, has now become available, it was of interest to compare some NMR parameters for this series (see Table 3). Although the majority of the parameters change regularly with increasing n, some parameters for CHF_2SiH_3 deviate from this pattern.

Infrared and Raman spectra

The IR spectra in the gas phase and Raman spectra in the liquid phase were recorded for I, $(CD_2F)SiD_3$, II, V, and IX; the spectra of I are illustrated in Figs. 3 and 4. Observed vibrational wavenumbers and assignments are set out in Tables 4 and 5.

Assignments for I and $(CD_2F)SiD_3$ are only qualitatively indicated in Table 4; they can be made in more detail from the normal coordinate analysis shown in Table 6, and by comparison with previous data for $(CH_2Cl)SiH_3$ and $(CH_2Br)SiH_3$ [18,19]. The assignments are particularly sensitive to resonance effects on bending and skeletal stretching vibrations ($\nu(CF)$, $\nu(SiC)$) which affect $(CD_2F)SiD_3$ more than I.

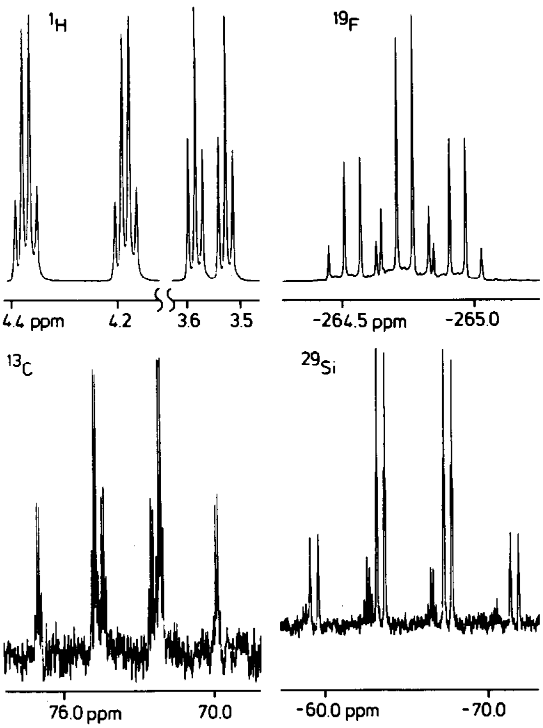


Fig. 1. ^{1}H, ^{19}F, ^{13}C and ^{29}Si NMR spectra of I.

The vibrational spectral data for II, V and IX are listed in Table 5, and interpreted in terms of the concept of group vibrations and by analogy with assignments for related compounds (I, CF_3SiH_3 [20], CHFClBr [21] and $CFCl_2Br$

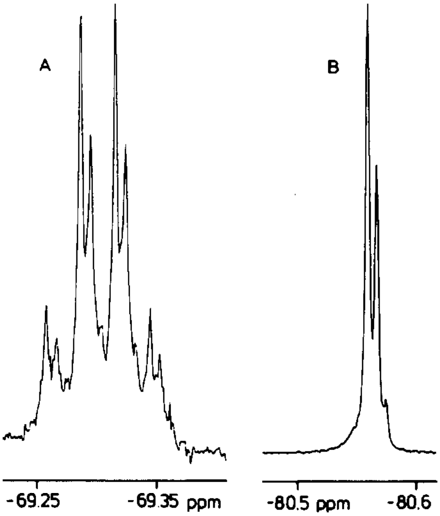


Fig. 2. ^{19}F NMR signals from V (A) and II (B), revealing $^{35/37}$Cl isotopic splitting.

Table 3

NMR data for (fluoromethyl)silanes [a]

	CH_3SiH_3 [b]	$(CH_2F)SiH_3$ [c]	$(CHF_2)SiH_3$ [d]	CF_3SiH_3 [e]
$\delta(^1H(C))$	0.12	4.28	5.81	–
$\delta(^1H(Si))$	3.55	3.55	3.53	3.92
$\delta(^{19}F)$	–	−263.7	−128.1	−56.1
$\delta(^{13}C)$	−12.3 [c]	73.4	120.2	129.9
$\delta(^{29}Si)$	−65.2	−65.5	−63.8	−71.1
$^1J(^1H^{13}C)$	122.1	142.8	171.3	–
$^1J(^1H^{29}Si)$	194.3	202.9	213.3	223
$^1J(^{19}F^{13}C)$	–	167.3	252.3	314.3
$^2J(^1H^{13}C)$	4.5 [c]	5.2	5.7	
$^2J(^1H^{29}Si)$	7.8	2.4	10.5	–
$^2J(^1H^{19}F)$	–	46.7	46.0	–
$^2J(^{19}F^{29}Si)$	–	24.6	34.1	48.8
$^3J(^1H^{19}F)$	–	14.4	11.1	7.5
$^3J(^1H^1H)$	4.7	3.4	1.8	–

