Novel (Fluoromethyl)silicon Derivatives from (Fluorodibromomethyl)silane Precursors

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Dibromofluoromethylation of $SiCl_4$ and organochlorosilanes R_nSiCl_{4-n} has been achieved with a reagent prepared from $(Me_2N)_2C{=}C(NMe_2)_2$ and $CFBr_3$, yields ranging from 27 to 54%. The reactivity of the silanes depends both on the nature of R and on n. Novel (dibromofluoromethyl)silicon derivatives (R = Me, n = 1–3; R = Et, n = 1, 2; R = n-Pr, i-Pr, i-Bu, and s-Bu, n = 1) as well as $CFBr_2SiCl_3$ were obtained and characterized. By treatment with $(n\text{-}Bu)_3SnH$ reduction of both the $CFBr_2$ and the SiR_nCl_{3-n} groups occurred, and the corresponding fluoromethylsilanes $CH_2FSiR_nH_{3-n}$ were obtained with yields ranging from 81 to 98%. Functional fluoromethylsilicon chlorides and bromides $CH_2FSiR_nX_{3-n}$, X = Cl and Br, were prepared by reaction of the hydrides with $SnCl_4$ and Br_2, respectively. Substitution reactions of CH_2FSiBr_3 take place selectively at the Si atom, and novel CH_2FSiY_3 derivatives, Y = F, Cl, NCO, OMe, and Ph, have been synthesized. The first di(fluoromethyl)diorganosilane, $(CH_2F)_2SiMe_2$, has been isolated from the dibromofluoromethylation of CH_2FSiMe_2Cl followed by reduction with $(n\text{-}Bu)_3SnH$. Several additional compounds emerging from partial substitution, rearrangement, and dismutation reactions have been identified, some of which were isolated. All compounds were characterized by their multinuclear NMR spectra and furthermore studied by IR, Raman, and mass spectroscopy.

Introduction

(Fluoromethyl)silanes $CH_{3-n}F_nSiR_3$ belong to the class of (α-halomethyl)silicon compounds which tend to decompose readily by elimination of carbene with concomitant formation of a strong silicon–halogen bond. The resulting low thermal stability, which can be increased by bulky and electron-releasing substituents, e.g. alkyl groups, is particularly pronounced for the fluoromethyl derivatives, and the number of fully-characterized examples has grown only slowly.

(Fluoromethyl)silanes $Si(CH_3)_a(CH_2F)_b(CHF_2)_c(CF_3)_d$, $a + b + c + d = 4$, have been obtained unselectively by low temperature fluorination of $SiMe_4$ with F_2 diluted by a noble gas.[1] Insertion of SiF_2 into the C–I bond of CF_3I has yielded CF_3SiF_2I[2] whose reaction with SbF_3 afforded CF_3SiF_3[2] while CF_3SiH_3 was obtained by its reduction with $LiAlH_4$.[3]

Since both reaction pathways are convenient for routine laboratory work much effort has been invested in the past to find easy, selective, and versatile syntheses of (fluoromethyl)silanes. However, attempts to convert, for example, CH_2ClSi derivatives into the corresponding (monofluoromethyl)silanes by treatment with AgF,[4a] KF,[4b] KF in toluene,[4c] and SbF_5[4d] resulted only in breakdown of the (halomethyl)silicon moiety. Furthermore organometallic reagents like $Hg(CF_3)_2$[5a] and $Cd(CF_3)_2D$[5b] had led to fluoro rather than (fluoromethyl)silicon derivatives.

Formation of species containing a CH_2FSi fragment was observed during thermal decomposition of CF_3SiH_3, and it was shown that CHF emerging from the decomposition of intermediate CHF_2Si derivatives had inserted into an SiH bond.[6] Although this reaction pathway is not very useful for the synthesis of CH_2FSi compounds[7] due to the lack of a readily available and suitable CHF source,[8] insertion of the carbene CFBr into the Si–H bond of triethylsilane has been used for the synthesis of $Et_3SiCHFBr$. Its selective reduction with tri-n-butyltin hydride afforded Et_3SiCH_2F, which is one of the first fully characterized (monofluoromethyl)silicon compounds.[9]

The reaction of a silyl chloride X_3SiCl with a reagent prepared from $P(NEt_2)_3$ and CF_3Br in a polar solvent (eq 1)[10] gives access to CF_3SiX_3 compounds on a large scale with a variety of substituents X.[11,12] Also, CF_2Br_2 and

$$CF_3Br + P(NEt_2)_3 + X_3SiCl \rightarrow X_3SiCF_3 + P(NEt_2)_3BrCl \quad (1)$$

$CFBr_3$ are known to form different kinds of (trihalomethyl)phosphonium salts when reacted with tertiary phosphines,[13] but these have not yet been used for transfer of a $CFBr_2$ group to silicon.

The strong electron donor tetrakis(dimethylamino)ethylene (**3**) has been shown to react with various polyhalomethanes to yield, in a first step, a trihalomethanide anion (eq 2).[14]

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$$3 + CCl_3Br \rightarrow [(Me_2N)_2CC(NMe_2)_2]^{2+} + Br^- + CCl_3^- \quad (2)$$

In an analogous reaction with CF_3I a reactive intermediate was obtained with which CF_3^- groups can be transferred to silicon, and accordingly Me_3SiCF_3 and $Me_2Si(CF_3)_2$ were prepared in yields of 94 and 63%, respectively.[15] Thus the reagent combination **3**/CF_3I is a promising alternative to the $P(NEt_2)_3/CF_3Br$ system.

Making use of the observation that (Si)C–F bonds are resistant toward reducing agents like $LiAlH_4$[3,16,17] and $(n\text{-}Bu)_3SnH$,[9] a novel route to (monofluoromethyl)silicon derivatives starting from fluorodichloromethyl precursors has been developed. Good yields of $Me_3SiCHFCl$ and Me_3SiCH_2F were obtained by treatment of $Me_3SiCFCl_2$ with stoichiometric amounts of $(n\text{-}Bu)_3SnH$.[17] Recently, $(n\text{-}Bu)_3SnH$ was also used to reduce $CFCl_2SiCl_3$[18] which is a suitable precursor for Si-functional (monofluoromethyl)silanes CHF_2SiX_3 (X = H, halogen, NR_2, etc.).[7] This reduction however does not proceed in a fully satisfactory fashion, at best a 1:1 mixture of CH_2FSiH_3 (**1**) and $CHFClSiH_3$ (**2**), with a total yield of ca. 55% being obtained.[7] In addition to the laborious separation of **1** and **2**, the optimized yield of $CFCl_2SiCl_3$ was not higher than 25%.[7,18] Thus better access to **1** and its derivatives appeared desirable; therefore we have tested whether replacement of $CFCl_2$ groups by $CFBr_2$ groups would be advantageous. We report here on the fluorodibromomethylation of chlorosilanes and describe the synthesis of many novel (monofluoromethyl)silicon compounds.

Results

(Dibromofluoromethyl)silanes. We have found that **3** combined with $CFBr_3$ will place $CFBr_2$ groups on silicon. Various organosilicon substrates were tested, and numerous novel (dibromofluoromethyl)silicon derivatives were obtained according to (eq 3) with yields of 27–54%, as reported in Table I.

$$R_{4-n}SiCl_n + 3 + CFBr_3 \rightarrow R_{4-n}SiCl_{n-1}(CFBr_2) + [(Me_2N)_2CC(NMe_2)_2]^{2+}Cl^-Br^- \quad (3)$$

With the exception of $t\text{-}BuSiCl_3$, monoalkyltrichlorosilanes reacted readily with the **3**/$CFBr_3$ reagent. Dialkyl- and trialkylsilicon chlorides are less reactive, dibromofluoromethylation occurring only in the case of primary alkyl substituents. Thus, steric shielding of the chlorosilane has a pronounced effect on its coupling with a $CFBr_2$ group. This behavior is in agreement with an S_N2-type substitution mechanism involving a ionic nucleophile $CFBr_2^-$, as suggested previously.[18]

Yields are somewhat curtailed by side reactions undergone by the **3**/$CFBr_3$ reagent, which involve irreversible formation of the salt $[(Me_2N)_2CC(NMe_2)_2]Br_2$ and the carbene CFBr, yielding polymeric, unidentified material. The intermediacy of CFBr has been confirmed by its reaction with vinyl bromide.[19]

Table I. Products from the Reaction of $R_{4-n}SiCl_n$ with 3 and $CFBr_3$

$R_{4-n}SiCl_n$	mmol of $R_{4-n}SiCl_n$:3:$CFBr_3$	product	% yield
$SiCl_4$	133:133:137	$CFBr_2SiCl_3$ (**4**)	30
$MeSiCl_3$	34:33:33	$CFBr_2SiMeCl_2$ (**5**)	44
Me_2SiCl_2	22:22:20	$CFBr_2SiMe_2Cl$ (**6**)	35
Me_3SiCl	24:27:23	$CFBr_2SiMe_3$ (**7**)	54
$EtSiCl_3$	26:24:26	$CFBr_2SiEtCl_2$ (**8**)	49
Et_2SiCl_2	20:19:21	$CFBr_2SiEt_2Cl$ (**9**)	51
$n\text{-}PrSiCl_3$	40:37:41	$CFBr_2Si(n\text{-}Pr)Cl_2$ (**10**)	42
$i\text{-}PrSiCl_3$	20:20:20	$CFBr_2Si(i\text{-}Pr)Cl$ (**11**)	36
$(i\text{-}Pr)_3SiCl$	23:25:21	no reaction	
$(n\text{-}Bu)_3SiCl$	50:51:53	$CFBr_2Si(n\text{-}Bu)_3$[a] (**12**)	
$i\text{-}BuSiCl_3$	31:29:32	$CFBr_2Si(i\text{-}Bu)Cl_2$ (**13**)	39
$(i\text{-}Bu)_3SiCl$	23:23:22	no reaction	
$s\text{-}BuSiCl_3$	34:32:34	$CFBr_2Si(s\text{-}Bu)Cl_2$ (**14**)	27
$(s\text{-}Bu)_2SiCl_2$	28:31:28	no reaction	
$t\text{-}BuSiCl_3$	41:42:40	no reaction	
Ph_3SiCl	16:18:15	no reaction	

[a] Could not be separated from $(n\text{-}Bu)_3SiCl$, yield unknown.

Table II. Physical Properties of Selected Compounds

compd	mp, °C	bp, °C/p, mbar	vapor pressure[a] $A/B/\Delta H_v$[b]$/\Delta S_v$[b]	T range, °C
4	58–60			
5	52–54			
6	51–54			
7	53–55			
8		<20/10^{-1}		
9		34–35/10^{-1}		
10		30–32/10^{-1}		
11		29–30/10^{-1}		
13		44–45/10^{-1}		
14		38–39/10^{-1}		
21		13.7[d]	3375/18.69/28.06/97.8	−78.1 to +9.8
22		79.2[d]	3854/17.86/32.05/91.0	−33.4 to +21.5
23		37.9[d]	3548/18.33/29.50/94.8	−61.3 to +22.6
24		48.7[d]	3186/16.82/26.48/82.3	−5.5 to +20.3
25		84.2/955		
26		79.2/1013		
27		68.6/1000		
28		102.3/993		
29		97.0/990		
30		40.2	3179/17.07/26.43/84.3	−26.3 to +17.7
33		1.5	3520/19.74/29.26/106.6	−35.5 to −1.5
34		63.4	3250/16.58/27.02/80.3	−3.5 to +17.8

[a] $\ln p$ (mbar) = $-A/T$ (K) + B. [b] In kJ mol^{-1}. [c] In J mol^{-1} K^{-1}. [d] Extrapolated, at 1013 mbar.

Compounds **4**–**7** are colorless solids at room temperature while **8**–**11**, **13**, and **14** are liquids. All compounds are volatile, vapor pressures of **4**–**8** at room temperature exceeding 10^{-1}–10^{-2} mbar. Melting and boiling points are set out in Table II. All compounds are somewhat photosensitive although the yellow color appearing is not associated with significant decomposition. Their moisture sensitivity decreases with increasing number and bulkiness of the alkyl substituents.

All novel compounds have been characterized by ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra which are discussed below. Infrared, Raman, and mass spectral data are reported in the Experimental Section.

Reduction of (Dibromofluoromethyl)silanes. Treatment of $CFCl_2SiCl_3$ with $(n\text{-}Bu)_3SnH$ in a 1:3.7 molar ratio for 15 min at room temperature had yielded all members of the series $CFCl_2SiH_nCl_{3-n}$ and $CHFClSiH_nCl_{3-n}$.[7] When $CFCl_2SiCl_3$ and $(n\text{-}Bu)_3SnH$ in a 1:10 ratio were heated for 3 days to 80 °C, the SiH_3 derivatives **1** and **2** had been obtained, after laborious separation, with yields of 26 and 28%, respectively.

