

## The synthesis and properties of $(\text{CH}_2\text{F})\text{SiH}_3$ and related monofluoromethylsilanes \*

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### Abstract

The reduction of  $(\text{CFCl}_2)\text{SiCl}_3$  by  $\text{LiAlH}_4$ ,  $\text{Me}_3\text{SnH}$ , and  $(^n\text{Bu})_3\text{SnH}$  has been studied. The compound  $(\text{CH}_2\text{F})\text{SiH}_3$  (I) and all the compounds of the series  $(\text{CFCl}_{2-m}\text{H}_m)\text{SiCl}_{3-n}\text{H}_n$ ,  $m = 0, 1$  and  $n = 0-3$  were detected and characterized by NMR spectroscopy. Conditions for the synthesis of I,  $(\text{CHFCl})\text{SiH}_3$  (IX) and  $(\text{CFCl}_2)\text{SiH}_3$  (V) with acceptable yields have been optimized. These novel compounds were studied by  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy; their infrared and Raman spectra were recorded and assigned with the assistance of a normal coordinate analysis of I and its isotopomer  $(\text{CD}_2\text{F})\text{SiD}_3$ . The thermolyses of I, IX and  $(\text{CHF}_2)\text{SiH}_3$  (X) which start at about 120, 200 and  $180^\circ\text{C}$ , respectively, have been studied. Whereas I decomposes by a migration of F from C to Si, compound X undergoes elimination of the carbene  $\text{CHF}$ , insertion of which into SiH bonds ultimately gives  $\text{CH}_3\text{Si}$  derivatives.

### Introduction

In spite of continuous efforts, only a very few fluoromethylsilicon compounds  $(\text{CF}_n\text{X}_{3-n})\text{Si}\equiv$ ,  $\text{X} = \text{H}, \text{Cl}, \text{Br}, \text{I}$ , have been described up to now. In contrast to their  $\text{CH}_3\text{Si}\equiv$  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  $\text{CF}_3\text{Si}$  moiety, which became accessible mainly through the pioneering work of Ruppert [1]. Silanes bearing  $\text{CHF}_2$  groups were selectively synthesized only recently, by  $\text{CF}_2$  insertion into SiH bonds [2].

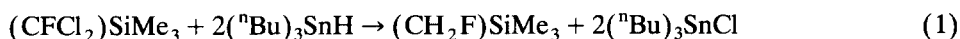
The monofluoro derivatives  $(\text{CH}_2\text{F})\text{Si}\equiv$  are still the least known of the fluoromethylsilanes, and the fluoro species were mostly excluded from systematic, particularly spectroscopic investigations of halomethylsilicon derivatives  $(\text{CH}_2\text{X})\text{Si}\equiv$ . Thus attempts to convert  $(\text{CH}_2\text{Cl})\text{SiH}_3$  into  $(\text{CH}_2\text{F})\text{SiH}_3$  (I) by use of  $\text{AgF}$  failed, only  $\text{H}_3\text{SiF}$  being obtained [3], and attempted fluorination of  $\text{Me}_3\text{SiCH}_2\text{Cl}$

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

with  $\text{SbF}_5$  [4],  $\text{Me}_3\text{SiCCl}_3$  with  $\text{KF}$  [5] or of  $\text{Me}_3\text{SiCHCl}_2$  with  $\text{KF}$  in toluene [6] was found to result in breakdown of the haloalkylsilicon moiety. Unselective formation of a large series of  $(\text{CH}_2\text{F})\text{Si}$  compounds has been observed in low temperature fluorination of  $\text{SiMe}_4$ , and characterization of some of the species containing the  $(\text{CH}_2\text{F})\text{Si}$  group was achieved mainly by NMR spectroscopy [7]. The insertion of  $\text{CHF}$  into a  $\text{SiH}$  bond in the gas phase was first observed during the thermolysis of  $\text{CF}_3\text{SiH}_3$  [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  $\text{CHF}$  than that provided by, for example, the thermolysis of difluoromethylsilane derivatives [2].

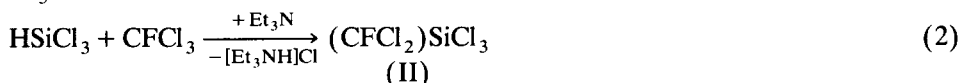
A convenient synthesis of I is a necessity if its chemical and spectroscopic properties and, in particular, its thermal and laser-induced decomposition are to be studied. To our knowledge  $\text{Me}_3\text{SiCH}_2\text{F}$  is the only fluoromethylsilane that has been fully characterized [9,10]. A variant of its recently reported synthesis



from a  $(\text{CFCl}_2)\text{Si}$  derivative might be used to synthesize I from  $\text{CFCl}_2\text{SiCl}_3$  [11] by selective and total  $\text{H}/\text{Cl}$  exchange. In this connection, we recall that reaction of  $\text{CF}_3\text{SiCl}_3$  with  $\text{LiAlH}_4$  leads to substitution at silicon, with preservation of the  $\text{CF}_3\text{Si}$  moiety [12]. We thus decided to study the reduction of  $(\text{CFCl}_2)\text{SiCl}_3$  (II) in detail, and report below on several novel fluoromethylsilicon derivatives.

### Synthesis of fluoromethylsilanes

(Fluorodichloromethyl)-trichlorosilane,  $(\text{CFCl}_2)\text{SiCl}_3$  (II) was first prepared by Josten and Ruppert [11] by the reaction of  $\text{CFCl}_3$  with  $\text{HSiCl}_3$  in the presence of  $\text{Et}_3\text{N}$



Attempts to synthesize II by nucleophilic fluorodichloromethylation of  $\text{SiCl}_4$  with the reagent  $\text{CFCl}_3/(\text{Et}_2\text{N})_3\text{P}$  failed [11]. This observation is somewhat surprising because analogous reactions have been successfully employed to synthesize fluorodichloromethyl-methylchlorosilanes,  $(\text{CFCl}_2)\text{Si}(\text{CH}_3)_n\text{Cl}_{3-n}$  from  $(\text{CH}_3)_n\text{SiCl}_{4-n}$  [11]. Furthermore  $\text{SiCl}_4$  reacts with  $\text{CF}_3\text{Br}/(\text{Et}_2\text{N})_3\text{P}$  to yield  $\text{CF}_3\text{SiCl}_3$  [12].

We have been able to reproduce the reported [11] synthesis of II; when  $\text{NMe}_3$  was used as the base, the yield of II was slightly increased from 21% [11] to 25%. Although the  $^{19}\text{F}$  NMR spectrum of our product was consistent with that previously reported its melting point was  $+24 \pm 2^\circ\text{C}$  rather than the previously reported  $-10^\circ\text{C}$  [11].

Traces of  $(\text{CFCl}_2)\text{SiHCl}_2$  (III) were detected by  $^1\text{H}$  and  $^{19}\text{F}$  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  $\text{H}/\text{Cl}$  redistribution reaction of II with  $\text{HSiCl}_3$ . 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  $\text{H}^-$  may occur at three different sites:

- (i) reduction of the  $\text{SiCl}_3$  group to yield  $(\text{CFCl}_2)\text{SiH}_{3-n}\text{Cl}_n$  species, such as III;
- (ii) reduction of the  $\text{CFCl}_2$  substituent, with preferential replacement of  $\text{Cl}$ ;

Table 1

Distribution of products <sup>a</sup> and NMR <sup>b</sup> data for the reaction of (CFCl<sub>2</sub>)SiCl<sub>3</sub> (II) with (nBu)<sub>3</sub>SnH, molar ratio 1:3.7, 15 min at room temperature

