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Reactions of methyl(pentafluorophenyl)- and methyl(pentafluorophenyl)phenylsilanes with electrophiles. A convenient preparative route to halogeno(methyl)pentafluorophenylsilanes $C_6F_5SiMe_2X$ and $C_6F_5SiMeX_2$ (X = F, Cl and Br)

H.-J. Frohn [a],*, A. Lewin [a], V.V. Bardin [b]

[a] *Fachgebiet Anorganische Chemie, Gerhard-Mercator-Universität Duisburg, Lotharstrasse 1, D-47048 Duisburg, Germany*
[b] *Institute of Organic Chemistry, 630090 Novosibirsk, Russia*

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Abstract

Halogeno(methyl)pentafluorophenylsilanes $C_6F_5SiMe_nX_{3-n}$ ($n = 1, 2$) (X = F, Cl, Br) were prepared in good yields from the corresponding phenylsilanes $C_6F_5SiMe_nPh_{3-n}$ by reactions with the electrophiles aHF, HCl–$AlCl_3$, Br_2–$AlBr_3$ or AlX_3 (X = Cl, Br) halogenated hydrocarbons. Additionally, reactions of $C_6F_5SiMe_3$ and $(C_6F_5)_2SiMe_2$ with selected electrophiles were studied. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

A well-known method of regiospecific functionalisation of aromatic hydrocarbons is the replacement of the alkylsilyl group $-SiAlk_3$ in $ArSiAlk_3$ under the action of electrophiles [1]. However, in the case of pentafluorophenylsilanes there are only few examples of electrophilic desilylation reactions known. Tetrakis(pentafluorophenyl)silane formed pentafluorobenzene when refluxed in 6 N HCl in THF [2] or bromopentafluorobenzene in low yield in reactions with excess of bromine in MeCN (reflux, 2 h) [3]. Sulfodesilylation of $C_6F_5SiMe_3$ with SO_3 in $CF_2ClCFCl_2$ (−196–25°C) showed a better conversion and gave $C_6F_5S(O)_2OSiMe_3$ in a 69% yield [4]. On the other hand, reactions of $(C_6F_5)_4Si$ with aq. 6 N HCl (reflux, 5 h) [2], of $(C_6F_5)_2SiMe_2$ and $(C_6F_5)_2SiMeH$ with $CF_3C(O)OH$ (reflux) [5,6], and of $C_6F_5SiMe_3$ with excess of iodine in MeCN (reflux, 2 h) [3] failed. Treatment of $C_6F_5Si(\alpha\text{-}Np)PhMe$ with BrCl in $CHCl_3$ (−78–20°C) led to the regiospecific cleavage of the naphthyl group and the formation of $C_6F_5SiPhMeCl$ [7]. It should be noted that reactions of pentafluorophenylsilanes with electrophiles can be promoted by Lewis base co-ordination at the silicon atom. By that procedure pentafluorophenyl derivatives of polyvalent bromine- [8] and iodinefluorides [9] were successfully prepared from the silanes $C_6F_5SiMe_3$, $(C_6F_5)_2SiMe_2$ and $C_6F_5SiF_3$. Some pentafluorophenylation reactions of other electrophilic substrates were known from literature [10] (see also review [11]).

Recently we reported the facile preparation of halogeno(pentafluorophenyl)silanes $(C_6F_5)_nSiX_{4-n}$ (X = F, Cl; $n = 1, 2$) by fluoridation and chloridation of the corresponding ethoxy(pentafluorophenyl)silanes and investigated some reactions of $C_6F_5SiF_3$ with elec-

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* Corresponding author.

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trophiles and nucleophiles [12]. The high resistance of the carbon–silicon bond in $C_6F_5SiF_3$ to the electrophilic desilylation allowed us to plan alternative syntheses of halogeno(pentafluorophenyl)silanes from either methyl(pentafluorophenyl)phenyl or methyl(pentafluorophenyl)silanes under the action of strong electrophilic reagents. Although the C–Si bond in $SiMe_4$ easily undergoes cleavage with superacids like FSO_3H or CF_3SO_3H under formation of the esters $FS(O)_2OSiMe_3$ or $CF_3S(O)_2OSiMe_3$, respectively [13], the favoured C–Si reaction site in silanes with C_6F_5–Si–Me fragments was not an obvious priority. However, the predominant cleavage of the phenyl group in $C_6F_5SiMe_nPh_{3-n}$ in reactions with electrophiles under formation of $C_6F_5SiMe_2X$ and $C_6F_5SiMeX_2$ (X = F, Cl, Br) was expected. While silanes $C_6F_5SiMe_2X$ can principally be obtained on pathways (1) and (2) [6,14–20], there was no convenient preparative route to the interesting bifunctional dihalogeno(methyl)pentafluorophenylsilanes.

$$C_6F_5MgBr + ClSiMe_2H \longrightarrow C_6F_5SiMe_2H$$
$$(X = Cl, Br)$$
$$X_2$$
$$\longrightarrow C_6F_5SiMe_2X \qquad (1)$$

$$C_6F_5MgBr + ClSiMe_2(OEt) \longrightarrow C_6F_5SiMe_2Cl + C_6F_5SiMe_2(OEt)$$
$$HCl$$
$$\longrightarrow C_6F_5SiMe_2Cl \qquad (2)$$

