

## A convenient preparation of pentafluorophenyl (fluoro) silanes: reactivity of pentafluorophenyltrifluorosilane <sup>☆</sup>

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### Abstract

Pentafluorophenyl(fluoro)silanes ( $C_6F_5)_nSiF_{4-n}$  ( $n = 1, 2$ ) were prepared from the corresponding ethoxysilanes by sequential chlorodeethoxylation with  $SOCl_2$  and fluoridation of chlorosilanes with  $SbF_3$ . The conversion of  $C_6F_5Si(OEt)_3$  and  $C_6F_5SiCl_3$  into  $C_6F_5SiF_3$  with anhydrous HF was described. Some reactions of  $C_6F_5SiF_3$  with electrophiles and nucleophiles were studied.

**Keywords:** Pentafluorophenylhalogenosilanes; C–Si bond cleavage; Nucleophilic arylation of electrophiles

### 1. Introduction

Pentafluorophenyltrialkylsilanes and tetrakis(pentafluorophenyl)silane are easily prepared by different methods [1] and their reactions with halogen fluorides [2,3], xenon difluoride [4], nucleophiles [5] and fluoride-catalysed reactions with electrophiles [6] have been described. Little is known about the reactivity of pentafluorophenylhalogenosilanes ( $C_6F_5)_nSiX_{4-n}$  ( $X = F, Cl, Br$ ;  $n = 1-3$ ). One reason for this is the absence of convenient or reliable preparative methods. While  $PhSiCl_3$  and  $Ph_2SiCl_2$  were obtained by phenylation of  $SiCl_4$  with  $PhMgBr$  or  $PhLi$  [7], the reaction of  $SiCl_4$  with  $C_6F_5MgBr$  or  $C_6F_5Li$  led mainly to  $(C_6F_5)_4Si$  [8]. Similar results were obtained by pentafluorophenylation of  $SiF_4$  [9] and  $SiBr_4$  [10]. In situ generated  $C_6F_5MgBr$  reacted with  $SiCl_4$  (in excess) to yield a mixture of  $(C_6F_5)_nSiCl_{4-n}$  ( $n = 1-4$ ) [11]. The first successful preparation of  $C_6F_5SiF_3$  was achieved by insertion of  $SiF_2$  into the C–F bond of hexafluorobenzene [12].  $C_6F_5SiFCl_2$  and  $C_6F_5SiCl_3$  were produced by UV-irradiation of  $C_6F_6$  and  $SiHCl_3$  [13] or gamma-irradiation of  $SiHCl_3$  and  $C_6F_5Cl$  [14,15], however, all the methods mentioned above have no preparative use. A

more convenient synthesis of  $(C_6F_5)_nSiBr_{4-n}$  ( $n = 1-3$ ) was offered by Weidenbruch [9,16] who passed bromopentafluorobenzene over a Si–Cu mixture at 600 °C and isolated  $C_6F_5SiBr_3$ ,  $(C_6F_5)_2SiBr_2$  and  $(C_6F_5)_3SiBr$  after rectification of the reaction mixture in 8%, 9% and 1% yields respectively. Reaction of the bromosilanes with  $SbF_3$  or  $Na_2SiF_6$  gave the corresponding fluorosilanes  $(C_6F_5)_nSiF_{4-n}$  ( $n = 1-3$ ) [10].

We report here new and convenient synthetic procedures for the preparation of pentafluorophenylchloro- and fluorosilanes  $(C_6F_5)_nSiX_{4-n}$  ( $X = Cl, F$ ;  $n = 1, 2$ ) and some reactions of  $C_6F_5SiF_3$  with electrophilic and nucleophilic reagents.

### 2. Results and discussion

#### 2.1. Synthesis of $(C_6F_5)_nSiX_{4-n}$ ( $X = Cl, F$ ; $n = 1, 2$ )

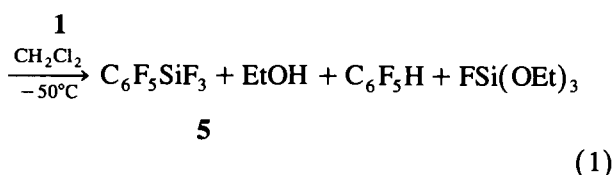
In 1968 Whittingham [11] published the preparation of pentafluorophenyl(ethoxy)silanes  $(C_6F_5)_nSi(OEt)_{4-n}$  from  $C_6F_5Br$ , Mg and  $Si(OEt)_4$ . This method may be scaled-up to 0.4 mol of bromopentafluorobenzene and pentafluorophenyltriethoxysilane (1) (55% yield), bis(pentafluorophenyl)diethoxysilane (3) (35% yield) and tris(pentafluorophenyl)ethoxysilane (trace) were isolated.

Several methods for the conversion of the Si–OEt into the Si–F bond were reported [7,17], but the most

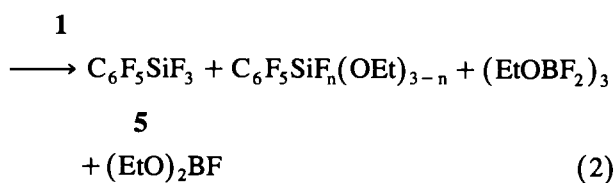
<sup>☆</sup> Dedicated to Prof. Dr. Herbert W. Roesky on the occasion of his 60th birthday.

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popular of them were unsuitable for the fluoridation of  $C_6F_5Si(OEt)_3$ . Heating of silane **1** with  $K[HF_2]$  or treatment with anhydrous HF (AHF) at room temperature gave  $C_6F_5H$ . Pentafluorophenyltrifluorosilane was obtained from  $C_6F_5Si(OEt)_3$  and AHF at  $-50^\circ C$ , but its yield was only 30% and the major product was pentafluorobenzene. Independent experiments have shown that the co-product ethanol reacts with  $C_6F_5Si(OEt)_3$  in AHF to give  $C_6F_5H$ .  $C_6F_5H$  is also formed from  $C_6F_5SiF_3$  and EtOH in AHF, but this reaction proceeds more slowly. To avoid the consumption of  $C_6F_5Si(OEt)_3$  and  $C_6F_5SiF_3$  by ethanol, the fluoridation of  $C_6F_5Si(OEt)_3$  with HF was carried out in the two-phase system AHF– $CH_2Cl_2$  at  $-50^\circ C$ . This modification gave trifluorosilane **5** in high yield and only a small admixture of pentafluorobenzene.



Other attempts to fluoridate triethoxysilane **1** were ineffective. Only a trace of  $C_6F_5SiF(OEt)_2$  was obtained by bubbling  $SF_4$  into a  $CH_2Cl_2$  solution of silane **1** at room temperature. From the reaction of  $C_6F_5Si(OEt)_3$  with  $BF_3 \cdot OEt_2$  or  $BF_3$  gas pentafluorophenyltrifluorosilane **5** was obtained only in complex mixtures together with partially substituted silanes  $C_6F_5SiF(OEt)_2$ ,  $C_6F_5SiF_2OEt$  and fluoroethoxyboranes.

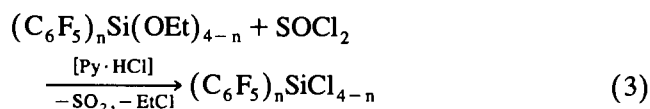


$n = 1, 2$

The fluoridation of  $C_6F_5Si(OEt)_3$  with  $SbF_3$  as well as with  $ZnF_2$  gave  $C_6F_5SiF_3$  (major),  $C_6F_5SiF_n(OEt)_{3-n}$  (admixture) and unrecognised fluoro-containing materials [18].