[a] Chemical shifts δ in ppm, absolute values of coupling constants J in Hz. [b] Refs. 15, 16. [c] This work; solvent and internal standard C_6D_6. [d] Ref. 2. [e] Ref. 17.

[22]). In these molecules vibrations of the heavy atom skeleton are severely coupled, and the assignments are very approximate. Vibrations of the CH and SiH_3 fragments are reasonably characteristic, with the exception of the CSiH bending modes which correspond to the $\rho(SiH_3)$ mode in $XSiH_3$ molecules. While the ν(CF) and ν(CCl) vibrations at ~ 1065 and 850 ± 60 cm^{-1}, respectively, show good agreement with those of CHFClBr and $CFCl_2Br$ (1075 ± 5 and 805 ± 25

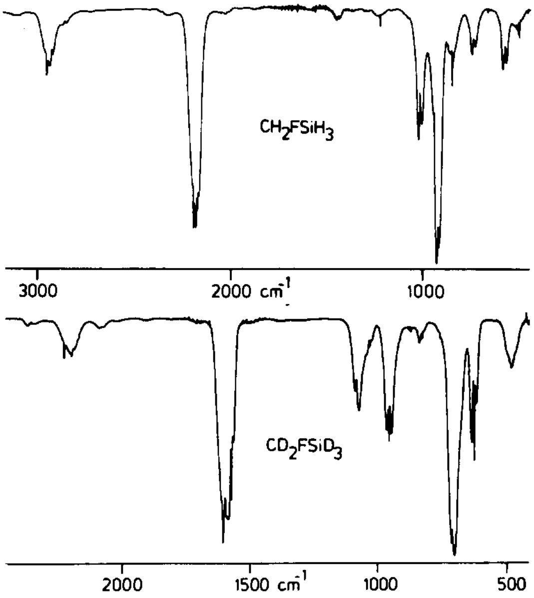


Fig. 3. Infrared spectra of I and $(CD_2F)SiD_3$ (18 cm gas cell, pressure ~ 6 mbar, resolution 4 cm^{-1}).

cm^{-1}), the "ν(SiC)" vibration adopted has the character of the "breathing mode" of the groups linked to the carbon atom, and the systematic increase in the associated wavenumber from 469 cm^{-1} in II to 530 cm^{-1} in IX is in line with a decrease of the molecular mass of the molecules. There is no basis at present for a detailed assignment of the bending vibrations below 400 cm^{-1}, the data being too scarce to justify a normal coordinate analysis.

Normal coordinate analysis of I

A normal coordinate analysis was performed by means of an iterative computer program [23], with starting force constants taken from CH_3SiH_3 [24] and $(CHF_2)SiH_3$ [2]. C_s symmetry and staggered conformation, $r(SiC) = 1.867$ Å, $r(SiH)$ 1.482 Å, $r(CF) = 1.333$ Å, $r(CH) = 1.095$ Å, H–C–Si = F–C–Si = 109.0°

Table 4

Infrared and Raman spectral data for $(CH_2F)SiH_3$ and $(CD_2F)SiD_3$ (cm^{-1})