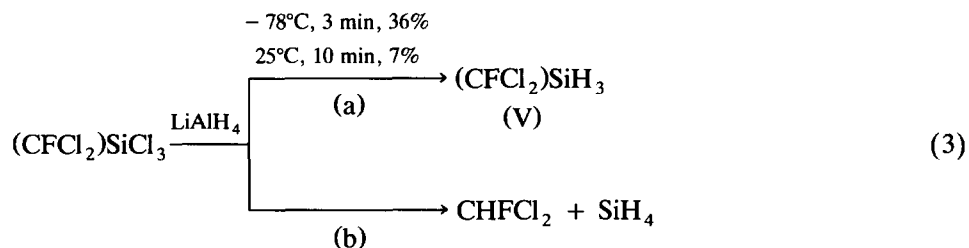
|                         | II    | III    | IV     | V      | VI      | VII      | VIII                | IX       |
|-------------------------|-------|--------|--------|--------|---------|----------|---------------------|----------|
| Product (%)             | 0.1   | 9.0    | 22.5   | 5.3    | 6.7     | 37.2     | 12.8                | 6.4      |
| δ( <sup>1</sup> H)(CH)  | —     | —      | —      | —      | 5.79d   | 5.77dd   | 5.87                | 5.92dq   |
| δ( <sup>1</sup> H)(SiH) | —     | 5.32d  | 4.68d  | 4.01d  | —       | 5.26dd   | ...                 | 3.70dd   |
| δ( <sup>19</sup> F)     | -80.5 | -81.4d | -78.1t | -69.5q | -170.1d | -173.3dd | -171.3 <sup>c</sup> | -163.5dq |
| <sup>2</sup> J(HF)      | —     | —      | —      | —      | 45.7    | 46.1     | 46.2                | 47.8     |
| <sup>3</sup> J(HF)      | —     | 3.7    | 6.2    | 6.7    | —       | 3.2      | 8.5 <sup>d</sup>    | 10.0     |
| <sup>3</sup> J(HH)      | —     | —      | —      | —      | —       | 2.2      | 2.2 <sup>e</sup>    | 2.2      |

<sup>a</sup> According to <sup>19</sup>F NMR spectrum. <sup>b</sup> In ppm, *J* in Hz. Measurements on neat sample, external standards TMS and CFCl<sub>3</sub>. Shifts and coupling constants may differ from those quoted in Table 2.

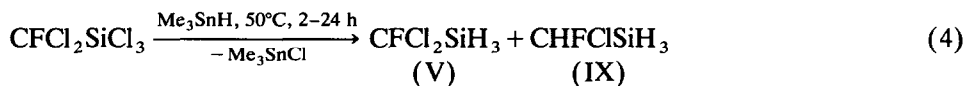
<sup>c</sup> ABMX spin system. <sup>d</sup> 1/2(<sup>3</sup>J(FH<sub>A</sub>) + <sup>3</sup>J(FH<sub>B</sub>)). <sup>e</sup> 1/2(<sup>3</sup>J(HH<sub>A</sub>) + <sup>3</sup>J(HH<sub>B</sub>)).

(iii) reductive cleavage of the C–Si bond with formation of CHFCl<sub>2</sub> and SiH<sub>4</sub>, along with concomitant complete reduction by process (i).

Whereas LiAlH<sub>4</sub> reacts with CF<sub>3</sub>SiCl<sub>3</sub> to yield CF<sub>3</sub>SiH<sub>3</sub> 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<sub>2</sub>)SiH<sub>3</sub> (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.



At and above room temperature Me<sub>3</sub>SnH is a more selective reducing agent, only V and CHFClSiH<sub>3</sub> (IX) being formed, in a ratio which depends on the reaction time (eq. 4).



Attempts to replace all the Cl atoms of II under more vigorous conditions, i.e. by treatment with Me<sub>3</sub>SnH 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)<sub>3</sub>SnH. Treatment of II with (nBu)<sub>3</sub>SnH 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<sub>2</sub>)SiH<sub>*n*</sub>Cl<sub>3-*n*</sub>

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

and  $(\text{CHFCl})\text{SiH}_n\text{Cl}_{3-n}$

$n = 0$  (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  $(^n\text{Bu})_3\text{SnH}$  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  $(\text{CD}_2\text{F})\text{SiD}_3$  was obtained analogously in a yield of 39% by use of  $(^n\text{Bu})_3\text{SnD}$ . 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  $\text{CH}_3\text{SiH}_3$  and  $(\text{CH}_2\text{Cl})\text{SiH}_3$ , respectively.

### Physical and chemical properties

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

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

I:  $A = 2655.3$ ,  $B = 17.227$  ( $176.7 \leq T \leq 246.3$  K),  $\Delta H = 22.08$  kJ mol<sup>-1</sup>,  
 $\Delta S = 85.7$  J mol<sup>-1</sup> K<sup>-1</sup>, 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<sup>-1</sup>,  
 $\Delta S = 82.9$  J mol<sup>-1</sup> K<sup>-1</sup>, 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<sup>-1</sup>,  
 $\Delta S = 103.2$  J mol<sup>-1</sup> K<sup>-1</sup>, extrapolated b.p. 21.3°C.

The starting material II is easily hydrolyzed. In contrast to IX and  $\text{SiH}_4$ , I is neither pyrophoric when exposed to air nor sensitive to moisture. In agreement with previously reported [2] observations on  $(\text{CHF}_2)\text{SiH}_2\text{Cl}$ , 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  $\text{CF}_3\text{SiH}_3$  [8] and  $\text{CH}_3\text{SiH}_3$  [13] we have investigated the thermal decomposition of I, IX and  $(\text{CHF}_2)\text{SiH}_3$  (X).

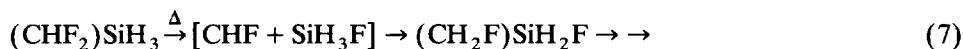
In the gas phase the decomposition of I becomes significant above 120°C; thus 96% of I decomposed within 7 days at 145°C according to



About 14% of the  $\text{CH}_3\text{SiH}_2\text{F}$  formed undergoes a ligand exchange to form  $\text{CH}_3\text{SiH}_3$  and  $\text{CH}_3\text{SiHF}_2$ . We assume that the decomposition of I has a dytopic 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  $\text{MeSiH}_{3-n}\text{F}_n$  (see Experimental section). Traces of additional compounds, assumed to be methyl-difluoromethylsilanes

$(\text{CHF}_2)\text{SiH}_n\text{Me}_{3-n}$  were detected, but no monofluoromethylsilane derivatives, even though these are likely to be the first intermediates in a carbene elimination/insertion process.



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  $\text{CF}_2$  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  $(\text{CHFCl})\text{SiH}_3$  (IX) was almost complete after 3 days at 230–240°C. Numerous decomposition products were identified, the  $^1\text{H}$  NMR spectrum of their mixture being very complex. Most constituents could be identified, and major components, listed in the order of decreasing abundance, were  $\text{MeSiHF}_2$ ,  $\text{MeSiHFCl}$ ,  $\text{MeSiCl}_3$ ,  $\text{MeSiHCl}_2$ ,  $\text{Me}_2\text{SiFCl}$ ,  $\text{Me}_2\text{SiCl}_2$ ,  $\text{MeSiH}_2\text{Cl}$  and  $\text{Me}_2\text{SiHCl}$ . (For minor constituents and quantitative data see the Experimental section.) A significant observation was that all the CHFCl groups were transformed to  $\text{CH}_3$  moieties, and the decomposition pathway is related to that of X. Of the possible elimination of the carbenes CHF,  $\text{CHCl}$ , and  $\text{CFCl}$  in the first step, obviously that of  $\text{CHCl}$  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  $(\text{CH}_2\text{F})\text{SiCl}_3$  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  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{29}\text{Si}$  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  $^{19}\text{F}$  chemical shift of I is sensitive to deuteration,  $\delta\delta(^{19}\text{F})$  being  $-0.15$  ppm per D atom bonded to Si and  $-0.58$  ppm per D atom bonded to C.