2. Results

2.1. Reactions of methyl(pentafluorophenyl)silanes

The complex trimethyl(pentafluorophenyl)silane **1** reacted with anhydrous HF (aHF) at room temperature (r.t.) under formation of pentafluorobenzene **2** and fluorotrimethylsilane. The stronger protic acids FSO_3H and CF_3SO_3H caused the same regiospecific aryl–silicon bond cleavage. In both cases the methyl–silicon bond remained uneffected.

$$\underset{\mathbf{1}}{C_6F_5SiMe_3} + aHF \xrightarrow[\text{RT, 30 h}]{} \underset{\mathbf{2}}{C_6F_5H} + FSiMe_3 \qquad (3)$$

$$\mathbf{1} + FSO_3H \xrightarrow[\text{-20 °C, 5 min}]{} \mathbf{2} + FS(O)_2OSiMe_3 \qquad (4)$$

$$\mathbf{1} + CF_3SO_3H \xrightarrow[\text{RT, ca. 1 min}]{} \mathbf{2} + CF_3S(O)_2OSiMe_3 \qquad (5)$$

Those results allowed us to carry out the simple preparation of deuterated polyfluoroaromatics. Indeed, 1,4-dideuterotetrafluorobenzene was obtained from 1,2,4,5-tetrafluoro[bis(trimethylsilyl)]benzene and CF_3SO_3D in high yield within a few minutes.

$$1{,}4\text{-}C_6F_4(SiMe_3)_2 + 2\,CF_3SO_3D \longrightarrow$$
$$1{,}4\text{-}C_6D_2F_4 + 2\,CF_3S(O)_2OSiMe_3 \qquad (6)$$

Weaker electrophiles (CF_3CO_2H, reflux, 4 h; $[NO_2]^+[BF_4]^-$ in CH_3CN, r.t., 3 days) did not react with silane **1**. However, nitrodesilylation of silane **1** was possible with $[NO_2]^+[BF_4]^-$ in sulfolane (100 °C, 2 h).

The aryl–silicon bond in $C_6F_5SiMe_3$ **1** and $(C_6F_5)_2SiMe_2$ **3** was successfully cleaved with electrophilic brominating agents. Bromodesilylation with liquid bromine at r.t. proceeded slowly and silane **3** showed less reactivity in comparison to silane **1**. Nevertheless, both silanes **1** and **3** were converted into bromopentafluorobenzene **4** within a few minutes under the action of liquid bromine and $AlBr_3$.

$$\mathbf{1} + Br_2 \xrightarrow[\text{RT, 3 d}]{} \underset{\mathbf{4}}{C_6F_5Br} + BrSiMe_3 \qquad (7)$$

(55 % conversion of 1)

$$\mathbf{1} + Br_2 \xrightarrow[\text{-20 °C to RT, 15 min}]{AlBr_3} C_6F_5Br + BrSiMe_3 \qquad (8)$$

(100 % conversion of 1)

$$\mathbf{3} + Br_2 \xrightarrow[\text{RT, 8 d}]{} 2\,C_6F_5Br + Br_2SiMe_2 \qquad (9)$$

(20 % conversion of 3)

$$\mathbf{3} + Br_2 \xrightarrow[\text{-20 °C to RT, 15 min}]{AlBr_3} 2\,C_6F_5Br + Br_2SiMe_2 \qquad (10)$$

(100 % conversion of 3)

Bromopentafluorobenzene **4** was also obtained from silane **3** in a fast reaction with a sub-stoichiometric amount of $AlBr_3$ and an excess of bromine in 1,2-dibromoethane (DBE) in a 93% yield as well as 7% pentafluorobenzene **2**.

Surprisingly, we found a slow reaction of silane **3** with $AlBr_3$ in DBE to pentafluorobenzene **2** and bromo(dimethyl)pentafluorophenylsilane **5** in a molar ratio of 1:1.

$$\mathbf{3} \xrightarrow[\text{RT, 0.5 h}]{0.5\,AlBr_3,\ DBE} \underset{\mathbf{5}}{C_6F_5SiMe_2Br} + \underset{\mathbf{2}}{C_6F_5H} \qquad (11)$$

(5 % conversion of 3)

Similar results were obtained in the reactions of silane **3** with $AlCl_3$ in CD_2Cl_2 or $CDCl_3$. In $CDCl_3$ the products **2** (H containing) and **6** were detected in the reaction mixture as well as traces of $C_6F_5CDCl_2$. The latter suggests the participation of carbocationic species as reactive intermediates. However, the main path in the slow reactions of $(C_6F_5)_2SiMe_2$ with AlX_3 in halogenated hydrocarbons (also in deuterated ones) was protodesilylation. In spite of careful handling the influence of moisture as a source of H can not be totally excluded, especially in the case of long-time reactions. Substantial acceleration of the protodesilylation reaction was achieved when gaseous HCl was passed into the suspension of $AlCl_3$ in the $CDCl_3$ solution of silane **3** at r.t.

$$\mathbf{3}\ \xrightarrow[\text{RT, 13 d}]{1.8\ AlCl_3,\ CD_2Cl_2}\ \underset{\mathbf{6}}{C_6F_5SiMe_2Cl} + \underset{\mathbf{2}}{C_6F_5H} \qquad (12)$$

$$\mathbf{3}\ \xrightarrow[\text{RT, 13 d}]{n\ AlCl_3,\ CDCl_3}\ \mathbf{6} + \mathbf{2} \qquad (13)$$

(n = 0.3, 1.9)

$$\mathbf{3} + HCl\ \xrightarrow[\text{RT, 1 h}]{AlCl_3,\ CDCl_3}\ \mathbf{6} + \mathbf{2} + Me_2SiCl_2 \qquad (14)$$