$(CH_2F)SiH_3$		$(CD_2F)SiD_3$		Assignment
IR (gas)	Raman (liquid)	IR (gas)	Raman (liquid)	
3100vw				
		2930vw		$\nu(CH)$
2950s	2960w, dp	2218m	2234w, dp	$\nu_{as}(CH_2)/(CD_2)$
2918sh	2928s, p	2188w, PQR, 17	2180s, p	$\nu_s(CH_2)/(CD_2)$
2850vw	2860w, p			2×1440
2315vw				
		2080vw	2067w, p	1030 + 1076
		1700vw		
2193vs, PQR, 20 [a]		1602vs, PQR	1597s, dp	$\nu_{as}(SiH_3)/(SiD_3)$
2172vs, PQR, 16	2178vs, p	1568vs, PQR	1568vs, p	$\nu_s(SiH_3)$
2028vw				
		1496vw		
			1268w, p	
		1099vw	1098w, p	
1440w, PQR	1441w, p	1076s, PQR	1056s, p	$\delta(CH_2)/(CD_2)$
1296vw, PQR	1300m, p	1030sh	1010w	$\gamma(CH_2)/(CD_2)$
1222w	1225w, dp	908sh	912w, dp	$\tau(CH_2)/(CD_2)$
		979sh		
1022m, PQR, 20	995w	955s, PQR, 18	939m, p	$\nu(CF)$
942sh	942m, dp			$\delta_{as}(SiH_3)(a', a'')$
		825vw		
		754w	752w, p	
921vs, PQR		692vs		$\delta_s(SiH_3)/(SiD_3)$
870vw				
		707vs	705m, p	$\delta_{as}(SiD_3)(a')$
		692vs		$\delta_s(SiD_3)$
			682m, dp	$\delta_{as}(SiD_3)(a'')$
850m	850w, dp		673m, dp	$\rho(CH_2)/(CD_2)$
	840w, p			
737m, PQR, 20	739vs, p	623s, PQR, 18	625s, p	$\nu(SiC)$
579m, PQR, 20	583vs, p	477m	475s, p	$\rho(SiH_3)/(SiD_3)(a')$
515w	515w, dp	372m	375m, dp	$\rho(SiH_3)/(SiD_3)(a'')$
238m, PQR, 20	255m, p	222m	228m, p	$\delta(FCSi)$

[a] PR separation in cm^{-1}.

Table 5

Infrared and Raman spectral data for $(CFCl_2)SiCl_3$, $(CFCl_2)SiH_3$ and $(CHFCl)SiH_3$ (cm^{-1})

$(CFCl_2)SiCl_3$		$(CFCl_2)SiH_3$		$(CHFCl)SiH_3$		Assignment
IR (gas)	Raman (liquid)	IR (gas)	Raman (liquid)	IR (gas)	Raman (liquid)	
				2957m, PQR	2963m, p	$\nu(CH)$
		2221vs, PQR	2223sh	2211vs		$\nu_{as}(SiH_3)$
				2202vs		
		2200vs, PQR	2202vs, p	2197vs, PQR, 14 [a]	2191vs, p	$\nu_s(SiH_3)$
				1305w	1310m, p	$\delta(HC)$
				1194w, PQR, 16	1197m, p	$\delta(HC)$
1070s	1062w, p	1069s, PQR	1061w, p	1062s, PQR, 11	1020w	$\nu(CF)$
		943sh	934m	941s	947s, p	$\delta_{as}(SiH_3)$
				935sh	937s	
		918vs, PQR	913w, p	912vs, PQR, 16	911sh	$\delta_s(SiH_3)$
906s	904w, p	868vs, PQR	861m, p			$\nu_s(CCl_2)$
793s	787w	790s	780m			$\nu_{as}(CCl_2)$
				793m, PQR, 5	790m	$\nu(CCl)$
841w		732vw	730vw			
824w						
681m	681vw					$\nu_{as}(SiCl_3)$
630vs	627w					
		639s, PQR, 16	644m, p	730m	731s, p	$\delta(CSiH)$
		606s, PQR	608m	627s, PQR, 12	623m	$\delta(CSiH)$
538vs	539vw					$\nu_s(SiCl_3)$
		550sh	561vw		577sh	
		530w	534vw			
469vs	486vs, p	486m	486vs, p	530s, PQR	532vs, p	$\nu(SiC)$
	375w	377w	370m	377m	380s, p	Heavy atom bending modes
335s	334s, p	341s	340s, p			
317m, sh	317m, p					
		278w	278m, p	278m	283m, p	
227m	227m					
	180m		191m		193m, p	
	163m		171w			
	111m					

[a] PQR separation in cm^{-1}.

and H–Si–H = 108.6°, were assumed, with the H(2) atom of the SiH(1)H(2)H(3) rotor *trans* to the F atom. The notation (HSiH^t), Table 6, refers to H(1)SiH(2) and H(2)SiH(3), (HSiH^t) to H(1)SiH(3). Correspondingly (HSiC^g) denotes (H(2)SiC) etc., while interactions of adjacent angles are denoted (α/β') and the opposite ones (α/β''). The 18 normal vibrations transform to $\Gamma_{\text{vib}} = 11a' + 7a''$; of these the a'' torsion was not considered because the relevant vibration was not observed. Of the diagonal force constants listed in Table 6, *f*(SiC) and *f*(CF) could not be satisfactorily refined, and so were fixed at plausible values.