The  $^{19}\text{F}$  NMR signals of the (chlorofluoromethyl)silanes II, V and IX reveal a significant  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopic shift, which is illustrated in Fig. 2. An isotopic shift,  $\delta\delta(^{19}\text{F}) - 5.6 \times 10^{-3}$  ppm, per  $^{35}\text{Cl}$  replaced by  $^{37}\text{Cl}$ , has been reported for  $\text{CFCl}_3$  at 305 K [14].

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

Table 2

NMR data for (monofluoromethyl)silanes <sup>a</sup>

|                                     | (CFCl <sub>2</sub> )SiCl <sub>3</sub> <sup>b</sup><br>(II) | (CFCl <sub>2</sub> )SiH <sub>3</sub><br>(V) | (CHFCl)SiH <sub>3</sub><br>(IX) | (CH <sub>2</sub> F)SiH <sub>3</sub><br>(I) |
|-------------------------------------|------------------------------------------------------------|---------------------------------------------|---------------------------------|--------------------------------------------|
| <sup>1</sup> H NMR <sup>c</sup>     |                                                            |                                             |                                 |                                            |
| δ(CH)                               |                                                            |                                             | 5.72                            | 4.28                                       |
| δ(SiH)                              |                                                            | 3.95                                        | 3.64                            | 3.55                                       |
| <sup>2</sup> J(HCF)                 |                                                            |                                             | 45.6                            | 46.7                                       |
| <sup>3</sup> J(HF)                  |                                                            | 6.8                                         | 10.3                            | 14.4                                       |
| <sup>3</sup> J(HH)                  |                                                            |                                             | 2.2                             | 3.4                                        |
| <sup>19</sup> F NMR <sup>d</sup>    |                                                            |                                             |                                 |                                            |
| δ(F)                                | -80.6                                                      | -69.3                                       | -163.4                          | -263.7                                     |
| <sup>13</sup> C NMR <sup>e</sup>    |                                                            |                                             |                                 |                                            |
| δ(C)                                | 114.5                                                      | 116.6                                       | 95.3                            | 73.4                                       |
| <sup>1</sup> J(H <sup>13</sup> C)   |                                                            |                                             | 168.8                           | 142.8                                      |
| <sup>1</sup> J(F <sup>13</sup> C)   | 316.4                                                      | 317.7                                       | 249.7                           | 167.3                                      |
| <sup>2</sup> J(HSi <sup>13</sup> C) |                                                            | 7.6                                         | 6.3                             | 5.2                                        |
| <sup>29</sup> Si NMR <sup>f</sup>   |                                                            |                                             |                                 |                                            |
| δ(Si)                               | -13.7                                                      | -40.4                                       | -54.0                           | -65.5                                      |
| <sup>1</sup> J(H <sup>29</sup> Si)  |                                                            | 224.9                                       | 214.3                           | 202.9                                      |
| <sup>2</sup> J(HC <sup>29</sup> Si) |                                                            |                                             | 4.6                             | 2.4                                        |
| <sup>2</sup> J(FC <sup>29</sup> Si) | 53.9                                                       | 34.6                                        | 30.3                            | 24.6                                       |

<sup>a</sup> Chemical shifts δ in ppm, absolute values of coupling constants *J* in Hz. <sup>b</sup> Ref. 11; δ(F) -81.5 ppm, <sup>2</sup>J(FC<sup>29</sup>Si) 53.4 Hz, δ(<sup>29</sup>Si) -13.7 ppm. <sup>c</sup> Solvent and internal standard C<sub>6</sub>D<sub>6</sub>. δ(C<sub>6</sub>D<sub>5</sub>H) = 7.27 ppm.

<sup>d</sup> In C<sub>6</sub>D<sub>6</sub>. External standard CFCl<sub>3</sub>. <sup>e</sup> Solvent and internal standard C<sub>6</sub>D<sub>6</sub>. δ(C) = 128.0 ppm. <sup>f</sup> In C<sub>6</sub>D<sub>6</sub>. 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<sub>*n*</sub>F<sub>3-*n*</sub>)SiH<sub>3</sub>, *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<sub>2</sub>SiH<sub>3</sub> 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<sub>2</sub>F)SiD<sub>3</sub>, 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<sub>2</sub>F)SiD<sub>3</sub> 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<sub>2</sub>Cl)SiH<sub>3</sub> and (CH<sub>2</sub>Br)SiH<sub>3</sub> [18,19]. The assignments are particularly sensitive to resonance effects on bending and skeletal stretching vibrations (ν(CF), ν(SiC)) which affect (CD<sub>2</sub>F)SiD<sub>3</sub> more than I.

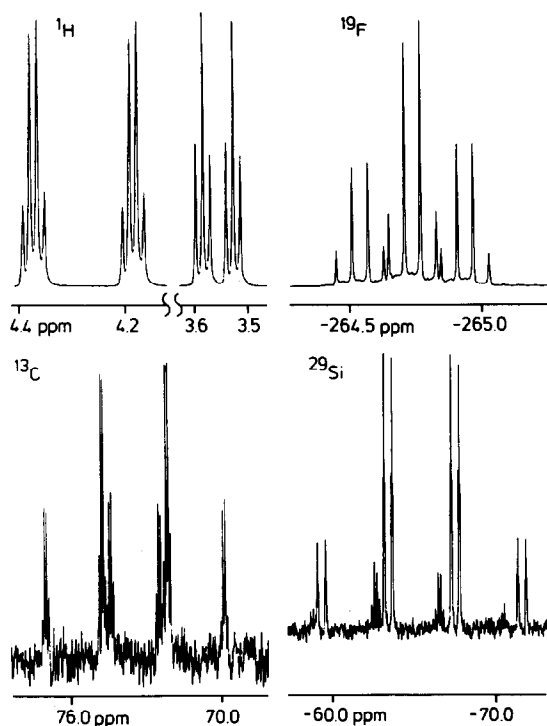


Fig. 1.  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra of I.

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,  $\text{CF}_3\text{SiH}_3$  [20],  $\text{CHFCIBr}$  [21] and  $\text{CFCl}_2\text{Br}$

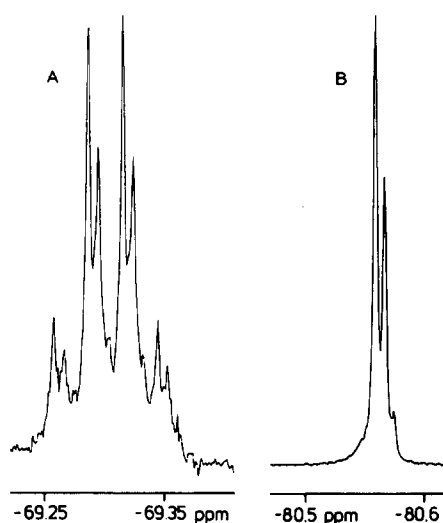


Fig. 2.  $^{19}\text{F}$  NMR signals from V (A) and II (B), revealing  $^{35}/^{37}\text{Cl}$  isotopic splitting.