2.2. Reactions of methyl(pentafluorophenyl)phenylsilanes

In contrast to methyl(pentafluorophenyl)silanes **1** and **3** the reactions of dimethyl(pentafluorophenyl) phenylsilane **7** and methyl(pentafluorophenyl)diphenylsilane **8** with electrophilic agents proceeded more readily and principally under phenyl–silicon bond cleavage. Treatment of silanes **7** and **8** with aHF gave in high yields fluoro(dimethyl)pentafluorophenylsilane **9** and difluoro(methyl)pentafluorophenylsilane **10**, respectively. Fluoro(methyl)pentafluorophenyl(phenyl)silane **11** was detected as an intermediate by ^{19}F-NMR spectrometry in the reaction of **8** to **10**.

$$\underset{\mathbf{7}}{C_6F_5SiMe_2Ph} + aHF\ \xrightarrow[\text{RT, 30 min}]{CH_2Cl_2}\ \underset{\mathbf{9}}{C_6F_5SiMe_2F} \qquad (15)$$

$$\underset{\mathbf{8}}{C_6F_5SiMePh_2} + aHF\ \xrightarrow[\text{RT, 4 h}]{CH_2Cl_2}\ \underset{\mathbf{11}}{C_6F_5SiMePhF} +$$

$$\underset{\mathbf{10}}{C_6F_5SiMeF_2}\ \xrightarrow[\text{RT, 24 h}]{aHF,\ CH_2Cl_2}\ \mathbf{10} \qquad (16)$$

Dichloro(methyl)pentafluorophenylsilane **12** was prepared in a similar way from silane **8**, HCl gas and $AlCl_3$ in hexane. However, the more convenient route to silane **12** is the reaction of silane **8** with $AlCl_3$ in CH_2Cl_2 at r.t. The initial reaction product was chloro(methyl)pentafluorophenyl(phenyl)silane **13** which finally underwent replacement of the residual phenyl group by chlorine. The same result was obtained in acetyl chloride.

$$\mathbf{8} + HCl\ \xrightarrow[\text{RT, 15 min}]{AlCl_3,\ \text{hexane}}\ \underset{\mathbf{12}}{C_6F_5SiMeCl_2} \qquad (17)$$

$$\begin{array}{lllll} \mathbf{8} & \xrightarrow{0.4-1\ AlCl_3,\ CH_2Cl_2} & C_6F_5SiMePhCl & +\ \mathbf{12} & (18) \\ & \text{RT, 25 - 30 min} & \mathbf{13}\ \ 80-84\ \% & 15-16\ \% & \\ & \text{45 min} & & 100\ \% & \end{array}$$

$$\begin{array}{llll} \mathbf{8} & \xrightarrow{7.7\ AlCl_3,\ AcCl} & \mathbf{13}\ +\ \mathbf{12} & (19) \\ & \text{RT, 5 min} & 43\ \%\ \ 57\ \% & \\ & \text{20 min} & 100\ \% & \end{array}$$

That useful approach was successfully extended to the synthesis of bromosilane **5** and dibromo(methyl)pentafluorophenylsilane **14**. Both compounds were easily prepared from the corresponding silanes **7** and **8** under the action of $AlBr_3$ in DBE at r.t.

$$\underset{\mathbf{7}}{C_6F_5SiMe_2Ph}\ \xrightarrow[\text{RT, 10 min}]{0.3\ AlBr_3,\ DBE}\ \underset{\mathbf{5}}{C_6F_5SiMe_2Br} \qquad (20)$$

$$\underset{\mathbf{8}}{C_6F_5SiMePh_2}\ \xrightarrow[\text{RT, 10 min}]{0.5\ AlBr_3,\ DBE}\ \underset{\mathbf{14}}{C_6F_5SiMeBr_2} \qquad (21)$$

It should be mentioned, that difluorosilane **10** can also be obtained in addition to the procedure described in equation 16 by the reaction of dichloro(methyl)pentafluorophenylsilane **12** with xenon difluoride similar to the preparation of $C_6F_5SiMe_2F$ from $C_6F_5SiMe_2Cl$ and XeF_2 [21].

$$\underset{\mathbf{12}}{C_6F_5SiMeCl_2} + XeF_2\ \xrightarrow[\text{RT, 10 min}]{CH_2Cl_2}\ \mathbf{10} + Xe + Cl_2 \qquad (22)$$

Table 1
^{1}H- and ^{29}Si-NMR spectra of pentafluorophenylsilanes C_6F_5SiXYZ ($CDCl_3$, 35°C)

X	Y	Z	δ(H)/ppm	δ(Si)/ppm	J/Hz
CH_3	CH_3	CH_3	0.42	−0.75	
CH_3	CH_3	Cl	0.83[a]	16.66	(CH_3, F2) 1.8
CH_3^b	CH_3	Br	[e]	−2.60	
CH_3^b	CH_3	C_6H_5	7.66–7.45 (C_6H_5), 0.81 (CH_3)	−7.03	(CH_3, F2) 1.8
CH_3	CH_3	C_6F_5	0.80 (CH_3)[c]	−9.58[d]	(CH_3, F2) 1.6, (Si, F2) 55.0, (Si, CH) 7.4
CH_3	F	F	0.75	−17.01	(HCSiF) 6.1, (CH_3, F2) 1.5, (Si, F) 288.2, (Si, F2) 6.4, (Si, F3) 3.4, (Si, F4) 1.0
CH_3	Cl	Cl	1.19	10.34	(CH_3, F2) 2.4
CH_3	Br	Br	1.51	−6.71	(CH_3, F2) 3.4, (Si, F2) 6.5, (Si, F3) 3.2, (Si, F4) 1.2
CH_3	C_6H_5	C_6H_5	7.57 (H-2, 6), 7.47 (H-4), 7.41 (H-3, 5), 0.98 (CH_3)	−12.78	(H3, H4) 7.4, (CH_3, F2) 2.3

[a] Lit. 0.92 ppm (in benzene) [27]. [b] In CD_2Cl_2. [c] Present work, lit. see [19,28,29]. [d] Lit. −8.3 ppm [30]. [e] Lit. see [19,28].