Chloroethoxylation of  $C_6F_5Si(OEt)_3$  or  $(C_6F_5)_2Si(OEt)_2$  with acetylchloride ( $20^\circ C$ , 48 h) was reported [11], but we were unable to reproduce these preparations. Only traces of the desired product were formed when silane **1** and  $CH_3COCl$  were stirred continuously at room temperature (96 h) or under reflux (44 h). Also the reaction of  $C_6F_5Si(OEt)_3$  with AcCl in the presence of HOAc ( $40^\circ C$ , 48 h) led only to traces of  $C_6F_5SiCl_n(OEt)_{3-n}$ , whereas a mixture of  $C_6F_5SiCl_3$ ,  $C_6F_5SiCl_2OEt$  and, probably,  $C_6F_5SiCl_n(OAc)_{3-n}$  was

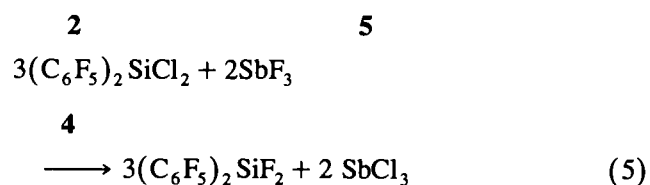
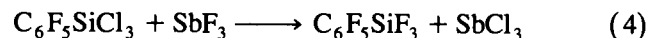
obtained in the presence of  $FeCl_3$  or  $ZnCl_2$ . That failure was unexpected taking into account the successful replacement of OEt groups for chlorine in  $C_6F_5SiMe(OEt)_2$  and  $C_6F_5Si(CH=CH_2)(OEt)_2$  under the action of AcCl and  $FeCl_3$  [19] and the conversion of  $C_6F_5SiBu_2OEt$  into  $C_6F_5SiBu_2Cl$  with AcCl and  $ZnCl_2$  (see Experimental section). Therefore we used thionylchloride in the presence of pyridinium hydrochloride (catalyst) as a more powerful reagent. The latter system was used earlier for the effective stepwise substitution of alkoxy groups by chlorine in  $Si(OR)_{4-n}$  [20]. Indeed, reflux of pentafluorophenyltriethoxysilane with  $SOCl_2$  and  $Py \cdot HCl$  for 24 h resulted in the formation of pentafluorophenyltrichlorosilane (**2**) in high yield. The intermediate silane  $C_6F_5SiCl_2OEt$  could be isolated when the reactants had been refluxed for 4 h only. A similar procedure was employed for the preparation of  $(C_6F_5)_2SiCl_2$  (**4**) from diethoxysilane  $(C_6F_5)_2Si(OEt)_2$  (**3**).



$(n = 1, 2)$

It is interesting that no reaction was observed between  $C_6F_5Si(OEt)_3$ ,  $SOBr_2$  and Py when heated at  $50^\circ C$  for 77 h.

Treatment of silanes **2** and **4** with  $SbF_3$  gave fluorosilanes **5** and **6** respectively. Niobium pentafluoride is also available for fluoridation [5]. With the two-phase system AHF– $CH_2Cl_2$  at  $-50^\circ C$  **2** could be converted also into **5**.



**6**

## 2.2. Reactivity of pentafluorophenyltrifluorosilane **5**

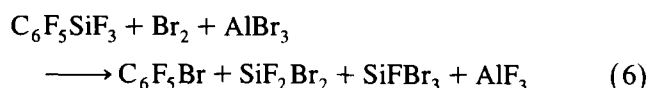
Recently  $C_6F_5SiF_3$  and related silanes were successfully used for the substitution of one fluorine atom for a  $C_6F_5$  group in  $IF_5$  [2],  $BrF_3$  [21] and  $BrF_5$  [3,22] in basic media. On the other hand no  $[C_6F_5Xe]^+$  cation was formed in the reaction of  $C_6F_5SiF_3$  with  $XeF_2$  in  $CH_2Cl_2$  nor in the presence of  $BF_3 \cdot OEt_2$ . Only ring fluorination without carbon–silicon bond cleavage took place when  $[XeF]^+$   $[NbF_6]^-$  was reacted with silane **5** in  $SO_2FCl$  [5]. Mechanistic details of these reactions are not known. This circumstance has prompted us to inves-

tigate interactions of pentafluorophenyltrifluorosilane (**5**) with simple electrophiles and nucleophiles.

The  $^{19}\text{F}$  NMR in either case spectra of  $\text{C}_6\text{F}_5\text{SiF}_3$  solutions in trifluoroacetic or fluorosulfonic acid exhibit the resonance of fluorine atoms bonded to silicon as triplet [ $^4J(\text{F}-\text{F})$ ]. In AHF trifluorosilane **5** is less soluble and this solution displays a very broad  $^{19}\text{F}$  NMR signal for the  $\text{SiF}_3$  group. No changes took place in these acidic solutions during a few days at room temperature.

Pentafluorophenyltrifluorosilane (**5**) did not react with bromine in MeCN at room temperature. Aryl–silicon bond cleavage proceeded very slowly in excess of liquid bromine (room temperature, 10 days) to give a mixture of trifluorosilane **5**, bromopentafluorobenzene and, presumably,  $\text{C}_6\text{F}_5\text{SiF}_2\text{Br}$  (1:1:0.6 mol). The latter compound was not isolated and only assumed by its  $^{19}\text{F}$  NMR spectrum:  $-126.90$  (F-2, 6),  $-143.63$  (F-4),  $-159.00$  (F-3, 5) and  $-131.00$  ( $\text{SiF}_2\text{Br}$ ) [ $t, ^4J(\text{F}-\text{F}) =$

11 Hz] ppm. Bromodesilylation was accelerated by  $\text{AlBr}_3$ . According to the  $^{19}\text{F}$  NMR data, the ratio of  $\text{C}_6\text{F}_5\text{SiF}_3$  to  $\text{C}_6\text{F}_5\text{Br}$  was 1:4 after 48 h and the total conversion of trifluorosilane **5** into bromopentafluorobenzene was completed after 76 h at room temperature. Co-products were mixed bromofluorosilanes  $\text{SiF}_n\text{Br}_{4-n}$  ( $n = 1, 2$ ) which were identified by their  $^{19}\text{F}$  NMR spectra. In the presence of  $\text{AlBr}_3$  exchange of silicon-bonded fluorine for bromine in trifluorosilane **5** was not observed.



Trifluorosilane **5** and nitronium tetrafluoroborate did not react in dichloromethane as well as in  $\text{HSO}_3\text{F}$ .

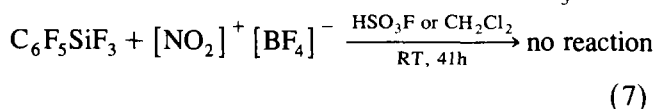
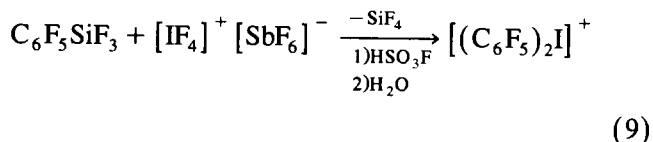
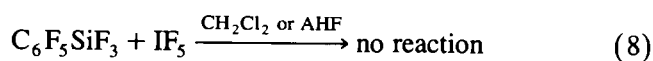


Table 1  
The  $^{19}\text{F}$  NMR spectra of pentafluorophenylsilanes  $\text{C}_6\text{F}_5\text{SiXYZ}$  ( $\text{CDCl}_3$ ,  $35^\circ\text{C}$ )