Table 3

NMR data for (fluoromethyl)silanes <sup>a</sup>

|                                    | CH <sub>3</sub> SiH <sub>3</sub> <sup>b</sup> | (CH <sub>2</sub> F)SiH <sub>3</sub> <sup>c</sup> | (CHF <sub>2</sub> )SiH <sub>3</sub> <sup>d</sup> | CF <sub>3</sub> SiH <sub>3</sub> <sup>e</sup> |
|------------------------------------|-----------------------------------------------|--------------------------------------------------|--------------------------------------------------|-----------------------------------------------|
| $\delta(^1\text{H}(\text{C}))$     | 0.12                                          | 4.28                                             | 5.81                                             | —                                             |
| $\delta(^1\text{H}(\text{Si}))$    | 3.55                                          | 3.55                                             | 3.53                                             | 3.92                                          |
| $\delta(^{19}\text{F})$            | —                                             | -263.7                                           | -128.1                                           | -56.1                                         |
| $\delta(^{13}\text{C})$            | -12.3 <sup>c</sup>                            | 73.4                                             | 120.2                                            | 129.9                                         |
| $\delta(^{29}\text{Si})$           | -65.2                                         | -65.5                                            | -63.8                                            | -71.1                                         |
| $^1J(^1\text{H}^{13}\text{C})$     | 122.1                                         | 142.8                                            | 171.3                                            | —                                             |
| $^1J(^1\text{H}^{29}\text{Si})$    | 194.3                                         | 202.9                                            | 213.3                                            | 223                                           |
| $^1J(^{19}\text{F}^{13}\text{C})$  | —                                             | 167.3                                            | 252.3                                            | 314.3                                         |
| $^2J(^1\text{H}^{13}\text{C})$     | 4.5 <sup>c</sup>                              | 5.2                                              | 5.7                                              | —                                             |
| $^2J(^1\text{H}^{29}\text{Si})$    | 7.8                                           | 2.4                                              | 10.5                                             | —                                             |
| $^2J(^1\text{H}^{19}\text{F})$     | —                                             | 46.7                                             | 46.0                                             | —                                             |
| $^2J(^{19}\text{F}^{29}\text{Si})$ | —                                             | 24.6                                             | 34.1                                             | 48.8                                          |
| $^3J(^1\text{H}^{19}\text{F})$     | —                                             | 14.4                                             | 11.1                                             | 7.5                                           |
| $^3J(^1\text{H}^1\text{H})$        | 4.7                                           | 3.4                                              | 1.8                                              | —                                             |

<sup>a</sup> Chemical shifts  $\delta$  in ppm, absolute values of coupling constants  $J$  in Hz. <sup>b</sup> Refs. 15, 16. <sup>c</sup> This work; solvent and internal standard C<sub>6</sub>D<sub>6</sub>. <sup>d</sup> Ref. 2. <sup>e</sup> 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<sub>3</sub> fragments are reasonably characteristic, with the exception of the CSiH bending modes which correspond to the  $\rho(\text{SiH}_3)$  mode in XSiH<sub>3</sub> molecules. While the  $\nu(\text{CF})$  and  $\nu(\text{CCl})$  vibrations at  $\sim 1065$  and  $850 \pm 60 \text{ cm}^{-1}$ , respectively, show good agreement with those of CHFCIBr and CFCl<sub>2</sub>Br ( $1075 \pm 5$  and  $805 \pm 25$

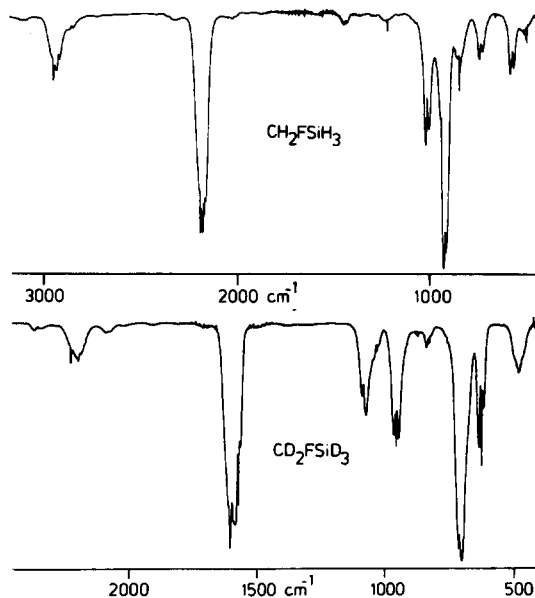


Fig. 3. Infrared spectra of I and (CD<sub>2</sub>F)SiD<sub>3</sub> (18 cm gas cell, pressure  $\sim 6$  mbar, resolution  $4 \text{ cm}^{-1}$ ).



$\text{cm}^{-1}$ ), the " $\nu(\text{SiC})$ " 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  $469 \text{ cm}^{-1}$  in II to  $530 \text{ cm}^{-1}$  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  $400 \text{ cm}^{-1}$ , 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  $\text{CH}_3\text{SiH}_3$  [24] and  $(\text{CHF}_2)\text{SiH}_3$  [2].  $C_s$  symmetry and staggered conformation,  $r(\text{SiC}) = 1.867 \text{ \AA}$ ,  $r(\text{SiH}) = 1.482 \text{ \AA}$ ,  $r(\text{CF}) = 1.333 \text{ \AA}$ ,  $r(\text{CH}) = 1.095 \text{ \AA}$ ,  $\text{H-C-Si} = \text{F-C-Si} = 109.0^\circ$

Table 4

Infrared and Raman spectral data for  $(\text{CH}_2\text{F})\text{SiH}_3$  and  $(\text{CD}_2\text{F})\text{SiD}_3$  ( $\text{cm}^{-1}$ )

| $(\text{CH}_2\text{F})\text{SiH}_3$ |                | $(\text{CD}_2\text{F})\text{SiD}_3$ |                | Assignment                                       |
|-------------------------------------|----------------|-------------------------------------|----------------|--------------------------------------------------|
| IR (gas)                            | Raman (liquid) | IR (gas)                            | Raman (liquid) |                                                  |
| 3100vw                              |                | 2930vw                              |                | $\nu(\text{CH})$                                 |
| 2950s                               | 2960w, dp      | 2218m                               | 2234w, dp      | $\nu_{\text{as}}(\text{CH}_2)/(\text{CD}_2)$     |
| 2918sh                              | 2928s, p       | 2188w, PQR, 17                      | 2180s, p       | $\nu_{\text{s}}(\text{CH}_2)/(\text{CD}_2)$      |
| 2850vw                              | 2860w, p       |                                     |                | $2 \times 1440$                                  |
| 2315vw                              |                | 2080vw                              | 2067w, p       | $1030 + 1076$                                    |
|                                     |                | 1700vw                              |                |                                                  |
| 2193vs, PQR, 20 <sup>a</sup>        |                | 1602vs, PQR                         | 1597s, dp      | $\nu_{\text{as}}(\text{SiH}_3)/(\text{SiD}_3)$   |
| 2172vs, PQR, 16                     | 2178vs, p      | 1568vs, PQR                         | 1568vs, p      | $\nu_{\text{s}}(\text{SiH}_3)$                   |
| 2028vw                              |                | 1496vw                              |                |                                                  |
|                                     |                |                                     | 1268w, p       |                                                  |
|                                     |                | 1099vw                              | 1098w, p       |                                                  |
| 1440w, PQR                          | 1441w, p       | 1076s, PQR                          | 1056s, p       | $\delta(\text{CH}_2)/(\text{CD}_2)$              |
| 1296vw, PQR                         | 1300m, p       | 1030sh                              | 1010w          | $\gamma(\text{CH}_2)/(\text{CD}_2)$              |
| 1222w                               | 1225w, dp      | 908sh                               | 912w, dp       | $\tau(\text{CH}_2)/(\text{CD}_2)$                |
|                                     |                | 979sh                               |                |                                                  |
| 1022m, PQR, 20                      | 995w           | 955s, PQR, 18                       | 939m, p        | $\nu(\text{CF})$                                 |
| 942sh                               | 942m, dp       |                                     |                | $\delta_{\text{as}}(\text{SiH}_3)(a', a'')$      |
|                                     |                | 825vw                               |                |                                                  |
|                                     |                | 754w                                | 752w, p        |                                                  |
| 921vs, PQR                          |                | 692vs                               |                | $\delta_{\text{s}}(\text{SiH}_3)/(\text{SiD}_3)$ |
| 870vw                               |                |                                     |                |                                                  |
|                                     |                | 707vs                               | 705m, p        | $\delta_{\text{as}}(\text{SiD}_3)(a')$           |
|                                     |                | 692vs                               |                | $\delta_{\text{s}}(\text{SiD}_3)$                |
|                                     |                |                                     | 682m, dp       | $\delta_{\text{as}}(\text{SiD}_3)(a'')$          |
| 850m                                | 850w, dp       |                                     | 673m, dp       | $\rho(\text{CH}_2)/(\text{CD}_2)$                |
|                                     | 840w, p        |                                     |                |                                                  |
| 737m, PQR, 20                       | 739vs, p       | 623s, PQR, 18                       | 625s, p        | $\nu(\text{SiC})$                                |
| 579m, PQR, 20                       | 583vs, p       | 477m                                | 475s, p        | $\rho(\text{SiH}_3)/(\text{SiD}_3)(a')$          |
| 515w                                | 515w, dp       | 372m                                | 375m, dp       | $\rho(\text{SiH}_3)/(\text{SiD}_3)(a'')$         |
| 238m, PQR, 20                       | 255m, p        | 222m                                | 228m, p        | $\delta(\text{FCSi})$                            |

<sup>a</sup> PR separation in  $\text{cm}^{-1}$ .