From the potential energy distribution the extent of the vibrational coupling becomes evident. With the exception of ν(CF) in I, all the skeletal (FCSi) vibrations are strongly coupled with $CH_2(CD_2)$ and $SiH_3(SiD_3)$ modes, and

Table 6

Potential energy distribution and diagonal force constants for $(CH_2F)SiH_3$ and $(CD_2F)SiD_3$

$(CH_2F)SiH_3$		$(CD_2F)SiD_3$		Potential energy distribution[a]
Obs.	Calc.	Obs.	Calc.	
a′				
2918	2942	2188	2137	98(CH)
2193	2194	1602	1592	101(SiH)
2172	2179	1568	1558	99(SiH)
1440	1434			77(HCH), 26(HCF), −15(HCH/HCF)
1296	1295			67(HCF), 42(HCSi), −15(HCF/HCSi′)[b]
		1076	1103	49(CF), 47(HCH), 32(HCF), −13(CF/HCF), −16(HCH/HCF)
		1030	1037	39(HCSi), 28(HCF), 23(SiC), 19(HCH), 18(CF), −10(SiC/HCSi)
1022	1028			100(CF)
		955	943	39(CF), 35(HCF), 15(CF/HCF), 11(HCH)
942	949			62(HSiH^g), 31(HSiH^t)[b]
921	913			56(HSiH^g), 18(HSiC^g), 11(HSiC^t), 11(HSiH/HSiC″)
737	727			68(SiC)
		707	701	49(HSiH^g), 30(SiC)
		692	690	68(HSiH^t), 16(HSiC^t)
		623	623	36(SiC), 35(HSiH^g)
579	585			43(HSiC^t), 25(HSiC^g), 21(SiC)
		477	465	48(HSiC^t), 24(HSiC^g)
255	255	222	228	79(FCSi), 13(HCSi), 10(HSiC^t), −15(FCSi/HSiC″)
a″				
2950	2950	2218	2195	103(CH)
2193	2194	1602	1591	101(SiH)
1222	1219	908	920	111(HCF), −11(HCF/HCF)
941	941			109(HSiH^t)
850	854			90(HCSi)
		682	686	81(HSiH^t), 24(HCSi)
		673	656	70(HCSi), 28(HSiH^t)
515	514	372	375	86(HSiC^g), 11(HCSi), 10(HSiC/HSiC)

Force constants (N cm^{-1}, scaled to 100 ppm)

f(SiC) = 2.98[c] *f*(SiH) = 2.75 *f*(HSiH^g) = 0.49 *f*(FCSi) = 0.55

f(CH) = 4.97 *f*(HCH) = 0.52 *f*(HSiH^t) = 0.51 *f*(HSiC^g) = 0.33

f(CF) = 5.05[c] *f*(FCH) = 0.98 *f*(HCSi) = 0.52 *f*(HSiC^t) = 0.48

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[a] In terms of inner force constants; only contributions > 10% are listed. H stands for H and D in $(CH_2F)SiH_3$ and $(CD_2F)SiD_3$, respectively. [b] See text for explanation. [c] Constrained.

