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Preparation of halogeno(pentafluorophenyl)silanes $(C_6F_5)_nSiX_{4-n}$ ($X = F$, Cl and Br; $n = 2, 3$) from pentafluorophenyl(phenyl)silanes $(C_6F_5)_nSiPh_{4-n}$

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Abstract

Halogeno(pentafluorophenyl)silanes $(C_6F_5)_nSiX_{4-n}$ ($X = F$, Cl and Br; $n = 2, 3$) were prepared in good yields from the corresponding phenylsilanes $(C_6F_5)_nSiPh_{4-n}$ by reactions with the electrophiles aHF, FSO_3H, HCl–$AlCl_3$ or with AlX_3 ($X = Cl$, Br)–halogenated hydrocarbons. The relative leaving ability of the organyl groups (C_6F_5, C_6H_5, Me) bonded to the silicon atom and the strength of the electrophilic reagent are discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silanes; Electrophilic substitution; Silicon

1. Introduction

Our previous paper dealt with the facile preparation of halogeno(methyl)pentafluorophenylsilanes $C_6F_5SiMe_nX_{3-n}$ ($X = F$, Cl, Br; $n = 1, 2$) in reactions of the corresponding phenylsilanes $C_6F_5SiMe_nPh_{3-n}$ with electrophilic reagents [1]. The substantial differences in the leaving ability of pentafluorophenyl and phenyl groups prompted us to extend that approach to the synthesis of halogeno(pentafluorophenyl)silanes $(C_6F_5)_nSiX_{4-n}$ starting with easily available compounds $(C_6F_5)_nSiPh_{4-n}$. All up to date known routes to halogeno(pentafluorophenyl)silanes have some disadvantages, e.g. multistep reactions, low yields of the desired products, formation of complex reaction mixtures or the use of specific laboratory equipment (see [2] and references cited there).

2. Results

The starting material pentafluorophenyl(phenyl)silanes $(C_6F_5)_2SiPh_2$ **1** and $(C_6F_5)_3SiPh$ **2** were readily produced by nucleophilic substitution of chlorine in the easily available chloro(phenyl)silanes Ph_2SiCl_2 and $PhSiCl_3$, respectively, with C_6F_5Li in ether–hexane using modified literature methods [3,4]. However, the situation was different for $C_6F_5SiPh_3$. We were not able to work out a preparative route to silane $C_6F_5SiPh_3$ by reaction of Ph_3SiCl with C_6F_5MgBr or with C_6F_5Br and $P(NEt_2)_3$. From C_6F_5Li and Ph_3SiCl [4] we always got a raw product of low purity in low yields. In the past the lack of a simple synthesis for $C_6F_5SiPh_3$ was already reported by Fearon and Gilman [3]. Because of the lack of availability of $C_6F_5SiPh_3$ we concentrated our investigations of the reactivity of pentafluorophenyl(phenyl)silanes with electrophiles exclusively on silanes **1** and **2**.

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2.1. Reactions of pentafluorophenyl(phenyl)silanes with protic acids

No reaction was detected between silane **1** and an excess of aHF at room temperature (r.t.) over 26 h, but a slow replacement of one phenyl group by fluorine took place in dichloromethane or chloroform solutions. However, the treatment of silane **1** with a mixture of aHF and FSO_3H led to the formation of difluoro-[bis-(pentafluorophenyl)]silane **3** in good yields within 1.5 h.

$$(C_6F_5)_2SiPh_2 + aHF\ (\mathbf{1}) \xrightarrow[\text{RT, 26 h}]{} \text{No reaction} \qquad (1)$$

$$\mathbf{1} + aHF \xrightarrow[\text{RT, 7 days}]{CHCl_3} (C_6F_5)_2SiPhF\ (\mathbf{4})\ (20\%\ \text{conversion of}\ \mathbf{1}) \qquad (2)$$

$$\mathbf{1} + aHF \xrightarrow[\text{RT, 8 days}]{CH_2Cl_2} (C_6F_5)_2SiPhF\ (\mathbf{4})\ (72\%\ \text{yield}) + (C_6F_5)_2SiF_2\ (\mathbf{3})\ (10\%\ \text{yield}) \qquad (3)$$

$$\mathbf{1} + aHF + FSO_3H \xrightarrow[\text{RT, 1.5 h}]{} \mathbf{3}\ (72\%\ \text{yield}) \qquad (4)$$

Silane **2** was unreactive towards aHF in dichloromethane, but reacted rapidly with fluorosulfonic acid to give fluoro[tris(pentafluorophenyl)]silane **5** and benzenesulfonyl fluoride. Likely, fluorosilane **5** was formed by thermal decomposition of the ester $(C_6F_5)_3SiOSO_2F$ in FSO_3H (cf. similar displacement of the fluorosulfato group by fluorine in Me_3SiOSO_2F and related compounds [5]).

$$(C_6F_5)_3SiPh + aHF \xrightarrow[\text{RT, 4 days}]{CH_2Cl_2} \text{No reaction} \qquad (5)$$

$$\mathbf{2} + FSO_3H \xrightarrow[\text{RT, 1.5 h}]{CH_2Cl_2} (C_6F_5)_3SiF + PhSO_2F\ (\mathbf{5})\ (83\%\ \text{yield}) \qquad (6)$$

