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Difluorocarbene insertion into Si–H bonds: the preparation and properties of difluoromethylsilanes *

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Abstract

Difluorocarbene, CF_2, generated by thermal decomposition of CF_3SiF_3 at 100 °C, has been found to insert into the Si–H bonds of halosilanes SiH_3X (X = F, Cl, Br, I), methylhalosilanes CH_3SiH_2X (X = Br, Cl) and $(CH_3)_2SiHCl$, and disiloxane $(SiH_3)_2O$. Use of excess of the CF_2-source CF_3SiF_3 and of pressure favour the formation of the di-insertion products $(CHF_2)_2SiHX$ and $(CHF_2)_2(CH_3)SiX$. $(CHF_2)_3SiCl$ was identified among the products formed in the co-thermolysis of CF_3SiF_3 and $(CHF_2)SiH_2Cl$. In contrast, organosilanes R_nSiH_{4-n} (R = Me, Ph; n = 0–4), dihalosilanes SiH_2X_2 and $RSiHX_2$, trihalosilanes $HSiX_3$ and tetrahalosilanes SiX_4 do not react with CF_2 under these conditions. The reactivity and selectivity of difluorocarbene is discussed in terms of steric and electronic parameters. A kinetic deuterium effect, $k(SiH)/k(SiD)$ 1.14, has been observed for the insertion into $MeSiH_2Cl$. The mostly novel products were characterized by vibrational and multinuclear NMR spectroscopy. Difluoromethylsilane, $(CHF_2)SiH_3$, has been obtained from $(CHF_2)SiH_2Cl$ and $LiAlH_4$ in almost quantitative yield, and its vibrational spectrum has been recorded and interpreted with the assistance of a normal coordinate analysis.

Introduction

The rapid elimination of difluorocarbene from trifluoromethylsilanes restricted preparation of such silanes for a long time [1]. Now that trifluoromethylsilanes are available in preparative-scale quantities [2–4], such elimination of difluorocarbene could have a synthetic potential. For example, CF_3SiF_3 [5] appears to be a particularly clean source of CF_2; thus SiF_4 is the only detectable by-product of the decomposition, which starts at 80 °C and has a half-life of 7 min at 100 °C. Alternative CF_2 generators such as tetrafluoroethylene oxide [6] or difluoroaziridine [7] require considerably higher temperatures or photolytic conditions [8]. Other convenient CF_2 sources such as $CF_3Sn(CH_3)_3$ [9], $CF_2ClCOONa$ [10] or CF_3Hg derivatives [11], in addition to requiring high temperatures, have the disadvantage of either forming solid by-products or needing polar solvents.

It was found [12] that CF_3SiH_3 decomposes selectively to form SiH_3F and CF_2 at about 200 °C. In the absence of an efficient carbene trap the latter formally

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* Dedicated to Professor M. Baudler on the occasion of her 70th birthday.

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undergoes an H/F exchange with the silane, and the CHF and CH_2 thus formed insert into Si–H bonds to form CH_2FSi and CH_3Si derivatives. Though no CHF_2Si species were detected under the conditions of the thermolysis all identified products could be explained in terms of a sequence of carbene insertion and elimination reactions. The primary step, the insertion of CF_2 into the Si–H bond of SiH_3F to yield CHF_2SiH_2F, was verified independently [12].

These observations prompted us to investigate in some detail the reaction of CF_2 with silanes which possess Si–H bonds and to explore the potential of CF_2 insertions for the selective synthesis of difluoromethylsilanes.

CF_2 insertion reactions

Trifluoro(trifluoromethyl)silane, CF_3SiF_3, is a particularly useful source for difluorocarbene. Firstly, its moderate thermal stability allows gas phase manipulations at ambient temperature, and secondly the gaseous byproduct of the decomposition, SiF_4, can be easily separated from any CF_2 insertion product. The handicap of CF_3SiF_3, its poor availability [3], has now been overcome by an improved synthesis of its precursor CF_3SiCl_3, which was obtained from $SiCl_4$ and $P(NEt_2)_3/CF_3Br$ [2] with a yield of 50% when benzonitrile was employed as a solvent (Eq. 1):

$$SiCl_4 \xrightarrow[\text{benzonitrile, 50\%}]{P(NEt_2)_3/CF_3Br} CF_3SiCl_3 \xrightarrow[(n\text{-Bu})_2O,\ 62\%]{SbF_3} CF_3SiF_3 \qquad (1)$$

Thermolysis of CF_3SiF_3 at 100 °C produces SiF_4, C_2F_4 and *cyclo*-C_3F_6, and the same products are obtained in the presence of SiH_4, $MeSiH_3$, Me_3SiH or $PhSiH_3$ – no products formed by insertion of CF_2 into either the Si–H or the Si–C bond being detected by NMR spectroscopy. In contrast, CF_2 inserts smoothly into the Si–H bond of methyl-monohalosilanes, $Me_nSiH_{3-n}X$ ($n = 0$–2), Table 1 (Eq. 2):

$$(CH_3)_nSiH_{3-n}X + CF_3SiF_3 \xrightarrow[7\text{–}60\ \text{bar}]{100\,°C,\ 2\ h} (CHF_2)(CH_3)_nSiH_{2-n}X + SiF_4 \qquad (2)$$
$$(n = 0;\ X = F, Cl, Br, I)$$
$$(n = 1;\ X = Cl, Br)$$
$$(n = 2;\ X = Cl)$$

For a 1 : 1 ratio of the reactants, the yields of the CHF_2Si products as determined by ^1H NMR spectroscopy were 60–75% for SiH_3X, 40% for $MeSiH_2X$, and 30% for Me_2SiHCl. For $PhSiH_2Cl$, insertion to yield $(CHF_2)PhSiHCl$ was proven by the observation of characteristic pattern of the latter in the ^{19}F NMR spectrum, but no more than 5% was formed.