The reduction of **4** by $(n\text{-}Bu)_3SnH$ proceeds faster, is more selective than that of $CFCl_2SiCl_3$, and can be brought to completeness. Treatment of **4** with 2.6 equiv $(n\text{-}Bu)_3SnH$ for 5 min at room temperature yields 64%

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Table III. Reduction of (Dibromofluoromethyl)silanes

$CFBr_2$-SiR_nCl_{3-n}	equiv of $(n\text{-Bu})_3SnH$	reacn time at 25 °C, h	product	% yield
4	7.0	24	CH_2FSiH_3 (**1**)	98
5	5.7	60	CH_2FSiH_2Me (**21**)	95
6	12	24	$CH_2FSiClMe_2$ (**22**)	81
6	6.7	120	$CH_2FSiHMe_2$ (**23**)	84
8	5.5	60	CH_2FSiH_2Et (**24**)	82
9	7.8	168	$CH_2FSiHEt_2$ (**25**)	83
10	6.6	96	$CH_2FSiH_2(n\text{-Pr})$ (**26**)	95
11	7.6	96	$CH_2FSiH_2(i\text{-Pr})$ (**27**)	90
13	7.2	72	$CH_2FSiH_2(i\text{-Bu})$ (**28**)	94
14	4.3	144	$CH_2FSiH_2(sec\text{-Bu})$ (**29**)	86

$CFBr_2SiH_3$ (**15**), 27% $CHFBrSiH_3$ (**16**), and 6% $CFBr_2SiH_2Cl$ (**17**), along with traces of **1**, $CFBr_2SiHCl_2$ (**18**), $CH_2FSiHCl_2$ (**19**), and CH_2FSiCl_3 (**20**). When **4** was reacted for 24 h at room temperature with 7 equiv $(n\text{-Bu})_3SnH$, quantitative conversion to **1** took place. No byproducts were found, and pure **1** was isolated in 98% yield.

Similarly, the alkyl(dibromofluoromethyl)silanes **5**, **6**, **8**–**11**, **13**, and **14** reacted with $(n\text{-Bu})_3SnH$ to form the corresponding alkyl(fluoromethyl)silanes **21**–**29**. Yields of isolated pure material ranged from 81 to 98%, Table III. However, prolonged reaction times were required for complete conversion when the bulkiness of the alkyl groups increased. Thus, **6** and $(n\text{-Bu})_3SnH$ yielded 81% **22** when the reduction was carried on for 24 h, while 84% **23** was obtained after 5 days. Obviously, the $CFBr_2$ group is reduced faster than the $SiMe_2Cl$ moiety while the above-mentioned yields of the incomplete reduction of **4** suggest that reduction of the $CFBr_2$ group is significantly slower than that of the $SiCl_3$ group.

Experiments aimed at replacing the reducing agent $(n\text{-Bu})_3SnH$ by $LiAlH_4$ were not successful. Thus, the reaction of **22** with $LiAlH_4$ in $(n\text{-Bu})_2O$ at room temperature gave Me_3SiH in quantitative yield. Whether the CH_2F group is reduced, or a dyotropic rearrangement of intermediate CH_2FSiMe_2H to Me_3SiF occurs, as was observed in the thermal decomposition of **1** ($\rightarrow CH_3SiH_2F$),[7] is not clear at present.

All compounds **21**–**29** were characterized by multinuclear NMR spectra (see below). Some physical properties are collected in Table II. Vibrational spectroscopic and mass spectral data are set out in the Experimental Section.

Reactions of (Fluoromethyl)silanes with $SnCl_4$. Since the reduction of organo(dibromofluoromethyl)silicon halides could not be directed selectively to the corresponding organo(fluoromethyl)silicon halides, **22** being a favorable exception, reactivity at silicon had to be recovered by functionalization of the Si–H bonds. Hydrogen/halogen exchange with electrophilic halides, e.g. of Sn and B, is well documented.[20]

We have investigated in some detail the reactions of **1**, **21**, and **23** with $SnCl_4$. It was found that **1** and $SnCl_4$ yield CH_2FSiH_2Cl (**30**) almost quantitatively when reacted for 5 h at room temperature in a 1:1 molar ratio (eq 4); see

$$CH_2FSiH_3 + SnCl_4 \rightarrow CH_2FSiH_2Cl + SnCl_2 + HCl \tag{4}$$

Table IV for details. An excess of $SnCl_4$, molar ratio 1:10, gave after 5 days at room temperature only a complex mixture of compounds rather than the desired dichloro species **19**, of which only minor amounts were found. Several products were identified by ^1H and ^{19}F NMR spectroscopy, among them as the main component **30**, and furthermore CH_2FCl ($\delta(^{19}F)$ −169.8 ppm, t, $^2J(FH)$ 47.9 Hz), CH_2FSiH_2F (**31**), $CH_2FSiHFCl$ (**32**), and CH_2FSiF_3 (**33**). Their NMR data are reported in the appropriate sections, and their constitutions have been, in part, confirmed by independent syntheses. Furthermore, the ^{19}F NMR resonance second in intensity is attributed to CH_2ClSiH_2F ($\delta(^{19}F)$ −187.9 ppm, tt, $^2J(FH)$ 49.2 Hz, $^3J(FH)$ 3.2 Hz), while a weak signal ($\delta(^{19}F)$ −143.4 pm, dt, $^2J(FH)$ 68.4 Hz, $^3J(FH)$ 3.2 Hz) was assigned to $CH_2ClSiHFX$, X = F or Cl. None of the resonances could be attributed to C_2H_5Si derivatives since no signals were present in the 0–1.6 ppm range of the ^1H NMR spectra, resonances at 2.6–2.9 ppm on the other hand strongly supporting the presence of CH_2ClSi groups. The component third in abundance, with $\delta(^{19}F)$ −146.5 ppm, tq, $^1J(F^{29}Si)$ 304.1 Hz, $^2J(FH)$ 65.3 Hz, $^3J(FH)$ 4.3 Hz, has not yet been identified.

This formation of CH_2ClSiF derivatives may be accounted for by a dyotropic rearrangement of a CH_2FSiCl entity. This is initiated by an insertion of CH_2 into a SiCl bond, with concomitant formation of an energetically favored SiF bond. The likelihood of this rearrangement is strongly supported by the analogous one of $CH_2FSiHClMe$ (**34**) and CH_2FSiBr_2Me occurring in C_6D_6 solution, by which $CH_2ClSiHFMe$ and $CH_2BrSiFBrMe$ are formed in the course of several months in a clean and quantitative reaction (see below).

While the reaction of **23** with $SnCl_4$ (see Table IV) gave 98% **22**, that of **21** proceeded less specifically. Reaction in a 1:0.9 ratio for 20 min at room temperature yielded ca. 40% of the desired product, **34**, and the excess of **21** could be recovered by fractional distillation. When **21** and $SnCl_4$ in a 1:1 molar ratio were kept at room temperature for 4 h, less **34** was obtained, and dismutation and rearrangement products were identified: $CH_2FSiHFMe$ (**35**) ($\delta(^{19}F)$ −276.3 ppm, tdd, CF, −179.9 ppm, dm, SiF, $^2J(HCF)$ 47.2 Hz, $^2J(HSiF)$ 51.8 Hz, $^3J(FCSiH)$ 11.3 Hz, $^3J(FCSiF)$ 3.9 Hz) and Me_2SiHF were found.

More forcing conditions, with $SnCl_4$ and **21** in a 2.2:1 molar ratio afforded a multicomponent mixtur after 2 days at room temperature. Its major constituent, CH_2FSiCl_2Me, was identified by its ^{19}F NMR spectrum, $\delta(^{19}F)$ −281.1 ppm, t, $^2J(FH)$ 47.2 Hz. However, separation from accompanying products, mostly **34** and **35**, was not possible.

Reactions of (Fluoromethyl)silanes with Bromine. The halogenation of SiH functions is a standard procedure for the synthesis of halosilanes under mild conditions.[21] However, the chlorination of **1** with Cl_2 in CH_2Cl_2 could not be controlled even when this was carried out at −100 °C. Repeatedly, explosions occurred, with concomitant deposition of carbon and complete decomposition.

In contrast bromination with Br_2 in CH_2Cl_2 proceeded smoothly at room temperature (Table IV), and CH_2FSiBr_3 (**36**) was isolated with a yield of 75%. Some minor amounts of $CH_2FSiHBr_2$ (**37**) were obtained as well. Analogously, the bifunctional derivative $CH_2FSiMeBr_2$ (**38**) was synthesized with a yield of 63% by the reaction of **21** with Br_2 for 16 h, Table IV.

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Table IV. Halogenation of (Fluoromethyl)silanes at Room Temperature

reactant	halogenating agent	reaction time	molar ratio	product	trapping *T*, °C	% yield
1	$SnCl_4$	5 h	1:1	CH_2FSiH_2Cl (**30**)	−115	98
21	$SnCl_4$	20 min	1:0.9	$CH_2FSiHClMe$ (**34**)	−90	40
23	$SnCl_4$	12 h	1:1.1	$CH_2FSiClMe_2$ (**22**)	−90	98
1	Br_2	2 days	1:3	CH_2FSiBr_3 (**36**)		75
				$CH_2FSiHBr_2$ (**37**)[a]		7
21	Br_2	16 h	1:2	CH_2FSiBr_2Me (**38**)		63

[a] Purity ca. 90%.

Table V. NMR Chemical Shifts δ (ppm) and Coupling Constants *J* (Hz)

	4	**15**	**23**	**34**	**46**	**44**
$\delta(\mathrm{C}H_3)$			0.09	0.31	0.10	0.03
$\delta(\mathrm{C}H_2\mathrm{F})$			4.37	4.27/4.31	4.42	4.36
$\delta(\mathrm{Si}H)$		4.43	4.08	4.77	3.98	
$\delta(^{13}C\mathrm{H_3})$			−7.0	−3.1		−7.8
$\delta(^{13}C\mathrm{F})$	90.4		79.0	78.1		78.0
$\delta(^{19}F)$	−86.0	−73.2	−270.5	−274.6	−268.6	−277.9
$\delta(^{29}Si)$	−5.1		−18.1			−4.6
$^1J(^{13}CF)$	333.4	335.8	160.7	163.7		159.8
$^1J(H^{29}Si)$			(−)179.1			
$^2J(H\mathrm{Si}D)$					1.0	
$^2J(HCH(\mathrm{F}))$				14.0		
$^2J(H\mathrm{Si}^{13}C(\mathrm{F}))$			9.3			
$^2J(HCF)$			47.3	47.1	47.1	47.4
$^2J(H_3\mathrm{C}^{29}Si)$			7.6			7.0
$^2J(H_2\mathrm{CF}^{29}Si)$			2.1			2.2
$^2J(F^{29}Si)$	49.3		(−)22.0	28.6		21.5
$^3J(H_3\mathrm{CSi}H)$			3.7	3.2	4.2	
$^3J(H_3\mathrm{CSi}D)$					0.6	
$^3J(H_2\mathrm{C(F)Si}H)$			2.3	2.8/1.6	2.9	
$^3J(H_2\mathrm{C(F)Si}D)$					0.4	
$^3J(H\mathrm{CSi}^{13}C(\mathrm{F}))$			2.5			
$^3J(F\mathrm{CSi}H)$		6.7	13.0	9.1	14.5	
$^3J(F\mathrm{CSi}^{13}C\mathrm{H_3})$			3.0	1.7		3.0
$^3J(F\mathrm{CSi}^{13}C\mathrm{F})$						3.4
$^4J(H_3\mathrm{CSiC}F)$			0.5	0.7		0.7

In summary, the halogenation of **1** and **21** with Br_2, and of **23** with $SnCl_4$, provides tri-, bi-, and monofunctional alkyl(fluoromethyl)silicon halides in good to excellent yields. These fluoro-substituted methylsilicon halides are now easily accessible and useful starting materials for the synthesis of methylsilicon derivatives which have been modified by a peripheral fluorine atom. Some substitution reactions of **36** will now be described.

Substitution Reactions of 36. In order to test the resistance of the CH_2FSi group toward nucleophilic substitution at silicon, we have studied the performance of **36** in some standard organosilicon reactions. According to the position of the Si–Br bond in the well-known conversion series,[22] **36** is expected to react with heavy metal halides MY_n, M = Ag, Hg; Y = Cl, NCO, NCS, F, O/2, etc. Furthermore, halogen exchange reactions with SbF_3 have been reported.[23]

The reaction of **36** with Ag[OCN], AgCl, and SbF_3 gave the corresponding CH_2FSiY_3 derivatives with Y = NCO (**39**), Cl (**20**), and F (**33**) in moderate to good yields. While the reactions with Ag[OCN] and SbF_3 proceed rapidly, that with AgCl required a reaction time of 12 h, and the trichloride **20** still contained a product with SiF bonds as evident from an infrared absorption at 936 cm^{-1}.

Nucleophilic substitution by methoxy and phenyl groups was achieved by reacting **36** with MeOH and PhLi, respectively. The triphenylsilane **40** is the first CH_2FSi derivative which is crystalline at room temperature. The methoxy derivative $CH_2FSi(OMe)_3$ (**41**) was difficult to separate from residual MeOH, which apparently catalyzed a slow decomposition of the CH_2FSi moiety. The residue of the reaction exerted ^{19}F NMR signals at −143 and −145 ppm, which indicates the presence of SiF groups.

Bis(fluoromethyl)dimethylsilane. A main aim of the present study was to link more than one single CH_2F group to silicon. The versatility of the reaction eq 3 is a promising entry into CH_2F polysubstitution. Investigations of $(CF_3)_nSi$ derivatives have shown however that their stability decreases significantly with increasing *n*.[6,12] In addition, the ease of CF_2 insertion into Si–H bonds to yield $(CHF_2)_nSi$ derivatives also decreases substantially with *n*.[24] Unfortunately, attempts to react $SiCl_4$ with a 2–3-fold excess of the reagent combination $CFBr_3$/**3** in CH_2Cl_2 at −20 °C did not yield any $CFBr_2Si$ derivatives at all. Since even **4** was not found among the reaction products, we conclude that **3** has attacked a CBr bond of **4** prior to any disubstitution. In addition, the reactions of **36** and **38** with $CFBr_3$/**3** in CH_2Cl_2 degraded the CH_2F groups completely and yielded numerous fluorine-containing products. The ^{19}F and ^1H NMR spectra of the crudely fractionated samples suggested the presence of $CH_2BrSiFBr_2$ ($\delta(^{19}F)$ −141.3 ppm, t, $\delta(^1H)$ 2.64 ppm, d, $^3J(FH)$ 2.8 Hz) and $CH_2BrSiFBrMe$ (**42**) (see NMR data below), which may be dyotropic rearrangement products of **36** and **38**, respectively.