3. Conclusions

The reactivity of methyl(pentafluorophenyl)silanes towards strong electrophiles like HY (Y = F, OSO_2F, OSO_2CF_3), HCl–$AlCl_3$, bromine, Br_2–$AlBr_3$ or AlX_3 (X = Cl, Br) halogenated hydrocarbons demonstrated that aryl–Si bond cleavage was also possible in the case of electron-poor phenyl groups like the C_6F_5-group. Under similar conditions phenylsilanes $C_6F_5Si(Me)_nPh_{3-n}$ underwent regiospecific replacement of the phenyl group(s) by halogen atom(s) while the C_6F_5–Si fragments stayed unchanged. Those circumstances allowed us to elaborate a general and simple preparative route to halogeno(methyl)pentafluorophenylsilanes. Considerations about the pathways and the rates of those reactions will be included in our next publication in the field of pentafluorophenylsilane chemistry [22].

4. Experimental section

NMR spectra were recorded on Bruker spectrometers WP 80 SY (^{1}H at 80.13, ^{19}F at 75.39 MHz), AM 400 (^{13}C at 100.58, ^{29}Si at 79.49 MHz) and Avance DRX 500 (^{1}H at 500.13, ^{13}C at 125.76, ^{19}F at 470.59, ^{29}Si at 99.36 MHz) with respect to TMS and C_6F_6. The ^{19}F chemical shifts were related to $CFCl_3$ using $\delta(F) = -162.9$ ppm for C_6F_6. IR spectra were measured on a Nicolet 20 DXB instrument (KBr pellets) and Raman spectra on a Bruker FT-spectrometer IFS 66 equipped with a Raman device FRA 106 (Nd: YAG laser ADLAS) (glass capillary sealed under dry argon). GCMS measurements of mixtures were performed with a gas chromatograph HP 5890 (HP 5 capillary, 30 m) combined with a mass spectrometer AMD 604.

Pentafluorophenylsilanes **1** [23] and **3** [19] were prepared by literature methods. Hydrogen fluoride was dried by electrolysis (stainless steel cell, Ni electrodes). HCl gas was dried by bubbling through concentrated H_2SO_4. FSO_3H, CF_3SO_3H and AcCl were distilled, $AlCl_3$ and $AlBr_3$ sublimed before use. $[NO_2]^+[BF_4]^-$ (Fluka) and CF_3CO_2H (Solvay) were used without additional purification. Hexane, ether, benzene, CH_2Cl_2, $CHCl_3$ and 1,2-dibromoethane were dried by

Table 2
^{19}F-NMR spectra of pentafluorophenylsilanes C_6F_5SiXYZ ($CDCl_3$, 35°C)

X	Y	Z	δ(F)/ppm			J(F, F)/Hz
			F-2, 6	F-4	F-3, 5	
CH_3	CH_3	Cl	−128.06	−150.60	−162.03	(2, 4) 4.5, (3, 4) 19.8
$CH_3^{a,b}$	CH_3	Br	−128.83	−152.30	−162.60	(2, 4) 3.6, (3, 4) 19.7
CH_3^a	CH_3	C_6H_5	−126.62	−152.60	−162.34	(2, 4) 3.7, (3, 4) 19.5
CH_3^c	CH_3	C_6F_5	−128.41	−150.92	−161.83	(2, 4) 3.9, (3, 4) 19.9
$CH_3^{a,d}$	C_6H_5	F	−127.80	−149.75	−161.31	(2, 4) 4.3, (3, 4) 19.7
CH_3^a	C_6H_5	Cl	−125.97	−149.58	−161.38	(2, 4) 4.7, (3, 4) 19.9
CH_3	C_6H_5	C_6H_5	−124.94	−151.42	−161.86	(2, 4) 4.0, (3, 4) 20.1
CH_3^e	F	F	−128.67	−147.30	−160.82	(2, 4) 5.2, (3, 4) 19.9, (F, Si) 288.2
CH_3	Cl	Cl	−127.28	−147.50	−160.73	(2, 4) 5.6, (3, 4) 20.1
CH_3	Br	Br	−126.72	−147.43	−160.67	(2, 4) 5.7, (3, 4) 20.1

[a] In CD_2Cl_2. [b] Present work, lit. see [19,28]. [c] Present work, lit. see [19,28,29]. [d] δ(F) (F–Si) −162.25 ppm. [e] δ(F) (F–Si) −131.17 ppm.

literature methods and stored over molecular sieves (ether over Na). All reactions were carried out in stoppered FEP traps under dry argon atmosphere except where alternative handling is described. Solid materials were manipulated in a Braun glove box with a gas purification MB-100.

NMR, IR and Raman spectral data are given in Tables 1–4.