The insertion strongly depends on the pressure under which the reaction is carried out [13]. While no silanes containing CHF_2 groups were observed in the reaction with SiH_3Cl at a pressure of 0.2 bar, 5% conversion was achieved at 1.2 bar, and this was further raised to 63% at 7.4 bar. Further pressure increases did not change the conversion rate, but instead enhanced the amounts of bis(difluoromethyl)silane, $(CHF_2)_2SiHCl$, being formed. Both the fraction of the latter and the total turnover were increased by employing an excess of the CF_2 source, Table 1 (Eq. 3).

$$Si(CH_3)_nH_{3-n}X \xrightarrow{\text{excess } CF_3SiF_3} (CHF_2)_2Si(CH_3)_nH_{1-n}X \qquad (3)$$
$$(n = 0;\ X = F, Cl, Br)$$
$$(n = 1;\ X = Cl)$$

Table 1

Conditions [a] and product distribution for the co-thermolysis of CF_3SiF_3 and monohalosilanes

Silane	CF_3SiF_3 : Silane molar ratio	Pressure [b]	Conversion [c]	Products (yield) [d]
SiH_3F	1.0	7	76	$(CHF_2)SiH_2F$ (35%)
	1.5	18	100	$(CHF_2)SiH_2F/(CHF_2)_2SiHF$ (95/5) [e]
SiH_3Cl	1.2	0.2	0	
	1.2	1.2	5	
	1.2	7	68	$(CHF_2)SiH_2Cl$ (60%)
	1.2	80	67	
	1.4	35	100	$(CHF_2)SiH_2Cl/(CHF_2)_2SiHCl$ (95/5) [e]
	3.5	14	100	$(CHF_2)SiH_2Cl/(CHF_2)_2SiHCl$ (75/25) [e]
SiH_3Br	1.9	18	66	$(CHF_2)SiH_2Br/(CHF_2)_2SiHBr$ (80/20) [e]
SiH_3I	1.0	21	60	$(CHF_2)SiH_2I$
CH_3SiH_2Cl	1.0	21	40	$(CHF_2)(CH_3)SiHCl$ (21%)
	1.6	65	52	$(CHF_2)(CH_3)SiHCl/$ $(CHF_2)_2(CH_3)SiCl$ (80/20) [e]
CH_3SiH_2Br	1.0	20	40	$(CHF_2)(CH_3)SiHBr$ (20%)
$(CH_3)_2SiHCl$	1.0	58	30	$(CHF_2)(CH_3)_2SiCl$ (19%)
$(CHF_2)SiH_2Cl$	3.0	31	60	$(CHF_2)_2SiHCl/$ $(CHF_2)_3SiCl$ (80/20) [e]
$(SiH_3)_2O$	2.8	32	100	$[(CHF_2)SiH_2]_2O$ (23%)
$C_6H_5SiH_2Cl$	1.0	11	< 5	

[a] Co-thermolysis at 100 °C for 2 h. [b] In bar, calculated throughout this investigation on the basis of the ideal gas law. [c] Percentage of reacted silane. [d] Yields for isolated silanes. [e] Molar ratios determined by ^{19}F NMR spectroscopy.

The co-thermolysis of $(CHF_2)SiH_2Cl$ with an excess of CF_3SiF_3 (1 : 2.9; 100 °C; 2 h) yielded 40% of $(CHF_2)_2SiHCl$ and also 10% of $(CHF_2)_3SiCl$.

Significant amounts of CH_2F-substituted silanes were detected in the co-pyrolysis of CF_3SiF_3 and SiH_3F, Table 2A. This presumably implies the formation via H/F scrambling of $(CHF_2)SiF_3$, which readily generates CHF. The latter can then insert into Si–H bonds to form the CH_2F groups [12].

The insertion of CF_2 is not limited to silyl halides. Disiloxane, $H_3SiOSiH_3$, is quantitatively converted into CHF_2-containing silanes with an excess of CF_3SiF_3 (3 : 1), viz.

$$(SiH_3)_2O \xrightarrow[100\,^\circ C,\ 2\ h]{CF_3SiF_3} \underset{(63\%)}{(CHF_2SiH_2)_2O} + \underset{(6\%)}{(CHF_2)SiH_2OSiH_3} + \underset{(15\%)}{(CHF_2)_2SiHOSiH_3} + \underset{(9\%)}{(CHF_2)_2SiH_2} \quad (4)$$

A further, as yet unidentified, compound containing a $(CHF_2)_2SiH$ unit makes up the remaining 7%. The predominance of the di-inserted symmetric over the asymmetric disiloxane clearly demonstrates that insertion of a second CF_2 at the same silicon atom is slower than that of the first CF_2 moiety.

Trisilylamine, $(H_3Si)_3N$, did not undergo insertion of CF_2 even when the CF_2-precursor CF_3SiF_3 was employed in excess under the same conditions.

The presence of a second halogen function completely suppresses the insertion of CF_2. Thus, SiH_2X_2, CH_3SiHX_2, $SiHX_3$ and SiX_4 (X = Cl, Br, I) were quantitatively recovered from the co-thermolysis with CF_3SiF_3.