Finally, the dibromofluorination of $CH_2FSiClMe_2$ (**22**) with 1 equiv **3** and 1.3 equiv $CFBr_3$ in CH_2Cl_2 at −20 °C gave 65% $CH_2F(CFBr_2)SiMe_2$ (**43**) whose reduction with 4.2 equiv $(n\text{-}Bu)_3SnH$ afforded a 73% yield of $(CH_2F)_2$-

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$SiMe_2$ (**44**). This is the first bis(fluoromethyl)silicon derivative to be isolated, although it had been previously identified by its NMR spectra among the products of the direct fluorination of $SiMe_4$ with a Xe/F_2 mixture.[1c,25] Likewise $(CH_2F)_2SiH_2$ and $(CH_2F)_2SiF_2$ have been detected among the thermal decomposition products of CF_3SiH_3 and $(CF_3)_2SiH_2$.[6]

Some Properties. While the $CFBr_2Si$ derivatives hydrolyze quite easily with evolution of $CHFBr_2$, the CH_2F group is almost as stable to hydrolysis and to nucleophilic attack as a methyl group. Thus, the reactivity of CH_2FSi derivatives generally resembles that of the corresponding CH_3Si derivatives.

We have found that CH_2FSi compounds are less volatile than their CH_3Si counterparts, **33** revealing a particularly low volatility, Table II. In view of the high vaporization entropy, $\Delta S_v = 106.6$ J mol^{-1} K^{-1}, we suppose that **33** is associated, presumably by H···F hydrogen bonds, although F···Si coordination cannot be ruled out. We note that **33** exhibits the largest shift of all compounds studied here of the ν(CF) stretching vibration to a small wavenumber (23 cm^{-1}) when going from the gaseous to the liquid phase.

The thermal decomposition of **1** has been studied previously.[7] At ca. 140 °C a dyotropic rearrangement occurs which is complete after 7 days and which yields CH_3SiH_2F as the primary product. While most CH_2FSi compounds are stable at room temperature for months, **34** and **38**, dissolved in C_6D_6, rearranged completely and selectively within several months at room temperature to yield $CH_2ClSiHFMe$ (**45**) and $CH_2BrSiFBrMe$ (**42**), respectively. This rearrangement resembles that occurring during the thermal decomposition of **1**.

NMR Spectra. A CH_2FSi group comprises four atoms which can be easily studied by ^1H, ^{13}C, ^{19}F, and ^{29}Si spectroscopy, and many of the other substituents linked to silicon have NMR active nuclei as well. Since almost all evidence for the identification, constitution, conformation and purity of the novel compounds is based on their NMR spectra, elemental analyses of gaseous material in general not being practicable and significant, the NMR spectra of representative examples will be discussed in some detail here. The data related to the other compounds are reported in the Experimental Section. Furthermore, attempts will be made to derive a set of increments with which the NMR parameters can be reproduced.

The examples discussed here include **4** and **15** as typical $CFBr_2Si$ derivatives and the "normal" CH_2FSi species **23**. Compound **34** is included as an example for magnetically nonequivalent CH_2F protons, while the monodeuteriosilane $CH_2FSiHDMe$ (**46**) (prepared from **34** and $(n\text{-}Bu)_3SnD$ with 83% yield) serves to derive the geminal ^2J(HD) coupling constant. Finally, **44** is included as an example for bis(fluoromethyl)silane derivatives. Chemical shifts and coupling constants are reported in Table V.

CFBr₂Si Derivatives. The NMR parameters of the Si–alkyl groups do not reveal any unexpected features. The ^{13}C signal of the $CFBr_2$ group is observed in the 90–105 ppm region and shifted 10–30 ppm to high field in comparison to analogous CF_3Si and $CFCl_2Si$ derivatives. Both the chemical shift and $^1J(^{13}CF)$ are sensitive to the other substituents at silicon, replacement of Cl by R in compounds $CFBr_2SiCl_nR_{3-n}$ producing a systematic ^{13}C low field shift and a 1–3-Hz increase of $^1J(^{13}CF)$ per replaced Cl atom. The ^{13}C resonances of the R groups of 8–11, 13, and 14 were assigned with the help of J-modulated spin echo spectra.[26]

Table VI. Substituent Increments β for $^2J(F^{29}Si)$ of Compounds $CFBr_2SiCl_nR_{3-n}$ (Hz)

x, y, z	β	x, y, z	β
Cl, Cl	16.5	Cl, *i*-Bu	9.6
Cl, Me	10.7	Cl, *s*-Bu	9.2
Cl, Et	9.8	Me, Me	8.2
Cl, *n*-Pr	9.8	Et, Et	5.6
Cl, *n*-Pr	9.5	*n*-Bu, *n*-Bu	6.4

The range of the ^{19}F chemical shift for the $CFBr_2$ group is from −76 to −90 ppm, and there is no apparent simple correlation of $\delta(^{19}F)$ with the electronic properties of the other substituents at silicon.

There is however a dependence of $\delta(^{29}Si)$ on the substituents at silicon. Likewise, the resonance of **4** is shifted from that of mono- and polyalkylated $CFBr_2Si$ species by 15 and 20–30 ppm to a high field, respectively. The absolute value of $^2J(F^{29}Si)$ increases with decreasing number of alkyl substituents. Group increments β were deduced according to ref 27 from eq 5, which reproduce $^2J(F^{29}Si)$ within about 1%, Table VI.

$$^2J(F^{29}Si)\ (Hz) = \beta_{xy} + \beta_{xz} + \beta_{yz} \qquad (5)$$

CH₂FSi Compounds. While the ^1H (3.86–5.24 ppm) and ^{29}Si chemical shifts (−72.9 to +22.2 ppm) of the CH_2FSi group are hardly characteristic, the ^{19}F and ^{13}C shifts, −252.7 to −285.0 and 68.8–80.7, ppm, respectively, exert quite narrow and specific ranges. The ^2J(HF), 46.5–47.4 Hz, and $^1J(F^{13}C)$ couplings, 156.9–181.0 Hz, are diagnostic of intact CH_2F groups. The $^2J(F^{29}Si)$ coupling constant has been shown to decrease in the series $CF_3SiH_3 \rightarrow CHF_2SiH_3 \rightarrow CH_2FSiH_3$ from 48.8 via 34.1 to 26.6 Hz,[7] but in spite of this apparent regularity its absolute value for CH_2FSi derivatives spans a quite large interval, 19.1–41.4 Hz.

In general the NMR spectra are of first order except for the alkyl groups. Unexpectedly, the ^1H coupled ^{29}Si spectrum of **23** appeared to be of higher order. However, inspection of its ^1H NMR spectrum reveals that for the given magnetic field, the ^{29}Si satellite of the SiH resonance happens to be close to the high frequency portion at 4.46 ppm of the CH_2F group. Hence the accidently almost degenerate transitions mix and perturb the ^{29}Si signal. This perturbation allows a determination of the coupling constants $^1J(H^{29}Si)$, ^2J(HCF), $^2J(HC(F)^{29}Si)$, $^2J(FC^{29}Si)$, ^3J(FCSiH), and ^3J(HC(F)SiH), Table V, by means of the simulation of the $\{CH_3\}$ decoupled ^{29}Si NMR spectrum. Assuming a negative sign[28] for $^1J(H^{29}Si)$, a negative sign was also deduced for $^2J(FC^{29}Si)$, while all other coupling constants were found to be positive. The observed and simulated $^{29}Si\{CH_3\}$ NMR spectra of **23** are illustrated in Figure 1.

Compound **34**, which disposes over four different substituents at silicon, represents an L_3ABMX spin system, with a pronounced AB structure for the magnetically nonequivalent protons of the CH_2FSi group, $\Delta\delta$ = 0.04 ppm. The geminal HH′ coupling constant and the vicinal ^3J(HH) constants were extracted from the spectrum.

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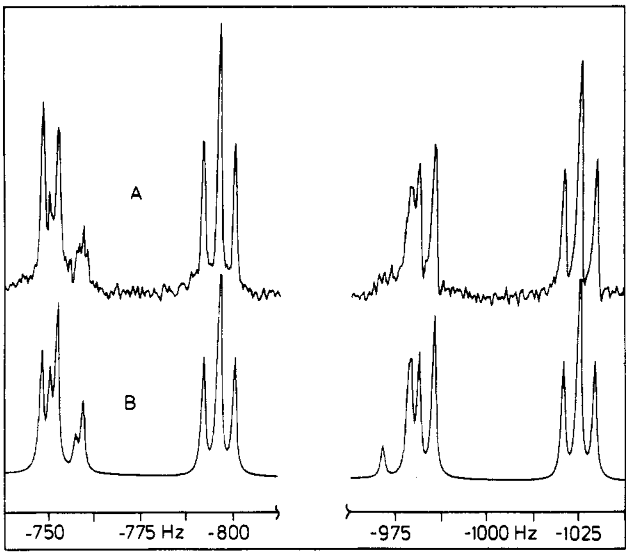

Figure 1. $^{29}Si\{CH_3\}$ NMR spectrum of **23**: (A) experimental spectrum; (B) simulated spectrum.

The analysis of the ^1H NMR spectrum of **46** gave access to the geminal coupling constant $^2J(HSiD)$ = 1.03 Hz. Employing the magnetogyric ratio $\gamma(H)/\gamma(D) = 6.5$,[26] the coupling constant $^2J(HSiH)$ is calculated to be 6.7 Hz.

The diagnostic value of the NMR spectra for the characterization of novel CH_2FSi species is nicely demonstrated by the ^{29}Si NMR spectrum of **44** (Figure 2). Here, a triplet of septets of quintets gives rise to a specific multiplet structure, Table V.

The ^1H-decoupled ^{29}Si NMR spectrum of **39** reveals a doublet at −72.6 ppm, $^2J(F^{29}Si)$ 33.5 Hz, whose lines show a half-width of ca. 30 Hz. This signal broadening is obviously caused by the quadrupole moment of the nuclear spin $I = 1$ nuclei of the nitrogen atoms directly bonded to silicon. This is a proof of Si–NCO rather than Si–OCN bonding.[29]

IR and Raman Spectra. We have recorded gas phase IR and in many cases also liquid phase Raman spectra of all mentioned compounds which were isolated. Diagnostic wavenumbers and corresponding intensities are reported in the Experimental Section. Some general comments will be made here.

The $CFBr_2Si$ group behaves as if it were a perturbed $CFBr_2Cl$ molecule whose spectrum has been analyzed,[30] and similarities are also evident with $CFBr_3$.[30] However, couplings with the other substituents X at silicon occur when these are heavy (X = Cl, Br), and furthermore the CBr_2 and CSi vibrations fall into the range of those of the SiX_3 group.

The CF stretching vibration, very strong in the IR and weak in the Raman effect, is quite characteristic and observed in the 1030–1080-cm^{-1} range (cf., $CFBr_2Cl$ 1075 and $CFBr_3$ 1069 cm^{-1}). The "upper" asymmetric CBr_2 stretching vibration spans the 600–880-cm^{-1} range. This dispersion is due to the fact that the CBr_2Si moiety exerts a "pulsation" near 400 cm^{-1} (4 396 cm^{-1}, $CFBr_3$ 398 cm^{-1}) and two (upper and lower) asymmetric stretches related to the degenerate stretch of $CFBr_3$ at 743 cm^{-1}. These may be described very approximately as ν_{as} and $\nu_s(CBr_2)$, respectively. They are sensitively balanced under the influence of further substituent vibrations and observed for example in **4** at 851 cm^{-1} (IR, Raman) and 629 cm^{-1} (IR). In the corresponding alkylsilicon species the "pulsation" is shifted with increasing number of alkyl groups to a small wavenumber while that of $\nu_{as}(CBr_2)$ is shifted to a large wavenumber, obviously as a consequence of repulsion by the Si–alkyl stretching vibrations occurring in the 600–750-cm^{-1} range.

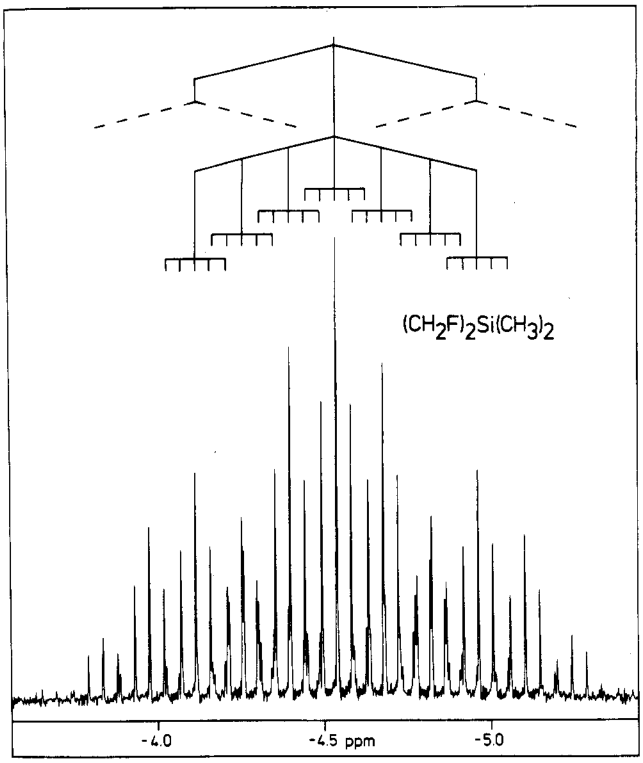

Figure 2. ^{29}Si NMR spectrum of **44**.