Anhydrous HCl reacted with both silanes **1** and **2** in the presence of $AlCl_3$ in hexane to give chlorosilanes **6**, **7** or **8**, respectively. Total consumption of silane **1** was achieved within 1 h, but further substitution of the residual phenyl group in silane **6** by chlorine proceeded slowly. Silane **2** with three electron-poor pentafluorophenyl groups was less reactive than silane **1** and the conversion of **2** into chlorosilane **8** was incomplete after 2–3 h even in the presence of five equivalents of $AlCl_3$.

$$\mathbf{1} + HCl + n AlCl_3 \xrightarrow{\text{Hexane}} (C_6F_5)_2SiPhCl + (C_6F_5)_2SiCl_2$$

$$\begin{array}{llll} n = 0.9, & 8\ \text{h}, & \mathbf{6}\ (27\%), & \mathbf{7}\ (73\%); \\ n = 3, & 3\ \text{h}, & & \mathbf{7}\ (100\%) \end{array} \qquad (7)$$

$$\mathbf{2} + HCl + n AlCl_3 \xrightarrow{\text{Hexane}} (C_6F_5)_3SiCl$$

$$\begin{array}{lll} n = 2, & 3\ \text{h}, & \mathbf{8}\ (59\%\ \text{conversion of}\ \mathbf{2}); \\ n = 5, & 2\ \text{h}, & \mathbf{8}\ (64\%\ \text{conversion of}\ \mathbf{2}) \end{array} \qquad (8)$$

Because of the negligible solubility of $AlCl_3$ in hexane, the low reaction rate can be assigned to the heterogeneous conditions of reaction. It was expected that the use of polar halogenated hydrocarbons such as dichloromethane, chloroform or 1,2-dichloroethane (DCE) should facilitate the reaction with HCl–$AlCl_3$ due to the higher solubility of the catalyst and the higher polarity of media. Indeed, quantitative formation of dichlorosilane **7** took place within a few min when silane **1** was treated with HCl and $AlCl_3$ in DCE at r.t.

$$\mathbf{1} + HCl + 1.4AlCl_3 \xrightarrow[\text{10 min}]{\text{DCE}} \mathbf{7}\ (100\%) \qquad (9)$$

It was surprising that the replacement of the C_6H_5 group by chlorine also occurred in the absence of HCl. We studied that unexpected reaction in detail and developed a convenient preparative route to halogeno (pentafluorophenyl)silanes.

2.2. Reactions of pentafluorophenyl(phenyl)silanes with aluminum trichloride and tribromide–halogenated hydrocarbons

Treatment of phenylsilane **1** with 0.5 equivalents of $AlCl_3$ in CH_2Cl_2 at r.t. for 1 h gave dichlorosilane **7**. In chloroform the analogous reaction was completed after 3 h. Increasing the amount of $AlCl_3$ accelerated the reaction rate in dichloromethane and chloroform. On no account was pentafluorophenyl–silicon bond cleavage detected.

$$\mathbf{1} + n\ AlCl_3 \xrightarrow[\text{RT}]{CH_2Cl_2\ \text{or}\ CHCl_3} \underset{\mathbf{7}\ (100\%)}{(C_6F_5)_2SiCl_2} \qquad (10)$$

$$\begin{array}{llll} \text{in}\ CH_2Cl_2: & n = 0.5\ (60\ \text{min}), & n = 1.0\ (35\ \text{min}), & n = 5.0\ (10\ \text{min}) \\ \text{in}\ CHCl_3: & n = 0.5\ (180\ \text{min}), & n = 1.0\ (40\ \text{min}), & n = 5.0\ (15\ \text{min}) \end{array}$$

A similar picture was observed in the reaction of phenylsilane **2** with $AlCl_3$. In CH_2Cl_2 the total conversion into chlorosilane **8** was achieved within 1 h whereas 4 h were required for the complete reaction in $CHCl_3$.

$$\mathbf{2} + 0.5\ AlCl_3 \xrightarrow[\text{RT}]{\substack{CH_2Cl_2\ (55\ \text{min})\ \text{or} \\ CHCl_3\ (240\ \text{min})}} (C_6F_5)_3SiCl\ (\mathbf{8})\ (100\%) \qquad (11)$$

Dibromo[bis(pentafluorophenyl)]silane **9** and bromo-[tris(pentafluorophenyl)]silane **10** were easily prepared by the homogenous reaction of the corresponding silanes **1** and **2** with less stoichiometric amounts of $AlBr_3$ in 1,2-dibromoethane (DBE).

$$\mathbf{1} + 0.5\ AlBr_3 \xrightarrow[\text{RT, 20 min}]{\text{DBE}} (C_6F_5)_2SiBr_2\ (\mathbf{9})\ (100\%) \qquad (12)$$

$$\mathbf{2} + 0.5\ AlBr_3 \xrightarrow[\text{RT, 90 min}]{\text{DBE}} (C_6F_5)_3SiBr\ (\mathbf{10})\ (100\%) \qquad (13)$$

3. Discussion

The results presented here have close relations to the formation of halogeno(methyl)pentafluorophenylsilanes reported in our previous paper [1] and that circumstance caused us to discuss both results together. The elaboration and understanding of simple synthetic routes to halogeno(pentafluorophenyl)silanes was the goal of our work. With phenylsilanes as starting material we have not analysed further the path of the phenyl leaving group under the influence of the different electrophiles.