Table 2

Typical product distribution for the reaction of SiH_3F and CF_3SiF_3 and NMR identification (8 ppm) (*A*) Immediately after co-thermolysis, 2 h at 100 °C. (*B*) After additional storage for 5 days at room temperature

A		
$(CHF_2)SiH_2F$	78%	[a]
$(CHF_2)SiHF_2$	3%	[b]
$(CH_2F)SiF_3$	8%	[b]
$(CH_2F)SiHF_2$	4%	[b]
$(CHF_2)(CH_3)SiHF$	< 0.5%	$\delta(H(CH_3))$ 0.5 ppm (ddt, 8.0, 2.7, 0.6 Hz)
$(CHF_2)SiH_2Cl$ [c]	4%	[a]
$(CH_2Cl)SiF_3$ [c]	1%	$\delta(H)$ 2.8 (q, 2.6 Hz); $\delta(F)$ −143.2 (t, 2.6 Hz)
B		
$(CHF_2)_2SiH_2$	37%	[b]
$(CHF_2)(CH_2F)SiF_2$	17%	$\delta(H(CHF_2))$ 5.9 (td, 44.8, 0.5 Hz); $\delta(H(CH_2F))$ 4.6 (d(t), 46.6, not resolved) $\delta(F(SiF_2))$ −151.2 [d]; $\delta(F(CHF_2))$ −143.5 (d, 44.8 Hz); $\delta(F(CH_2F))$ −285.4 (t, 46.7 Hz)
$(CHF_2)SiF_3$	14%	[b,d]
$(CHF_2)SiH_3$	3%	[b]
$(CHF_2)_2SiF_2$	3%	$\delta(H)$ 5.8 (t, 44.3 Hz); $\delta(F(CHF_2))$ −142.8 (dm [e], 44.9 Hz); $\delta(F(SiF_2))$ −148 [d]
$(CH_2F)SiF_3$	3%	[b]
$(CHF_2)(CH_2F)SiH_2$	%	[b]
$(CH_2Cl)SiF_3$ [c]	2%	$\delta(H)$ 2.8 (q, 2.6 Hz); $\delta(F)$ −143.2 (t, 2.6 Hz)
$(CHF_2)(CH_2Cl)SiF_2$	7%	$\delta(H(CH_2Cl))$ 2.9 (t, 3.5 Hz); $\delta(F(CHF_2))$ −142.8 (dt, 44.8, 3.7 Hz) $\delta(F(SiF)_2))$ −149.9 (ttd, 3.7, 3.5, 1.6 Hz)

[a] See Table 3. [b] See Ref. 12. [c] Cl originating from CF_3SiF_2Cl, present as impurity in CF_3SiF_3. [d] Broad signal due to fluorine exchange. [e] $AA'X_2X_2'$ spin system.

A kinetic H/D isotope effect was revealed by means of ^{19}F NMR spectroscopy in the co-thermolysis of equal amounts of CH_3SiH_2Cl and CH_3SiD_2Cl with CF_3SiF_3. Although the starting materials undergo H/D exchange with formation of $CH_3SiHDCl$ even a ambient temperature, the ratio of the sum of the CHF_2-containing products $(CHF_2)(CH_3)SiHCl$ and $(CHF_2)(CH_3)SiDCl$ with respect to that of CDF_2 species gives $k(SiH)/k(SiD) = 1.14$. This determination was made possible by the large H/D isotope effect on the ^{19}F NMR shifts, $\delta(CHF_2) - \delta(CDF_2) = 0.70$ and $\delta(CHF_2SiH) - \delta(CHF_2SiD) = 0.07$ ppm.

Physical and chemical properties

The (difluoromethyl)halosilanes are colourless volatile liquids which should be handled with great caution, e.g. $(CHF_2)SiH_2Cl$ is prone to explode at or below room temperature. The fluoride $(CHF_2)SiH_2F$ has a relatively high boiling point, 45 °C as extrapolated from vapour pressure measurements, which lies above that, i.e. 27 °C, of the chloride $(CHF_2)SiH_2Cl$. This is indicative of intermolecular interactions and these may also favour the facile decomposition of the fluoride, which proceeds quantitatively at 25 °C within 5 days. The fast exchange on the NMR time scale of the silicon-bonded fluorine atoms of $(CHF_2)SiF_3$ or $(CHF_2)_2SiF_2$, which are present in the reaction mixture, indicates that this decomposition is catalyzed by HF which is presumably formed by reaction with the glass walls. Among the complex decomposition products (see Table 2B) $(CHF_2)_2SiH_2$ was identified as the major component (37%), along with considerable amounts of $(CHF_2)(CH_2F)SiF_2$. The formation of these dimethylsilyl derivatives presumably involves participation of the CHF_2 group in an intermolecular exchange process. Generation of CF_2, followed by its insertion into an Si–H bond of $(CHF_2)SiH_2F$ and H/F scrambling, or alternatively preferential insertion of CHF into an Si–F bond, is unlikely to occur under the conditions used. Furthermore the amount of CH_2F-containing silanes remains essentially unaltered. The unexpected appearance of CH_2Cl groups (see Table 2B) is due to the presence of some CF_3SiF_2Cl as an impurity in the starting material CF_3SiF_3. After thermolysis the chlorine is found in $(CHF_2)SiH_2Cl$; in the subsequent decomposition it selectively replaces the fluorine of a CH_2F group.

$(CHF_2)SiH_2Cl$ can be readily converted into difluoromethylsilane, $(CHF_2)SiH_3$ (Eq. 5), which is colourless, stable gas, b.p. −15 °C. The latter was also detected as a final product in a scrambling process.

$$(CHF_2)SiH_2Cl \xrightarrow[-20\,^\circ C,\ (n\text{-}Bu_2O)]{LiAlH_4} (CHF_2)SiH_3 \qquad (5)$$

Spectra

The variety and abundance of NMR-active nuclei (^1H, ^{19}F, ^{13}C and ^{29}Si) facilitates the unambiguous identification of even minor components in complex mixtures. In $H–CF_2–SiH_2–X$ species the common CF_2SiH_2 moiety forms an $AA'XX'$ spin system which, because of the large $^2J(FF)$ coupling of ca. 400 Hz, gives rise to "first-order" triplets with an effective coupling constant of $(J_{AX} + J_{AX'})/2$. In the case of the disiloxane small long-range couplings induce slight distortions of the respective triplet structures.