Table 5

Infrared and Raman spectral data for  $(\text{CFCl}_2)_2\text{SiCl}_3$ ,  $(\text{CFCl}_2)_2\text{SiH}_3$  and  $(\text{CHFCl})\text{SiH}_3$  ( $\text{cm}^{-1}$ )

| $(\text{CFCl}_2)_2\text{SiCl}_3$ |                  | $(\text{CFCl}_2)_2\text{SiH}_3$ |                            | $(\text{CHFCl})\text{SiH}_3$                      |                                      | Assignment                                                                                                   |
|----------------------------------|------------------|---------------------------------|----------------------------|---------------------------------------------------|--------------------------------------|--------------------------------------------------------------------------------------------------------------|
| IR (gas)                         | Raman (liquid)   | IR (gas)                        | Raman (liquid)             | IR (gas)                                          | Raman (liquid)                       |                                                                                                              |
| 1070s                            | 1062w, p         | 2221vs, PQR                     | 2223sh                     | 2957m, PQR<br>2211vs<br>2202vs                    | 2963m, p                             | $\nu(\text{CH})$<br>$\nu_{\text{as}}(\text{SiH}_3)$                                                          |
| 906s                             | 904w, p          | 2200vs, PQR                     | 2202vs, p                  | 2197vs, PQR, 14 <sup>a</sup><br>1305w             | 2191vs, p<br>1310m, p                | $\nu_s(\text{SiH}_3)$<br>$\delta(\text{HC})$                                                                 |
| 793s                             | 787w             | 1069s, PQR<br>943sh             | 1061w, p<br>934m           | 1194w, PQR, 16<br>1062s, PQR, 11<br>941s<br>935sh | 1197m, p<br>1020w<br>947s, p<br>937s | $\delta(\text{HC})$<br>$\nu(\text{CF})$<br>$\delta_{\text{as}}(\text{SiH}_3)$                                |
| 841w                             |                  | 918vs, PQR                      | 913w, p                    | 912vs, PQR, 16                                    | 911sh                                | $\delta_s(\text{SiH}_3)$                                                                                     |
| 824w                             |                  | 868vs, PQR                      | 861m, p                    |                                                   |                                      | $\nu_s(\text{CCl}_2)$                                                                                        |
| 681m                             |                  | 790s                            | 780m                       |                                                   |                                      | $\nu_{\text{as}}(\text{CCl}_2)$                                                                              |
| 630vs                            | 681vw<br>627w    | 732vw                           | 730vw                      | 793m, PQR, 5                                      | 790m                                 | $\nu(\text{CCl})$                                                                                            |
| 538vs                            | 539vw            | 639s, PQR, 16<br>606s, PQR      | 644m, p<br>608m            | 730m<br>627s, PQR, 12                             | 731s, p<br>623m                      | $\nu_{\text{as}}(\text{SiCl}_3)$<br>$\delta(\text{CSiH})$<br>$\delta(\text{CSiH})$<br>$\nu_s(\text{SiCl}_3)$ |
| 469vs                            | 486vs, p<br>375w | 550sh<br>530w<br>486m           | 561vw<br>534vw<br>486vs, p |                                                   | 577sh                                |                                                                                                              |
| 335s                             | 334s, p          | 377w                            | 370m                       | 530s, PQR<br>377m                                 | 532vs, p<br>380s, p                  | $\nu(\text{SiC})$                                                                                            |
| 317m, sh                         | 317m, p          | 341s                            | 340s, p                    |                                                   |                                      |                                                                                                              |
| 227m                             | 227m             | 278w                            | 278m, p                    | 278m                                              | 283m, p                              | Heavy atom bending modes                                                                                     |
|                                  | 180m             |                                 | 191m                       |                                                   | 193m, p                              |                                                                                                              |
|                                  | 163m             |                                 | 171w                       |                                                   |                                      |                                                                                                              |
|                                  | 111m             |                                 |                            |                                                   |                                      |                                                                                                              |

<sup>a</sup> PQR separation in  $\text{cm}^{-1}$ .

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<sup>1</sup>), Table 6, refers to H(1)SiH(2) and H(2)SiH(3), (HSiH<sup>1</sup>) to H(1)SiH(3). Correspondingly (HSiC<sup>8</sup>) denotes (H(2)SiC) etc., while interactions of adjacent angles are denoted ( $\alpha/\beta'$ ) and the opposite ones ( $\alpha/\beta''$ ). 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,  $f(\text{SiC})$  and  $f(\text{CF})$  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  $\nu(\text{CF})$  in I, all the skeletal (FCSi) vibrations are strongly coupled with  $\text{CH}_2(\text{CD}_2)$  and  $\text{SiH}_3(\text{SiD}_3)$  modes, and

Table 6

Potential energy distribution and diagonal force constants for  $(\text{CH}_2\text{F})\text{SiH}_3$  and  $(\text{CD}_2\text{F})\text{SiD}_3$

| $(\text{CH}_2\text{F})\text{SiH}_3$                      |       | $(\text{CD}_2\text{F})\text{SiD}_3$ |                           | Potential energy distribution <sup>a</sup>                                                          |
|----------------------------------------------------------|-------|-------------------------------------|---------------------------|-----------------------------------------------------------------------------------------------------|
| Obs.                                                     | Calc. | Obs.                                | Calc.                     |                                                                                                     |
| <i>a'</i>                                                |       |                                     |                           |                                                                                                     |
| 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) <sup>b</sup>                                                       |
|                                                          |       | 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 <sup>8</sup> ), 31(HSiH <sup>1</sup> ) <sup>b</sup>                                         |
| 921                                                      | 913   |                                     |                           | 56(HSiH <sup>8</sup> ), 18(HSiC <sup>8</sup> ), 11(HSiC <sup>1</sup> ), 11(HSiH/HSiC <sup>1</sup> ) |
| 737                                                      | 727   |                                     |                           | 68(SiC)                                                                                             |
|                                                          |       | 707                                 | 701                       | 49(HSiH <sup>8</sup> ), 30(SiC)                                                                     |
|                                                          |       | 692                                 | 690                       | 68(HSiH <sup>1</sup> ), 16(HSiC <sup>1</sup> )                                                      |
|                                                          |       | 623                                 | 623                       | 36(SiC), 35(HSiH <sup>8</sup> )                                                                     |
| 579                                                      | 585   |                                     |                           | 43(HSiC <sup>1</sup> ), 25(HSiC <sup>8</sup> ), 21(SiC)                                             |
|                                                          |       | 477                                 | 465                       | 48(HSiC <sup>1</sup> ), 24(HSiC <sup>8</sup> )                                                      |
| 255                                                      | 255   | 222                                 | 228                       | 79(FCSi), 13(HCSi), 10(HSiC <sup>1</sup> ), –15(FCSi/HSiC <sup>1</sup> )                            |
| <i>a''</i>                                               |       |                                     |                           |                                                                                                     |
| 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 <sup>1</sup> )                                                                             |
| 850                                                      | 854   |                                     |                           | 90(HCSi)                                                                                            |
|                                                          |       | 682                                 | 686                       | 81(HSiH <sup>1</sup> ), 24(HCSi)                                                                    |
|                                                          |       | 673                                 | 656                       | 70(HCSi), 28(HSiH <sup>1</sup> )                                                                    |
| 515                                                      | 514   | 372                                 | 375                       | 86(HSiC <sup>8</sup> ), 11(HCSi), 10(HSiC/HSiC)                                                     |
| Force constants (N cm <sup>–1</sup> , scaled to 100 ppm) |       |                                     |                           |                                                                                                     |
| $f(\text{SiC}) = 2.98^c$                                 |       | $f(\text{SiH}) = 2.75$              | $f(\text{HSiH}^8) = 0.49$ | $f(\text{FCSi}) = 0.55$                                                                             |
| $f(\text{CH}) = 4.97$                                    |       | $f(\text{HCH}) = 0.52$              | $f(\text{HSiH}^1) = 0.51$ | $f(\text{HSiC}^8) = 0.33$                                                                           |
| $f(\text{CF}) = 5.05^c$                                  |       | $f(\text{FCH}) = 0.98$              | $f(\text{HCSi}) = 0.52$   | $f(\text{HSiC}^1) = 0.48$                                                                           |