4.1. *Methyl(pentafluorophenyl)diphenylsilane* ***8***

Bromopentafluorobenzene (13.6 g, 54.9 mmol) and ether (100 ml) were placed in a flask equipped with dropping funnel, reflux condenser and magnetic stirrer under dry argon and cooled to −78°C. A sample of BuLi (1.6 M in hexane, 34.5 ml, 54.9 mmol) was added dropwise under stirring. The reaction mixture was maintained at −78°C for 3 h before a solution of $Ph_2SiMeCl$ (12.8 g, 54.9 mmol) in ether (100 ml) was added. Overnight the reaction mixture was allowed to warm to r.t. After hydrolysis the organic phase was separated, the aqueous phase was extracted with ether and the combined extracts were dried with $MgSO_4$. Silane **8** (15.4 g, 77%) was isolated by vacuum-distillation, b.p. 117 − 120°C (0.04 hPa).

Found: C 62.3, H 3.46, F 26.1. $C_{19}H_{13}F_5Si$. Required: C 62.6, H 3.57, F 26.1.

4.2. *Dimethyl(pentafluorophenyl)phenylsilane* ***7***

Within 15 min $P(NEt_2)_3$ (7.7 g, 31 mmol) was added dropwise under stirring to a 5–8°C cold solution (flask) of bromopentafluorobenzene (6.5 g, 26 mmol) and $PhMe_2SiCl$ (3.7 g, 26 mmol) in benzene (20 ml). The resulting suspension was stirred for a further 1 h, washed with concentrated H_2SO_4 (2 × 5 ml) and finally with water till neutral. After drying with $MgSO_4$ silane **7** (4.3 g, 55%) was isolated by vacuum-distillation, b.p. 142–145°C (3 hPa) (lit. 94.5–95.5°C (0.2 hPa) [24]).

4.3. *Reactions of pentafluorophenyltrimethylsilane* ***1*** *with electrophiles*

4.3.1. *With aHF*

Silane **1** (200 mg, 0.83 mmol) and aHF (0.4 ml) were stirred at r.t. The conversion of silane **1** into pentafluorobenzene **2** was 30% after 12 h and 100% after 30 h (^{19}F-NMR).

4.3.2. *With FSO_3H*

Silane **1** (200 mg, 0.83 mmol) was added to FSO_3H (0.4 ml) under stirring at −60°C. At −60°C no reaction was detected after 5 min while at −20°C the total conversion of silane **1** into pentafluorobenzene **2** and $FS(O)_2OSiMe_3$ had taken place after 5–7 min (^1H-, ^{19}F-NMR).

4.3.3. *With CF_3SO_3H*

At r.t. silane **1** (250 mg, 1.04 mmol) was added to CF_3SO_3H (0.3 ml) under stirring. Within a few minutes the total conversion of silane **1** into pentafluorobenzene **2** and $CF_3S(O)_2OSiMe_3$ was observed (^{19}F-NMR).

4.3.4. *With CF_3CO_2H*

Silane **1** (2.0 g, 8.3 mmol) and CF_3CO_2H (5 ml) were refluxed for 4 h. The system was diluted with water (10 ml), the phases were separated, the organic phase was washed with aq. $NaHCO_3$ and water and finally dried with $MgSO_4$. In total 1.8 g (90%) of silane **1** were recovered.

4.3.5. *With $[NO_2]^+[BF_4]^-$ in sulfolane*

A solution of silane **1** (84 mg, 0.35 mmol) and $[NO_2]^+[BF_4]^-$ (70 mg, 0.53 mmol) in sulfolane (0.2 ml) was stirred in a flask at 100°C for 2 h. After cooling to 30–35°C a mixture of silane **1**, nitropentafluorobenzene (1:1.5, M) and a resonance at $\delta(F) = -144.9$ ppm, possibly the result of an addition between sulfalane and BF_3, was observed by ^{19}F-NMR spectrometry.

4.3.6. *With $[NO_2]^+[BF_4]^-$ in acetonitrile*

No reaction was detected between silane **1** (61 mg, 0.25 mmol) and $[NO_2]^+[BF_4]^-$ (60 mg, 0.45 mmol) in acetonitrile (0.15 ml) at 22°C after stirring for 3 days in a glass NMR tube (^{19}F-NMR).

4.3.7. *With bromine*

A mixture of silane **1** (180 mg, 0.75 mmol) and bromine (247 mg, 1.54 mmol) was stirred at r.t. ^1H- and ^{19}F-NMR monitoring showed the slow formation of C_6F_5Br and $BrSiMe_3$ (20, 28 and 55% conversion of silane **1** after 13, 22 and 90 h, respectively).

4.3.8. *With bromine and $AlBr_3$*

Silane **1** (68 mg, 0.28 mmol) was added to a solution of $AlBr_3$ (58 mg, 0.22 mmol) in bromine (0.1 ml) at −20°C. After warming to r.t. (15 min) the ^{19}F-NMR spectrum showed the total conversion of silane **1** into bromopentafluorobenzene **4**. A violent reaction took place when the reactants were mixed at r.t.