The ^{19}F NMR spectra of the chiral silanes $(CHF_2)(CH_3)SiHX$ (X = Cl, Br) are characterized by well separated AB systems ($\delta_A - \delta_B = 1.53$ ppm (Cl), 1.80 ppm (Br) with $^2J(FF)$ couplings of 391.9 and 387.8 Hz, respectively, Fig. 1. A simulation of the spectrum of the CH_3-proton decoupled ABXY system yields different $^3J(HF)$ coupling constants, +4.5 and +8.7 Hz (X = Cl) and +4.8 and +9.2 Hz (X = Br), Table 3. An ABX-type pattern with slightly different $^1J(CF)$ couplings is also revealed by the ^{13}C NMR spectra.

Significant four-bond couplings ($^4J(FF)$, 2–4 Hz and $^4J(FH)$, ca. 1 Hz) yield characteristic $AA'X_2X'_2$ patterns for bis(difluoromethyl)silanes. These might be further complicated by additional "first-order" couplings over three bonds, as in $(CHF_2)_2SiH_2$ [12], or the fluorines in a CF_2 group are magnetically inequivalent, as found in $(CHF_2)_2SiMeCl$. Simulation of the spectrum of the latter yielded $(\delta_A - \delta_B) = 0.82$ ppm and $^2J(FF)$ +402.1 Hz, $^2J(HF)$ +45.7 Hz, $^4J(FF)$ +2.2 and +3.4 Hz, $^4J(FH)$ +0.5 Hz – the signs of the ^2J constants being adopted from the literature [12]. For the halides $(CHF_2)_2SiHX$, the AB-type pattern of the prochiral CF_2 units is hardly detectable. Thus, the difference of the ^{19}F chemical shifts $\Delta(\delta(F^A) - \delta(F^B))$ is only 0.15 ppm for X = Br, and the central line of the multiplet in the proton-decoupled spectrum at a resonance frequency of 235 MHz shows a 1.4 Hz splitting.

Infrared and Raman spectra of the novel fluoromethyl silanes have been recorded. Those of difluoromethylsilane, $(CHF_2)SiH_3$, can be readily assigned by

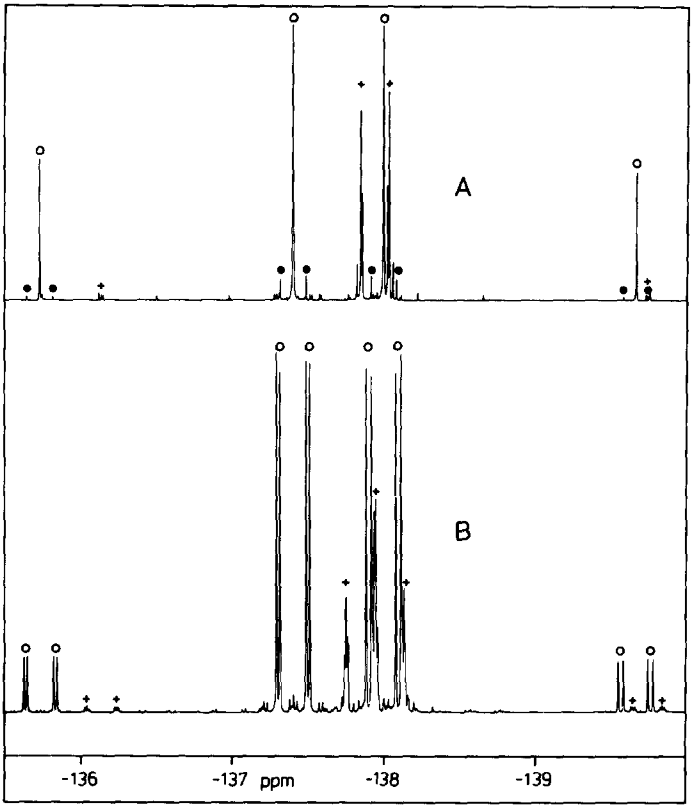


Fig. 1. ^{1}H-decoupled (A) and undecoupled ^{19}F NMR spectrum (B). $(CHF_2)SiHCl(CH_3)$: circles, with ^{29}Si satellites denoted by full dots. $(CHF_2)_2SiCl(CH_3)$: crosses.

comparison with CHF_2Cl [13] and CF_3SiH_3 [14]. In order to achieve a more quantitative description of the vibrational fundamentals and to obtain information on the strength of the Si–C bond, we performed a normal coordinate analysis [15], the results of which are shown in Table 4. The molecular geometry was based on that of CF_3SiH_3, and the mutual force field for the iteration procedure was constructed from those for CHF_2Cl [13] and CF_3SiH_3 [14]. The fact that the calculated SiC stretching force constant, 2.69 N cm^{-1}, exceeds that of CF_3SiH_3, 2.54 N cm^{-1}, is consistent with the lower positive charges in CHF_2SiH_3 both on the carbon and silicon atoms. The SiC force constant is, however, still considerably smaller than that of CH_3SiH_3, 2.98 N cm^{-1} [16].

The large number of bands in the low wavenumber region of the spectra of $(CHF_2)SiH_2F$ and $(CHF_2)SiH_2Cl$ indicates that the compounds exist as a mixture of conformers.