<sup>a</sup> In terms of inner force constants; only contributions > 10% are listed. H stands for H and D in  $(\text{CH}_2\text{F})\text{SiH}_3$  and  $(\text{CD}_2\text{F})\text{SiD}_3$ , respectively. <sup>b</sup> See text for explanation. <sup>c</sup> Constrained.

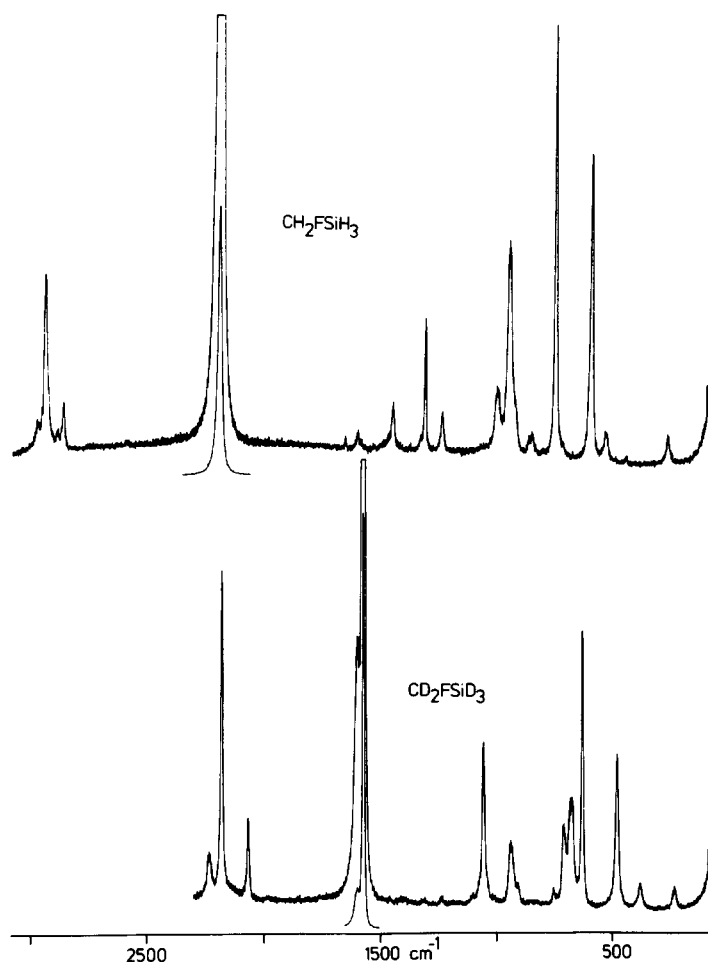


Fig. 4. Liquid phase Raman spectra of I and  $(\text{CD}_2\text{F})\text{SiD}_3$ , at  $-60^\circ\text{C}$  (excitation Kr 647.1 nm).

reference to group vibrations is not justified here. We note that in the series  $(\text{CH}_3-n\text{F}_n)\text{SiH}_3$ ,  $f(\text{CF})$  increases with  $n$ , while  $f(\text{SiC})$  decreases:  $f(\text{CF})/f(\text{SiC})$ ,  $n = 0$ ,  $-/3.22$  [24];  $n = 1$ ,  $5.05/2.98$ ;  $n = 2$ ,  $5.37/2.69$  [2];  $n = 3$ ,  $5.602/2.537$   $\text{N cm}^{-1}$  [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 ( $^1\text{H}$ , 250.1 MHz;  $^{13}\text{C}$ , 62.9 MHz;  $^{19}\text{F}$ , 235.4 MHz;  $^{29}\text{Si}$ , 49.7 MHz) or, in routine work, with a Varian EM 390 spectrometer ( $^1\text{H}$ , 90.0 MHz;  $^{19}\text{F}$ , 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  $1\text{--}2\text{ cm}^{-1}$ .

(Fluorodichloromethyl)trichlorosilane (II) was obtained as described previously [11] but with use of  $\text{NMe}_3$  instead of  $\text{NEt}_3$ ; yield 25%, m.p.  $+24 \pm 2^\circ\text{C}$  ([11]  $-10^\circ\text{C}$ ). Tri-*n*-butylstannane- $d_1$  was made as described previously [25] from  $(^n\text{Bu})_3\text{SnCl}$  and  $\text{LiAlD}_4$  in  $^t\text{BuOMe}$  (yield, approx. 80%).

### Reduction of II

*With  $(^n\text{Bu})_3\text{SnH}$ .* In a typical experiment a mixture of 0.76 mmol of  $(^n\text{Bu})_3\text{SnH}$  and 0.09 mmol of II was sealed in a 4 mm glass tube (volume  $\sim 1\text{ cm}^3$ ) and kept at 20 or  $80^\circ\text{C}$  for various times. The compositions of the product mixtures obtained at  $20^\circ\text{C}$  and 15 min are shown in Table 1. When the reaction mixture was kept at  $20^\circ\text{C}$  for 30 min, IX was mainly obtained. Heating at  $80^\circ\text{C}$  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  $\text{CH}_3\text{SiH}_3$ ,  $(\text{CH}_2\text{Cl})\text{SiH}_3$ , butane and 1-butene.

*With  $\text{Me}_3\text{SnH}$ .* Analogously, 2.63 mmol of  $\text{Me}_3\text{SnH}$  were treated with 0.42 mmol of II. After 2 h at  $50^\circ\text{C}$ , V and IX were present and IX was the main product after 1 day. Heating at  $80^\circ\text{C}$  for 3 days resulted in formation of black material which did not contain any I.

*With  $\text{LiAlH}_4$  at room temperature.* Compound II (12.4 mmol) was condensed onto a suspension of 1.73 g (45.6 mmol) of  $\text{LiAlH}_4$  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  $-196^\circ\text{C}$ . Formation of a non-condensable gas ( $\text{H}_2$ ) was noted. Compound V (0.89 mmol, 7%) was obtained by fractional condensation of the volatile products. The by-products  $\text{SiH}_4$  and  $\text{CH}_2\text{Cl}_2$  were identified by IR and NMR spectroscopy.