The vibrational spectra of the (fluoromethyl)silane derivatives reveal great similarities to that of **1**, which has been analyzed in detail with the assistance of a normal coordinate analysis.[7] The CF stretching vibration is associated with a strong IR absorption, coincident with a weak Raman line, in the 990–1045-cm^{-1} range. In comparison to the $CFBr_2$ derivatives this vibration is shifted to a small wavenumber due to a reversal of the coupling repulsion, $\delta(CH_2)$ above $\nu(CF)$ rather than $\nu(CF)$ above $\nu(CBr_2)$. Evidence for coupling effects across the silicon atom is clearly evident. Likewise, **33** reveals the highest $\nu(CF)$ vibration (1045 cm^{-1}) of all CH_2FSi compounds so far studied, the SiF stretching vibrations at 992 cm^{-1} (species e for C_{3v} symmetry) and 889 cm^{-1} (a_1) causing this high wavenumber shift. The IR spectrum of **33** is illustrated in Figure 3, the high intensity of the SiF_3 vibrations clearly exceeding that of $\nu(CF)$. The degeneracy of $\nu_{as}(SiF_3, e)$ is apparently not raised. The SiC stretching vibration, 693 cm^{-1}, is associated with an extremely strong Raman line, the corresponding IR absorption being too weak to be observed. On the other hand, both SiF stretching vibrations are very strong in the IR, which is evidence of pseudotetrahedral behavior of the $CSiF_3$ group, with $\nu(SiC)$ corresponding to the a_1 mode, and the two SiF_3 stretches (a_1 + e) correlating with the tetrahedral f_2 mode.

On the other hand, the CH_2F group has a significant effect on SiH_n vibrations. This is particularly evident for the monohydrides **23** and **25** whose $\nu(SiH)$ vibration is associated with two and three bands at 2153/2134 and 2140/2128/2118 cm^{-1}, respectively. Correspondingly, $\nu(CF)$ of **23** is associated with two absorptions at 1008 and 996 cm^{-1}. These effects are due to the presence of *trans* and

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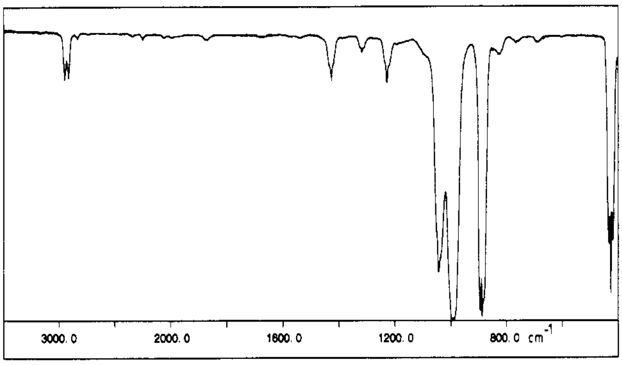

Figure 3. Gas phase IR spectrum of **33**.

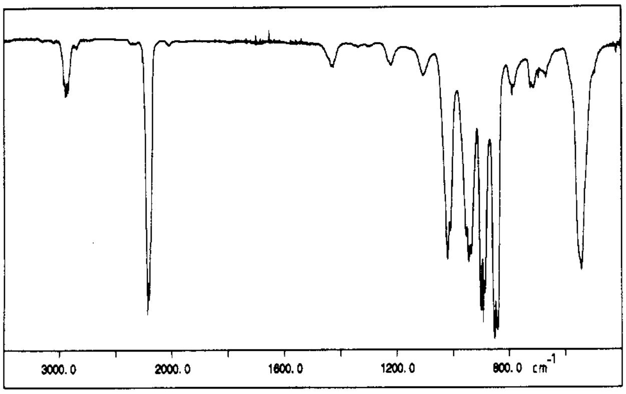

Figure 4. Gas phase IR spectrum of **30**.

gauche conformers, and in addition the two Et groups of **25** cause further conformational multiplicity. Such conformational effects have been studied for deuterated RSiHD$_2$ species and their germane and stannane analogs by McKean *et al.*[31] For example, two ν(SiH) IR absorptions at 2193 and 2166 cm^{-1} observed in CH$_2$ClSiHD$_2$ were assigned to the *gauche* and *trans* (SiH/CCl) species.

The IR (Figure 4) and Raman spectra of **30** may illustrate the vibrational behavior of CH$_2$FSiH$_2$X-type molecules. The Si–X bond is associated with the intense SiCl stretching vibration at 541 cm^{-1}, while the four strong absorptions in the 1100–800-cm^{-1} region are assigned to ν(CF) (1018 cm^{-1}), δ(SiH$_2$) (946 cm^{-1}), ω(SiH$_2$) (894 cm^{-1}), and ρ(CH$_2$) (847 cm^{-1}).

As a general observation the substantial phase shifts should be mentioned. These are evident from a comparison of the gas phase IR with liquid phase Raman wavenumbers and are particularly pronounced for CF and SiX stretching vibrations. Typically, these amount to ~15–20 cm^{-1} for ν(CF) and, e.g., 20 cm^{-1} for ν(SiCl) in **30**, the Raman lines lying consistently at smaller wavenumbers.

Diagnostic (incomplete) IR absorptions and Raman lines of the investigated compounds are quoted in the Experimental Section, and some assignments are given there.

Mass Spectra. We have recorded EI mass spectra of **23**, **24**, **27**, and **28**. Major fragments and their relative intensities are set out in the Experimental Section. In view of the detailed characterization of the compounds by multinuclear NMR spectra, it seemed sufficient to study only a representative series of compounds.

The M$^+$ ion has low to medium intensity while the [M – CH$_2$F]$^+$ ion is either the base peak (**23**, **24**) or second (**27**) and third (**28**) in intensity. Fragmentation of the alkyl group competes with CH$_2$F–Si bond fission, the former gaining importance with increasing size of the alkyl group. Thus, the fragment [M – CH$_2$F – C$_2$H$_4$]$^+$ is the base peak of **27** and **28**. Interestingly, the ions [SiH$_2$F]$^+$ and [SiF]$^+$ are of considerable intensity; these ions originate, however, from secondary reactions involving a dyotropic CF/SiH rearrangement. Analogous reactions of SiH$_4$ with CF$_3$$^+$ and SiH$_3$$^+$ with CHF$_3$ have been reported.[32]

Experimental Section

General Remarks. Reactions were in general carried out either in standard glass equipment under dried N$_2$ or in sealed ampules which were connected to a standard vacuum line operated at a pressure of 10^{-2}–10^{-3} mbar. Molecular weights of **24**–**27** were determined by the Regnault method using a MKS Baratron 315 BHS capacitance manometer and a Pt 100 resistance thermometer. NMR spectra were recorded on solutions in C$_6$D$_6$ or CDCl$_3$ with the following instruments: ^{1}H, Varian EM 390, 90.0 MHz, and Bruker AC 250, 250.0 MHz, C$_6$D$_6$ or CDCl$_3$ as internal standards, δ(^{1}H) 7.27 ppm; ^{13}C, Bruker AC 250, 62.8 MHz, C$_6$D$_6$ or CDCl as internal standards, δ(^{13}C) 128.0 and 77.0 ppm, respectively; ^{19}F, Varian EM 390, 84.7 MHz, and Bruker AC 250, 235.4 MHz, external standard CFCl$_3$; ^{29}Si, Bruker AC 250, 49.7 MHz, external standard TMS. IR spectra were recorded of gaseous or liquid samples (**41** as CsI pellet) with a Perkin-Elmer 580 B (4000–200 cm^{-1}) grating and Bruker IFS 25 FT spectrometer (4000–400 cm^{-1}); wavenumber accuracy ±2 cm^{-1}. Raman spectra were obtained with a Cary 82 spectrometer, excitation Kr$^+$ 647.1 nm, of samples in 1- or 4-mm glass tubes. EI mass spectra were measured with a Varian MAT 311a instrument, ionization energy 70 eV.

Materials. Solvents were purified and dried by standard methods. The starting materials **3**, CBr$_4$, SbF$_3$, SiCl$_4$, SnCl$_4$, Me$_n$SiCl$_{4-n}$, *n*-PrSiCl$_3$, (*i*-Pr)$_3$SiCl, (*n*-Bu)$_3$SiCl, (*i*-Bu)$_3$SiCl, Ph$_3$SiCl, and (*n*-Bu)$_3$SnH were commercially available, *t*-BuSiCl$_3$ and *i*-BuSiCl$_3$ were taken from the laboratory stock. The compounds *i*-PrSiCl$_3$, *s*-BuSiCl$_3$, and (*s*-Bu)$_2$SiCl$_2$ were prepared according to standard procedures.[33] CFBr$_3$ was obtained in an 84% yield from CBr$_4$ and SbF$_3$.[34]

Reaction of 3/CFBr$_3$ with SiCl$_4$ and Alkylchlorosilanes. An equimolar quantity of **3** was added at –20 °C within 1 h to a solution of CFBr$_3$ and a chlorosilane (mole ratio 1:1) in CH$_2$Cl$_2$ (1 mL/mmol). Stirring was continued at room temperature for 1 h and thereafter the reaction mixture fractionated in vacuo. Products **4**–**8**, **10**, and **11** were trapped at –40 °C. The less volatile compounds **9**, **12** (contained (*n*-Bu)$_3$SiCl), **13**, and **14** were worked up by filtration of the reaction mixture, extraction of the unsoluble salts with CH$_2$Cl$_2$, evaporation of the solvent at ambient pressure, and distillation in vacuo. For boiling points see Table II, for yields Table I.

(Dibromofluoromethyl)trichlorosilane (4). For NMR see Table V. IR (gas)/Raman (solid), cm^{-1}; 1060 (s)/1055 (w), ν(CF); 851 (m)/855 (m), ν_{as}(CBr$_2$); 714 (s)/709 (m), 683 (m)/685 (w), ν_{as}(SiCl$_3$); 629 (vs)/630 (w), ν_s(CBr$_2$); 508 (vs)/507 (w), ν_s(SiCl$_3$); –/396 (vs), ν(Si–CFBr$_2$).

(Dibromofluoromethyl)methyldichlorosilane (5). NMR: δ(^{1}H) 1.10 ppm, ^2J(H^{29}Si) 8.1 Hz; δ(^{19}F) –90.1 ppm, ^2J(F^{29}Si) 37.6 Hz; ^{13}C δ(CH$_3$) 1.5 ppm, δ(CFBr$_2$) 94.1 ppm, d, ^1J(F^{13}C) 336.5 Hz; δ(^{29}Si) 10.4 ppm, d. IR (gas)/Raman (solid), cm^{-1}: 2994 (w)/–, 2986 (w)/–, –/2918 (m), ν(CH); 1410 (w)/1402 (w), δ_{as}(CH$_3$); 1269 (m)/–, δ_s(CH$_3$); 1077 (s)/1056 (w), 1046 (s)/–, ν(CF); 860 (m)/854 (m), ν_{as}(CBr$_2$); 804 (vs)/–; 780 (s)/–; 749 (s)/756 (m); 707 (s)/–; 690 (m)/685 (m); 588 (vs)/584 (m), 509 (vs)/499 (m), ν(SiCl$_2$); 417 (w)/419 (vs), ν(Si–CFBr$_2$). Anal. Calcd for C$_2$H$_3$Br$_2$Cl$_2$FSi: Br, 52.43; Cl, 23.26; F, 6.23. Found: Br, 53.86; Cl, 21.34; F, 7.51.

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(34) Rathsburg, H. *Chem. Ber.* **1918**, *51*, 669.

(Dibromofluoromethyl)dimethylchlorosilane (6). NMR: $\delta(^{1}H)$ 0.73 ppm, $^{2}J(H^{29}Si)$ 7.2 Hz; $\delta(^{19}F)$ −81.3 ppm, $^{2}J(F^{29}Si)$ 29.9 Hz; ^{13}C $\delta(CH_3)$ −1.1 ppm, $\delta(CFBr_2)$ 98.9 ppm, d, $^{1}J(F^{13}C)$ 338.7 Hz; $\delta(^{29}Si)$ 15.0 ppm, d, $^{1}J(^{13}C^{29}Si)$ 63.3 Hz. IR (gas)/Raman (solid), cm^{-1}: 2980 (m)/2984 (w), 2918 (w)/2918 (s), $\nu(CH_3)$; 1408 (w)/1402 (w), $\delta_{as}(CH_3)$; 1264 (vs)/1268 (w), $\delta_{s}(CH_3)$; 1091 (m)/−; 1064 (vs)/1055 (w), ν(CF); 870 (s)/887 (w), $\nu_{as}(CBr_2)$; 840 (s)/838 (w); 803 (vs)/806 (m); 798 (vs)/794 (m); 752 (m)/−; 709 (s)/709 (w); 684 (vs)/683 (s), $\nu_{s}(CBr_2)$; 515 (vs)/506 (s), ν(SiCl); 408 (m)/411 (vs), $\nu(Si{-}CFBr_2)$. Anal. Calcd for $C_3H_6Br_2ClFSi$: C, 12.67; H, 2.13; Br, 56.19; Cl, 12.46; F, 6.68. Found: C, 12.99; H, 2.15; Br, 56.18; Cl, 11.46; F, 7.20.