| X                      | Y                            | Z                                   | $\delta(^{19}\text{F})/\text{ppm}$ |         |         |                      | $J(^{19}\text{F}-^{19}\text{F})/\text{Hz}$                |
|------------------------|------------------------------|-------------------------------------|------------------------------------|---------|---------|----------------------|---|
|                        |                              |                                     | F-2,6                              | F-4     | F-3,5   | F-Si                 |   |
| F                      | F                            | F                                   | -125.14                            | -142.93 | -158.97 | -134.32 <sup>a</sup> | (2,4) 6.5; (3,4) 19.1;<br>(F-Si-C-C-F) 10.2               |
| F                      | F                            | F <sup>b</sup>                      | -125.64                            | -144.14 | -160.08 | <sup>c</sup>         | (2,4) 6.5; (3,4) -18.1;<br>(F-Si-C-C-F) 11.6 <sup>1</sup> |
| F                      | F                            | F <sup>d</sup>                      | -124.82                            | -143.03 | -159.04 | -134.19 <sup>a</sup> | (2,4) 6.5; (3,4) 18.5;<br>(F-Si-C-C-F) 10.9               |
| F                      | F                            | F <sup>e</sup>                      | -125.93                            | -143.84 | -159.52 | -132.76 <sup>f</sup> | (2,4) 6.2; (3,4) 19.7                                     |
| F                      | F                            | OE <sup>t</sup> <sup>d</sup>        | -126.0                             | -144.3  | -159.4  | -130.1               |   |
| F                      | F                            | OE <sup>t</sup> <sup>g</sup>        | -126.2                             | -146.5  | -160.3  | -132.9               |   |
| F                      | OE <sup>t</sup>              | OE <sup>t</sup> <sup>d</sup>        | -126.0                             | -147.0  | -160.8  | -132.6               |   |
| F                      | OE <sup>t</sup>              | OE <sup>t</sup> <sup>g</sup>        | -126.2                             | -149.1  | -161.1  | -132.2               |   |
| OE <sup>t</sup>        | OE <sup>t</sup>              | OE <sup>t</sup>                     | -127.00                            | -151.38 | -162.17 |                      | (2,4) 3.5; (3,4) 19.3                                     |
| F                      | F                            | NR <sub>2</sub> <sup>i</sup>        | -126.2                             | -148.2  | -160.9  | -135.7               |   |
| F                      | NR <sub>2</sub> <sup>i</sup> | NR <sub>2</sub> <sup>i</sup>        | -126.9                             | -151.2  | -162.0  | -137.1               |   |
| Cl                     | Cl                           | Cl <sup>d</sup>                     | -125.59                            | -145.09 | -159.90 |                      | (2,4) 6.8; (3,4) 19.4                                     |
| Cl                     | Cl                           | OE <sup>t</sup>                     | -126.40                            | -147.14 | -160.75 |                      | (2,4) 5.8; (3,4) 19.6                                     |
| $\text{C}_6\text{F}_5$ | F                            | F <sup>b</sup>                      | -127.19                            | -144.39 | -159.33 | <sup>c</sup>         | (2,4) 6.0; (3,4) -18.5;<br>(F-Si-C-C-F) 12.0              |
| $\text{C}_6\text{F}_5$ | F                            | F <sup>d</sup>                      | -126.81                            | -143.91 | -159.37 | -129.81              | (2,4) 6.0; (3,4) 19.2;<br>(F-Si-C-C-F) 12.0               |
| $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$       | F <sup>d</sup>                      | -127.53                            | -144.91 | -159.70 | -158.13              | (2,4) 5.6; (3,4) 19.8;<br>(F-Si-C-C-F) 11.3               |
| $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$       | F <sup>b</sup>                      | -127.66                            | -144.74 | -159.22 | <sup>c</sup>         |   |
| $\text{C}_6\text{F}_5$ | Cl                           | Cl <sup>d</sup>                     | -126.34                            | -145.51 | -159.98 |                      | (2,4) 6.3; (3,4) 19.4                                     |
| $\text{C}_6\text{F}_5$ | Cl                           | OE <sup>t</sup> <sup>d</sup>        | -127.4                             | -147.6  | -160.9  |                      | (3,4) 18.8  |
| $\text{C}_6\text{F}_5$ | OE <sup>t</sup>              | OE <sup>t</sup> <sup>d</sup>        | -128.07                            | -149.48 | -161.57 |                      | (3,4) 18.8  |
| $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$       | Cl <sup>b</sup>                     | -127.06                            | -145.33 | -157.50 |                      | (2,4) 5.8; (3,4) -19.8                                    |
| $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$       | $\text{C}_6\text{F}_5$ <sup>d</sup> | -127.15                            | -146.68 | -160.16 |                      | (2,4) 5.2; (3,4) 19.9                                     |
| $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$       | $\text{C}_6\text{F}_5$ <sup>b</sup> | -127.50                            | -146.21 | -159.66 |                      |   |
| Bu                     | Bu                           | Bu                                  | -127.44                            | -153.11 | -162.35 |                      | (2,4) 3.7; (3,4) 18.0                                     |
| Bu                     | Bu                           | F                                   | -128.44                            | -150.52 | -161.45 | -168.32 <sup>h</sup> | (2,4) 3.8; (3,4) 19.4                                     |
| Bu                     | Bu                           | OE <sup>t</sup>                     | -128.18                            | -152.24 | -162.13 |                      | (2,4) 3.7; (3,4) 20.0                                     |
| Bu                     | Bu                           | Bu <sup>k</sup>                     | -129.47                            |         | -145.88 |                      |   |

<sup>a</sup>  $^1J(^{19}\text{F}-^{29}\text{Si})$  248 Hz; <sup>b</sup> in  $\text{CCl}_4$  [27]; <sup>c</sup> no data; <sup>d</sup> in  $\text{CH}_2\text{Cl}_2-\text{CD}_2\text{Cl}_2$ ; <sup>e</sup> in  $\text{CD}_3\text{CN}-\text{EtCN}$ ; <sup>f</sup> sharp singlet; <sup>g</sup> neat liquid; <sup>h</sup>  $^1J(^{19}\text{F}-^{29}\text{Si})$  296 Hz; <sup>i</sup> NR<sub>2</sub> means piperidino group, solution in hexane; <sup>k</sup> 4-Bu $\text{C}_6\text{F}_4$ ; <sup>1</sup> see [28].

Previously no reaction of trifluorosilane **5** with  $\text{IF}_5$  (acidic media) as well as in chlorofluorocarbons (neutral media) was found [2]. In this paper the inertness of trifluorosilane **5** toward  $\text{IF}_5$  in  $\text{CH}_2\text{Cl}_2$  or AHF is shown. On the other hand, the interaction of compound **5** with  $[\text{IF}_4]^+ [\text{SbF}_6]^-$  in  $\text{HSO}_3\text{F}$  led to evolution of  $\text{SiF}_4$  (identified by its  $^{19}\text{F}$  NMR spectrum and as adduct  $\text{SiF}_4 \cdot 2 \text{Py}$ ) and formation of the bis(pentafluorophenyl)iodonium cation (identified by IR and  $^{19}\text{F}$  NMR spectrum).



The introduction of the second aryl group and the reduction of I(V) to I(III) are subjects for future investigations. The salt  $[\text{IF}_4]^+ [\text{SbF}_6]^-$  was dissolved in  $\text{HSO}_3\text{F}$  at room temperature and this solution was characterized by a sharp singlet resonance at 19.5 ppm ( $[\text{IF}_4]^+$  cation), a broad signal at ca.  $-110$  ppm ( $[\text{SbF}_6]^-$  anion) of correct relative intensity besides the singlet of  $\text{HSO}_3\text{F}$  ( $^{19}\text{F}$  NMR) [23]. During the conversion of trifluorosilane **5** into the bis(pentafluorophenyl)iodonium cation  $\text{C}_6\text{F}_5\text{IF}_4$  could not be detected. Furthermore,  $\text{C}_6\text{F}_5\text{IF}_4$

did not give the  $[(\text{C}_6\text{F}_5)_2\text{I}]^+$  cation under the action of  $\text{HSO}_3\text{F}$  or  $[\text{IF}_4]^+ [\text{SbF}_6]^-$  in  $\text{HSO}_3\text{F}$  under the same conditions.

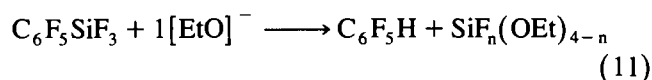
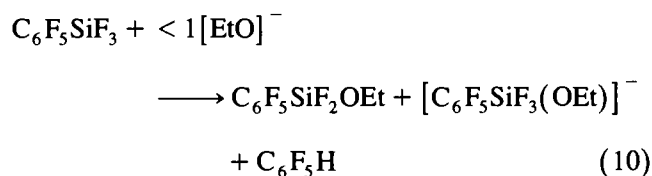
Similar to the reactivity of pentafluorophenyl-halogenosilanes with electrophiles only a few examples of reactivity with nucleophiles were known from the literature. From pentafluorophenyltrifluorosilane (**5**) only its hydrolysis to polymeric material  $[\text{C}_6\text{F}_5\text{SiO}_{1.5}]_n$  was reported [12]. The same product was obtained from  $\text{C}_6\text{F}_5\text{SiFCl}_2$  [13]. The exhaustive replacement of chlorine by ethoxy groups in  $\text{C}_6\text{F}_5\text{SiCl}_3$  or  $(\text{C}_6\text{F}_5)_2\text{SiCl}_2$  using anhydrous EtOH and Py in ether was described by Whittingham [11]. Weidenbruch converted bromosilanes  $\text{C}_6\text{F}_5\text{SiBr}_3$  and  $(\text{C}_6\text{F}_5)_2\text{SiBr}_2$  into  $\text{C}_6\text{F}_5\text{SiR}_3$  or  $(\text{C}_6\text{F}_5)_2\text{SiR}_2$  using Grignard reagents  $\text{RMgBr(I)}$  ( $\text{R} = \text{Me}, \text{Et}$ ) [9,16]. It was known that the reaction products of  $\text{C}_6\text{F}_5\text{SiMe}_3$  with nucleophiles depends on “hardness” of nucleophile: “hard”  $[\text{PrO}]^-$  gave pentafluorobenzene and “soft” BuLi led to formation of  $4\text{-BuC}_6\text{F}_4\text{SiMe}_3$  [5]. The “borderline” nucleophiles (piperidine, lithium piperidide and lithium propanethiolate) reacted at both electrophilic centres of  $\text{C}_6\text{F}_5\text{SiMe}_3$  (silicon and carbon C-4) [5]. Taking into account the high bond energy of silicon–fluorine and the strong electron pair acceptor character of the  $\text{SiF}_3$  group, the favoured attack of nucleophiles at  $\text{C}_6\text{F}_5\text{SiF}_3$  was not obvious.