4.4. *1,4-Dideuterotetrafluorobenzene*

At −20°C 1,2,4,5-tetrafluoro[bis(trimethylsilyl)]benzene (1.0 g, 3.4 mmol) was added to a stirred solution of CF_3SO_3D, obtained from D_2O (0.2 g, 10

Table 3
^{13}C-NMR spectra of pentafluorophenylsilanes C_6F_5SiXYZ ($CDCl_3$, 35°C)

X	*Y*	*Z*	δ (C)/ppm	*J*/Hz
CH_3	CH_3	CH_3	C_6F_5: 149.37 (C-2, 6), 142.25 (C-4), 137.52 (C-3, 5), 111.23 (C-1); CH_3: 1.98	C_6F_5: (C2, F2) 241.5, (C4, F4) 253.9, (C4, F3) 13.6, (C4, F2) 6.0, (C3, F3) 253.5, (C1, F2) 29.5
CH_3[a]	CH_3	C_6H_5	C_6F_5: 149.88 (C-2, 6), 142.81 (C-4), 137.96 (C-3, 5), 110.47 (C-1); C_6H_5: 136.63 (C-1), 134.29 (C-3, 5), 130.43 (C-4), 128.65 (C-2, 6); CH_3: −1.03	C_6F_5: (C2, F2) 241.8, (C3, F3) 250.8, (C4, F4) 253.8, (C4, F3) 13.5, (C4, F2) 6.0, (C1, F2) 32.4, (C1, F3) 3.5, (C1, F4) 3.5; C_6H_5: (C3, H3) 158.6, (C4, H4) 160.1, (C4, H3) 7.0, (C2, H2) 159.6; CH_3: (C, F2) 3.5, (C, H) 121.7, (C, Si) 56.8
CH_3	CH_3	C_6F_5	C_6F_5: 148.99 (C-2, 6), 142.74 (C-4), 137.33 (C-3, 5), 107.84 (C-1); CH_3: −0.14	C_6F_5: (C2, F2) 243.3, (C4, F4) 256.3, (C4, F3) 13.5, (C4, F2) 6.0, (C3, F3) 252.8, (C1, F2) 30.7; CH_3: (C, F2) 3.1, (C, Si) 58.8
CH_3	C_6H_5	C_6H_5	C_6F_5: 149.25 (C-2, 6), 142.48 (C-4), 137.32 (C-3, 5), 108.27 (C-1); C_6H_5: 134.63 (C-3, 5), 133.79 (C-1), 130.12 (C-4), 128.10 (C-2, 6); CH_3: −1.52	C_6F_5: (C2, F2) 251.8, (C4, F4) 255.8, (C4, F3) 13.5, (C4, F2) 5.8, (C3, F3) 244.3, (C1, F2) 31.1, (C1, F3) 3.4, (C1, F4) 3.4; C_6H_5: (C3, H3) 160.6, (C4, H4) 160.6, (C4, H3) 7.4, (C2, H2) 162.1; CH_3: (C, F2) 4.0, (C, H) 122.3
CH_3	F	F	C_6F_5: 149.34 (C-2, 6), 144.23 (C-4), 137.47 (C-3, 5), 102.59 (C-1); CH_3: −2.49	C_6F_5: (C2, F2) 247.8, (C3, F3) 254.8, (C4, F4) 259.3, (C4, F3) 13.2, (C4, F2) 5.9; CH_3: (C, Si*F*) 15.7
CH_3	Cl	Cl	C_6F_5: 148.78 (C-2, 6), 144.03 (C-4), 137.54 (C-3, 5), 106.47 (C-1); CH_3: 7.92	C_6F_5: (C2, F2) 249.1, (C3, F3) 254.3, (C4, F4) 259.3, (C4, F3) 13.3, (C4, F2) 6.6, (C1, F2) 26.6, (C1, F3) 3.1, (C1, F4) 3.1; CH_3: (C, F2) 3.5, (C, Si) 75.8
CH_3	Br	Br	C_6F_5: 148.63 (C-2, 6), 144.08 (C-4), 137.51 (C-3, 5), 106.90 (C-1); CH_3: 10.77	C_6F_5: (C2, F2) 249.3, (C3, F3) 254.8, (C4, F4) 259.8, (C4, F3) 13.2, (C4, F2) 5.9, (C1, F2) 26.2, (C1, F3) 3.2, (C1, F4) 3.2; CH_3: (C, F2) 3.7

[a] In CD_2Cl_2.

mmol) and $(CF_3SO_2)_2O$ (2.0 g, 7 mmol). After 10–15 min the ^{19}F-NMR spectrum showed the formation of 1,4-$C_6D_2F_4$. The compound 1,4-$C_6D_2F_4$ (0.4 g, 77%) was isolated by distillation, b.p. 84–86°C.

*4.5. Reactions of dimethyl[bis(pentafluorophenyl)]silane **3** with electrophiles*

4.5.1. With bromine

In a reaction with bromine (0.3 ml) at r.t. 20% of silane **3** (34 mg, 0.08 mmol) were converted into bromopentafluorobenzene **4** and traces of pentafluorobenzene **2** (^{19}F-NMR) within 8 days.

4.5.2. With bromine and $AlBr_3$

A sample of $AlBr_3$ (23 mg, 0.09 mmol) was added at r.t. to a solution of silane **3** (57 mg, 0.15 mmol) in bromine (0.3 ml). After 15 min the reaction mixture was diluted with $CDCl_3$ (0.05 ml). The ^{1}H- and ^{19}F-NMR spectra showed the total conversion of silane **3** into bromopentafluorobenzene and Me_2SiBr_2.