(Dibromofluoromethyl)trimethylsilane (7). NMR: $\delta(^{1}H)$ 0.32 ppm, $^{2}J(H^{29}Si)$ 6.8 Hz; $\delta(^{19}F)$ −76.1 ppm, $^{2}J(F^{29}Si)$ 24.4 Hz; ^{13}C $\delta(CH_3)$ −3.7 ppm, $\delta(CFBr_2)$ 104.9 ppm, d, $^{1}J(F^{13}C)$ 339.7 Hz; $\delta(^{29}Si)$ 18.9 ppm, d, $^{1}J(^{13}C^{29}Si)$ 55.0 Hz. IR (gas)/Raman (solid), cm^{-1}: 2983 (w)/−, 2969 (m)/2979 (w), 2913 (w)/2910 (m), $\nu(CH_3)$; 1418 (w)/1417 (vw), $\delta_{as}(CH_3)$; 1260 (vs)/1258 (vw), $\delta_{s}(CH_3)$, 1072 (m)/−; 1046 (vs)/−, ν(CF); 877 (vs)/−, $\nu_{as}(CBr_2)$; 853 (vs)/−, $\rho(Si(CH_3)_3)$; 797 (s)/794 (m); 758 (m)/762 (w), $\rho(Si(CH_3)_3)$; 712 (s)/−; 670 (s)/664 (m), $\nu_{s}(CBr_2)$; 624 (m)/625 (m), $\nu_{s}(SiC_3)$; −/398 (vs), $\nu(Si{-}CFBr_2)$. Anal. Calcd for $C_4H_9Br_2FSi$: C, 18.20; H, 3.44; Br, 60.52; F, 7.20. Found: C, 18.55; H, 3.62; Br, 59.83; F, 7.40.

(Dibromofluoromethyl)ethyldichlorosilane (8). NMR: ^{1}H $\delta(CH_3)$ 1.05 ppm, tm, $\delta(CH_2)$ 1.23 ppm, qm, ^{3}J(HH) 7.2 Hz; $\delta(^{19}F)$ −82.3 ppm, $^{2}J(F^{29}Si)$ 35.7 Hz; ^{13}C $\delta(CH_3)$ 9.3 ppm, $\delta(CH_2)$ 6.1 ppm, $\delta(CFBr_2)$ 94.2 ppm, d, $^{1}J(F^{13}C)$ 336.5 Hz; $\delta(^{29}Si)$ 10.9 ppm. IR (gas)/Raman (liquid), cm^{-1}: 2982 (m)/2979 (w), 2954 (w)/2950 (m, p), −/2940 (sh), −/2907 (m, p), 2899 (w)/2893 (m, p), ν(CH); 1469 (w)/1465 (w), 1295 (w)/−, δ(HCH); 1172 (m)/−; 1070 (s)/1063 (w, p), ν(CF); 1044 (m)/1040 (w, p); 1016 (m)/1015 (w, p); 850 (w)/846 (m, p); 839 (w)/838 (m, p); 751 (m)/742 (w, p); 712 (vs, PQR)/714 (w); −/682 (w); 602 (s)/−; 507 (s)/505 (m, p), $\nu_{s}(SiCl_3)$; −/429 (vs, p); −/420 (vs, p); −/394 (vs, p), $\nu(Si{-}CFBr_2)$.

(Dibromofluoromethyl)diethylchlorosilane (9). NMR: $\delta(^{1}H)$ 1.18 ppm; $\delta(^{19}F)$ −76.5 ppm, $^{2}J(F^{29}Si)$ 25.2 Hz; ^{13}C $\delta(CH_3)$ 5.7 ppm, $\delta(CH_2)$ 6.4 ppm, $\delta(CFBr_2)$ 98.5 ppm, d, $^{1}J(F^{13}C)$ 340.2 Hz; $\delta(^{29}Si)$ 24.4 ppm, d. IR (liquid)/Raman (liquid), cm^{-1}: 2968 (s)/2977 (w), 2941 (m)/2949 (m, p), 2916 (m)/−, 2884 (s)/2891 (s, p), ν(CH); 1460 (m)/1467 (m), 1410 (m)/1416 (w), 1385 (m)/1389 (w), 1243 (m)/1245 (m, p), δ(HCH); 1046 (s)/1050 (w, p), 1022 (s)/1016 (m, p), ν(CF); 970 (w)/981 (m); 825 (m)/830 (s, p); 737 (s)/743 (m, p); 680 (vs)/680 (m); 638 (m)/640 (m, p); 498 (s)/504 (m, p), ν(SiCl); 448 (w)/452 (m, p); 422 (w)/414 (vs, p), $\nu(Si{-}CFBr_2)$.

(Dibromofluoromethyl)-*n*-propyldichlorosilane (10). NMR: ^{1}H $\delta(CH_3)$ 0.86 ppm, td, $\delta(CH_2(CH_2))$ 1.15–1.23 ppm, m, $\delta(CH_2(CH_3))$ 1.42–1.54 ppm, sext, $^{3}J(CH_3CH_2)$ 7.2 Hz, $^{3}J(CH_2CH_2)$ 7.2 Hz; $\delta(^{19}F)$ −82.5 ppm, $^{2}J(F^{29}Si)$ 36.0 Hz; ^{13}C $\delta(CH_3)$ 16.2 ppm, $\delta(C(CH_3))$ 17.0 ppm, $\delta(C(CH_2))$ 18.7 ppm, $\delta(CFBr_2)$ 94.5 ppm, d, $^{1}J(F^{13}C)$ 336.3 Hz; $\delta(^{29}Si)$ 9.4 ppm, d, $^{1}J(^{13}C^{29}Si)$ 75.0 Hz. IR (liquid)/Raman (liquid), cm^{-1}: 2963 (s)/2971 (w), 2931 (m)/2941 (s, p), −/2915 (m, p), 2900 (w)/2895 (s, p), 2975 (m)/2879 (s, p), ν(CH); 1463 (m)/−, 1457 (sh)/1454 (m), 1210 (w)/1210 (m, p), δ(HCH); 1061 (vs, b)/1067 (m, p), ν(CF); 1037 (s)/1034 (m, p); 1008 (m)/1013 (w, p); 843 (s)/846 (m, p); 741 (s)/742 (w, p); 690 (vs)/692 (m); 580 (s)/583 (w), $\nu_{as}(SiCl_2)$; 509 (s)/508 (m, p), $\nu(SiCl_2)$; 453 (m)/455 (m, p); 435 (m)/436 (s, p); 395 (w)/399 (s, p), $\nu(Si{-}CFBr_2)$.

(Dibromofluoromethyl)isopropyldichlorosilane (11). NMR: ^{1}H $\delta(CH_3)$ 1.28 ppm, d, δ(CH) 1.85 ppm, sept, ^{3}J(HH) 7.3 Hz; $\delta(^{19}F)$ −79.4 ppm, $^{2}J(F^{29}Si)$ 35.3 Hz; ^{13}C $\delta(CH_3)$ 16.7 ppm, δ(CH) 16.6 ppm, $\delta(CFBr_2)$ 93.9 ppm, d, $^{1}J(F^{13}C)$ 336.2 Hz; $\delta(^{29}Si)$ 10.7 ppm, d. IR (liquid)/Raman (liquid), cm^{-1}: 2960 (s)/2964 (w), 2940 (s)/2943 (m, p), 2898 (s)/2903 (w, p), 2878 (s)/2878 (m, p), ν(CH); 1458 (s)/1452 (w), 1397 (m)/1397 (w), 1362 (m)/−, 1249 (w)/1249 (m, p), δ(HCH); 1040 (s, b)/1040 (w, p), ν(CF); 1008 (s)/1012 (w, p); 880 (s)/883 (w, p); 838 (s)/840 (m, p); 700 (s)/703 (w); 670 (vs)/677 (w, p); 597 (vs)/600 (w), $\nu_{as}(SiCl_2)$; 505 (vs)/508 (w, p), $\nu_{s}(SiCl_2)$; 435 (m)/440 (s, p); 395 (w)/402 (vs, p), $\nu(Si{-}CFBr_2)$.

(Dibromofluoromethyl)tri-*n*-butylsilane (12). NMR: $\delta(^{19}F)$ −78.9 ppm, $^{2}J(F^{29}Si)$ 19.2 Hz; ^{13}C $\delta(CFBr_2)$ 103.0 ppm, d, $^{1}J(F^{13}C)$ 340.0 Hz.

(Dibromofluoromethyl)isobutyldichlorosilane (13). NMR: ^{1}H $\delta(CH_3)$ 1.11 ppm, d, $\delta(CH_2)$ 1.47 ppm, d, δ(CH) 2.17 ppm, tsept, $^{3}J(CH_3CH)$ 6.7 Hz, $^{3}J(CH_2CH)$ 6.9 Hz; $\delta(^{19}F)$ −83.1 ppm, $^{2}J(F^{29}Si)$ 35.6 Hz; ^{13}C $\delta(CH_3)$ 24.2 ppm, $\delta(CH_2)$ 25.9 ppm, δ(CH) 25.4 ppm, $\delta(CFBr_2)$ 94.5 ppm, d, $^{1}J(F^{13}C)$ 336.9 Hz; $\delta(^{29}Si)$ 9.1 ppm, d, IR (liquid)/Raman (liquid), cm^{-1}: 2961 (vs)/2968 (w), 2935 (s)/2940 (m, p), −/2908 (m, p), 2895 (s)/−, 2878 (s)/2879 (m, p), ν(CH); 1468 (s)/1467 (w), 1395 (m)/1399 (w), 1385 (m)/1389 (w), 1337 (m)/1340 (w), 1223 (m)/1226 (w, p), δ(HCH); 1165 (m)/1169 (w); 1096 (s)/1100 (w); 1040 (vs, b)/1040 (w), ν(CF); 840 (s)/847 (m, p); 829 (sh)/830 (m, p); 751 (s)/754 (w); 732 (vs)/738 (m, p); 696 (vs)/697 (w); 682 (vs)/686 (w); 582 (vs)/585 (w), ν_{as} $(SiCl_2)$; 505 (vs)/511 (m, p), $\nu_{s}(SiCl_2)$; −/490 (m, p); 463 (s)/467 (w, p); 453 (s)/454 (w, p); −/390 (s, p), $\nu(Si{-}CFBr_2)$.

(Dibromofluoromethyl)-*sec*-butyldichlorosilane (14). NMR: ^{1}H $\delta(CH_3(CH_2))$ 1.07 ppm, t, $\delta(CH_3(CH))$ 1.28 ppm, dd, $\delta(CH_2)$ 1.38–1.75 ppm, m, δ(CH) 1.90–2.01 ppm, m, $^{3}J(CH_3CH_2)$ 7.3 Hz, $^{3}J(CH_3CH)$ 7.2 Hz; $\delta(^{19}F)$ −79.2 ppm, $^{2}J(F^{29}Si)$ 34.8 Hz; ^{13}C $\delta(CH_3)$ 12.6/23.7 ppm, $\delta(CH_2)$ 23.4 ppm, δ(CH) 12.7 ppm, $\delta(CFBr_2)$ 94.3 ppm, d, $^{1}J(F^{13}C)$ 336.3 Hz; $\delta(^{29}Si)$ 9.8 ppm, d. IR (liquid)/Raman (liquid), cm^{-1}: 2967 (vs)/2950 (w), 2933 (s)/2943 (m, p), 2874 (s)/2880 (m, p), ν(CH); 1463 (s)/1462 (m), −/1447 (m), 1386 (m)/1389 (m), 1216 (w)/1217 (m, p), δ(HCH); 1041 (vs)/1033 (m, p), ν(CF); 1008 (s)/1012 (w); 851 (s)/850 (w); 833 (s)/834 (m, p); 688 (vs)/691 (m); 662 (s)/665 (w); 599 (vs)/600 (w), $\nu_{as}(SiCl_2)$; 515 (vs)/518 (m, p), $\nu_{s}(SiCl_2)$; 442 (s)/444 (m, p); 421 (w)/422 (m, p); −/410 (s, p); 373 (m)/375 (vs, p), $\nu(Si{-}CFBr_2)$.

Reduction of (Dibromofluoromethyl)silanes. This was performed by reacting a $CFBr_2Si$ compound with an excess of $(n\text{-}Bu)_3SnH$ at room temperature in a screw cap vial. After completion of the reaction (see Table III for details), volatile products were collected in vacuo and purified by fractional condensation. Usually, it was sufficient to remove traces of excessive $(n\text{-}Bu)_3SnH$ which was condensed in a −30 °C trap.

Reaction of 4 with 2.6 equiv $(n\text{-}Bu)_3SnH$, 5 min at 25 °C, afforded a mixture of products containing 64% (dibromofluoromethyl)silane (15) [NMR data, Table V], 6% (dibromofluoromethyl)chlorosilane (17) [NMR: $\delta(^{1}H)$ 4.78 ppm, d; $\delta(^{19}F)$ −82.8 ppm, t, ^{3}J(HF) 6.4 Hz], 27% (bromofluoromethyl)silane (16) [NMR: ^{1}H δ(CH) 6.16 ppm, dq, δ(SiH) 3.99 ppm, dd, ^{3}J(HH) 2.4 Hz, ^{2}J(HF) 46.3 Hz; $\delta(^{19}F)$ −169.9 ppm, dq, ^{3}J(FH) 10.0 Hz], furthermore traces, altogether 3%, of (dibromofluoromethyl)dichlorosilane (18) [NMR: $\delta(^{19}F)$ −87.0 ppm, d, ^{3}J(FH) 4.3 Hz], (fluoromethyl)silane (1),[7] (fluoromethyl)dichlorosilane (19) [NMR: $\delta(^{19}F)$ −266.4 ppm, td, ^{2}J(FH) 47.0 Hz, ^{3}J(FH) 3.8 Hz], and (fluoromethyl)trichlorosilane (20) [NMR see below].