Table 2  
The  $^{13}\text{C}$  NMR spectra of pentafluorophenylsilanes  $\text{C}_6\text{F}_5\text{SiXYZ}$  ( $\text{CD}_2\text{Cl}_2$ ,  $35^\circ\text{C}$ )

| X                      | Y                      | Z                      | $\delta(^{13}\text{C})/\text{ppm}$ |        |        |        | $J(^{13}\text{C}-^{19}\text{F})/\text{Hz}$   |
|------------------------|------------------------|------------------------|------------------------------------|--------|--------|--------|--|
|                        |                        |                        | C-1                                | C-2,6  | C-3,5  | C-4    |  |
| F                      | F                      | F                      | 96.13                              | 151.24 | 139.07 | 146.90 | (1,2) 27.0; (2,2) 253.1; (2,4) 5.7; (3,3) 257.6; (3,4) 13.2; (4,4) 261.9                       |
| Cl                     | Cl                     | Cl <sup>a</sup>        | 106.27                             | 150.41 | 139.37 | 146.48 | (1,2) 21.8; (2,2) 252.1; (2,4) 5.8; (3,3) 256.5; (3,4) 13.2; (4,4) 261.1                       |
| Cl                     | Cl                     | Cl <sup>b,g</sup>      | 105.07                             | 148.88 | 137.83 | 144.92 |  |
| Cl                     | Cl                     | OEt <sup>b,c</sup>     | 105.61                             | 149.80 | 138.39 | 145.03 | (1,2) 25.8; (1,4) 2.8; (2,2) 251.3; (2,4) 5.4; (3,3) 256.2; (3,4) 13.2; (4,4) 259.7            |
| OEt                    | OEt                    | OEt <sup>b,d</sup>     | 105.92                             | 150.39 | 138.25 | 143.69 | (1,2) 31.1; (1,3) 3.3; (1,4) 3.3; (2,2) 246.3; (2,4) 5.7; (3,3) 244.8; (3,4) 13.4; (4,4) 255.4 |
| $\text{C}_6\text{F}_5$ | F                      | F                      | 100.73                             | 150.20 | 138.23 | 145.78 | (1,2) 26.5; (2,2) 248.5; (2,4) 5.7; (3,3) 256.8; (3,4) 13.3; (4,4) 261.1                       |
| $\text{C}_6\text{F}_5$ | Cl                     | Cl                     | 105.86                             | 149.83 | 138.58 | 145.51 | (1,2) 24.4; (2,2) 250.8; (2,4) 5.8; (3,3) 258.9; (3,4) 13.3; (4,4) 260.9                       |
| $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$ | Cl <sup>a</sup>        | 106.27                             | 150.47 | 139.37 | 146.48 | (1,2) 21.8; (2,2) 252.1; (2,4) 5.8; (3,3) 256.5; (3,4) 13.2; (4,4) 261.1                       |
| $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$ | $\text{C}_6\text{F}_5$ | 103.5                              | 150.0  | 138.0  | 145.0  | (2,2) 248.6; (3,3) 257.5; (4,4) 257.5  |
| Bu                     | Bu                     | OEt <sup>b,e</sup>     | 108.82                             | 149.50 | 137.46 | 142.38 | (1,2) 35.2; (2,2) 242.7; (3,3) 253.3; (4,4) 254.9  |
| Bu                     | Bu                     | F <sup>b,f</sup>       | 106.98                             | 149.09 | 137.56 | 143.09 | (1,2) 29.0; (2,2) 244.1; (2,4) 5.9; (3,3) 252.6; (3,4) 13.4; (4,4) 256.6                       |

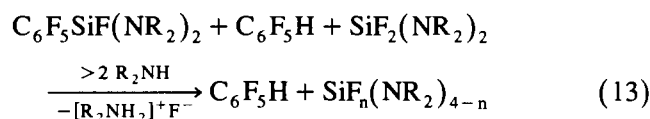
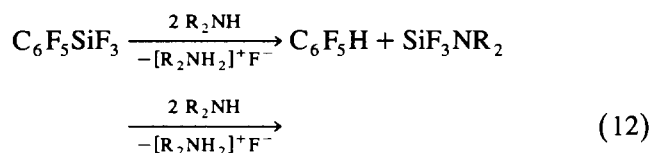
<sup>a</sup> in  $\text{CD}_3\text{CN}$ ; <sup>b</sup> in  $\text{CDCl}_3$ ; <sup>c</sup> 62.38 ( $\text{OCH}_2$ ), 17.69 ( $\text{CH}_3$ ) ppm; <sup>d</sup>  $^1J(\text{OC-H})$  141.7 Hz,  $^1J(\text{C-H})$  122.1 Hz; <sup>e</sup> 59.97 ( $\text{OCH}_2$ ), 18.34 ( $\text{CH}_3$ ) ppm; <sup>f</sup>  $^1J(\text{OC-H})$  143.7 Hz,  $^1J(\text{C-H})$  135.1 Hz; <sup>g</sup> 59.61 ( $\text{OCH}_2$ ), 26.48 ( $\text{CH}_3$ ), 25.02 ( $\text{CH}_2$ ), 18.27 ( $\text{CH}_3\text{CH}_2\text{O}$ ), 14.65, 13.72 ( $\text{CH}_2\text{CH}_2\text{Si}$ ) ppm; <sup>h</sup> 26.20 ( $\text{CH}_3$ ), 24.43 ( $\text{CH}_2$ ), 15.19 ( $\text{CH}_2$ ), 13.67 ( $\text{CH}_2$ ) ppm, <sup>i</sup>  $^2J(\text{C-Si-F})$  15.5 Hz; <sup>j</sup>  $^{13}\text{C}\{^{19}\text{F}\}$  decoupled spectrum.

For detection of intermediates at the interaction of trifluorosilane **5** with nucleophiles, all reactions were checked by  $^{19}\text{F}$  NMR spectrometry (Tables 1–3). Addition of 0.34 equivalents EtONa (“hard” nucleophile) to the solution of trifluorosilane **5** in diglyme gave pentafluorobenzene and, probably, a mixture of  $\text{C}_6\text{F}_5\text{SiF}_3$ ,  $\text{C}_6\text{F}_5\text{SiF}_2\text{OEt}$  and  $[\text{C}_6\text{F}_5\text{SiF}_3(\text{OEt})]^-$ , which underwent fast Si–F exchange. This assumption arises from comparison of the  $^{19}\text{F}$  NMR spectra of the neutral silanes  $\text{C}_6\text{F}_5\text{SiF}_n(\text{OEt})_{3-n}$  ( $n = 1-3$ ) where F–Si signals were located at  $-130$  to  $-134$  ppm and the spectrum of  $[\text{Me}_4\text{N}]^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$   $\{-104.2$  ( $[\text{SiF}_4]^-$ ),  $-129.2$  (F-2, 6),  $-159.9$  (F-4),  $-164.2$  (F-3, 5) ppm (in diglyme) [25] with the observed resonances at  $-123.2$  (Si–F, broad),  $-126.6$  (F-2, 6),  $-147.6$  (F-4) and  $-160.7$  (F-3, 5) ppm. Finally, under the action of ca. 1 equivalent of EtONa pentafluorobenzene became the only polyfluoroaromatic product.