3.1. Relative rate of carbon–silicon bond cleavage in $C_6F_5(Ph)SiXY$

In all pentafluorophenyl(phenyl)silanes $C_6F_5(Ph)SiXY$ only substitution of the phenyl group by halogen took place, independent of the nature of the electrophile. Comparison of the time for the total consumption of the starting silanes under similar conditions (temperature, concentration) gave the following sequences.

Electrophile	Rate of consumption of $C_6F_5(Ph)SiXY$
$HF–CH_2C1_2$	X, Y: C_6F_5, $C_6F_5 \ll C_6F_5$, Ph $<$ Ph, Me $<$ Me, Me
1 $AlCl_3–CH_2C1_2$	X, Y: C_6F_5, $C_6F_5 < C_6F_5$, Ph $\sim$ Ph, Me
0.5 $AlBr_3$–DBE	X, Y: C_6F_5, $C_6F_5 < C_6F_5$, Ph $<$ Ph, Me $\sim$ Me, Me.

It is noteworthy, that only strong electrophilic reagents like CF_3SO_3H, FSO_3H, $Br_2–AlBr_3$ or $Br_2–AlBr_3$–DBE were reactive enough to cleave the pentafluorophenylsilicon bond in the methyl(pentafluorophenyl)silanes $(C_6F_5)_nSiMe_{4-n}$ ($n = 1, 2$). The methyl–silicon bond stayed unchanged in all cases [1]. The rate of carbon–silicon bond cleavage by electrophiles increased in the series: $CH_3 \ll C_6F_5 < C_6H_5$.

The electrophilic character of those processes was proved by the following considerations: (a) replacement of the phenyl group in phenyl(pentafluorophenyl) silanes occurred more readily than the pentafluorophenyl group while the latter was preferentially eliminated in the silicate anion $[C_6F_5Si(C_6H_5)XYNu]^-$ and (b) the rate of the C_6F_5–Si bond cleavage in methyl (pentafluorophenyl)silanes depended clearly on the strength of the protic acids ($CF_3SO_3H > FSO_3H >$ aHF) and Lewis acids ($Br_2–AlBr_3 > AlBr_3$–DBE $> AlCl_3–CH_2C1_2$).

3.2. Role of solvent and AlX_3 ($X = Cl$, Br)

Solvents can influence the conversion rate of pentafluorophenylsilanes under the action of electrophiles in three ways. The first aspect is the solubility of the electrophilic reagent or catalyst. Indeed, the conversion of silane **1** in aHF–CH_2Cl_2 was 36% (21 h) and only 20% in aHF–$CHC1_3$ (7 days). Those results correlate with the lower solubility of aHF in chloroform with respect to that in dichloromethane (see Section 4). The second aspect is the positive influence of a high dielectric constant of the solvent on the electrophilic bond cleavage, e.g. in CH_2Cl_2 with the higher dielectric constant ($\varepsilon = 8.9$) reactions are faster than in $CHCl_3$ ($\varepsilon = 4.8$). The third important factor is the direct participation of halogenated hydrocarbon solvents in the reactions when AlX_3 was present. Reactions of pentafluorophenylsilanes with AlX_3 in halogenated hydrocarbons probably proceeded via an intermediate generation of a carbocationic species like $[ClCH_2^{\delta+} \cdot Cl_4Al^{\delta-}]$ which are the reactive electrophilic key agents. The higher electrophilicity of carbocation $[ClCH_2]^+$ with respect to $[Cl_2CH]^+$ and the higher dielectric constant of CH_2Cl_2 were responsible for the higher reactivity of $AlCl_3$ in CH_2Cl_2 in comparison to $CHCl_3$. Moreover, the high solubility of the stronger Lewis acid $AlBr_3$ in DBE ($\varepsilon = 4$) and the higher polarisation of the carbon–bromine bond in $[BrCH_2CH_2^{\delta+} \cdot Br_4Al^{\delta-}]$ made that system the most effective electrophile in the series $AlCl_3–CHCl_3$, $AlCl_3–CH_2Cl_2$ and $AlBr_3$–DBE.

Principally, catalytic amounts of AlX_3 were satisfactory to run those processes. Our previous [1] and present work demonstrated clearly the acceleration of the reaction rate with increasing relative amounts of aluminum trihalide. In the case of the high soluble system $AlBr_3$–DBE a higher relative amount of $AlBr_3$ increased the concentration of the electrophile. In CH_2Cl_2, $CHCl_3$, DCE and hexane with very low solubilities of $AlCl_3$ the reaction rate depended mainly on the active surface of the catalyst. In the course of the reaction the active surface could be reduced by deposition of by-side products like $[-CHCl(C_6H_4)]_n$ which resulted from consecutive reactions of the phenyl leaving group under electrophilic conditions. By-side alkylation of the phenyl group in the case of the reagent halogenated alkane $AlHal_3$, is a source of H–Hal which forms H^+ as additional electrophile in the presence of $AlHal_3$. Our observation that in such cases the operation in a closed system compared with an open one is accompanied by a faster cleavage of the C_6H_5–Si bond means that the protolytic cleavage is faster than the carbocationic.