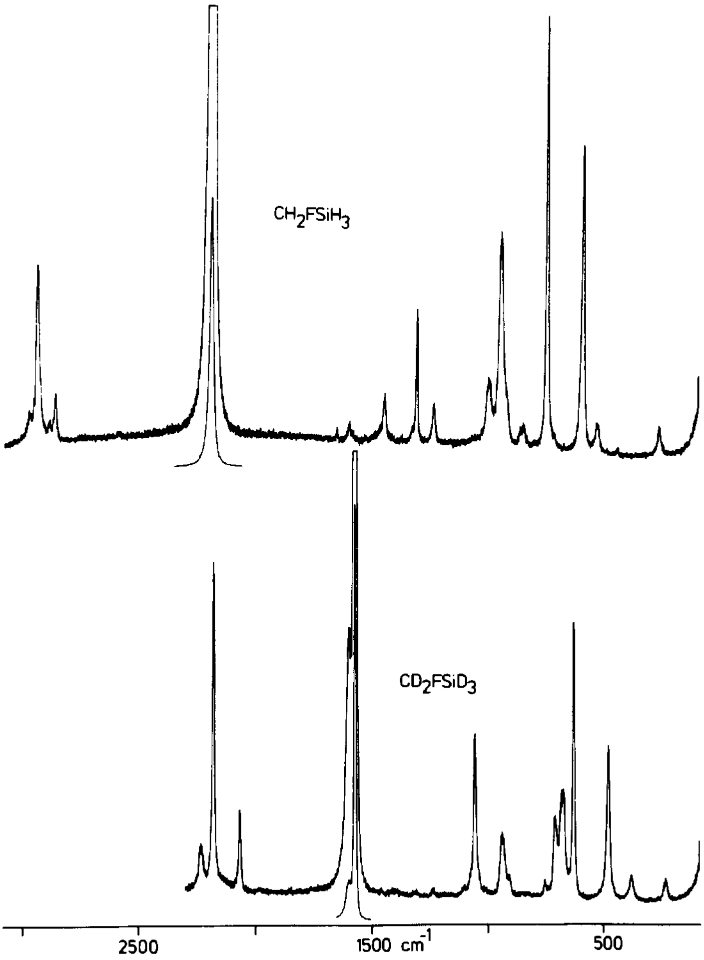

Fig. 4. Liquid phase Raman spectra of I and $(CD_2F)SiD_3$, at −60°C (excitation Kr 647.1 nm).

reference to group vibrations is not justified here. We note that in the series $(CH_{3-n}F_n)SiH_3$, $f(CF)$ increases with n, while $f(SiC)$ decreases: $f(CF)/f(SiC)$, $n = 0$, −/3.22 [24]; $n = 1$, 5.05/2.98; $n = 2$, 5.37/2.69 [2]; $n = 3$, 5.602/2.537 N cm^{-1} [20].

Experimental

Volatile materials were handled in a vacuum system equipped with greaseless valves. Gas volumes were determined by use of an MKS Baratron 315 BKS pressure gauge or with an Edwards pressure sensor, NMR spectra were recorded either with a Bruker AC 250 spectrometer (^1H, 250.1 MHz; ^{13}C, 62.9 MHz; ^{19}F, 235.4 MHz; ^{29}Si, 49.7 MHz) or, in routine work, with a Varian EM 390 spectrometer (^1H, 90.0 MHz; ^{19} F, 84.7 MHz). IR spectra were recorded with a Perkin–Elmer 580 B grating spectrometer or a Bruker IFS 25 FT spectrometer; gas cells of 10 or 18 cm length equipped with KBr or polythene windows were employed. Raman spectra of liquefied samples were measured with a Cary 82 spectrograph, excitation Kr 647.1 nm, wavenumber accuracy of IR and Raman data 1-2 cm^{-1}.

(Fluorodichloromethyl)trichlorosilane (II) was obtained as described previously [11] but with use of NMe_3 instead of NEt_3; yield 25%, m.p. $+24 \pm 2$°C ([11] -10°C). Tri-n-butylstannane-d_1 was made as described previously [25] from $(^nBu)_3SnCl$ and $LiAlD_4$ in ^tBuOMe (yield, approx. 80%).

Reduction of II

With $(^nBu)_3SnH$. In a typical experiment a mixture of 0.76 mmol of $(^nBu)_3SnH$ and 0.09 mmol of II was sealed in a 4 mm glass tube (volume ~ 1 cm^3) and kept at 20 or 80°C for various times. The compositions of the product mixtures obtained at 20°C and 15 min are shown in Table 1. When the reaction mixture was kept at 20°C for 30 min, IX was mainly obtained. Heating at 80°C for 1 h yielded IX and traces of I, while after 2.5 h, I and IX were present in approximately 1:1 molar ratio, along with traces of CH_3SiH_3, $(CH_2Cl)SiH_3$, butane and 1-butene.

With Me_3SnH. Analogously, 2.63 mmol of Me_3SnH were treated with 0.42 mmol of II. After 2 h at 50°C, V and IX were present and IX was the main product after 1 day. Heating at 80°C for 3 days resulted in formation of black material which did not contain any I.