*With  $\text{LiAlH}_4$  at  $-78^\circ\text{C}$ .* A mixture of 4.57 mmol of II and 8.43 mmol of  $\text{LiAlH}_4$  in 7.5 ml of di-*n*-butylether was treated analogously for 3 min at  $-78^\circ\text{C}$ . Volatile products were evaporated off, trapped at  $-196^\circ\text{C}$ , and worked up by trap-to-trap condensation *in vacuo*. V (containing  $\leq 2\%$  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  $(^n\text{Bu})_3\text{SnH}$  and 9.65 mmol of II was heated in a 50 ml ampoule at  $80^\circ\text{C}$  for 3 days, after which the  $^1\text{H}$  NMR spectrum indicated that the mixture contained 46% of I, 48% of IX, 3% of  $(\text{CH}_2\text{Cl})\text{SiH}_3$ , 3% of  $\text{CH}_3\text{SiH}_3$ , and traces of 1-butene. The ampoule was then connected to a vacuum line, and volatile products were taken off through a  $-126^\circ\text{C}$  trap, in which IX and some  $(\text{CH}_2\text{Cl})\text{SiH}_3$  condensed, and I along with some  $\text{CH}_3\text{SiH}_3$  were condensed in a  $-196^\circ\text{C}$  trap. I and IX were purified by isothermal distillation at  $-60^\circ\text{C}$ , 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  $120^\circ\text{C}$ . I (0.50 mmol), sealed in a glass ampoule (volume  $1.0\text{ cm}^3$ ) was kept at  $140\text{--}150^\circ\text{C}$  for 7 days. The extrapolated pressure was about 30 bar. Gaseous decomposition products identified by  $^1\text{H}$

Table 7

Products of the thermal decomposition of X and their NMR spectral data <sup>a</sup>

| Product <sup>b</sup>                        | %  | $\delta(\text{H}(\text{CF}))$ | $\delta(\text{H}(\text{Si}))$ | $\delta(\text{H}(\text{CH}_3))$ | $\delta(\text{FC})$ | $\delta(\text{F}(\text{Si}))$ | $^1\text{J}(\text{F}^{29}\text{Si})$ | $^2\text{J}(\text{HF})$ | $^3\text{J}(\text{HF})$ | $^3\text{J}(\text{HH})$ | Ref. |
|---------------------------------------------|----|-------------------------------|-------------------------------|---------------------------------|---------------------|-------------------------------|--------------------------------------|-------------------------|-------------------------|-------------------------|------|
| $\text{SiF}_4$                              | 1  |                               |                               |                                 |                     | -163.2s <sup>c</sup>          | 174.3                                |                         |                         |                         | 26   |
| $\text{SiHF}_3$                             | 8  |                               | 3.97q                         |                                 |                     | -134.7d                       |                                      | 95.8                    |                         |                         | 26   |
| $\text{SiH}_2\text{F}_2$                    | 5  |                               | 4.31t                         |                                 |                     | -146.2t                       |                                      | 60.8                    |                         |                         | 26   |
| $\text{SiH}_3\text{F}$                      | 2  |                               | 4.54d                         |                                 |                     | -213.9q                       |                                      | 46.5                    |                         |                         | 26   |
| $\text{CH}_3\text{SiF}_3$                   | 6  |                               |                               | -0.06q                          |                     | -134.3q                       |                                      |                         | 4.3                     |                         | 26   |
| $\text{CH}_3\text{SiHF}_2$                  | 43 |                               | 4.66tq                        | 0.00td                          |                     | -137.1dq                      | 295.3                                | 68.1                    | 6.8                     | 1.2                     | 26   |
| $\text{CH}_3\text{SiH}_2\text{F}$           | 8  |                               | 4.78dq                        | 0.14dt                          |                     | -130.2tq                      |                                      | 48.3                    | 8.3                     | 3.4                     | 26   |
| $\text{CH}_3\text{SiH}_3$                   | 1  |                               | 3.67q                         | n.o.                            |                     |                               |                                      |                         |                         | 4.6                     | 15   |
| $(\text{CH}_3)_2\text{SiF}_2$               | 7  |                               |                               | 0.08t                           |                     | -131.5sept                    | 289.5                                |                         | 6.2                     |                         | 26   |
| $(\text{CH}_3)_2\text{SiHF}$                | 8  |                               | 4.95dsept                     | 0.18dt                          |                     | -171.2dsept                   | 277.0                                | 53.1                    | 7.8                     | 2.7                     | 26   |
| $(\text{CH}_3)_3\text{SiF}$                 | 3  |                               |                               | 0.17d                           |                     | -157.5dec                     | 275.1                                |                         | 7.3                     |                         | 26   |
| $(\text{CHF}_2)_2\text{SiH}_3$              | 1  | 5.71tq                        | 3.46td                        |                                 | -129.4dq            |                               |                                      | 46.0                    | 11.0                    | 1.8                     | 2    |
| $(\text{CHF}_2)_2\text{SiH}_2\text{CH}_3$   | 3  | 5.77tt                        | 3.77m                         | n.o.                            | -134.0dt            |                               |                                      | 46.1                    | 10.3                    | 1.3                     |      |
| $(\text{CHF}_2)_2\text{SiH}(\text{CH}_3)_2$ | 1  | 5.76td                        | 3.98                          | n.o.                            | n.o.                |                               |                                      | 46.2                    | 8.5                     | 1.0                     |      |
| $(\text{CHF}_2)_2\text{Si}(\text{CH}_3)_3$  | 1  | 5.70t                         |                               | n.o.                            | -139.6d             |                               |                                      | 46.3                    |                         |                         |      |
| $\text{CH}_2\text{F}_2$                     | 1  | n.o.                          |                               |                                 | -142.4t             |                               |                                      | 50.3                    |                         |                         | 27   |

<sup>a</sup> Chemical shift  $\delta$  in ppm, absolute value of coupling constant  $J$  in Hz.  $\delta(^1\text{H})$  internal standard  $\text{C}_6\text{D}_6\text{H} = 7.27$  ppm,  $\delta(^{19}\text{F})$  external standard  $\text{CFCl}_3$ . <sup>b</sup> About 7% of products not identified. <sup>c</sup> 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 <sup>a</sup>