The unexpected and very slow reaction of $AlCl_3$ with $(C_6F_5)_2SiMe_2$ in CD_2Cl_2 and $CDCl_3$ under formation of C_6F_5H and $C_6F_5SiMe_2Cl$ [1] is explainable if we assume–despite of a dry argon atmosphere–that small amounts HCl were formed by partial hydrolysis of $AlCl_3$ by penetration of water vapour into the FEP trap with PTFE stopper during the long-time processes (13 days).

4. Experimental section

The NMR spectra were recorded on Bruker spectrometers WP 80 SY (^1H at 80.13 MHz, ^{19}F at 75.39 MHz) and Avance DRX 500 (^1H at 500.13 MHz, ^{13}C at 125.76 MHz, ^{19}F at 470.59 MHz, ^{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. The IR spectra were measured on a Nicolet 20 DXB instrument (KBr pellets) and the 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).

Pentafluorophenylsilanes $(C_6F_5)_2SiPh_2$ **1** and $(C_6F_5)_3SiPh$ **2** were obtained by modified literature methods [3] (see below). Hydrogen fluoride was dried by electrolysis (stainless steel cell, Ni electrodes), HCl by bubbling through H_2SO_4. FSO_3H was distilled and aluminum trihalogenides AlX_3 were sublimed before use. Ether, hexane, dichloromethane, chloroform, 1,2-dichloroethane and 1,2-dibromoethane were dried by literature methods and stored over molecular sieves (ether over Na). All reactions were carried out in stoppered FEP or PFA traps under dry argon atmosphere except when alternative handling is described. Solid materials were manipulated in a Braun glovebox with a gas purification MB-100.

The solubility of aHF in $CDCl_3$ (4.0 mg ml^{-1}, 0.19 mmol ml^{-1}), CD_2Cl_2 (14.4 mg ml^{-1}, 0.72 mmol ml^{-1}) and in DCE (38.5 mg ml^{-1}, 1.92 mmol ml^{-1}) at 1°C was determined by ^{19}F-NMR spectrometry using C_6F_6 as a quantitative internal reference.

4.1. *Bis(pentafluorophenyl)diphenylsilane* ***1***

Bromopentafluorobenzene (13.0 g, 52.6 mmol) and ether (50 ml) were placed in a flask equipped with a dropping funnel, a reflux condenser and a magnetic stirrer and cooled to -78°C under dry argon. BuLi (1.6 M in hexane, 34 ml, 54.4 mmol) was added dropwise under stirring. The reaction mixture was maintained at -78°C for 1 h before Ph_2SiCl_2 (7.42 g, 29.3 mmol) 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 **1** was isolated by vacuum-distillation, b.p. 140–155°C (0.04 hPa) and crystallised from hexane (yield 7.85 g, 58%), m.p. 149–151°C (lit. m.p. 151–152°C [3], b.p. 175°C (0.15 hPa), m.p. 152°C [4]). Found: C 55.9, H 2.03. $C_{24}H_{10}F_{10}Si$. Required: C 55.8, H 1.95.

4.2. *Tris(pentafluorophenyl)phenylsilane* ***2***

A sample of bromopentafluorobenzene (23.0 g, 93.0 mmol) and ether (70 ml) were placed in a flask equipped with a dropping funnel, a reflux condenser and a magnetic stirrer and cooled to -78°C under dry argon. BuLi (1.6 M in hexane, 60 ml, 96.0 mmol) was added dropwise under stirring. The reaction mixture was maintained at -78°C for 1 h before a solution of $PhSiCl_3$ (7.15 9, 33.8 mmol) in ether (40 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 $MgSO_4$. The solvent was distilled off and the residue was sublimed at 130°C (0.04 hPa). Sublimate **2** was purified by crystallisation from hexane and re-sublimation at 110°C (0.04 hPa) (yield 12.6 9, 67%), m.p. 138°C (lit. m.p. 136–137°C [3], b.p. 180°C (0.8 hPa), m.p. 149°C [4]).

4.3. *Reactions of bis(pentafluorophenyl)diphenylsilane* ***1*** *with electrophiles*

4.3.1. *With aHF*

A suspension of silane **1** (80 mg, 2.4 mmol) in aHF (0.5 ml) was stirred at r.t. for 26 h. After removal of aHF in vacuum at -20°C and dissolution of the solid residue (74 mg) in CH_2Cl_2 silane **1** was recovered unchanged (^{19}F-NMR).

4.3.2. *With aHF in dichloromethane*

A sample of aHF (2 ml) was added to a stirred solution of silane **1** (1.21 g, 2.4 mmol) in CH_2Cl_2–CD_2Cl_2 (2:1) (3 ml) at -78°C. The two phase system was warmed to r.t. After 3 days the reaction mixture contained silanes **1, 4** and **3** (15, 80 and 5 M%). After 8 days only **4** and **3** were present in a molar ratio of

Table 1
^1H and ^{29}Si-NMR spectra of pentafluorophenylsilanes $(C_6F_5)_2SiXY$ ($CDCl_3$, 35°C)

X	Y	δ(H)/ppm	δ(Si)/ppm	J/Hz
$C_6H_5^a$	C_6H_5	7.71 (H-2, 6), 7.60 (H-4), 7.51 (H-3, 5)	-25.11	(H2, H4) 1.6, (H3, H4) 7.5
C_6F_5	C_6H_5	7.58 (H-2, 6), 7.52 (H4), 7.42 (H-3, 5)	-33.17	(H2, H4) 1.3, (H3, H4) 7.5
C_6H_5	F	7.71 (H-2, 6) 7.60 (H-4), 7.50 (H-3, 5)	-14.40	(H3, H4) 6.9, (Si, F) 286.1
$C_6F_5^a$	F	—	-20.23	(Si, F) 288.5
C_6F_5	Cl	—	-22.70	
C_6F_5	Br	—	-33.39	

[a] In CD_2Cl_2.