(Fluoromethyl)methylsilane (21). NMR: ^{1}H $\delta(CH_3)$ 0.10 ppm, t, $\delta(SiH_2)$ 3.87 ppm, dqt, $\delta(CH_2F)$ 4.43 ppm, dt, $^{1}J(H^{29}Si)$ 195.6 Hz, ^{2}J(HCF) 47.1 Hz, ^{3}J(HSiCF) 14.1 Hz, ^{3}J(H(CF)H) 2.8 Hz, $^{3}J(HSiCH_3)$ 4.2 Hz; $\delta(^{19}F)$ −268.9 ppm, tt; ^{13}C $\delta(CH_3)$ −11.3 ppm, d, $\delta(CH_2F)$ 76.6 ppm, d, $^{1}J(F^{13}C)$ 161.0 Hz, $^{3}J(F^{13}C)$ 3.0 Hz; $\delta(^{29}Si)$ −39.5 ppm, d, $^{2}J(F^{29}Si)$ 23.1 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2970 (m)/2980 (w), 2946 (m)/−, 2938 (m)/−, 2921 (sh)/2921 (s, p), ν(CH); 2165 (vs)/2165 (vs, p), $\nu(SiH_2)$; 1435 (w)/1433 (m), $\delta_{as}(CH_3)$; 1425 (w)/1423 (m), $\delta(CH_2)$; −/1303 (m, p), $\omega(CH_2)$; 1263 (m, PQR 12 [$\Delta\nu_{PR}$ 12 cm^{-1}])/1262 (m, p), $\delta_{s}(CH_3)$; 1223 (w)/1226 (w), $\tau(CH_2)$; 1007 (s, PQR 12)/986 (w), ν(CF); 948 (s, PQR 12)/950 (m), $\delta(SiH_2)$; 908 (vs, PQR 16)/−, $\omega(SiH_2)$; 766 (m)/767 (m, p); 719 (w)/718 (m, p); 694 (w)/696 (s, p); 637 (m, PQR 16)/642 (vs, p); 605 (w)/608 (m, p); 490 (m, PQR)/495 (w, p).

(Fluoromethyl)dimethylchlorosilane (22). NMR: ^{1}H $\delta(CH_3)$ 0.30 ppm, d, $\delta(CH_2F)$ 4.28 ppm, d, ^{2}J(HCF) 47.2 Hz, ^{4}J(FH) 0.8 Hz; $\delta(^{19}F)$ −268.2 ppm, t; ^{13}C $\delta(CH_3)$ −0.9 ppm, d, $\delta(CH_2F)$ 79.6 ppm, d, $^{1}J(F^{13}C)$ 162.7 Hz, $^{3}J(F^{13}C)$ 1.3 Hz; $\delta(^{29}Si)$ 22.2 ppm, d, $^{2}J(F^{29}Si)$ 27.0 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2979 (s)/2979 (m), 2952 (s)/2955 (w), 2919 (s)/2916 (vs, p), ν(CH); 1456 (sh)/1446 (w), $\delta_{as}(CH_3)$; 1421 (m)/1416 (s), $\delta(CH_2)$; −/1300 (w, p), $\omega(CH_2)$; 1262 (vs)/1267 (w, p), $\delta_{s}(CH_3)$; 1213 (m)/1223 (w), $\tau(CH_2)$; 997 (vs, PQR 11)/987 (w, p), ν(CF); 847 (vs)/848 (w, p); 810 (vs)/814 (w, p); 762 (m)/766 (w); 735 (m)/731 (w, p); 640 (s)/640 (vs, p); 502 (vs)/494 (s, p), $\nu(SiCl)$; –/481 (s, p). Anal. Calcd for C_3H_8ClFSi: C, 28.44; H, 6.37; F, 15.01. Found: C, 28.80; H, 6.27; F, 16.8.

(Fluoromethyl)dimethylsilane (23). For NMR, see Table V. IR (gas)/Raman (liquid), cm^{-1}: 2973 (s)/2976 (m), 2932 (s)/–, 2914 (sh)/2915 (vs, p), $\nu(CH)$; 2153 (vs, PQR)/–, –/2144 (vs, p), 2134 (vs, PQR)/–, $\nu(SiH)$, see text; 1428 (m, PQR)/1428 (m), $\delta_{as}(CH_3)$; –/1298 (m, p), $\omega(CH_2)$; 1260 (s, PR)/1264 (w, p), $\delta_s(CH_3)$; 1219 (w, PR)/1224 (w), $\tau(CH_2)$; 1008 (s)/–, 996 (vs)/983 (m), $\nu(CF)$; 903 (w)/895 (vs); 848 (s, PR)/850 (w); 775 (m)/779 (w); 718 (w, PR)/715 (m); 684 (w, PQR)/687 (m, p); 664 (w)/667 (s, p); 635 (sh)/640 (s, p); 616 (m, PQR)/611 (vs, p). MS [*m*/*e* (relative intensity)]: 92 (M^+, 0.5), 77 ($M - CH_3$, 5), 63 ($M - C_2H_5$, 21), 61 ($M - CF$, 5), 60 ($M - CHF$, 8), 59 ($M - CH_2F$, 100), 57 (C_2H_5Si, 5), 49 (SiH_2F, 21), 47 (SiF, 16), 45 (CH_3SiH_2, 6), 43 (CH_3Si, 11), 31 (CF, 11). Anal. Calcd for C_3H_9FSi: C, 39.08; H, 9.84; F, 20.61. Found: C, 38.95; H, 9.63; F, 20.8.

(Fluoromethyl)ethylsilane (24). NMR: ^1H $\delta(CH_3)$ 0.99 ppm, t, $\delta(CH_2)$ 0.65 ppm, qt, $\delta(SiH_2)$ 3.86 ppm, dqui, $\delta(CH_2F)$ 4.45 ppm, dt, ${}^1J(H^{29}Si)$ 195.1 Hz, ${}^2J(HF)$ 47.3 Hz, ${}^3J(HF)$ 15.0 Hz, ${}^3J(H(CF)H)$ 2.9 Hz, ${}^3J(CH_3SiH)$ 3.1 Hz, ${}^3J(CH_3CH)$ 7.8 Hz; $\delta(^{19}F)$ –268.3 ppm, tt; ^{13}C $\delta(CH_3)$ 8.70 ppm, $\delta(CH_2)$ –0.6 ppm, d, $\delta(CH_2F)$ 75.8 ppm, d, ${}^1J(F^{13}C)$ 161.2 Hz, ${}^3J(F^{13}C)$ 2.3 Hz; $\delta(^{29}Si)$ –33.2 ppm, d, ${}^2J(F^{29}Si)$ 22.0 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2969 (s)/2965 (m), 2938 (s)/2944 (s, p), –/2920 (s, p), –/2886 (s, p), $\nu(CH)$; 2150 (vs, PQR)/2155 (vs, p), $\nu(SiH)$; –/1298 (m, p), $\omega(CH_2)$; 1221 (w, PQR)/1225 (sh), $\tau(CH_2)$; –/1025 (m, p); 1008 (s)/992 (sh), $\nu(CF)$; 974 (s, PR)/975 (m, p); 939 (s, PR)/940 (m); 879 (vs, PR)/880 (w); –/703 (m, p); –/645 (s, p); –/623 (vs, p); 609 (w)/608 (vs, p). MS [*m*/*e* (relative intensity)]: 92 (M^+, 0.1), 63 ($M - C_2H_5$, 19), 62 ($M - C_2H_6$, 8), 60 ($M - CHF$, 8), 59 ($M - CH_2F$, 100), 58 ($M - CH_3F$, 15), 57 ($M - CH_2F - 2H$, 5), 49 (SiH_2F, 8), 47 (SiF, 23), 45 (CH_3SiH_2, 6), 43 (CH_3Si, 8), 31 (CF, 28), 29 (SiH/C_2H_5, 7), 27 (C_2H_3, 8). Anal. Calcd for C_3H_9FSi: C, 39.08; H, 9.84; F, 20.61. Found: C, 39.05; H, 9.78; F, 20.4.

(Fluoromethyl)diethylsilane (25). NMR: ^1H $\delta(CH_3)$ 1.02 ppm, tm, $\delta(CH_2)$ 0.51–0.64 ppm, $\delta(SiH)$ 3.94 ppm, dtqui, $\delta(CH_2F)$ 4.50 ppm, dd, ${}^1J(H^{29}Si)$ 182.1 Hz, ${}^2J(HF)$ 47.3 Hz, ${}^3J(FH)$ 14.7 Hz, ${}^3J(H(CF)H)$ 2.2 Hz, ${}^3J(HC(CH_3)SiH)$ 3.4 Hz, ${}^3J(CH_3CH_2)$ 7.9 Hz; $\delta(^{19}F)$ –271.2 td; ^{13}C $\delta(CH_3)$ 8.0 ppm, $\delta(CH_2)$ 1.3 ppm, , $\delta(CH_2F)$ 77.3 ppm, d, ${}^1J(F^{13}C)$ 160.6 Hz, ${}^3J(F^{13}C)$ 2.6 Hz; $\delta(^{29}Si)$ –8.6 ppm, d, ${}^2J(F^{29}Si)$ 19.8 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2966 (vs)/2958 (sh), 2930 (s)/2942 (s, p), –/2917 (s, p), 2898 (s)/2900 (s, p), –/2884 (s, p), 2850 (m)/–, $\nu(CH)$; 2140 (s, PQR)/–, 2128 (s)/2129 (s, p), 2118 (s, PQR)/–, $\nu(SiH)$, see text; 1472 (m)/1466(m); 1422 (m)/1420 (w); –/1296 (w, p), $\omega(CH_2)$; 1006 (s)/–, $\nu(CF)$; 978 (sh)/977 (s, p); 830 (vs, b)/832 (w); 743 (m)/750 (w, p), 607 (w)/588 (vs, p).

(Fluoromethyl)-*n*-propylsilane (26). NMR: ^1H $\delta(CH_3)$ 0.98 ppm, t, $\delta(CH_2(CH_3))$ 1.46 ppm, qt, $\delta(CH_2(CH_2))$ 0.68–0.79 ppm, $\delta(SiH_2)$ 3.85 ppm, dtt, $\delta(CH_2F)$ 4.52 ppm, dt, ${}^1J(H^{29}Si)$ 192.7 Hz, ${}^2J(HCF)$ 47.2 Hz, ${}^3J(HSiCF)$ 14.6 Hz, ${}^3J(CH_2(F)SiH_2)$ 2.9 Hz, ${}^3J((C)CH_2SiH_2)$ 3.6 Hz, ${}^3J(HCCH)$ 7.3 Hz; $\delta(^{19}F)$ –268.4 ppm, tt; ^{13}C $\delta(CH_3)$ 18.8 ppm, $\delta(CH_2(CH_3))$ 17.3 ppm, $\delta(CH_2(CH_2))$ 9.6 ppm, d, $\delta(CH_2F)$ 75.9 ppm, d, ${}^1J(F^{13}C)$ 161.8 Hz, ${}^3J(F^{13}C)$ 2.1 Hz; $\delta(^{29}Si)$ –33.4 ppm, d, ${}^2J(F^{29}Si)$ 22.2 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2968 (s)/2968 (m), 2938 (s)/2939 (vs, p), 2921 (sh)/2918 (vs, p), –/2897 (vs, p), 2886 (s)/2878 (vs, p), $\nu(CH)$; 2151 (vs)/2153 (vs, p), $\nu(SiH_2)$; –/1299 (m, p), $\omega(CH_2)$; 1223 (m)/1225 (w), $\tau(CH_2)$; 1006 (s)/986 (w), $\nu(CF)$; 940 (vs)/942 (m), $\delta(SiH_2)$; –/897 (m, p), $\omega(SiH_2)$; 888 (vs)/883 (m, p); –/617 (vs, p).

(Fluoromethyl)isopropylsilane (27). NMR: ^1H $\delta(CH_3)$ and $\delta(CH)$ 1.06 ppm, $\delta(SiH_2)$ 3.81 ppm, dm, $\delta(CH_2F)$ 4.49 ppm, dt, ${}^1J(H^{29}Si)$ 192.9 Hz, ${}^2J(HCF)$ 47.2 Hz, ${}^3J(HSiCF)$ 15.2 Hz, ${}^3J(CH_2(F)SiH_2)$ 2.7 Hz; $\delta(^{19}F)$ –268.2 ppm, tt; ^{13}C $\delta(CH_3)$ 18.9 ppm, $\delta(CH)$ 8.7 ppm, d, $\delta(CH_2F)$ 75.5 ppm, d, ${}^1J(F^{13}C)$ 161.5 Hz, ${}^3J(F^{13}C)$ 1.8 Hz; $\delta(^{29}Si)$ –27.6 ppm, d, ${}^2J(F^{29}Si)$ 20.9 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2952 (vs)/2955 (sh), –/2922 (s, p), 2910 (s)/2900 (s, p), 2876 (s)/2872 (vs, p), $\nu(CH)$; 2151 (vs)/2152 (vs, p), $\nu(SiH_2)$; –/1297 (m, p), $\omega(CH_2)$; 1223 (w)/1225 (w), $\tau(CH_2)$; 1006 (s)/990 (w), $\nu(CF)$; 938 (s)/937 (w), $\delta(SiH_2)$; 881 (vs)/884 (m, p); –/595 (vs, p); 538 (s)/542 (m, p); –/479 (m, p). MS [*m*/*e* (relative intensity)]: 106 (M^+, 6), 77 ($M - C_2H_5$, 11), 76 ($M - C_2H_6$, 9), 74 ($M - CHF$, 8), 73 ($M - CH_2F$, 86), 72 ($M - CH_3F$, 7), 62 ($M - C_3H_8$, 10), 61 ($M - C_3H_9$, 8), 59 ($M - C_2H_4F$, 5), 49 (SiH_2F, 15), 47 (SiF, 52), 46 ($M - C_3H_5F$, 10), 45 ($M - C_3H_6F$, 100), 44 ($M - C_3H_7F$, 9), 43 (C_3H_7/CH_3Si, 61), 42 (C_3H_6/CH_2Si, 28), 41 (C_3H_5/CHSi, 49), 39 (C_3H_3, 17), 31 (CF, 6), 28 (C_2H_4, 6), 27 (C_2H_3, 27). Anal. Calcd for $C_4H_{11}FSi$: F, 17.89. Found: F, 18.5.