4.5.3. With bromine and $AlBr_3$ in DBE

A solution of silane **3** (52 mg, 0.13 mmol) in DBE (0.2 ml) was added to $AlBr_3$ (19 mg, 0.07 mmol) and the resulting solution was stirred for 0.5 h at r.t. Bromosilane **5**, pentafluorobenzene **2** (1:1, M) and silane **3** (5% conversion) were detected by ^{19}F-NMR spectrometry. A total of 0.5 h after the addition of bromine (65 mg, 0.4 mmol) C_6F_5Br and C_6F_5H (93:7, M) were the only polyfluoroaromatic products (^{19}F-NMR).

4.5.4. With $AlCl_3$ (1.9 equivalents) in CD_2Cl_2

The reaction of silane **3** (57 mg, 0.15 mmol) with $AlCl_3$ (35 mg, 0.26 mmol) and CD_2Cl_2 (0.2 ml) led to a mixture of compounds **3**, **6** and **2** (42.9, 28.6 and 28.6 molar%, respectively) as well as Me_2SiCl_2 (^{1}H- and ^{19}F-NMR).

4.5.5. With $AlCl_3$ (0.33 equivalents) in $CDCl_3$

A sample of $AlCl_3$ (11 mg, 0.08 mmol) was added at r.t. to a solution of silane **3** (99 mg, 0.25 mmol) in $CDCl_3$ (0.4 ml) and the resulting reaction mixture was stirred for 13 days. The organic phase contained silanes **3**, **6**, **2** and $C_6F_5CDCl_2$ (62, 18, 18 and 2 molar%, respectively) as well as Me_2SiCl_2 (^{1}H-, ^{19}F-NMR and GCMS).

4.5.6. With $AlCl_3$ (1.9 equivalents) in $CDCl_3$

The reaction of silane **3** (36 mg, 0.09 mmol) with $AlCl_3$ (22 mg, 0.16 mmol) and $CDCl_3$ (0.4 ml) gave a mixture of **3**, **6**, **2** and $C_6F_5CDCl_2$ (29, 29, 29 and 13 molar%, respectively) as well as Me_2SiCl_2 (^{1}H-, ^{19}F-NMR and GCMS).

4.5.7. With HCl and $AlCl_3$ in $CDCl_3$

Gaseous HCl was bubbled into a stirred suspension of $AlCl_3$ (29 mg, 0.22 mmol) in a $CDCl_3$ (2 ml) solution of silane **3** (157 mg, 0.40 mmol) at r.t. After 1 h silanes **3**, **6** and pentafluorobenzene **2** (24, 29 and 47 molar%, respectively) were detected along with Me_2SiCl_2 (^{1}H- and ^{19}F-NMR).

Table 4
IR and Raman spectra of pentafluorophenylsilanes C_6F_5SiXYZ

X	Y	Z	IR/cm^{-1}	Raman/cm^{-1}
$CH_3^{a,b}$	F	F	2924, 1649, 1603, 1586, 1522, 1472, 1407, 1390, 1300, 1276, 1183, 1125, 1100, 1073, 1056, 1024, 977, 944, 900, 859, 785, 755, 732, 715, 628, 585, 505, 413, 394, 336	2988 (26.2), 2918 (91.0), 2795 (4.5), 2540 (3.7), 1649 (18.4), 1411 (5.7), 1389 (10.2), 1277 (3.3), 1144 (4.5), 895 (4.9), 860 (13.9), 716 (3.9), 586 (4.3), 506 (100.0), 445 (35.2), 396 (35.7), 337 (8.2), 280 (5.7), 216 (23.8), 157 (4.1)
$CH_3^{a,c}$	Cl	Cl	1645, 1521, 1473, 1407, 1386, 1297, 1269, 1143, 1114, 1096, 1023, 977, 857, 801, 758, 738, 628, 587, 564, 527, 482	2981 (7.0), 2916 (46.5), 1645 (14.0), 1384 (7.0), 857 (9.3), 587 (37.2), 482 (100.0), 444 (19.8), 394 (18.6), 369 (18.6), 314 (9.3), 234 (16.3), 146 (10.5)
CH_3^{a}	Br	Br	2969, 2932, 2916, 1644, 1611, 1588, 1521, 1468, 1403, 1384, 1296, 1264, 1143, 1092, 1033, 1020, 976, 854, 805, 796, 754, 732, 626, 586, 508, 464, 444, 421	2980 (25.0), 2913 (100.0), 1644 (25.0), 1383 (25.0), 853 (35.7), 732 (21.4), 586 (67.9), 508 (58.9), 445 (35.7), 421 (85.7), 350 (76.8), 294 (64.3), 278 (23.2), 209 (14.3), 199 (17.9), 170 (57.1)
CH_3^{d}	CH_3	C_6F_5	2972, 2914, 1644, 1584, 1519, 1463, 1410, 1383, 1377, 1290, 1264, 1137, 1088, 1018, 972, 864, 857, 820, 810, 802, 740, 726, 680, 627, 585, 507, 401	2973 (14.6), 2914 (61.5), 2798 (3.5), 1644 (20.0), 1404 (5.4), 1383 (13.9), 1269 (4.6), 1137 (3.9), 864 (6.2), 822 (15.4), 679 (24.6), 627 (6.2), 584 (59.2), 496 (100.0), 446 (36.2), 395 (30.8), 359 (8.9), 298 (8.1), 279 (5.4), 250 (6.9), 227 (12.3), 161 (6.9), 134 (6.2)
CH_3^{a}	C_6H_5	C_6H_5	3073, 3052, 3025, 3003, 1642, 1591, 1518, 1462, 1430, 1411, 1376, 1286, 1261, 1193, 1110, 1086, 1030, 1018, 1000, 971, 801, 755, 735, 726, 968, 622, 509, 474, 448, 441	3138 (4.5), 3054 (52.4), 2968 (9.7), 2909 (18.0), 1642 (5.2), 1591 (21.2), 1570 (8.0), 1376 (3.9), 1193 (5.8), 1159 (6.4), 108 (7.4), 1030 (27.0), 1000 (100.0), 837 (6.4), 672 (20.6), 585 (14.8), 509 (16.7), 476 (3.9), 446 (8.7), 395 (8.7), 350 (8.4), 328 (3.2), 243 (7.7), 200 (7.7), 88 (42.8)

[a] Neat liquid. [b] Lit. see [25]. [c] Lit. see [26]. [d] Lit. see [19].