Discussion

Difluorocarbene, which can be cleanly generated by thermolysis of CF_3SiF_3, inserts readily and selectively into Si–H bonds of silanes provided the silicon atom carries a single halogen or oxygen atom as a further substituent. No evidence was

Table 3

NMR data for (difluoromethyl)silanes [a] (δ ppm)

	$\delta(H(CHF_2))$	$\delta(H(SiH))$	$\delta(F(CHF_2))$	$\delta(C(CHF_2))$ [b]	$\delta(Si)$ [c]	$^2J(HCF)$	$^3J(FCSiH)$	$^3J(HCSiH)$	$^1J(HC(F_2))$	$^1J(SiH)$	$^1J(CF)$	$^2J(SiCF)$
$(CHF_2)SiH_3$	5.81	3.53	−128.1	120.2	−63.8	46.0	11.1	1.8	171.2	213.3	252.3	34.1
$(CHF_2)SiH_2F$ [d]	6.03	4.81	−140.8	117.5	−16.0	45.5	7.4 [e]	1.5	173.9	248.8	250.3	41.9
$(CHF_2)SiH_2Cl$	6.01	4.75	−135.0	118.3	−24.8	46.0	7.7 [e]	1.7	173.8	251.8	254.4	42.2
$(CHF_2)SiH_2Br$	5.92	4.66	−133.0	117.3	−32.9	46.2	7.9 [e]	1.7	174.7	251.9	255.7	42.2
$(CHF_2)SiH_2I$	5.90	4.62	−130.1	f	f	46.7	8.0 [e]	1.7	f	f	f	f
$(CHF_2)(CH_3)SiHCl$ [g]	5.88	4.82	−136.9	118.9	−1.4	46.2	4.5/8.9	1.3	171.7	243.0	253.8	39.8
			−138.5									
$(CHF_2)(CH_3)SiHBr$ [h]	5.90	4.67	−134.9	118.8	−7.9	46.4	4.8/9.2	1.2	f	246.1	253.8	40.3
			−136.7									
$(CHF_2)(CH_3)_2SiCl$ [i]	5.97	–	−138.5	119.7	18.3	46.3	–	–	f	–	253.9	37.1
$[(CHF_2)SiH_2]_2O$	5.55	4.43	−138.6	119.4	−32.4	45.8	8.0 [e]	1.3	170.1	239.8	251.9	39.3
$(CHF_2)_2SiH_2$	5.85	3.85	−131.1		−45.4	45.4	9.4 [e]	1.9			f	33.8
$(CHF_2)_2SiHF$ [k]	5.75	4.94	−142.8			45.4	f	f			f	
$(CHF_2)_2SiHCl$	6.07	4.88	−136.2			46.0	5.5	1.9				
$(CHF_2)_2SiHBr$	5.96	4.88	−134.2	116.3 [l]	−25.3	46.3	6.4	1.7			255.4	40.5
$(CHF_2)_2(CH_3)SiCl$ [m]	5.96	–	−137.5	117.4	1.0	45.7					253.2	38.0
			−138.3								253.4	
$(CHF_2)_3SiCl$	6.16	–	−136.5			46.3	–	–				

[a] Chemical shifts δ in ppm, coupling constants J in Hz. [b] In C_6D_6, δ 128.0. [c] Ext. std. TMS. [d] $\delta(F(SiF))$ −201.8, $^1J(SiF)$ 295.1 Hz, $^2J(FSiH)$ 47.6 Hz, $^3J(FCSiF)$ < 0.2 Hz. [e] $(J(AX)+J(AX'))/2$. [f] Not determined. [g] $^3J(H_3CSiH)$ 3.2 Hz, $^2J(FCF)$ 392.0 Hz, $\delta(C(CH_3))$ −5.8, $\delta(H(CH_3))$ 0.62. [h] $^3J(H_3SiCH)$ 3.3 Hz, $^2J(FCF)$ 387.8 Hz, $\delta(C(CH_3))$ −5.9, $\delta(H(CH_3))$ 0.68. [i] $\delta(C(CH_3))$ −3.5, $\delta(H(CH_3))$ 0.67. [k] $\delta(F(SiF)$ −194.2, $^2J(FSiH)$ 46.3 Hz. [l] $^3J(CSiC)$ 3.2 Hz. [m] $^2J(FCF)$ 402.1 Hz, $^4J(FCSiCF)$ +2.2 Hz/+3.4 Hz, $^4J(FCSiCH)$ +0.5 Hz, $\delta(H(CH_3))$ 0.71.

Table 4

Infrared and Raman spectra [a], potential energy distribution [b], and diagonal force constants [c] of CHF_2SiH_3

IR, gas	Raman, liquid	Approximate description	Potential energy distribution
2928 m, PQR	2940 w, p	$\nu(CH)$	100 (CH)
2211 vs	2210 sh	$\nu_{as}(SiH_3)(a', a'')$	101 (SiH)
2193 vs, PQR	2196 vs, p	$\nu_s(SiH_3)$	99 (SiH)
1378 w	1363 w	$\delta(HCF)(a'')$	99 (HCF)
1326 m	1327 m, p	$\delta(HCF)(a')$	45 (HCF), 40 (HCSi), 11 (CF), 10 (HCSi/HCF)
1097 vs	1093 w, p	$\nu_s(CF_2)$	64 (CF), 13 (FCF)
1035 vs	1016 w	$\nu_{as}(CF_2)$	133 (CF), −15 (CF/CF′)
941 s	937 m	$\delta_{as}(SiH_3)(a', a'')$	109 (HSiH)
907 vs	910 sh	$\delta_s(SiH_3)$	48 (HSiC), 45 (HSiH), 18 (HSiH/HSiC)
766 m, PQR	763 s, p	$\rho(SiH_3)(a')$	35 (SiC), 33 (HSiC), 11 (FCSi)
631 m	634 m	$\rho(SiH_3)(a'')$	90 (HSiC)
587 w	589 vs, p	$\nu(SiC)$	48 (SiC), 46 (HSiC)
481 m, PQR	486 m, p	$\delta(CF_2)$	64 (FCF), 12 (HCSi)
301 m, PQR	305 s, p	$\omega(CF_2)$	46 (FCSi), 18 (HCSi), 15 (SiC), 14 (HCF), 11 (HCSi), −12 (FCSi/HCSi), −12 (F′CSi/HCSi)
222 w	-	$\tau(CF_2)$	134 (FCSi), −12 (CF/FCSi), −12 (CF′/FCSi) −19 (FCSi/FCSi)