Table 2
^{19}F-NMR spectral data of pentafluorophenylsilanes $(C_6F_5)_2SiXY$($CDCl_3$, 35°C)

X	Y	δ(F)/ppm			J(F,F)/Hz
		F-2,6	F-4	F-3,5	
$C_6H_5^{a,b}$	C_6H_5	−123.89	−149.41	−160.91	(2, 4) 4.4, (3, 4) 19.9
$C_6F_5^{b}$	C_6H_5	−125.86	−147.86	−160.51	(2, 4) 4.7, (3, 4) 20.2
C_6H_5	F^{c}	−127.12	−147.13	−160.57	(2, 4) 5.0, (3, 4) 20.0, (F, Si) 285.8, (*F*SiCCF) 12.4
C_6H_5	Cl	−125.81	−147.39	−160.47	(2, 4) 5.2, (3, 4) 19.9
$C_6F_5^{a,b}$	Br	−126.88	−145.80	−160.03	(2, 4) 5.9, (3,4) 20.3

[a] In CD_2Cl_2.
[b] Present work, lit. see [14].
[c] δ(F) −163.43 ppm.

85:15 (^{19}F-NMR). The volatile compounds were removed in vacuum at −50°C. Product **4** was isolated by vacuum distillation in 72% yield (788 mg) (b.p. 90°C (10 hPa)) and characterised by ^{1}H, ^{13}C, ^{19}F, ^{29}Si-NMR, IR and Raman spectra (Tables 1–4).

4.3.3. With aHF in $CDCl_3$

A sample of aHF (0.4 ml) was added to a solution of silane **1** (25 mg, 0.05 mmol) in $CDCl_3$ (0.4 ml) at −78°C and kept at r.t. for 7 days. The organic phase contained silanes **1** and **4** (80 and 20 M%). No additional resonances of polyfluoroaromatics were detected in the acidic phase (^{19}F-NMR).

4.3.4. With aHF and FSO_3H

A sample of aHF (6 ml) and FSO_3H (1 ml) were added in sequence to silane **1** (1.10 g, 2.12 mmol) in a FEP trap ($\phi_i = 23$ mm) at −10°C. The reaction mixture was stirred at r.t. for 1.5 h until the solid silane disappeared. The acidic phase was extracted with CH_2Cl_2 (2 × 3 ml). The combined extracts were treated with NaF, filtered and the solvent was removed in vacuum. Silane **3** (0.61 g, 72%) was isolated by vacuum distillation, b.p. 76–78°C (6.7 hPa) (lit. b.p. 90°C (13.3 hPa), 207°C [6], 126°C (80 hPa) [2]) and identified by ^{19}F-NMR spectrometry [2].

4.3.5. With HCl and $AlCl_3$ (0.9 equivalent) in hexane

HCl was bubbled into a stirred suspension of $AlCl_3$ (161 mg, 1.21 mmol) in a hexane (10 ml) solution of silane **1** (663 mg, 1.28 mmol) at r.t. After 1 h ^{19}F-NMR spectrometry showed the total conversion of silane **1** into **6** and **7** (88 and 12 M%). Further treatment of the reaction mixture with HCl for 8 h gave compounds **6** and **7** in a molar ratio of 27:73.

4.3.6. With HCl and $AlCl_3$ (3.2 equivalent) in hexane

In a similar way, the bubbling of HCl into a stirred suspension of $AlCl_3$ (82 mg, 0.62 mmol) in a hexane (2 ml) solution of silane **1** (101 mg, 0.20 mmol) at r.t. led to the formation of **6** and **7** in a molar ratio of 54:46 (1 h) and 11:89 (2 h). After 3 h only silane **7** was detected in the reaction mixture by ^{19}F-NMR spectrometry.

4.3.7. With HCl and $AlCl_3$ (1.4 equivalent) in DCE

HCl was bubbled into a stirred suspension of $AlCl_3$ (73 mg, 0.55 mmol) in a DCE (1 ml) solution of silane **1** (194 mg, 0.38 mmol) at r.t. Silane **7** was formed in quantitative yield within 10 min (^{19}F-NMR).

4.3.8. With $AlCl_3$ (0.5 equivalent) in CH_2Cl_2

A sample of $AlCl_3$ (54 mg, 0.41 mmol) was added to a stirred solution of silane **1** (421 mg, 0.82 mmol) in CH_2Cl_2 (2 ml). After 50 min the total consumption of silane **1** was detected and **6** and **7** were formed in a molar ratio of 18:82. Complex **7** was the only polyfluoroaromatic reaction product after 60 min.