*4.6. Reactions of dimethyl(pentafluorophenyl)phenylsilane **7** with electrophiles*

4.6.1. With aHF

A two phase system of silane **7** (1.25 g, 4.12 mmol), aHF (1 ml) and CH_2Cl_2 (3 ml) was stirred at r.t. After 0.5 h aHF was evaporated under argon and the residual solution was treated with NaF. Compound **9** (0.95 g, 94%) was isolated by distillation, b.p. 155–158°C (lit. 157–159°C [21]).

4.6.2. With $AlBr_3$ in DBE

A sample of $AlBr_3$ (109 mg, 0.41 mmol) was added to a stirred solution of silane **7** (433 mg, 1.43 mmol) in DBE (2 ml) at 5°C. After 10 min the suspension was diluted with hexane (8 ml) and filtered. The filtrate was washed with 10% HCl and water and dried with $MgSO_4$. Separation of the mother liquid and evaporation of the solvent gave product **5** (380 mg, 87%).

*4.7. Reactions of methyl(pentafluorophenyl)diphenylsilane **8** with electrophiles*

4.7.1. With aHF

A sample of aHF (2 ml) was added to a solution of silane **8** (1.25 g, 3.4 mmol) in CH_2Cl_2–CD_2Cl_2 (3:1) (4 ml) at -78°C. The two phase system was stirred and warmed to r.t. Periodic control of the reaction mixture by ^{19}F-NMR spectrometry showed the following composition (molar%):

Reaction time, h	Silane **8** (%)	Silane **11** (%)	Silane **10** (%)
0.5	78	22	—
4	—	51	49
23.5	—	—	100

When the total conversion of silane **8** into silane **10** was achieved, aHF was removed in vacuum at -30°C and product **10** (531 mg, 63%) was isolated by distillation, b.p. 150°C (lit. 144°C [25]).

4.7.2. With HCl and $AlCl_3$ in hexane

At r.t. gaseous HCl was bubbled into a stirred suspension of $AlCl_3$ (100 mg, 0.75 mmol) in a hexane (10 ml) solution of silane **8** (525 mg, 1.44 mmol) for 60 min. The ^{19}F-NMR spectrum of the mother liquid showed the quantitative conversion of silane **8** into product **12**.

4.7.3. With $AlCl_3$ (one equivalent) in CH_2Cl_2

A solution of silane **8** (1.21 g, 3.3 mmol) in CH_2Cl_2 (3 ml) was added to a stirred suspension of $AlCl_3$ (429 mg, 3.2 mmol) in CH_2Cl_2 (1 ml). Periodic control of the reaction mixture by ^{19}F-NMR spectrometry showed the following composition (molar%):

Reaction time, minutes	Silane **8** (%)	Silane **13** (%)	Silane **12** (%)
15	52	48	—
30	—	50	50
45	—	—	100

4.7.4. With $AlCl_3$ (0.7 equivalents) in CH_2Cl_2

A solution of silane **8** (1.18 g, 3.2 mmol) in CH_2Cl_2 (3 ml) was added to a stirred suspension of $AlCl_3$ (297 mg, 2.2 mmol) in CH_2Cl_2 (1 ml). After 45 min the ^{19}F-NMR spectrum showed the total conversion of silane **8** into product **12** which was isolated in a 66% yield (603 mg) by distillation, b.p. 171°C (lit. 63–65°C (4 hPa) [26], 71°C (10 hPa) [18]).

4.7.5. With $AlCl_3$ (7.7 equivalents) in AcCl

A solution of silane **8** (26 mg, 0.07 mmol) in AcCl (0.1 ml) was added to a stirred solution of $AlCl_3$ (73 mg, 0.55 mmol) in AcCl (0.15 ml). After 20 min the ^{19}F-NMR spectrum showed the total conversion of silane **8** into product **12**.

4.7.6. With $AlBr_3$ (0.5 equivalent) in DBE

A solution of silane **8** (1.36 g, 3.7 mmol) and $AlBr_3$ (498 mg, 1.9 mmol) in DBE (25 ml) was stirred for 10 min. The ^{19}F-NMR spectrum showed the total conversion of silane **8** into product **14** which was isolated in a 65% yield (897 mg) by distillation, b.p. 199°C.

*4.8. Reaction of dichloro(methyl)pentafluorophenylsilane **12** with XeF_2*

A sample of xenon difluoride (0.80 g, 4.73 mmol) was added in one portion to a stirred solution of dichlorosilane **12** (1.28 g, 4.55 mmol) in CH_2Cl_2 (5 ml) at r.t. Within a few minutes xenon started to evolve. After 30 min the reaction mixture was warmed to reflux, the solvent was distilled off and difluorosilane **10** (0.83 g, 74%) was isolated by distillation, b.p. 137–138°C (lit. 144°C [25]).

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