Force constants

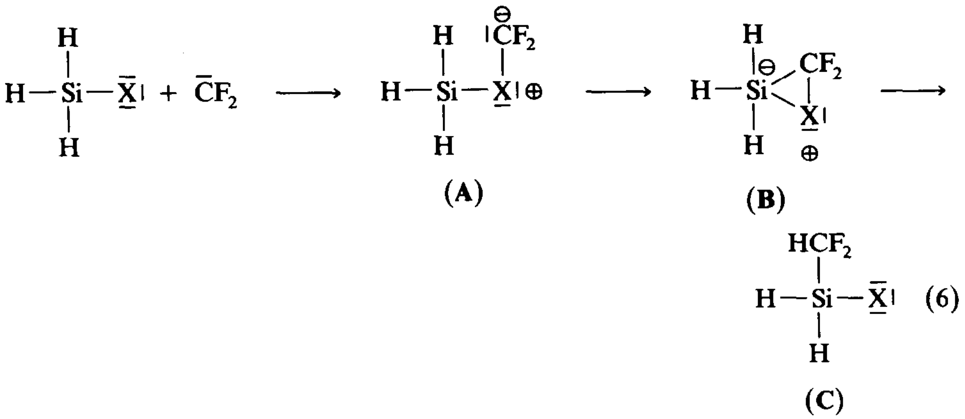
f(SiC)	2.69	f(FCF)	1.22	f(FCSi)	0.56
f(CF)	5.37	f(HSiC)	0.48	f(HSiH)	0.48
f(CH)	4.70	f(HCF)	0.81	f(HCSi)	0.45

[a] In cm^{-1}. [b] Contributions >10%. [c] In N cm^{-1}, scaled to 100 pm.

found for incorporation into any other silicon-element bond. This contrasts with the reported insertion of CF_2 (generated from Me_3SnCF_3) into the Si–Si bond of $FMe_2Si–SiMe_2F$ to yield the carbasilane $(FMe_2Si)_2CF_2$ [17].

Since the insertion reaction must compete with the oligomerization of CF_2 to form C_2F_4 and *cyclo*-C_3F_6, a high yield of the CHF_2Si derivative implies that the insertion rate is relatively high. Thus CF_2 inserts most rapidly into the Si–H bonds of silyl halides SiH_3X. Replacement of one or two hydrogen atoms by methyl groups lowers the insertion rate significantly, and this rate becomes barely detectable for phenylchlorosilanes. A second CF_2 group inserts more slowly than the first at the same silicon atom. This is underlined by the favoured formation of $(CHF_2SiH_2)_2O$ with respect to $(CHF_2)_2SiHOSiH_3$.

Although the Si–H bond character of CF_3SiH_3 is similar to that of SiH_3Cl and SiH_3Br, CF_2 does not insert into the Si–H bonds of CF_3SiH_3. This suggests that neither the polarity of the Si–H bond nor the charge on the Si atom are of crucial importance for the reactivity towards CF_2. On the other hand, the presence on silicon of a substituent with available lone pairs seems to be necessary for a sufficiently fast CF_2 insertion rate. This observation may be rationalized by a mechanism in which insertion is preceded by formation of a donor–acceptor complex **A**:



Such a charge transfer interaction is favoured by the low-lying acceptor orbital of singlet-CF_2, and has also been suggested by ab initio calculations for the insertion of CH_2 and CF_2 [18]. The introduction of CF_2 is followed by Si–C bond formation (**B**) by interaction of the CF_2 HOMO with an empty orbital at Si (σ^*(SiH)). This step is assisted by a positive charge on the silicon atom and the polarity $\overset{\delta+}{\mathrm{Si}}-\overset{\delta-}{\mathrm{H}}$. The latter facilitates hydride transfer to carbon with concomitant loss of the C–X overlap. Bulky substituents attached to the Si atom will both reduce the stability of the charge transfer complex **A** and hinder Si–C bond formation.

The proposed mechanism makes the failure of CF_2 to insert into $(H_3Si)_3N$ understandable. The nitrogen lone pair of the planar NSi_3 skeleton is generally not available for coordination, and the positive charge on silicon, which assists Si–C bond formation, is smaller than in silyl fluoride and disiloxane [19].

The reluctance of dihalosilanes SiH_2X_2 to insert CF_2 cannot be ascribed to enhanced steric shielding. Furthermore, the effect of the second halide on the charge distribution is not likely to be crucial in view of the fact that CF_2 can be forced to insert into $(CHF_2)_2SiHCl$, and so CF_2 should be able to form an adduct with SiH_2X_2. However, this adduct apparently cannot rearrange to a transition state capable of hydrogen transfer, such as **B**. This may be the case if the adduct is formed by donation of electrons from the b_2 MO of SiH_2X_2, which is formed by the lone pairs of the two X atoms, into the CF_2 LUMO.

The possibility that formation of a charge transfer complex **A** may precede insertion of CF_2 into a Si–Si bond is also suggested by the behaviour of $Me_3SiSiMe_3$. This, in contrast to $FMe_2SiSiMe_2F$ [17], gave no CF_2 insertion products when treated according to our standard procedure with CF_3SiF_3, or under more forcing conditions [17] with Me_3SnCF_3.