4.3.9. With $AlCl_3$ (0.9 equivalent) in CH_2Cl_2

Similarly, the reaction of $AlCl_3$ (241 mg, 1.8 mmol) with silane **1** (1.07 g, 1.2 mmol) in CH_2Cl_2 (3 ml) gave silanes **6** and **7** in a molar ratio of 25:75 (30 min). After 40 min silane **7** was the only product. Product **7** (622 mg, 69%) was isolated by vacuum-distillation, b.p. 100–105°C (1.0 hPa) (lit. b.p. 100–103°C (2.0 hPa) [2], 180–182°C (21.3 hPa) [8]) and was identified by ^{13}C, ^{19}F and ^{29}Si-NMR spectra [2].

4.3.10. With $AlCl_3$ (5.0 equivalent) in CD_2Cl_2

The treatment of silane **1** (32 mg, 0.06 mmol) in CD_2Cl_2 (0.3 ml) with $AlCl_3$ (45 mg, 0.34 mmol) at r.t. resulted after 10 min in the quantitative formation of silane **7** (^{19}F-NMR).

4.3.11. With $AlCl_3$ in $CHCl_3$

Reactions of $AlCl_3$ (*n* equivalents) with silane **1** (0.4 mmol) in $CHCl_3$ (2 ml) were performed in a

Table 3
^{13}C-NMR spectra of pentafluorophenylsilanes $(C_6F_5)_2SiXY(CDCl_3$, 35°C)

X	Y	δ(C)/ppm	J/Hz
$C_6F_5^a$	C_6H_5	C_6F_5: 149.63 (C-2, 6), 143.56 (C-4), 137.99 (C-3, 5), 106.83 (C-1) C_6H_5: 135.93 (C-3, 5) 131.45 (C-4), 128.66 (C-2, 6), 129.90 (C-1)	C_6F_5: (C2, F2) 245.3, (C4, F4) 256.3, (C4, F3) 13.6, (C4, F2) 5.9, (C3, F3) 252.3, (C1, F2) 28.7
C_6F_5	C_6H_5	C_6F_5: 149.24 (C-2, 6), 143.69 (C-4), 137.57 (C-3, 5), 104.54 (C-1) C_6H_5: 134.45 (C-3, 5) 131.56 (C-4), 128.44 (C-2, 6), 127.60 (C-1)	C_6F_5: (C2, F2) 246.8, (C4, F4) 258.9, (C4, F3) 13.3, (C4,F2) 6.4, (C3,F3) 254.1, (C1, F2) 27.4 C_6H_5: (C3, H3) 160.6, (C4, H4) 161.1, (C4, H3) 6.9), (C2, H2) 163.1
C_6H_5	F	C_6F_5: 149.29 (C-2, 6), 144.17 (C4), 137.56 (C-3, 5), 104.22 (C-1) C_6H_5: 133.66 (C-3, 5), 132.54 (C-4), 128.66 (C-2, 6), 128.56 (C-1)	C_6F_5: (C2, F2) 247.8, (C4, F4) 259.4, (C4, F3) 13.2, (C4, F2) 6.8, (C3, F3) 255.3 C_6H_5: (C3, H3) 159.6, (C4, H4) 161.6, (C4, H3) 7.6, (C2, H2) 161.1
C_6F_5	F	C_6F_5: 149.92 (C-2, 6), 145.34 (C-4), 138.19 (C-3, 5), 103.10 (C-1)	C_6F_5: (C2, F2) 246.8, (C4, F4) 260.3, (C4,F3) 13.0, (C4, F2) 6.0, (C3, F3) 254.8, (C1, F2) 26.9, (C1, SiF)16.0
C_6F_5	Br	C_6F_5: 149.21 (C-2, 6), 144.53 (C-4), 137.65 (C-3, 5), 103.77 (C-1)	C_6F_5: (C2, F2) 248.8, (C4, F4) 261.3, (C4, F3) 13.3, (C4, F2) 5.8, (C3, F3) 255.3, (C1, F2) 24.2

[a] In CD_2C1_2.

similar manner and showed the following results (^{19}F-NMR).

n	Time (min)	Silane **6** (%)	Silane **7** (%)
0.5	30	47	53
0.5	55	24	76
0.5	70	18	82
0.5	190	—	100
1.0	30	40	60
1.0	40	—	100

Similarly, the treatment of silane **1** (27 mg, 0.05 mmol) with $AlCl_3$ (36 mg, 0.27 mmol) in $CDCl_3$ (0.4 ml) gave silane **7** (100% yield, ^{19}F-NMR) within 15 min.

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

A solution of silane **1** (223 mg, 0.43 mmol) in DBE (2 ml) was added to a stirred solution of $AlBr_3$ (56 mg, 0.21 mmol) in DBE (1 ml) at r.t. After 20 min the ^{19}F-NMR spectrum showed the quantitative conversion of silane **1** into dibromosilane **9** [7,14].

4.3.13. With $AlBr_3$ (1.0 equivalent) in DBE

Similarly, after 10 min dibromosilane **9** was obtained in quantitative yield by the reaction of silane **1** (114 mg, 0.22 mmol) with $AlBr_3$ (59 mg, 0.22 mmol) in DBE (2 ml) at r.t. (^{19}F-NMR).