With $LiAlH_4$ at room temperature. Compound II (12.4 mmol) was condensed onto a suspension of 1.73 g (45.6 mmol) of $LiAlH_4$ in 30 ml of di-n-butylether and the suspension was warmed to room temperature and stirred for 15 min. The vapour pressure was adjusted to 100 mbar and the volatile materials were trapped at -196°C. Formation of a non-condensable gas (H_2) was noted. Compound V (0.89 mmol, 7%) was obtained by fractional condensation of the volatile products. The by-products SiH_4 and $CHFCl_2$ were identified by IR and NMR spectroscopy.

With $LiAlH_4$ at -78°C. A mixture of 4.57 mmol of II and 8.43 mmol of $LiAlH_4$ in 7.5 ml of di-n-butylether was treated analogously for 3 min at -78°C. Volatile products were evaporated off, trapped at -196°C, and worked up by trap-to-trap condensation *in vacuo*. V (containing $\leqq 2\%$ IV) was obtained in a yield of 36%.

(Fluorodichloromethyl)silane (V). M, found 134.8 (by gas density) (calc. 133.02).

(Fluoromethyl)silane (I) and (chlorofluoromethyl)silane) (IX). A mixture of 96.2 mmol of $(^nBu)_3SnH$ and 9.65 mmol of II was heated in a 50 ml ampoule at 80°C for 3 days, after which the ^1H NMR spectrum indicated that the mixture contained 46% of I, 48% of IX, 3% of $(CH_2Cl)SiH_3$, 3% of CH_3SiH_3, and traces of 1-butene. The ampoule was then connected to a vacuum line, and volatile products were taken off through a -126°C trap, in which IX and some $(CH_2Cl)SiH_3$ condensed, and I along with some CH_3SiH_3 were condensed in a -196°C trap. I and IX were purified by isothermal distillation at -60°C, at which they had vapour pressures of 130 and 8.2 mbar, respectively. Yields 26 and 28%. M, by gas density: I, found 63.8 (calc. 64.13); IX, found 99.0 (calc. 98.58).

Thermolysis

Thermolyses were carried out as described previously [8]. I: Test experiments showed that the thermolysis of I starts at about 120°C. I (0.50 mmol), sealed in a glass ampoule (volume 1.0 cm^3) was kept at 140–150°C for 7 days. The extrapolated pressure was about 30 bar. Gaseous decomposition products identified by ^1H

Table 7

Products of the thermal decomposition of **X** and their NMR spectral data [a]

Product [b]	%	δ(H(CF))	δ(H(Si))	δ(H(CH$_3$))	δ(F(C))	δ(F(Si))	^1J(F^{29}Si)	^2J(HF)	^3J(HF)	^3J(HH)	Ref.
SiF_4	1					−163.2s [c]	174.3				26
$SiHF_3$	8		3.97q			−134.7d		95.8			26
SiH_2F_2	5		4.31t			−146.2t		60.8			26
SiH_3F	2		4.54d			−213.9q		46.5			26
CH_3SiF_3	6			−0.06q		−134.3q			4.3		26
CH_3SiHF_2	43		4.66tq	0.00td		−137.1dq	295.3	68.1	6.8	1.2	26
CH_3SiH_2F	8		4.78dq	0.14dt		−130.2tq		48.3	8.3	3.4	26
CH_3SiH_3	1		3.67q	n.o.						4.6	15
$(CH_3)_2SiF_2$	7			0.08t		−131.5sept	289.5		6.2		26
$(CH_3)_2SiHF$	8		4.95dsept	0.18dt		−171.2dsept	277.0	53.1	7.8	2.7	26
$(CH_3)_3SiF$	3			0.17d		−157.5dec	275.1		7.3		26
$(CHF_2)SiH_3$	1	5.71tq	3.46td		−129.4dq			46.0	11.0	1.8	2
$(CHF_2)SiH_2CH_3$	3	5.77tt	3.77m	n.o.	−134.0dt			46.1	10.3	1.3	
$(CHF_2)SiH(CH_3)_2$	1	5.76td	3.98	n.o.	n.o.			46.2	8.5	1.0	
$(CHF_2)Si(CH_3)_3$	1	5.70t		n.o.	−139.6d			46.3			
CH_2F_2	1	n.o.			−142.4t			50.3			27

[a] Chemical shift δ in ppm, absolute value of coupling constant J in Hz. $\delta(^1H)$ internal standard C_6D_5H = 7.27 ppm, $\delta(^{19}F)$ external standard $CFCl_3$. [b] About 7% of products not identified. [c] s, d, t, q, sept, dec, m = singlet, doublet, triplet, quartet, septet, decet, multiplet.