(Fluoromethyl)isobutylsilane (28). NMR: ^1H $\delta(CH_3)$ 0.96 ppm, d, $\delta(CH_2)$ 0.69 ppm, dt, $\delta(CH)$ 1.76 ppm, qtt, $\delta(SiH_2)$ 3.91 ppm, dtt, $\delta(CH_2F)$ 4.45 ppm, dt, ${}^1J(H^{29}Si)$ 191.7 Hz, ${}^2J(HCF)$ 47.2 Hz, ${}^3J(HSiCF)$ 14.3 Hz, ${}^3J(CH_2(F)SiH_2)$ 2.9 Hz, ${}^3J(CHSiH_2)$ 3.9 Hz, ${}^3J(CH_3CH)$ 6.7 Hz, ${}^3J(CHCH_2)$ 6.7 Hz; $\delta(^{19}F)$ –266.9 ppm, tt; ^{13}C $\delta(CH_3)$ 25.3 ppm, $\delta(CH_2)$ 17.5 ppm, d, $\delta(CH)$ 25.7 ppm, $\delta(CH_2F)$ 76.2 ppm, ${}^1J(F^{13}C)$ 161.9 Hz, ${}^3J(F^{13}C)$ 2.1 Hz; $\delta(^{29}Si)$ –38.6 ppm, d, ${}^2J(F^{29}Si)$ 22.3 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2963 (vs)/2964 (m), 2942 (sh)/2935 (s, p), 2912 (s)/2919 (vs, p), 2882 (s)/2878 (vs, p), $\nu(CH)$; 2157 (vs), 2157 (vs, p), $\nu(SiH_2)$; –/1299 (w, p), $\omega(CH_2)$; 1224 (m)/1220 (m, p); 1006 (s)/984 (w, p), $\nu(CF)$; 942 (vs)/949 (m, p), $\delta(SiH_2)$; 886 (vs)/882 (w); 639 (w)/641 (vs, p); 610 (s)/615 (vs, p); 504 (m)/–; –/427 (m, p). MS [*m*/*e* (relative intensity)]: 120 (M^+, 0.1), 105 ($M - CH_3$ 10), 88 ($M - CHF$, 7), 87 ($M - CH_2F$, 69), 86 ($M - CH_3F$, 13), 77 ($M - C_3H_7$, 55), 75 ($M - C_3H_9$, 6), 64 ($M - C_4H_8$, 7), 63 ($M - C_4H_9$, 94), 62 ($M - C_4H_{10}$, 6), 61 ($M - C_4H_{11}$, 8), 60 ($M - C_3H_5F$, 11), 59 ($M - C_3H_6F$, 100), 58 ($M - C_3H_7F$, 8), 55 (C_4H_7, 30), 49 (SiH_2F, 59), 47 (SiF, 27), 45 (CH_3SiH_2, 38), 43 (C_3H_7/CH_3Si, 17), 41 (C_3H_5/CHSi, 27), 31 (CF, 6), 29 (SiH, 27), 27 (C_2H_3, 21). Anal. Calcd for $C_5H_{13}FSi$: C, 49.94; H, 10.90; F, 15.80. Found: C, 49.80; H, 10.89; F, 15.6.

(Fluoromethyl)-*sec*-butylsilane (29). NMR: ^1H $\delta(CH_3(CH_2))$ 0.94 ppm, t, $\delta(CH_3(CH))$ 1.05 ppm, d, $\delta(CH_2)$ 1.22–1.59 ppm, $\delta(CH)$ 0.89–1.02 ppm, $\delta(SiH)$ 3.88/3.92 ppm, $\delta(CH_2F)$ 4.50 ppm, dt, ${}^1J(H^{29}Si)$ 193.6 Hz, ${}^2J(HCF)$ 47.2 Hz, ${}^3J(HSiCF)$ 15.2 Hz, ${}^3J(CH_2(F)SiH_2)$ 2.8 Hz, ${}^3J(CHSiH_2)$ 3.1 Hz, ${}^3J(CH_3CH_2)$ 7.4 Hz, ${}^3J(CH_3CH)$ 7.0 Hz; $\delta(^{19}F)$ –267.3 ppm, tt; ^{13}C $\delta(CH_3)$ 15.2/15.9 ppm, $\delta(CH_2)$ 26.8 ppm, $\delta(CH)$ 16.3 ppm, d, $\delta(CH_2F)$ 75.5 ppm, d, ${}^1J(F^{13}C)$ 161.9 Hz, ${}^3J(F^{13}C)$ 1.8 Hz; $\delta(^{29}Si)$ –267.3 ppm, d, ${}^2J(F^{29}Si)$ 21.1 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2966 (s)/2964 (m, p), 2943 (s)/2941 (vs, p), 2920 (s)/2919 (vs, p), 2878 (s)/2877 (vs, p), –/2863 (vs, p), $\nu(CH)$; 2153 (vs)/2152 (vs, p), $\nu(SiH_2)$; –/1299 (m, p), $\omega(CH_2)$; 1006 (s)/981 (w), $\nu(CF)$; 940 (s)/940 (m), $\delta(SiH_2)$; 882 (vs)/–; –/615 (vs, p); 598 (w)/592 (vs, p); 536 (m)/542 (s, p).

Halogenation of (Fluoromethyl)silanes. (a) With $SnCl_4$. The respective (fluoromethyl)silane and $SnCl_4$ were condensed into a screw cap vial and reacted at room temperature; for details see Table IV. Volatile products were collected at –196 °C and separated by fractional condensation *in vacuo*.

(Fluoromethyl)chlorosilane (30). NMR: ^1H $\delta(CH_2F)$ 4.28 ppm, dt, $\delta(SiH)$ 4.54 ppm, dt, ${}^1J(H^{29}Si)$ 241.1 Hz, ${}^2J(HF)$ 46.7 Hz, ${}^3J(HSiCF)$ 11.2 Hz, ${}^3J(HH)$ 2.4 Hz; $\delta(^{19}F)$ –268.8 ppm, tt; $\delta(^{13}C)$ 76.4 ppm, d, ${}^1J(F^{13}C)$ 165.0 Hz, ${}^1J(H^{13}C)$ 144.0 Hz, ${}^2J(H^{13}C)$ 10.1 Hz; $\delta(^{29}Si)$ –19.1 ppm, d, ${}^2J(F^{29}Si)$ 29.5 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2962 (m, PQR)/2970 (w), $\nu_{as}(CH_2)$; 2949 (m, PQR)/–; 2925 (m)/2930 (m, p), $\nu_s(CH_2)$; 2234 (s, sh)/–, $\nu_{as}(SiH_2)$; 2208 (vs)/2204 (vs, p), $\nu_s(SiH_2)$; 1427 (w)/1430 (w), $\delta(CH_2)$; –/1301 (m, p), $\omega(CH_2)$; 1223 (w)/1225 (w), $\tau(CH_2)$; 1018 (s, PQR 10)/1001 (w, p), $\nu(CF)$; 946 (s, PQR 17)/940 (m, p), $\delta(SiH_2)$; 894 (vs, PQR 12)/880 (vw, p), $\omega(SiH_2)$; 847 (vs, PQR 10)/844 (vw), $\rho(CH_2)$; 720 (w)/719 (s, p), $\nu(SiC)$; 695 (w)/700 (sh), $\tau(SiH_2)$; 541 (s)/520 (vs, p), $\nu(SiCl)$.

(Fluoromethyl)fluorosilane (31). NMR: ^{19}F $\delta(CF)$ –274.9 ppm, ttd, $\delta(SiF)$ –198.9 ppm, ttd, ${}^2J(HCF)$ 46.8 Hz, ${}^2J(HSiF)$ 49.0 Hz, ${}^3J(FCSiH)$ 13.2 Hz, ${}^3J(FCSiF)$ 4.8 Hz, ${}^3J(HCSiF)$ 7.6 Hz.

(Fluoromethyl)fluorochlorosilane (32). NMR: ^{19}F $\delta(CF)$ –275.0 ppm, tdt, $\delta(SiF)$ –150.9 ppm, dtd, ${}^2J(HCF)$ 46.9 Hz, ${}^2J(HSiF)$ 61.1 Hz, ${}^3J(FCSiH)$ 6.4 Hz, ${}^3J(FCSiF)$ 4.4 Hz, ${}^3J(HCSiF)$ 6.5 Hz.

(Fluoromethyl)methylchlorosilane (34). For NMR, see Table V. IR (gas)/Raman (liquid), cm^{-1}: 2983 (m)/2982 (w), 2960 (m)/–, 2937 (m)/–, 2920 (m)/2916 (vs, p), $\nu(CH)$; 2195 (vs, PQR)/2192 (vs, p), 2176 (vs, PQR)/–, $\nu(SiH)$; see text; 1430 (m)/1425 (w), $\delta_{as}(CH_3)$; –/1415 (sh), $\delta(CH_2)$; –/1300 (w, p), $\omega(CH_2)$; 1266 (s, PR 8)/1261 (w, p), $\delta_s(CH_3)$; 1215 (w)/1222 (w), $\tau(CH_2)$;

1007 (s, PQR 11)/992 (w, p), $\nu(CF)$; 895 (vs)/887 (w); 871 (vs, PQR)/865 (w); 852 (vs, PQR)/852 (w); 820 (vs)/–; 671 (w)/674 (vs, p); –/633 (m, p); 521 (vs)/502 (vs, p), $\nu(SiCl)$.

(Chloromethyl)methylfluorosilane (45) is formed from **34** in benzene after several months at room temperature in quantitative yield. NMR: ^1H $\delta(CH_3)$ 0.20 ppm, dd, $\delta(CH_2Cl)$ 2.54–2.56 ppm m, $\delta(SiH)$ 4.73 ppm, dtq, $^1J(H^{29}Si)$ 293.5 Hz, $^2J(HSiF)$ 49.7 Hz, $^3J(HSiCH)$ 2.4 Hz, $^3J(H_3CSiF)$ 7.7 Hz; $\delta(^{19}F)$ –171.9 ppm, dm.

(b) With Br_2. A 1.30-g (20.3-mmol) sample of **1**, 10 mL of CH_2Cl_2, and 5 mmol of Br_2 were condensed into a 450-mL screw cap ampule, the solution was brought to room temperature, and stirring was continued until the bromine color had almost disappeared. Then a second 5-mmol portion of Br_2 was condensed onto the mixture and the procedure repeated until 10.0 g (62.8 mmol) of Br_2 had been consumed. From time to time HBr was removed by fractional condensation of the reaction mixture. After a total reaction time of ca. 2 days products were separated by fractional condensation *in vacuo*. For details see Table IV.

(Fluoromethyl)tribromosilane (36). NMR: $\delta(^1H)$ 4.14 ppm, d, $^2J(FCH)$ 46.6 Hz; $\delta(^{19}F)$ –252.7 ppm, t; $\delta(^{13}C)$ 80.7 ppm, d, $^1J(F^{13}C)$ 181.0 Hz; $\delta(^{29}Si)$ –25.2 ppm, d, $^2J(F^{29}Si)$ 41.4 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2955 (w)/2955 (w), $\nu_{as}(CH_2)$; 2916 (m)/2913 (m, p), $\nu_s(CH_2)$; 1424 (m, PQR)/1421 (w), $\delta(CH_2)$; 1297 (w)/1296 (w, p), $\omega(CH_2)$; 1222 (w, PQR)/1220 (w), $\tau(CH_2)$; 1034 (s, PQR)/1016 (w, p), $\nu(CF)$; 783 (s)/–, $\rho(CH_2)$; 721 (m)/722 (m, p), $\nu(SiC)$; 504 (vs)/504 (w, p), $\nu_{as}(SiBr_3)$, a′; 484 (vs)/475 (w), $\nu_{as}(SiBr_3)$, a″; 362 (s)/361 (vs, p), $\nu_s(SiBr_3)$. Anal. Calcd for CH_2Br_3FSi: C, 3.99; H, 0.67; F, 6.31. Found: C, 4.19; H, 0.78; F, 6.1.

(Fluoromethyl)dibromosilane (37). NMR: ^1H $\delta(CH_2F)$ 4.26 ppm, dd, $\delta(SiH)$ 5.27 ppm, dt, $J(H^{29}Si)$ 293.6 Hz, $^2J(HCF)$ 46.8 Hz, $^3J(HSiCF)$ 4.5 Hz, $^3J(HCSiH)$ 2.2 Hz; $\delta(^{19}F)$ –259.6 ppm, td; $\delta(^{13}C)$ 77.6 ppm, d, $^1J(F^{13}C)$ 173.8 Hz; $\delta(^{29}Si)$ –13.8 ppm, d, $^2J(F^{29}Si)$ 36.8 Hz.