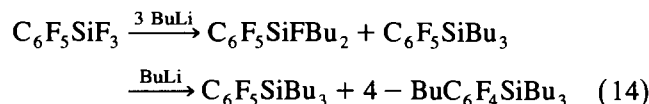
The interaction of trifluorosilane **5** with piperidine (2 equivalents) in hexane led to formation of pentafluorobenzene and pentafluorophenylpiperidinodifluorosilane (1:1 mol). Further treatment of the reaction mixture with piperidine (2 equivalents) resulted in pentafluorophenylbis(piperidino)fluorosilane and  $\text{C}_6\text{F}_5\text{H}$  (1:2

mol). In excess of that amine pentafluorobenzene was the only polyfluoroaromatic product.



In contrast to the interaction with EtONa, the generation of arylaminofluorosilicates was not observed here. One of the possible reasons is their fast reaction with acidic protons of the  $[\text{R}_2\text{NH}_2]^+$  cation to give  $\text{C}_6\text{F}_5\text{H}$ .

Addition of BuLi (3 equivalents) to  $\text{C}_6\text{F}_5\text{SiF}_3$  in hexane gave a mixture of  $\text{C}_6\text{F}_5\text{SiFBu}_2$  and  $\text{C}_6\text{F}_5\text{SiBu}_3$  (2:1 mol). Further alkylation with BuLi led to the formation of  $\text{C}_6\text{F}_5\text{SiBu}_3$  and 4-Bu $\text{C}_6\text{F}_4\text{SiBu}_3$ . When  $\text{C}_6\text{F}_5\text{SiF}_3$  was alkylated with 4.3 equivalents of BuLi in a mixture of hexane–diglyme, 4-butyltetrafluorophenyltributylsilane was the only polyfluoroaromatic reaction product. In both cases no pentafluorobenzene was detected. It should be mentioned that alkylation of  $\text{C}_6\text{F}_5\text{SiMe}_3$  with BuLi in hexane led to formation of 4-Bu $\text{C}_6\text{F}_4\text{SiMe}_3$  [5].



These data point out the attack of nucleophiles at the silicon atom in  $\text{C}_6\text{F}_5\text{SiF}_3$  independently from the “hardness” of the nucleophiles. However, the “hard”

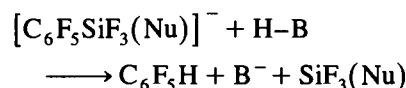
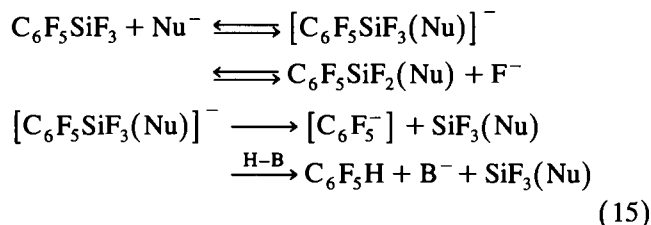
Table 3  
The  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra of pentafluorophenylsilanes  $\text{C}_6\text{F}_5\text{SiXYZ}$  ( $\text{CDCl}_3$ ,  $35^\circ\text{C}$ )

| X                      | Y   | Z              | $\delta(^{29}\text{Si})/\text{ppm}$ | $J(^{29}\text{Si}-^{19}\text{F})/\text{Hz}$                          | $\delta(^1\text{H})/\text{ppm}$   | $J(^1\text{H}-^{19}\text{F})/\text{Hz}$ |
|------------------------|-----|----------------|-------------------------------------|--|---|---|
| F                      | F   | F <sup>a</sup> | -77.78                              | 248.0 (Si–F)<br>6.1 (Si–C–C–F)<br>6.1 (Si–C–C–C–F)<br>6.9 (Si–C–C–F) |   |   |
| Cl                     | Cl  | Cl             | -12.10                              |  |   |   |
| Cl                     | Cl  | OEt            | -33.91                              |  | 1.46 (CH <sub>3</sub> )<br>4.24 (OCH <sub>2</sub> )   | 7<br>7                                  |
| OEt                    | OEt | OEt            | -67.27                              | 3.7 (Si–C–C–F)<br>3.7 (Si–C–C–C–F)                                   | 1.30 (CH <sub>3</sub> )<br>3.95 (OCH <sub>2</sub> )   | 7<br>7                                  |
| $\text{C}_6\text{F}_5$ | F   | F <sup>a</sup> | -39.85                              | 281.5 (Si–F)   |   |   |
| $\text{C}_6\text{F}_5$ | Cl  | Cl             | -8.23                               |  |   |   |
| $\text{C}_6\text{F}_5$ | OEt | OEt            |                                     |  | 1.35 (CH <sub>3</sub> )<br>4.10 (OCH <sub>2</sub> )   | 6                                       |
| Bu                     | Bu  | Bu             | -3.78                               |  | 1.32, 0.86  |   |
| Bu                     | Bu  | F              | 19.64                               | 293.0 (Si–F)   | 1.39, 1.04, 0.88  |   |
| Bu                     | Bu  | OEt            | 4.95                                |  | 1.33, 0.95, 0.87 (C <sub>4</sub> H <sub>9</sub> ),<br>3.74 (OCH <sub>2</sub> ), 1.19 (CH <sub>3</sub> ) | 7                                       |

<sup>a</sup> in  $\text{CD}_2\text{Cl}_2$ .

oxygen- and nitrogen-containing nucleophiles seem to form arylfluorosilicates intermediately which lose  $[C_6F_5]^-$  irreversibly under formation of  $C_6F_5H$ . In the case of piperidine pentafluorobenzene can be formed alternatively by protodesilylation of the intermediate silicate with the acidic  $[R_2NH_2]^+$  cation. The absence of  $C_6F_5H$  in the alkylation of  $C_6F_5SiF_3$  with BuLi indicates the predominant elimination of  $F^-$  from  $[C_6F_5SiF_3Bu]^-$  rather than  $[C_6F_5]^-$ ; also no protodesilylation of the intermediate silicate takes place.

A general scheme for the interaction of **5** with nucleophiles  $Nu^-$  is shown in Eq. (15).



Desilylation of  $C_6F_5SiF_3$  with electrophiles in neutral or acidic media should proceed via addition of the electron-deficient species to the C-1 carbon atom. However, the substituent  $[F_3Si^+]$  is a very poor leaving group and therefore its successful displacement requires nucleophilic assistance.

This proposal rationalises the observed inertness of trifluorosilane **5** to strong anhydrous acids and  $[NO_2]^+$   $[BF_4]^-$  (weak nucleofuge counteranions  $[H_nF_{n+1}]^-$ ,  $[FSO_3]^-$ ,  $[BF_4]^-$ ), whereas electrophilic bromine in the adduct  $Br_2-AlBr_3$  was more reactive due to the transfer of bromide from  $[AlBr_4]^-$  to silicon. In liquid bromine a second molecule of pentafluorophenyltrifluorosilane can principally assist as Lewis acid instead of  $AlBr_3$  to give  $C_6F_5Br$  and  $C_6F_5SiF_2Br$ . Hence every desilylation of  $C_6F_5SiF_3$  by electrophiles should include the participation of whether a nucleophilic counteranion or the solvent when the reaction is carried out in basic media.

### 3. Experimental section

The  $^1H$  and  $^{19}F$  NMR spectra were recorded on a Varian EM 360 L ( $^1H$  at 60.0 MHz and  $^{19}F$  at 56.4

MHz), a Bruker WP 80 SY ( $^{19}F$  at 75.4 MHz), WP 200 SY ( $^1H$  at 200.0 MHz,  $^{19}F$  at 188.3 MHz) and AM 400 ( $^{13}C$  at 100.6 MHz,  $^{29}Si$  at 79.5 MHz) spectrometer (TMS and  $C_6F_6$  as internal references). The  $^{19}F$  chemical shifts were assigned to  $CFCl_3$  using  $\delta(F) = -162.9$  ppm for  $C_6F_6$ . The IR spectra were registered on a Specord M 80, a Perkin Elmer 557 and a Nicolet 20 DXB instrument and the Raman spectra on a Ramalog 5 M spectrometer (Kr laser, red line at  $15453.5\text{ cm}^{-1}$ ).