*4.4. Reactions of tris(pentafluorophenyl)phenylsilane **2** with electrophiles*

4.4.1. With aHF in dichloromethane

A sample of aHF (3 ml) was added to a stirred solution of silane **2** (710 mg, 1.2 mmol) in CH_2Cl_2–CD_2Cl_2 (2:1) (3 ml) at -78°C and kept at r.t. for 4 days. After removal of aHF and dichloromethane in vacuum the unchanged silane **2** was recovered quantitatively.

4.4.2. With FSO_3H in CH_2Cl_2

A sample of FSO_3H (0.7 ml) was added at r.t. to a stirred solution of silane **2** (550 mg, 0.90 mmol) in CH_2Cl_2 (1 ml) (PFA trap: $\phi_i = 11.7$ mm). After 1 h the ^{19}F-NMR spectrum of the organic phase showed the quantitative formation of silane **5** and $PhSO_2F$ [δ(F) 64.1 ppm)] (1:1, molar). The organic phase was separated and the acidic phase was extracted with CH_2Cl_2 (2 ml). The combined extracts were treated with NaF, filtered and the volatile substances were removed in vacuum at <90°C. Silane **5** (0.41 g, 83%) was obtained as residue and was identified by ^{19}F-NMR [2] and additionally characterised by ^{13}C and ^{29}Si-NMR spectrometry (Tables 1 and 3).

4.4.3. With HCl and $AlCl_3$ (2.0 equivalent) in hexane

A sample of HCl was bubbled into a stirred suspension of $AlCl_3$ (52 mg, 0.39 mmol) in a hexane (10 ml) solution of silane **2** (119 mg, 0.20 mmol) at r.t. The molar ratio of silane **2** to chlorosilane **8** was 41:59 (3 h) and 38:62 (4 h) (^{19}F-NMR).

4.4.4. With HCl and $AlCl_3$ (5.1 equivalent) in hexane

A sample of HCl was bubbled into a stirred suspension of $AlCl_3$ (112 mg, 0.84 mmol) in a hexane (2.5 ml) solution of silane **2** (101 mg, 0.17 mmol) at r.t. After 2 h the molar ratio of silane **2** to chlorosilane **8** was 36:64 (^{19}F-NMR).

4.4.5. With $AlCl_3$ (0.5 equivalent) in CH_2Cl_2

A solution of silane **2** (344 mg, 0.57 mmol) in CH_2Cl_2

Table 4
IR and Raman spectra of pentafluorophenylsilanes $(C_6F_5)_2SiXY$

X	Y	IR/cm^{-1}	Raman/cm^{-1}
C_6H_5	C_6H_5	3078, 3025, 3020, 3006, 1666, 1644, 1592, 1571, 1519, 1465, 1431, 1380, 1336, 1308, 1286, 1270, 1196, 1162, 1135, 1115, 1089, 1020, 1000, 969, 920, 851, 836, 757, 738, 727, 711, 694, 626, 586, 517, 485, 477, 468, 445, 433, 406, 339, 313	3180 (3.4), 3145 (6.8), 3077 (23.8), 3055 (45.6), 3035 (4.8), 1643 (17.0), 1592 (36.7), 1572 (11.9), 1379 (8.5), 1195(6.8), 1163(8.2), 1107(6.1), 1028 (32.7), 1001 (87.8), 832 (15.7), 694 (12.2), 619 (10.9), 586 (29.6), 518 (26.5), 478 (16.3), 446 (27.6), 392 (23.8), 346 (5.4), 281 (4.8), 254 (11.9), 231 (4.1), 207 (21.1), 191 (23.5), 133 (20.8), 85 (100.0)
C_6F_5	C_6H_5	3081, 3053, 2924, 1646, 1590, 1523, 1467, 1431, 1380, 1292, 1143, 1111, 1099, 1089, 1029, 1022, 999, 972, 760, 739, 728, 700, 695, 633, 626, 588, 526, 521, 504, 477, 460, 449, 442, 414, 337, 316	3058 (40.4), 3004 (3.6), 1645 (22.9), 1590 (16.1), 1570 (8.2), 1389 (9.3), 1195 (3.6), 1159 (6.4), 1140 (3.6), 1111 (36.0), 1029 (12.8), 1000 (45.4), 848 (4.3), 828 (16.3), 702 (9.6), 619 (6.0), 586 (44.4), 523 (8.5), 505 (47.5), 461 (22.0), 446 (38.7), 415 (9.2), 398 (37.6), 375 (8.2), 350 (5.7), 339 (5.0), 282 (5.4), 237 (9.3), 204 (12.9), 189 (15.0), 176 (13.6), 106 (100.0)
$C_6H_5^a$	F	3081, 3057, 3032, 1645, 1594, 1520, 1471, 1433, 1384, 1296, 1258, 1195, 1124, 1094,1028, 997, 974, 892, 835, 758, 742, 729, 705, 697, 630, 588, 530, 514, 477, 464, 444, 423	3184 (4.2), 3144 (7.8), 3062 (67.3), 2974 (6.3), 2527 (3.9), 1645 (31.3), 1594 (28.2), 1572 (10.2), 1389 (15.5), 1196 (5.6), 1162 (6.3), 1125 (8.1), 1031 (24.7), 999 (100.0), 889 (4.9), 835 (14.8), 706 (17.3), 620 (9.9), 586 (6.2), 514 (5.9), 464 (27.5), 445 (38.0), 396 (38.7), 350 (11.3), 280 (4.9), 236 (6.7), 192 (22.9), 85 (43.0)
$C_6F_5^b$	Cl	1648, 1524, 1467, 1382, 1298, 1262, 1143, 1099,1028, 972, 875, 847, 812, 759, 730, 634, 589, 568, 525, 490, 449, 436, 398, 334, 314, 303	1646 (44.6), 1394 (17.6), 1383 (6.8), 856 (6.8), 831 (25.7), 587 (77.0), 523 (12.2), 491 (100.0), 447 (63.5), 430 (20.3), 395 (60.8), 333 (6.1), 281 (8.1), 249 (20.3), 234 (12.8), 220 (13.5), 142 (39.9)
$C_6F_5^b$	Br	1648, 1524, 1469, 1381, 1298, 1264, 1143, 1099, 1027, 972, 874, 846, 812, 757, 730, 634, 589, 525, 450, 439, 396, 338, 321	1645 (61.6), 1393 (22.2), 1146 (6.6), 855 (7.1), 830 (32.8), 630 (5.6), 589 (100.0), 525 (16.2), 510 (45.0), 471 (80.3), 447 (88.9), 429 (31.3), 395 (82.8), 383 (23.2), 349 (7.6), 333 (7.6), 281 (11.1), 233 (21.7), 189 (47.0), 172 (18.2), 135 (30.3), 97 (20.2), 78 (4.0)