Apparently these vigorous conditions (~ 160 °C) do not make Me_3SnCF_3 a more efficient reagent for CF_2 insertion into silicon–element bonds. Thus, after 3 days at 160 °C, the reaction of Me_3SnCF_3 with Me_3SiCl yielded Me_3SnCl and Me_3SiF along with C_2F_4 and *cyclo*-C_3F_6, while that with $HSiCl_3$ gave only Me_3SnCl, SiF_4, C_2F_4 and *cyclo*-C_3F_6 – no $CF_2ClSiHCl_2$ or CHF_2SiCl_3 being detected.

Keeping in mind the thermal instability of fluoromethylsilanes, the main advantage of CF_3SiF_3 with regard to Me_3SnCF_3 for CF_2 insertion reaction are the mild conditions under which a Si–C bond can be formed. These conditions allow the insertion products to survive, which makes the reported insertion reactions useful for syntheses of hitherto inaccessible CHF_2Si derivatives on a preparative scale.

Experimental

Volatile materials were handled in a standard vacuum system equipped with greaseless valves. Gas volumes and vapour pressures were measured with a MKS Baratron 315 BHS pressure gauge. NMR spectra were recorded with a Varian EM 390 (^1H, 90.0 MHz; ^{19}F, 84.7 MHz) and a Bruker AC 250 spectrometer (^1H 250.13 MHz; ^{19}F, 235.36 MHz; ^{13}C, 62.90 MHz; ^{29}Si, 49.70 MHz). Infrared spectra were recorded with a Perkin Elmer 580 B spectrometer with 10 cm gas cells, and Raman spectra with a Cary 82 model, excitation Kr^+ 647.1 nm.

Starting materials. Silyl halides were obtained by cleavage of arylsilanes with gaseous HX, SiH_3F by fluorination of SiH_3Br with SbF_3 at −30 °C. Dichlorosilane was prepared from SiH_3Cl and $SnCl_4$ (ratio 1/1.3) at 100 °C, di- and tri-fluorosilane by low-temperature fluorination of corresponding chlorides with SbF_3. Methyl-chloro- and -bromo-silanes were obtained from the corresponding methylsilanes and stoichiometric amounts of $SnCl_4$ or $SnBr_4$, in sealed ampoules at 100 °C. Me_3SnCF_3 was prepared as previously described [20].

(Trifluoromethyl)trifluorosilane. Under an atmosphere of CF_3Br, 253 g (1.02 mol) $P(NEt_2)_3$ were added at 0 °C during 2 h to a solution of 170 g (1.00 mol) $SiCl_4$ in 200 ml benzonitrile. After 2 h of vigorous stirring at 0 °C all volatile products were evaporated off in vacuo during 2 days and condensed at −78 °C while the reaction mixture was slowly warmed to 40 °C. Isothermal distillation yielded 102.5 g (0.50 mol) CF_3SiCl_3. This was converted to CF_3SiF_3 with a yield of 62% by treatment with a twofold excess of freshly sublimated SbF_3 in dibutyl ether under 0.8 bar of dry nitrogen as the temperature was raised from −78 °C to −45 °C. The product obtained after passing the volatile products through a −126 °C trap was contaminated with SiF_4 (15%) and traces of CF_3SiF_2Cl.

(Difluoromethyl)silanes, general procedure. The appropriate silane and CF_3SiF_3 were co-condensed either into a 4 mm o.d. glass ampoule (volume 1.2 ml) or, for preparative scale experiments, into stainless steel cylinders equipped with Hoke valves. After 2 h heating at 100 °C the products were either identified by NMR spectroscopy, or separated by fractional condensation in vacuo from the more volatile materials, which consisted mainly of SiF_4, *cyclo*-C_3F_6 and C_2F_4.

No indication for CF_2 insertion was found in the reaction with SiH_4, $MeSiH_3$, Me_2SiH_2, Me_3SiH, $PhSiH_3$, SiH_2F_2, SiH_2Cl_2, SiH_2Br_2, $SiHCl_3$, $MeSiHCl_2$, Me_2SiCl_2, Me_3SiCl, Me_3SiBr, $SiCl_4$, $SiBr_4$ and $Me_3SiSiMe_3$. Decomposition of the silane was observed in the case of SiH_3CN and $Et_2NSiHCl_2$.

Reactions with Me_3SnCF_3. Ca. 4 mmol Me_3SnCF_3 and ca. 3.5 mmol of the silane were condensed in a 30 ml glass ampoule and the mixture was heated to 160 °C for 3 days. Volatile products were evaporated off, separated by fractional condensation in vacuo, and investigated by IR and NMR spectroscopy.

(a) From Si_2Me_6, ca. 3.5 mmol $SnMe_4$ were obtained and, in addition, C_2F_4, *cyclo*-C_3F_6 and Me_3SiF in a 3 : 1 : 1 molar ratio. Traces of material revealing peaks in the ^{19}F NMR spectrum at −24.0 s, −42.8 s, and −64.3 ppm, s, were found in the −78 °C trap.

(b) Me_3SiCl formed ca. 4 mmol Me_3SnCl, 3 mmol Me_3SiF, and C_2F_4 and *cyclo*-C_3F_6 in a molar ratio of ca. 1 : 1.

(c) $HSiCl_3$ converted Me_3SnCF_3 quantitatively into Me_3SnCl. 3 mmol volatile products collected in a −196 °C trap consisted of SiF_4, C_2F_4 and *cyclo*-C_3F_6 in a 2 : 3 : 2 molar ratio. Weak additional peaks were observed in the ^{19}F NMR spectrum at −143.7 s, −120.5 s, and −81.7 ppm, d.