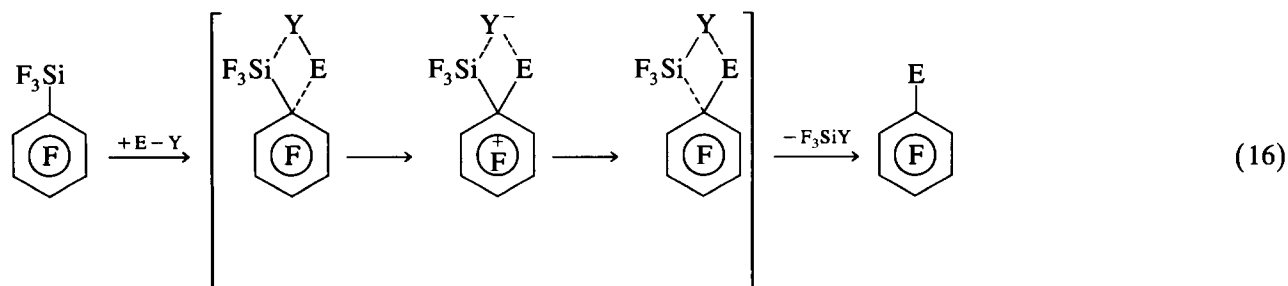
The compounds  $SbF_5$ ,  $IF_5$ ,  $SO_2FCl$ ,  $SOCl_2$ ,  $HSO_3F$  and piperidine were distilled before use. EtONa was prepared from sodium and anhydrous EtOH and kept at  $140-150\text{ }^\circ\text{C}$  in high vacuum for 4 h.  $[NO_2]^+$   $[BF_4]^-$  (Fluka) was used without further purification. Pentafluorophenyltriethoxysilane (**1**), bis(pentafluorophenyl)diethoxysilane (**3**) [11] and  $[IF_4]^+$   $[SbF_6]^-$  [26] were synthesised by known methods. All manipulations with pentafluorophenylfluorosilanes were carried out in FEP tube reactors.

#### 3.1. Pentafluorophenyltriethoxysilane (1)

IR (neat liquid): 2981, 2932, 1644, 1519, 1468, 1386, 1292, 1169, 1116, 1092, 973, 792, 688, 636, 620, 522,  $469\text{ cm}^{-1}$ . Raman: 2985 (29.5), 2935 (37.7), 2900 (19.3), 1645 (18.7), 1480 (15.5), 1470 (25.3), 1447 (23.8), 1385 (10.4), 1300 (18.0), 1143 (9.8), 1100 (19.8), 1093 (19.3), 975 (10.4), 942 (9.2), 846 (23.6), 800 (15.1), 687 (11.4), 627 (7.9), 587 (55.2), 520 (21.4), 472 (12.8), 448 (95.7), 400 (100), 352 (20.4), 287 (12.2), 238 (16.1), 205 (16.7)  $\text{cm}^{-1}$ .

#### 3.2. Pentafluorophenyltrichlorosilane (2)

Pentafluorophenyltriethoxysilane **1** (35.7 g, 0.108 mol), thionylchloride (48 ml, 0.658 mol) and pyridinium hydrochloride (1.6 g, 0.014 mol) were refluxed and stirred for 24 h. Excess of  $SOCl_2$  was distilled off and pentafluorophenyltrichlorosilane isolated by vacuum-distillation. Yield 27.2 g (83%), bp  $45\text{ }^\circ\text{C}$  (1.5 Torr) (lit.  $64-65\text{ }^\circ\text{C}$  (5 Torr) [14,15],  $80-84\text{ }^\circ\text{C}$  (14 Torr) [11]). Raman: 1650 (9.0), 1393 (4.0), 1148 (2.2), 859 (5.4), 593 (76.0), 546 (2.6), 480 (90.3), 450 (93.7), 398 (89.9), 363 (13.2), 310 (12.0), 281 (3.7), 236 (9.7), 218 (13.7), 204 (9.8), 173 (100.0), 148 (96.8)  $\text{cm}^{-1}$ .



### 3.3. Bis(pentafluorophenyl)dichlorosilane (4)

4 was obtained in a similar way as  $(C_6F_5)_2Si(OEt)_2$  (4.94 g, 10.9 mmol),  $SOCl_2$  (3.3 ml, 45 mmol) and pyridinium hydrochloride (0.15 g, 1.3 mmol). Yield 3.05 g (64 %), bp 100–103 °C (1.5 Torr) (lit. 180–182 °C (16 Torr) [11]). The intermediate formation of  $(C_6F_5)_2SiClOEt$  was detected by  $^{19}F$  NMR spectrometry (not isolated).

### 3.4. Pentafluorophenyldichloro(ethoxy)silane

Pentafluorophenyltriethoxysilane 1 (39 g, 0.118 mol), thionyl chloride (55 ml, 0.76 mol) and pyridinium hydrochloride (1.5 g, 1.4 mmol) were refluxed and stirred for 4 h. Silane  $C_6F_5SiCl_2OEt$  (18 g, 49%) was isolated by vacuum-distillation, bp 96–99 °C (4 Torr). Found: C 30.6, H 1.91, Cl 23.0, F 30.4.  $C_8H_5Cl_2F_5OSi$ . Required: C 30.9, H 1.61, Cl 22.8, F 30.5. IR (neat liquid): 2985, 2941, 2908, 1644, 1530, 1473, 1460, 1386, 1298, 1168, 1100, 976, 780, 752, 730  $cm^{-1}$ .

### 3.5. Fluoridation of $C_6F_5Si(OEt)_3$ with AHF

#### 3.5.1. In neat AHF

A mixture of  $C_6F_5Si(OEt)_3$  (170 mg, 0.51 mmol) and AHF (anhydrous HF, 0.25 ml) was shaken at –50 °C for 3 h. After 3 h the acidic phase was separated and the organic phase was diluted with dichloromethane (0.15 ml). The solution contained  $C_6F_5SiF_3$  (8%) and  $C_6F_5H$  (22%). The acidic phase contained  $C_6F_5SiF_3$  (26%) and  $C_6F_5H$  (41%). The total yields of  $C_6F_5SiF_3$  and  $C_6F_5H$  were 34 and 63% respectively ( $^{19}F$  NMR, quantitative reference  $C_2F_3Cl_3$  (organic phase) and  $CF_3CO_2Na$  (acidic phase)).

#### 3.5.2. In $CH_2Cl_2$

AHF (0.3 ml) was added to a solution of  $C_6F_5Si(OEt)_3$  (91.5 mg, 0.28 mmol) in dichloromethane (0.2 ml) at –50 °C and stirred for 4 h. The organic phase contained  $C_6F_5SiF_3$  (48%) and  $C_6F_5H$  (9%).  $C_6F_5SiF_3$  (26 %) and  $C_6F_5H$  (18 %) were found in the AHF phase. The total yields of  $C_6F_5SiF_3$  and  $C_6F_5H$  were 74% and 26% respectively.

### 3.6. Pentafluorophenyltrifluorosilane (5)

Method A. Freshly sublimed antimony trifluoride (12.3 g, 68.8 mmol) was added in one portion to pentafluorophenyltrichlorosilane (2) (17.02 g, 56.5 mmol) into a round bottom flask equipped with reflux condenser. After a short inductive period the exothermic reaction started. The reaction mixture was refluxed for 1 h. Pentafluorophenyltrifluorosilane was distilled off at reduced pressure and re-distilled. Yield of  $C_6F_5SiF_3$  13.47 g (94%), bp 44 °C (64 Torr) (lit. 105 °C [12]).

Raman: 1653, 1403, 1154, 908, 630, 586, 518, 445, 410, 399, 345, 323, 280, 238, 219, 158  $cm^{-1}$ .

Method B. AHF (0.35 ml) was added into a solution of trichlorosilane 2 (251 mg, 0.83 mmol) in dichloromethane (0.2 ml) at –50 °C and stirred for 3 h. When the evolution of HCl subsided, trifluorosilane 5 was found in the organic (91%) and AHF (11%) phase (quantitative yield).