[a] Neat liquid.
[b] Present work, lit. see [9].

(2 ml) was added to a stirred suspension of $AlCl_3$ (38 mg, 0.28 mmol) in CH_2Cl_2 (1 ml). After 35 min the molar ratio of silane **2** to chlorosilane **8** was 13:87. Complex **8** was the only polyfluoroaromatic product after 55 min (^{19}F-NMR).

4.4.6. With $AlCl_3$ (1.2 equivalent) in CH_2Cl_2

A solution of silane **2** (923 mg, 1.5 mmol) in CH_2Cl_2 (6 ml) was added to a stirred suspension of $AlCl_3$ (246 mg, 1.8 mmol) in CH_2Cl_2 (1 ml). After 55 min chlorosilane **8** was the only polyfluoroaromatic product. The reaction mixture was evaporated to dryness in vacuum (0.04 hPa) and after repeated sublimation at 92°C (0.04 hPa) silane **8** was obtained in 82% yield (700 mg), m.p. 93–95°C (lit. 78.5–79.5°C [9], 83–85°C [10], 83–86°C [11], 91–93°C [12]). Compound **8** was identified by ^{13}C, ^{19}F [2] and ^{29}Si-NMR spectra, IR and Raman spectra (Tables 1 and 4).

4.4.7. With $AlCl_3$ (0.5 equivalent) in $CHCl_3$

A solution of silane **2** (361 mg, 0.60 mmol) in $CHCl_3$ (1 ml) was added to a stirred suspension of $AlCl_3$ (40 mg, 0.30 mmol) in $CHCl_3$ (1 ml) at r.t. ^{19}F-NMR monitoring showed the following results.

Reaction time (min)	Silane **2** (%)	Silane **8** (%)
35	78	22
55	51	49
240	—	100

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

Silane **2** (121 mg, 0.20 mmol) dissolved in DBE (1 ml) was added to a stirred solution of $AlBr_3$ (26 mg, 0.10 mmol) in DBE (1 ml) at r.t. ^{19}F-NMR monitoring showed the following results.

Reaction time (min)	Silane **2** (%)	Silane **10** (%)
20	43	57
35	19	81
45	9	91
90	—	100

4.4.9. With $AlBr_3$ (1.0 equivalent) in DBE

A solution of silane **2** (647 mg, 1.2 mmol) in DBE (10 ml) was added to a stirred solution of $AlBr_3$ (302 mg, 1.1 mmol) in DBE (1 ml) at r.t. After 25 min the molar ratio of silane **2** to bromosilane **10** was 30:70 and after 40 min **10** was the only polyfluoroaromatic product (^{19}F-NMR). The reaction mixture was evaporated to dryness in a vacuum (50°C, 0.04 hPa) and the residue was sublimed at 110°C (0.04 hPa) to give bromosilane **10** (543 mg, 83%), m.p. 108–110°C (lit. 83–85°C [9,13], 103–107°C [10]). Compound **10** was identified by ^{19}F- [14], ^{13}C and ^{29}Si-NMR spectra, IR and Raman spectra (Tables 1–4).

4.4.10. With $AlBr_3$ (4.1 equivalent) in DBE

$AlBr_3$ (38 mg, 0.14 mmol) dissolved in DBE (0.15 ml) was added to a stirred solution of silane **2** (21 mg, 0.04 mmol) in DBE (0.1 ml) at r.t. After 10 min a quantitative conversion of silane **2** into bromosilane **10** was detected by ^{19}F-NMR spectrometry.

4.5. Conversion of chlorotris(pentafluorophenyl)silane into fluorotris(pentafluorophenyl)silane

A sample of chlorosilan **8** (32 mg, 0.06 mmol) was dissolved in CD_2Cl_2 (0.3 ml). At −78°C 0.3 ml aHF was added. The two-phase system was stirred and warmed to r.t. After 90 min the CD_2Cl_2 phase was separated. Compound **8** was quantitatively converted into fluorosilane **5** (^{19}F-NMR).

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