| Product                                             | %            | $\delta(\text{H}(\text{C}))$ | $\delta(\text{H}(\text{Si}))$ | $\delta(\text{F})$   | $^2J(\text{HF})$ | $^2J(\text{HSi})$ | $^3J(\text{HF})$ | $^3J(\text{HH})$ | Ref.   |
|-----------------------------------------------------|--------------|------------------------------|-------------------------------|----------------------|------------------|-------------------|------------------|------------------|--------|
| $\text{SiH}_3\text{F}$                              | 3            |                              | n.o.                          | -214.8q <sup>b</sup> | 45.9             |                   |                  |                  | 26     |
| $\text{SiH}_2\text{F}_2$                            | 1            |                              | 4.79t                         | -147.2t              | 60.9             |                   |                  |                  | 26     |
| $\text{SiH}_2\text{FCl}$                            | 2            |                              | 5.24d                         | -155.7t              | 56.5             |                   |                  |                  |        |
| $\text{SiHF}_3$                                     | <sup>c</sup> |                              | n.o.                          | -134.8d              | 95.7             |                   |                  |                  | 26     |
| $\text{SiHF}_2\text{Cl}$                            | <sup>c</sup> |                              | n.o.                          | -122.5d              | 84.6             |                   |                  |                  |        |
| $\text{CH}_3\text{SiCl}_3$                          | 10           | 1.15s                        |                               |                      |                  | 9.1               |                  |                  | 28     |
| $(\text{CH}_3)_2\text{SiCl}_2$                      | 6            | 0.82s                        |                               |                      |                  | 7.5               |                  |                  | 28     |
| $(\text{CH}_3)_3\text{SiCl}$                        | 1            | 0.45s                        |                               |                      |                  | 7.0               |                  |                  | 29     |
| $\text{CH}_3\text{SiF}_3$                           | 1            | 0.53q                        |                               | -134.9q              |                  | n.o.              | 4.1              |                  | 26     |
| $(\text{CH}_3)_2\text{SiF}_2$                       | 2            | 0.35t                        |                               | -132.3sept           |                  | n.o.              | 6.2              |                  | 26     |
| $(\text{CH}_3)_3\text{SiF}$                         | 2            | 0.24d                        |                               | -157.9dec            |                  | n.o.              | 7.5              |                  | 26     |
| $\text{CH}_3\text{SiFCl}_2$                         | 3            | 0.93d                        |                               | -108.6q              |                  | n.o.              | 5.0              |                  | 30     |
| $\text{CH}_3\text{SiF}_2\text{Cl}$                  | <sup>c</sup> | n.o.                         |                               | -117.8q              |                  | n.o.              | 4.5              |                  | 30     |
| $(\text{CH}_3)_2\text{SiFCl}$                       | 8            | 0.59d                        |                               | -132.0sept           |                  | n.o.              | 6.4              |                  | 30     |
| $\text{CH}_3\text{SiH}_3$                           | <sup>c</sup> | n.o.                         | 3.53q                         |                      |                  | n.o.              |                  | 4.6              |        |
| $\text{CH}_3\text{SiH}_2\text{F}$                   | 3            | 0.19dt                       | 4.82dq                        | -131.1tq             | 49.2             | n.o.              | 7.8              | 3.2              | 15, 26 |
| $\text{CH}_3\text{SiH}_2\text{Cl}$                  | 4            | 0.61t                        | 4.76q                         |                      |                  | n.o.              |                  | 3.6              | 15     |
| $\text{CH}_3\text{SiHF}_2$                          | 27           | 0.44td                       | 4.84tq                        | -137.8dq             | 68.0             | n.o.              | 6.9              | 1.1              | 26     |
| $\text{CH}_3\text{SiHFCI}$                          | 12           | 0.69dd                       | 5.34dq                        | -141.0dq             | 62.2             | n.o.              | 6.5              | 1.7              |        |
| $\text{CH}_3\text{SiHCl}_2$                         | 8            | 0.89d                        | 5.59q                         |                      |                  | n.o.              |                  | 2.3              | 31     |
| $(\text{CH}_3)_2\text{SiHF}$                        | 1            | n.o.                         | n.o.                          | -171.3dsept          | 53.4             | n.o.              | 8.5              | n.o.             | 26     |
| $(\text{CH}_3)_2\text{SiHCl}$                       | 4            | 0.52d                        | 4.30sept                      |                      |                  | n.o.              |                  | 3.2              | 32, 33 |
| $(\text{CH}_2\text{F})\text{SiCl}_3$ ? <sup>c</sup> |              | n.o.                         | n.o.                          | -262.2t              | 46.8             | n.o.              |                  |                  |        |

<sup>a</sup> Chemical shift  $\delta$  in ppm, absolute value of coupling constant  $J$  in Hz. Solvent  $\text{CDCl}_3$ ,  $\delta(^1\text{H})$  internal standard  $\text{CHCl}_3 = 7.27$  ppm.  $\delta(^{19}\text{F})$  external standard  $\text{CFCl}_3$ . <sup>b</sup> See Table 7. <sup>c</sup> Traces. Sum of identified products about 2%.

and  $^{19}\text{F}$  NMR spectroscopy were  $\text{CH}_3\text{SiH}_2\text{F}$ , 82%,  $\text{CH}_3\text{SiH}_3$ , 7%,  $\text{CH}_3\text{SiHF}_2$ , 7% and undecomposed I, 4%.

X: A sample of X (0.49 mmol) sealed in an ampoule, (volume 1  $\text{cm}^3$ ) 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  $\text{cm}^3$  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  $^{19}\text{F}$  NMR spectrum).

IX: A sample of IX (0.47 mmol) sealed in a 1  $\text{cm}^3$  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  $\text{cm}^3$  sealed tube yielded, in the order of decreasing abundance,  $\text{HSiF}_3$ ,  $\text{H}_2\text{SiF}_2$ ,  $\text{H}_3\text{SiF}$ , and  $\text{SiF}_4$ . Neither 7-fluorobicyclo[4.1.0]heptane nor bicyclo[4.1.0]heptane could be detected in the products.

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## References

- 1 I. Ruppert, K. Schlich and W. Volbach, *Tetrahedron Lett.*, 25 (1984) 2195.
- 2 H. Bürger, R. Eujen and P. Moritz, *J. Organomet. Chem.*, 401 (1991) 249.
- 3 J.M. Bellama and A.G. MacDiarmid, *J. Organomet. Chem.*, 18 (1969) 275.
- 4 T.J. Hairston and D.H. O'Brien, *J. Organomet. Chem.*, 23 (1970) C41.
- 5 R.F. Cunico and B.B. Chou, *J. Organomet. Chem.*, 154 (1978) C45.
- 6 R. Damrauer, V.E. Yost, S.E. Danahey and B.K. O'Connell, *Organometallics*, 4 (1985) 1779.
- 7 R.J. Lagow and J.A. Morrison, *Adv. Inorg. Chem. Radiochem.*, 23 (1980) 177.
- 8 H. Beckers and H. Bürger, *J. Organomet. Chem.*, 385 (1990) 207.
- 9 J. Vcelak, V. Chvalovsky, M.G. Voronkov, V.B. Pukhnarevich and V.A. Pestunovich, *Collect. Czech. Chem. Commun.*, 41 (1976) 386.
- 10 V. Broicher and D. Geffken, *J. Organomet. Chem.*, 381 (1990) 315.
- 11 R. Josten and I. Ruppert, *J. Organomet. Chem.*, 329 (1987) 313.
- 12 H. Beckers, H. Bürger, P. Bursch and I. Ruppert, *J. Organomet. Chem.*, 316 (1986) 41.
- 13 P.S. Neudorfl and O.P. Strausz, *J. Phys. Chem.*, 82 (1977) 241.
- 14 W.S. Brey, K.H. Ladner, R.E. Block and W.A. Tallon, *J. Magn. Res.*, 8 (1972) 406.
- 15 E.A.V. Ebsworth and S.G. Frankiss, *Trans. Faraday Soc.*, 59 (1963) 1518.
- 16 R. Löwer, M. Vongehr and H.C. Marsmann, *Chem.-Ztg.*, 99 (1975) 33.
- 17 H. Beckers, H. Bürger and R. Eujen, *J. Fluorine Chem.*, 27 (1985) 461.
- 18 J.R. Durig and C.W. Hawley, *J. Chem. Phys.*, 59 (1973) 1.
- 19 K. Ohno and H. Murata, *Bull. Chem. Soc. Jpn.*, 45 (1972) 3333.
- 20 H. Beckers, H. Bürger, R. Eujen, B. Rempfer and H. Oberhammer, *J. Mol. Struct.*, 140 (1986) 281.
- 21 M. Diem and D.F. Burow, *J. Chem. Phys.*, 64 (1976) 5179.
- 22 R.C. Gilbert, G.A. Piatowski, J.M. Dowling and F.F. Cleveland, *J. Chem. Phys.*, 31 (1956) 1633.
- 23 D. Christen, *J. Mol. Struct.*, 48 (1978) 101.
- 24 E.A. Clark and A. Weber, *J. Chem. Phys.*, 45 (1966) 1759.
- 25 H.G. Kuivila and O.F. Beumel Jr., *J. Am. Chem. Soc.*, 89 (1967) 5861.
- 26 S.G. Frankiss, *J. Phys. Chem.*, 71 (1967) 3418.
- 27 P. Sartori and W. Habel, *J. Fluorine Chem.*, 16 (1980) 265.
- 28 E.V. Van den Berghe and G.P. Van der Kelen, *J. Organomet. Chem.*, 59 (1973) 175.
- 29 H. Schmidbaur, *J. Am. Chem. Soc.*, 85 (1963) 2337.
- 30 J.G. Riess and S.C. Pace, *Inorg. Chim. Acta*, 9 (1970) 61.
- 31 J.W. Ryan and J.L. Speier, *J. Am. Chem. Soc.*, 86 (1964) 895.
- 32 S.S. Danyluk, *J. Am. Chem. Soc.*, 87 (1965) 2300.
- 33 D.E. Webster, *J. Chem. Soc.*, (1960) 5132.