### 3.7. Reaction of $C_6F_5Si(OEt)_3$ with EtOH in AHF

Triethoxysilane 1 (210 mg, 0.636 mmol) was dissolved in a solution of EtOH (0.074 ml, 1.27 mmol) in AHF (0.2 ml) at –40 °C. After 1 h the ratio  $C_6F_5H$ :  $C_6F_5SiF_3$  was equal 35:1 (mol) and no  $C_6F_5Si(OEt)_3$  was found.

### 3.8. Reaction of $C_6F_5SiF_3$ with EtOH in AHF

Ethanol (0.01 mmol) was added to  $C_6F_5SiF_3$  (25 mg, 0.01 mmol) in AHF (0.3 ml) at –50 °C. No reaction was detected after shaking for 1 h ( $^{19}F$  NMR). Then an excess of EtOH (0.1 ml) was added and the reaction mixture was kept at –10 °C for 1 d and at –78 °C for 2 d. Pentafluorobenzene and pentafluorophenyltrifluorosilane were found in 86 and 14% yields ( $^{19}F$  NMR).

### 3.9. Bis(pentafluorophenyl)difluorosilane (6)

6 was obtained similarly to trifluorosilane 5 (method A) from  $(C_6F_5)_2SiCl_2$  (7.65 g, 17 mmol) and  $SbF_3$  (3.34 g, 18.7 mmol) at ca. 60 °C (bath). Yield of  $(C_6F_5)_2SiF_2$  was 4.42 g (65%), bp 126 °C (60 Torr) (lit. 207 °C [10]).

### 3.10. Attempted reaction of triethoxysilane 1 with $SOBr_2$

A mixture of  $C_6F_5Si(OEt)_3$  (5.0 g, 15 mmol), freshly distilled  $SOBr_2$  (8 ml, 103 mmol) and pyridine (1.2 g, 15 mmol) was stirred at 45–50 °C for 7 h. No reaction was detected ( $^{19}F$  NMR).

### 3.11. Reaction of $C_6F_5Si(OEt)_3$ with $BF_3$ or $BF_3 \cdot OEt_2$

Method A. Triethoxysilane 1 (6.0 g, 18 mmol) and  $BF_3 \cdot OEt_2$  (7.5 g, 53 mmol) were stirred for 30 h at room temperature. According to the  $^{19}F$  NMR spectrum, trifluorosilane 5 was the main product together with  $C_6F_5SiF(OEt)_2$ ,  $C_6F_5SiF_2OEt$  and  $(EtOBF_2)_3$ . The isolation of  $C_6F_5SiF_3$  from the reaction mixture by distillation failed (azeotrope formation with boron ethoxyfluorides; bp 78–83 °C).

Method B. Triethoxysilane 1 (8.0 g, 24 mmol) and  $BF_3 \cdot OEt_2$  (10.0 g, 70 mmol) were refluxed for 11 h. The composition of the reaction mixture was similar to that mentioned above.

Method C. Pentafluorophenyltriethoxysilane (12.48 g, 37.8 mmol) was added dropwise to  $\text{BF}_3 \cdot \text{OEt}_2$  (4.8 ml, 38.2 mmol) at 108–110 °C during 5 min. After 30 min the volatile products were distilled off and the residue was distilled in vacuum to give  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $(\text{EtOBF}_2)_3$  and  $(\text{EtO})_2\text{BF}$  (identified by their  $^{19}\text{F}$  NMR) and a mixture of  $\text{C}_6\text{F}_5\text{SiF}_3$ ,  $\text{C}_6\text{F}_5\text{SiF}_2\text{OEt}$  and  $\text{C}_6\text{F}_5\text{SiF}(\text{OEt})_2$ , bp 23–98 °C (24 Torr) (7.24 g, 1:7.4:2.7 mol) (not separated).

Method D. Boron trifluoride was bubbled through a solution of  $\text{C}_6\text{F}_5\text{Si}(\text{OEt})_3$  (1.0 g, 3 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 ml) at room temperature during 5 h. The excess of  $\text{BF}_3$  was removed by a stream of argon and the solvent was distilled off. The residue (1.8 g) (bp 78–80 °C) contained  $\text{C}_6\text{F}_5\text{SiF}_3$ ,  $\text{C}_6\text{F}_5\text{SiF}_2\text{OEt}$  (1.6:1 mol) and  $(\text{EtOBF}_2)_3$ .

### 3.12. Reaction of $\text{C}_6\text{F}_5\text{Si}(\text{OEt})_3$ with $\text{SF}_4$

A solution of triethoxysilane **1** (1.0 g, 3 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was treated with  $\text{SF}_4$  (HF free) for 1.5 h at room temperature. Only traces of  $\text{C}_6\text{F}_5\text{SiF}(\text{OEt})_2$  were detected ( $^{19}\text{F}$  NMR).

### 3.13. Attempted reactions of trifluorosilane **5** with acids

A solution of  $\text{C}_6\text{F}_5\text{SiF}_3$  (0.5–0.6 mmol) in acid ( $\text{AHF}$ ,  $\text{HSO}_3\text{F}$  or  $\text{CF}_3\text{CO}_2\text{H}$ ) (0.15–0.5 mmol) was kept at room temperature for 3 days. No reaction was detected ( $^{19}\text{F}$  NMR).

### 3.14. Attempted reactions of $\text{C}_6\text{F}_5\text{SiF}_3$ with $\text{IF}_5$

A solution of  $\text{C}_6\text{F}_5\text{SiF}_3$  and  $\text{IF}_5$  (1:1 mol) in  $\text{CH}_2\text{Cl}_2$  or HF (0.1–0.2 ml) was kept at room temperature for 24–36 h. No reactions were detected ( $^{19}\text{F}$  NMR).

### 3.15. Interaction of $\text{C}_6\text{F}_5\text{SiF}_3$ with $[\text{NO}_2]^+ [\text{BF}_4]^-$

Method A. A suspension of  $\text{C}_6\text{F}_5\text{SiF}_3$  and  $[\text{NO}_2]^+ [\text{BF}_4]^-$  (1:1 mol) in dichloromethane was shaken at room temperature for 41 h. No reaction was detected ( $^{19}\text{F}$  NMR).

Method B. The same result was obtained for the clear colourless solution of  $\text{C}_6\text{F}_5\text{SiF}_3$  (88 mg, 0.35 mmol) and  $[\text{NO}_2]^+ [\text{BF}_4]^-$  (73 mg, 0.55 mmol) in 0.15 ml of  $\text{HSO}_3\text{F}$  after 41 h.

### 3.16. Reactions of $\text{C}_6\text{F}_5\text{SiF}_3$ with bromine

Method A. No reaction was detected between  $\text{C}_6\text{F}_5\text{SiF}_3$  (44 mg, 0.17 mmol) and bromine (122 mg, 0.77 mmol) in acetonitrile (0.1 ml) at room temperature within 42 h.

Method B.  $\text{C}_6\text{F}_5\text{SiF}_3$  (69 mg, 0.27 mmol) and bromine (588 mg, 3.67 mmol) were kept for 10 days at

room temperature to give a mixture of  $\text{C}_6\text{F}_5\text{SiF}_3$ ,  $\text{C}_6\text{F}_5\text{Br}$  and  $\text{C}_6\text{F}_5\text{SiF}_2\text{Br}$  (1:1:0.6 mol).

Method C. A mixture of bromine (1.24 mmol) and  $\text{AlBr}_3$  (0.62 mmol) was cooled down to –20 °C and  $\text{C}_6\text{F}_5\text{SiF}_3$  (120 mg, 0.47 mmol) was added. The reaction mixture was kept at room temperature for 48 h to give  $\text{C}_6\text{F}_5\text{SiF}_3$ ,  $\text{C}_6\text{F}_5\text{Br}$  (1:4 mol) and bromofluorosilanes  $\text{SiF}_2\text{Br}_2$  and  $\text{SiFBr}_3$  ( $^{19}\text{F}$  resonances at –96.1 and –77.4 ppm (singlets) respectively [29]). After 76 h all  $\text{C}_6\text{F}_5\text{SiF}_3$  was converted to  $\text{C}_6\text{F}_5\text{Br}$ .