(Fluoromethyl)methyldibromosilane (38) was prepared analogously. NMR: ^1H $\delta(CH_3)$ 0.75 ppm, d, $\delta(CH_2F)$ 4.28 ppm, d, $^2J(HCF)$ 46.9 Hz, $^4J(HCSiCF)$ 0.6 Hz; $\delta(^{19}F)$ –258.6 ppm, t; ^{13}C $\delta(CH_3)$ 13.8 ppm, $\delta(CH_2F)$ 79.7 ppm, d, $^1J(F^{13}C)$ 171.5 Hz; $\delta(^{29}Si)$ 10.4 ppm, d, $^2J(F^{29}Si)$ 34.6 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2959 (m)/–, 2918 (m)/2914 (s, p), $\nu(CH)$; 1438 (sh)/–, $\delta_{as}(CH_3)$; 1408 (m)/1406 (w, p), $\delta(CH_2)$; –/1297 (w, p), $\omega(CH_2)$; 1265 (s)/1262 (w), $\delta_s(CH_3)$; 1216 (w)/1221 (w), $\tau(CH_2)$; 1015 (s)/1000 (w, p), $\nu(CF)$; 829 (vs)/–; 791 (vs)/–; 469 (vs)/466 (w), $\nu_{as}(SiBr_2)$; 393 (s)/388 (vs, p), $\nu_s(SiBr_2)$. Anal. Calcd for $C_2H_5Br_2FSi$: C, 10.18; H, 2.14; F, 8.05. Found: C, 10.33; H, 2.17; F, 8.2.

(Bromomethyl)methylfluorobromosilane (42) was obtained quantitatively from **38** in benzene after several months at room temperature. NMR: ^1H $\delta(CH_3)$ 0.48 ppm, d, $\delta(CH_2Br)$ 1.93–2.17 ppm, m, $^1J(H^{29}Si)$ 327.6 Hz, $^3J(H_3CSiF)$ 6.6 Hz; $\delta(^{19}F)$ –133.8 ppm, m.

Substitution Reactions of 36. A 0.58-g (1.93-mmol) sample of **36** was condensed onto 3.25 g (18.2 mmol) of freshly sublimated SbF_3 and reacted for 2 min at room temperature. Volatile products were separated *in vacuo* and 88% (fluoromethyl)trifluorosilane (**33**) was obtained. NMR: $\delta(^1H)$ 3.86 ppm, dq, $^2J(HCF)$ 46.5 Hz, $^3J(HCSiF)$ 3.3 Hz; ^{19}F $\delta(CF)$ –285.0 ppm, tq, $\delta(SiF)$ –143.1 ppm, dt, $^3J(FCSiF)$ 5.2 Hz; $\delta(^{13}C)$ 68.8 ppm, dq, $^1J(F^{13}C)$ 156.9 Hz, $^2J(F^{13}C)$ 27.7 Hz; $\delta(^{29}Si)$ –72.9 ppm, qdt, $^1J(F^{29}Si)$ 280.2 Hz, $^2J(F^{29}Si)$ 31.8 Hz, $^2J(H^{29}Si)$ 3.7 Hz. IR (gas)/Raman (liquid), cm^{-1}: 2961 (m)/2962 (m), $\nu_{as}(CH_2)$; 2927 (m)/2937 (s, p), $\nu_s(CH_2)$; 1430 (m)/1433 (w), $\delta(CH_2)$; 1321 (w)/1325 (w, p), $\omega(CH_2)$; 1230 (m)/1230 (w), $\tau(CH_2)$; 1045 (s)/1022 (m, p), $\nu(CF)$; 992 (vs)/988 (w, p), $\nu_{as}(SiF_3)$; 889 (vs, PQR 14)/885 (w, p), $\nu_s(SiF_3)$; 770 (w)/–, $\rho(CH_2)$; –/693 (vs, p), $\nu(SiC)$; 428 (vs, PQR 14)/426 (w, p), $\delta_s(SiF_3)$.

(Fluoromethyl)triisocyanatosilane (39) was prepared analogously from **36** and AgOCN, 5 min at room temperature, yield 67%. NMR: $\delta(^1H)$ 4.81 ppm, d, $^2J(HCF)$ 46.5 Hz; $\delta(^{19}F)$ –273.4 ppm, t; ^{13}C $\delta(CH_2F)$ 76.8 ppm, d, $\delta(NCO)$ 124.4 ppm, $^1J(F^{13}C)$ 160.2 Hz, $^1J(^{13}C^{29}Si)$ 112.0 Hz; $\delta(^{29}Si)$ –72.6 ppm, d, $^2J(F^{29}Si)$ 33.5 Hz. IR (gas)/Raman (liquid), cm^{-1}: –/2976 (sh), $\nu_{as}(CH_2)$; –/2938 (s, p), $\nu_s(CH_2)$; 2332 (s)/2330 (w, p), 2297 (vvs)/2286 (w), $\nu_{as}(NCO)$; 1440 (m)/1445 (vvs), $\nu_s(NCO)$; –/1428 (sh, p), $\delta(CH_2)$; –/1311 (w, p), $\omega(CH_2)$; –/1225 (m), $\tau(CH_2)$; 1025 (m)/1004 (m, p), $\nu(CF)$; 804 (s)/–, $\rho(CH_2)$; 624 (m)/619 (m), $\nu_{as}(SiN_3)$; 527 (m)/525 (vvs, p), $\nu_s(SiN_3)$.

(Fluoromethyl)trichlorosilane (20) was prepared from **36** and AgCl, 12 h at room temperature, yield 75%, purity 95%. NMR: $\delta(^1H)$ 3.98 ppm, d, $^2J(HCF)$ 46.6 Hz; $\delta(^{19}F)$ –262.1 ppm, t; $\delta(^{13}C)$ 78.2 ppm, dt, $^1J(F^{13}C)$ 174.2 Hz, $^1J(H^{13}C)$ 145.2 Hz; $\delta(^{29}Si)$ 0.5 ppm, d, $^2J(F^{29}Si)$ 38.6 Hz. IR (gas)/Raman (liquid) cm^{-1}: 2955 (m)/2955 (w), $\nu_{as}(CH_2)$; 2919 (m)/2922 (m, p), $\nu_s(CH_2)$; 1426 (m)/1427 (w), $\delta(CH_2)$; 1300 (w)/1301 (w, p), $\omega(CH_2)$; 1220 (w)/1220 (w), $\tau(CH_2)$; 1035 (s)/1017 (w, p), $\nu(CF)$; 790 (s)/–, $\rho(CH_2)$; 737 (s)/738 (m, p), $\nu(SiC)$; 601 (vs)/596 (m, p), $\nu_{as}(SiCl_3)$; 463 (s)/464 (vs, p), $\nu_s(SiCl_3)$; 329 (s)/330 (vs, p), $\delta_s(SiCl_3)$.

(Fluoromethyl)triphenylsilane (40), mp 68–70 °C, was prepared from **36** and PhLi. Purification by repeated sublimation and crystallization from CH_2Cl_2 gave colorless needles, yield 56%. NMR: ^1H $\delta(CH_2F)$ 5.24 ppm, d, $\delta(H_o)$ 7.67 ppm, dd, $\delta(H_m,H_p)$ 7.42–7.58 ppm, $^2J(HCF)$ 47.0 Hz, $^3J(H_oH_m)$ 5.9 Hz, $^4J(H_oH_p)$ 1.9 Hz; $\delta(^{19}F)$ –266.8 ppm, t; ^{13}C $\delta(CH_2F)$ 79.0 ppm, d; $\delta(C_i)$ 131.9 ppm, d, $\delta(C_o)$ 135.7 ppm, d, $\delta(C_m)$ 128.1 ppm, $\delta(C_p)$ 130.1 ppm, $^1J(F^{13}C)$ 164.4 Hz, $^3J(F^{13}C_i)$ 2.2 Hz, $^4J(F^{13}C_o)$ 0.6 Hz; $\delta(^{29}Si)$ –17.9 ppm, d, $^2J(F^{29}Si)$ 19.1 Hz. IR (CsI pellet)/Raman (solid), cm^{-1}: 3135 (w)/–; 3090 (w)/–, z_4; 3073 (m)/–, z_1; 3053 (m)/3059 (s), z_2; 3013 (m)/–, z_5; 2986 (w)/–, z_3; 2924 (w)/–, $\nu_{as}(CH_2)$; 2900 (w)/2904 (w), $\nu_s(CH_2)$; 1589 (m)/1593 (vs), k; 1570 (w)/1573 (vs), l; 1487 (s)/1490 (w), m; 1429 (vs)/1433 (w), n; –/1424 (w), $\delta(CH_2)$; 1330 (w)/1335 (w), o; 1298 (w)/1295 (w), $\omega(CH_2)$; 1263 (w)/–, e; 1220 (m)/1225 (w), $\tau(CH_2)$; 1190 (m)/1196 (m), a; 1158 (w)/1163 (m), c; 1114 (vs)/1117 (sh), q; –/1108 (m), q′; 1068 (w)/–, d; 1029 (m)/1032 (vs), b; 999 (m)/1004 (vs), p; 981 (s)/988 (sh), h; 920 (w)/925 (w), i; 859 (w)/865 (w), g; 777 (s)/–, $\rho(CH_2)$; 736 (s)/–, f; 719 (s)/723 (w), r; 698 (vs)/701 (w), r′; 658 (m)/662 (s), v; 619 (w)/622 (m), s; 511 (s)/–, y; 436 (m)/–, t; –/253 (sh), u; –/238 (s), u′. MS [*m*/*e* (relative intensity)]: 292 (M^+, 22), 260 (M – CHF, 26), 259 (M – CH_2F, 100), 201 (M – Ph – CH_2, 50), 181 (M – C_6H_6 – CH_2F, 10).

(Fluoromethyl)trimethoxysilane (41) was prepared from **36** and MeOH, yield 80%. NMR: ^1H $\delta(CH_3O)$ 3.68 ppm, $\delta(CH_2F)$ 4.50 ppm, d, $^2J(HCF)$ 46.5 Hz; $\delta(^{19}F)$ –262.4 ppm, t.

(Fluoromethyl)(fluorodibromomethyl)dimethylsilane (43). An 8.3-mmol sample of **22**, 10.3 mmol of **3**, and 7.7 mmol of $CFBr_3$ were reacted as described above. Volatile products were worked up by fractional condensation *in vacuo*, and **43** was obtained as a colorless solid, yield 65%. NMR: ^1H $\delta(CH_3)$ 0.26 ppm, d, $\delta(CH_2F)$ 4.48 ppm, d, $^2J(HCF)$ 47.3 Hz, $^4J(H_3CSiCF)$ 0.7 Hz; ^{19}F $\delta(CFBr_2)$ –77.0 ppm, $\delta(CH_2F)$ –263.8 ppm, t; ^{13}C $\delta(CH_3)$ –7.0 ppm, d, $\delta(CH_2F)$ 76.6 ppm, d, $\delta(CFBr_2)$ 100.6 ppm, dd, $^1J(F^{13}CBr)$ 338.0 Hz, $^1J(F^{13}CH)$ 162.9 Hz, $^3J(C(H_3)SiCF)$ 2.1 Hz, $^3J(C(FBr_2)SiCF)$ 5.4 Hz; $\delta(^{29}Si)$ 10.9 ppm, dd, $^2J(F(CH_2)^{29}Si)$ 24.5 Hz, $^2J(F(CBr_2)^{29}Si)$ 23.5 Hz. IR (gas)/Raman (solid), cm^{-1}: 2977 (m)/2978 (w), 2959 (m)/–, 2925 (m)/–, 2909 (sh)/2912 (s), $\nu(CH)$; 1418 (w)/1427 (w), $\delta_{as}(CH_3)$; –/1405 (w), $\delta(CH_2)$; 1295 (w)/1300 (w), $\omega(CH_2)$; 1262 (s)/1263 (w), $\delta_s(CH_3)$; 1218 (w)/1224 (w), $\tau(CH_2)$; 1046 (vs)/1041 (w), $\nu(F–CBr_2)$; 996 (s)/997 (w), $\nu(F–CH_2)$; 413 (m)/405 (vs), $\nu(Si–CFBr_2)$.

Bis(fluoromethyl)dimethylsilane (44) was prepared from 0.87 g (3.09 mmol) **43** and 3.80 g (13.1 mmol) of $(n\text{-}Bu)_3SnH$, 16 h at room temperature, yield 73%; bp 85.2 °C/1010 mbar. For NMR, see Table V. IR (gas)/Raman (liquid), cm^{-1}: 2970 (m)/–, 2940 (m)/–, 2933 (m)/–, 2914 (m)/2912 (vs, p), $\nu(CH)$; 1428 (w)/1433 (w), $\delta_{as}(CH_3)$; 1419 (sh)/1430 (w), $\delta(CH_2)$; 1295 (w)/1301 (w, p), $\omega(CH_2)$; 1260 (s, PQR)/1250 (w), $\delta_s(CH_3)$; 1219 (w, PQR)/1223 (w), $\tau(CH_2)$; 1001 (vs)/–, $\nu(CF)$; 856 (vs)/860 (w); –/623 (vvs, p), $\nu_s(SiC_4)$. Anal. Calcd for $C_4H_{10}F_2Si$: C, 38.69; H, 8.11; F, 30.59. Found: C, 38.76; H, 8.07; F, 30.2.

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