Table 8

Products of the thermal decomposition of **IX** and their NMR spectral data [a]

Product	%	δ(H(C))	δ(H(Si))	δ(F)	^2J(HF)	^2J(HSi)	^3J(HF)	^3J(HH)	Ref.
SiH_3F	3		n.o.	−214.8q [b]	45.9				26
SiH_2F_2	1		4.79t	−147.2t	60.9				26
SiH_2FCl	2		5.24d	−155.7t	56.5				
$SiHF_3$	[c]		n.o.	−134.8d	95.7				26
$SiHF_2Cl$	[c]		n.o.	−122.5d	84.6				
CH_3SiCl_3	10	1.15s				9.1			28
$(CH_3)_2SiCl_2$	6	0.82s				7.5			28
$(CH_3)_3SiCl$	1	0.45s				7.0			29
CH_3SiF_3	1	0.53q		−134.9q		n.o.	4.1		26
$(CH_3)_2SiF_2$	2	0.35t		−132.3sept		n.o.	6.2		26
$(CH_3)_3SiF$	2	0.24d		−157.9dec		n.o.	7.5		26
CH_3SiFCl_2	3	0.93d		−108.6q		n.o.	5.0		30
CH_3SiF_2Cl	[c]	n.o.		−117.8q		n.o.	4.5		30
$(CH_3)_2SiFCl$	8	0.59d		−132.0sept		n.o.	6.4		30
CH_3SiH_3	[c]	n.o.	3.53q			n.o.		4.6	
CH_3SiH_2F	3	0.19dt	4.82dq	−131.1tq	49.2	n.o.	7.8	3.2	15, 26
CH_3SiH_2Cl	4	0.61t	4.76q			n.o.		3.6	15
CH_3SiHF_2	27	0.44td	4.84tq	−137.8dq	68.0	n.o.	6.9	1.1	26
$CH_3SiHFCl$	12	0.69dd	5.34dq	−141.0dq	62.2	n.o.	6.5	1.7	
CH_3SiHCl_2	8	0.89d	5.59q			n.o.		2.3	31
$(CH_3)_2SiHF$	1	n.o.	n.o.	−171.3dsept	53.4	n.o.	8.5	n.o.	26
$(CH_3)_2SiHCl$	4	0.52d	4.30sept			n.o.		3.2	32, 33
$(CH_2F)SiCl_3$? [c]		n.o.	n.o.	−262.2t	46.8	n.o			

[a] Chemical shift δ in ppm, absolute value of coupling constant *J* in Hz. Solvent $CDCl_3$. δ(^1H) internal standard $CHCl_3$ = 7.27 ppm. δ(^{19}F) external standard $CFCl_3$. [b] See Table 7. [c] Traces. Sum of identified products about 2%.

and ^{19}F NMR spectroscopy were CH_3SiH_2F, 82%, CH_3SiH_3, 7%, CH_3SiHF_2, 7% and undecomposed I, 4%.

X: A sample of X (0.49 mmol) sealed in an ampoule, (volume 1 cm^3) was kept at 210–220°C for 7 days. Details of the decomposition products and their NMR data are given in Table 7. The cothermolysis of 0.46 mmol of X with 2.12 mmol of cyclohexene in a 1 cm^3 ampoule for 3 days at 240°C yielded 45% of 7-fluorobicyclo[4.1.0]heptane, with an *endo/exo* ratio of 3:4 (according to the ^{19}F NMR spectrum).

IX: A sample of IX (0.47 mmol) sealed in a 1 cm^3 ampoule, was kept for 3 days at 230–240°C. Volatile products were collected in traps at −85, −122 and −196°C, and investigated by NMR spectroscopy. The results are set out in Table 8. The cothermolysis of 0.54 mmol of IX with 1.43 mmol of cyclohexene for 3 days at 230–240°C, in a 1 cm^3 sealed tube yielded, in the order of decreasing abundance, $HSiF_3$, H_2SiF_2, H_3SiF, and SiF_4. Neither 7-fluorobicyclo[4.1.0]heptane nor bicyclo[4.1.0]heptane could be detected in the products.

Acknowledgements

We thank the Fonds der Chemie and the Ministerium für Wissenschaft und Forschung NW for support. Bayer AG is thanked for generous gifts of valuable chemicals.

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