### 3.17. Reaction of $\text{C}_6\text{F}_5\text{SiF}_3$ with $[\text{IF}_4]^+ [\text{SbF}_6]^-$

Trifluorosilane **5** (83 mg, 0.33 mmol) and  $[\text{IF}_4]^+ [\text{SbF}_6]^-$  (177 mg, 0.40 mmol) were dissolved in  $\text{HSO}_3\text{F}$  (0.2 ml) forming a green solution which displayed  $^{19}\text{F}$  resonances at 19.3 ( $[\text{IF}_4]^+$ ), –125.2, –133.9, –143.4 and –159.4 ppm ( $\text{C}_6\text{F}_5\text{SiF}_3$ ) (4:2:3:1:2 mol) together with signals of  $\text{SiF}_4$  (–163.0 ppm),  $[\text{SbF}_6]^-$  (–109 ppm, very broad) and  $\text{HSO}_3\text{F}$  (42.3 ppm). After 2 d the solution became red–brownish. Resonances at 18.3, –117.7, –135.3 and –152.8 ppm (4:2:1:2 mol) and signals of  $\text{SiF}_4$ ,  $\text{HSO}_3\text{F}$  and  $[\text{SbF}_6]^-$  were observed in the  $^{19}\text{F}$  NMR spectrum. No further changes took place during the next 4 days. Evolved  $\text{SiF}_4$  was identified as  $\text{SiF}_4 \cdot 2 \text{Py}$  adduct. The reaction mixture was poured onto ice frozen with liquid nitrogen. The solid was separated by centrifugation and dried in high vacuum at room temperature (76 mg). Its IR spectrum (in  $\text{AgCl}$ ) and  $^{19}\text{F}$  NMR spectrum [30] displayed the presence of the  $[(\text{C}_6\text{F}_5)_2\text{I}]^+$  cation.

### 3.18. Reaction of $\text{C}_6\text{F}_5\text{SiF}_3$ with $\text{BuLi}$

Method A. Trifluorosilane **5** (252 mg, 1.00 mmol) in hexane (0.5 ml) was treated with 1 M  $\text{BuLi}$  in hexane (3 ml) at –20 °C and warmed up to room temperature. The  $^{19}\text{F}$  NMR spectrum showed the presence of  $\text{C}_6\text{F}_5\text{SiFBu}_2$  and  $\text{C}_6\text{F}_5\text{SiBu}_3$  (2:1 mol). Further treatment with  $\text{BuLi}$  (1 ml) led to the formation of  $\text{C}_6\text{F}_5\text{SiBu}_3$  and admixture of 4- $\text{BuC}_6\text{F}_4\text{SiBu}_3$ .

Method B. The addition of 1.6 M  $\text{BuLi}$  in hexane (1.5 ml, 2.4 mmol) into a solution of  $\text{C}_6\text{F}_5\text{SiF}_3$  (140 mg, 0.55 mmol) in diglyme (0.5 ml) at –25 °C and the following warming up to room temperature resulted in the complete conversion of trifluorosilane **5** into 4- $\text{BuC}_6\text{F}_4\text{SiBu}_3$  ( $^{19}\text{F}$  NMR).

### 3.19. Reaction of $\text{C}_6\text{F}_5\text{SiF}_3$ with piperidine

The solution of  $\text{C}_6\text{F}_5\text{SiF}_3$  (68 mg, 0.27 mmol) in hexane (0.5 ml) was cooled down to –20 °C and a solution of piperidine in hexane (2 equivalents) was added in one portion by syringe. The resulting suspension was warmed up to room temperature and centrifuged. The  $^{19}\text{F}$  NMR spectrum showed the presence of



$C_6F_5SiF_2(NR_2)$  and  $C_6F_5H$  (1:1 mol). Further treatment of this solution with piperidine (2 equivalents) caused the appearance of  $C_6F_5SiF(NR_2)_2$  and  $C_6F_5H$  (1:2 mol). Treatment of this solution with piperidine (excess) gave pentafluorobenzene as the only polyfluoroaromatic product (quantitative yield).

### 3.20. Reaction of $C_6F_5SiF_3$ with sodium ethoxide

Solid EtONa (10 mg, 0.15 mmol) was added to a solution of  $C_6F_5SiF_3$  (109 mg, 0.43 mmol) in 0.2 ml of diglyme at  $-30^\circ C$ . The reaction mixture was heated to room temperature with shaking. The  $^{19}F$  NMR spectrum displayed signals of  $C_6F_5H$  and resonances at  $-123.2$  (Si–F, broad),  $-126.6$  (F 2, 6),  $-147.6$  (F-4) and  $-160.7$  (F-3, 5) ppm (the molar ratio of  $C_6F_5H$  to silanes and silicate was 1 to 3). Further addition of EtONa (total amount 32 mg, 0.47 mmol) led to the formation of pentafluorobenzene only.

### 3.21. Pentafluorophenyldibutylethoxysilane

Pentafluorophenyltriethoxysilane (3.30 g, 10 mmol) was added dropwise to a solution of BuMgBr prepared from BuBr (4.00 g, 30 mmol) and magnesium (0.72 g, 30 mmol) in ether (13 ml). The reaction mixture was refluxed for 5 h and kept overnight at room temperature. After extraction with hexane (3 x 10 ml) and filtration the solvent was distilled off in vacuum to give 2.4 g (68%) of  $C_6F_5SiBu_2OEt$ , bp  $125-128^\circ C$  (8 Torr).

Found: C 54.9, H 6.66, F 27.4.  $C_{16}H_{23}F_5OSi$ . Required: C 54.2, H 6.50, F 26.8. IR (neat liquid): 2958, 2927, 2870, 2854, 1636, 1511, 1455, 1405, 1368, 1280, 1192, 1158, 1104, 1075, 964, 877, 780, 765, 733, 693,  $496\text{ cm}^{-1}$ .

### 3.22. Pentafluorophenyldibutylfluorosilane

$C_6F_5SiBu_2OEt$  (1.8 g, 5.0 mmol) was refluxed in acetylchloride (1.2 g, 15 mmol) with  $ZnCl_2$  (ca. 0.2 g) for 8 h. The liquid phase was decanted and the volatile products removed at  $50-70^\circ C$  (bath). Crude  $C_6F_5SiBu_2Cl$  was heated with  $ZnF_2$  (3.0 g, 29 mmol) at  $200-220^\circ C$  (bath) for 30 min and  $C_6F_5SiBu_2F$  was distilled off in vacuum. Yield 1.1 g (67%), bp  $142^\circ C$  (30 Torr).

Found: C 51.7, H 5.75, F 34.9.  $C_{14}H_{18}F_6Si$ . Required: C 51.2, H 5.49, F 34.8. IR (neat liquid): 2965, 2937, 2880, 2869, 1645, 1534, 1466, 1404, 1380, 1285, 1200, 1087, 970, 893, 855, 790, 700,  $505\text{ cm}^{-1}$ .

### 3.23. Pentafluorophenyltributylsilane

A solution of BuLi in hexane (0.9 M, 26 ml, 23.4 mmol) was added dropwise to a stirred solution of

triethoxysilane 1 (2.20 g, 6.7 mmol) in hexane (2 ml) at  $-20^\circ C$ . The reaction mixture was stirred at room temperature for 2 h and poured into diluted HCl. The organic layer was washed with water, dried with  $CaCl_2$  and the solvent removed. Distillation of the residual oil in vacuum gave  $C_6F_5SiBu_3$  (1.25 g, 51%), bp  $148-151^\circ C$  (5 Torr).

Found: C 58.5, H 7.00, F 26.1.  $C_{18}H_{27}F_5Si$ . Required: C 59.0, H 7.38, F 26.0.

### 3.24. 4-Butyltetrafluorophenyltributylsilane

A solution of triethoxysilane 1 (1.10 g, 3.3 mmol) in hexane (2 ml) was transferred by syringe into a solution of 0.9 M BuLi in hexane (22.5 mmol) at  $0^\circ C$ . Then the reaction mixture was treated as mentioned above to yield 4-Bu $C_6F_4SiBu_3$  (0.62 g, 46%), bp  $185-188^\circ C$  (5 Torr).

Found: C 65.0, H 8.71, F 19.0.  $C_{22}H_{36}F_4Si$ . Required: C 65.3, H 8.91, F 18.8.

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