(Difluoromethyl)fluorosilane. B.p. 45 °C; $\ln p$ (mbar) $= -3100/T$ (K) $+ 16.670$; M, by gas density, found 101.3 (calcd. 101.1). IR see Ref. 12. Additional far infrared absorptions (cm^{-1}): 547 w, 400 m, 279 m. Raman, liquid (cm^{-1}) 2960 m, p, 2235 sh, 2218 vs, p, 1400 w, 1333 s, p, 1100 m, p, ν_s (CF_2), 1015 m, ν_{as} (CF_2), 950 w, p, 920 w, 901 w, p, ν(SiF), 777 m, 727 m, 661 vs, p, ν(SiC), 598 w, 547 s, p, $\delta(CF_2)$, 393 m, p, 296 m, p, 260 vs, p, 230 m, 192 w.

(Difluoromethyl)chlorosilane. B.p. 27 °C; $\ln p$ (mbar) $= -3482/T$ (K) $+ 18.536$; M, by gas density, found 114.0 (calcd. 116.6). IR, gas (cm^{-1}) 2938 m, PQR, ν(CH), 2229 vs, ν_{as} (SiH_2), 2217 vs, ν_s (SiH_2), 1385 w, 1324 m, PQR, 1094 s, PQR, $\Delta\nu$(PR) 11 cm^{-1}, ν_s (CF_2), 1037 vs, ν_{as} (CF_2), 936 s, PQR, 880 s, 847 vs, PQR, $\Delta\nu$(PR) 10 cm^{-1}, 795 vw, 721 m, 674 w, PQR, ν(SiC), 587 m, 562 s, PQR, $\Delta\nu$(PR) 10 cm^{-1}, ν(SiCl), 498 m, PQR, 286 m, 256 w. Raman, liquid (cm^{-1}) 2955 m, p, 2220 vs, p, 1330 s, p, 1101 m, p, 1030 w, 936 w, p, 848 vw, 782 s, 719 m, p, 664 m, p, 564 vs, p, 520 vs, p, 418 w, 324 s, p, 293 s, p, 261 s, p, 173 m, 124 s.

(Difluoromethyl)methylchlorosilane. B.p. 62 °C; $\ln p$ (mbar) $= -3241/T$ (K) $+ 16.600$; M, by gas density, found 125.5 (calcd. 130.6). IR, gas (cm^{-1}) 2982 m, 2932 m, 2922 sh, 2208 vs, ν(SiH), 1409 vw, 1324 s, 1270 s, δ_s (CH_3), 1095 s, ν_s (CF_2), 1025 vs, ν_{as} (CF_2), 887 s, 839 sh, 834 vs, $\rho(CH_3)$, 829 sh, 784 m, 758 w, 684 vw, 644 vw, 541 sh, 535 s, ν(SiCl), 368 w, 317 m, 313 w, 307 w, 282 vw, 202 m. Raman, liquid (cm^{-1}) 2987 w, 2921 m, 2211 vs, 1410 w, 1331 sh, 1325 m, 1267 w, 1090 m, 1016 w, 881 w, 832 w, 778 w, 757 m, 745 sh, 690 m, 673 w, 644 s, 642 sh, 542 s, 525 vs, 452 m, 380 sh, 370 m, 315 s, 310 m, 284 s, 262 w, 203 s, 185 m, 158 w, 125 w.

(Difluoromethyl)methylbromosilane. M, by gas density, found 171.3 (calcd. 175.1). IR, gas (cm^{-1}) 2984 w, 2935 m, 2929 sh, 2208 vs, ν(SiH), 1408 w, 1320 s, 1265 s, δ_s (CH_3), 1129 m, 1092 vs, ν_s (CF_2), 1024 vs, ν_{as} (CF_2), 886 vs, 826 vs, $\rho(CH_3)$, 780 s, 744 s, 695 w, 643 m, 535 w, 440 vs, ν(SiBr), 414 w, 365 m, 305 w, 256 w. Raman, liquid (cm^{-1}) 2985 m, 2919 s, 2207 vs, 1412 m, 1325 m, 1264 m, 1089 m, 1010 m, 908 w, 877 w, 823 w, 795 w, 778 w, 751 s, 729 sh, 682 s, 643 vs, 583 m, 546 m, 531 w, 437 vs, 410 vs, 382 s, 366 m, 310 s, 260 vs, 222 w, 187 s, 119 sh, 110 s.

(Difluoromethyl)dimethylchlorosilane. B.p. 90 °C; $\ln p$ (mbar) $= -3582/T$ (K) $+ 16.793$; M, by gas density, found 144.2 (calcd. 144.6). IR, gas (cm^{-1}) 2980 m, 2927 m, 1411 w, 1331 w, 1323 m, 1318 m, 1269 sh, 1264 s, δ_s (CH_3), 1126 sh, 1095 s, ν_s (CF_2), 1019 vs, ν_{as} (CF_2), 848 vs, $\rho(CH_3)$, 822 sh, 814 vs, 809 sh, 762 w, 714 m, 692 w, 644 m, 547 m, 541 m, 509 s, ν(SiCl), 472 w, 347 m, 296 w, 216 m, 196 w. Raman, liquid (cm^{-1}) 2982 w, 2918 s, 1408 w, 1332 w, 1323 m, 1268 w, 1090 w, 1005 w, 813 w, 713 m, 692 m, 647 vs, 545 m, 506 vs, 469 m, 367 m, 350 s, 300 m, 223 s, 203 s, 147 m, 123 m.

(Difluoromethyl)silane. 1.97 mmol $(CHF_2)SiH_2Cl$ were condensed onto a suspension of 320 mg (8.43 mmol) $LiAlH_4$ in 5 ml di-n-butylether, the mixture then warmed to −20 °C and stirred for 15 min. The product was evaporated off and purified in a vacuum line by passing through a −126 °C trap. Yield 1.95 mmol

(99%) $(CHF_2)SiH_3$, b.p. −15 °C; ln p (mbar) = $2999/T$ (K) +18.515; M, by gas density, found 81.3 (calcd. 82.1).

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