

Preparation, NMR spectra and reactivity of pentafluorophenyltetrafluorosilicates $M^+ [C_6F_5SiF_4]^-$ [☆]

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Abstract

Pentafluorophenyltetrafluorosilicates $M^+ [C_6F_5SiF_4]^-$ were obtained from pentafluorophenyltrifluorosilane $C_6F_5SiF_3$ and ionic fluorides MF ($M = K, Cs, Me_4N$) in anhydrous MeCN or diglyme. The reactivity of $M^+ [C_6F_5SiF_4]^-$ toward electrophiles was studied.

Keywords: Pentafluorophenyl; Fluorosilicate anion; Desilylation

1. Introduction

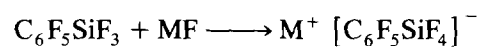
Recently we reported a convenient procedure for the synthesis of $C_6F_5SiF_3$ (**1**) and studied its NMR spectra and reactivity toward electrophiles and nucleophiles [1]. It was assumed that reactions of aryltrifluorosilane **1** with “hard” nucleophiles (NaOEt, piperidine) proceeds via the intermediate formation of pentafluorophenylfluorosilicates, which contain five-coordinated silicon. Participation of pentafluorophenyltrimethylfluorosilicates as highly reactive intermediates in fluoride-catalyzed reactions of $C_6F_5SiMe_3$ with electrophiles was proposed earlier [2], but proof of their existence had not been obtained at this stage. However, preparations, structures, spectral properties and reactivities of fluorosilicates $M^+ [R_nSiF_{5-n}]^-$ and $M_2^+ [R_nSiF_{6-n}]^{2-}$ ($n = 1-3$) were well documented for the different types of hydrocarbons and, to a lesser extent, for partially fluorinated organyl groups R [3,4].

This paper deals with the syntheses, NMR spectra and reactivities of pentafluorophenyltetrafluorosilicates $M^+ [C_6F_5SiF_4]^-$ ($M = [Me_4N], Cs$ and K).

2. Results and discussion

2.1. Synthesis and reactivity of pentafluorophenyltetrafluorosilicates

The general route to organylfluorosilicates consists of the interaction of the corresponding organylfluorosilane with a fluoride donor (alkali metal fluoride, ammonium fluoride, tetraalkylammoniumfluoride hydrate) in protic or aprotic solvents [3,4]. Reaction of HF-free pentafluorophenyltrifluorosilane with anhydrous $[Me_4N]F$, KF or CsF in dry CH_3CN , CD_3CN – $EtCN$ or diglyme gave the corresponding pentafluorophenyltetrafluorosilicates.



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($M = [Me_4N]$ **2**, Cs **3** or K **4**)

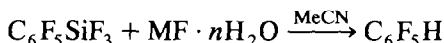
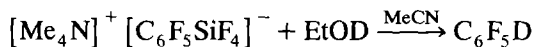
Fluorosilicates such as $Cs^+ [C_6F_5SiF_4]^-$ and $[Me_4N]^+ [C_6F_5SiF_4]^-$ are white moisture-sensitive solids that are slightly soluble in polar aprotic solvents, whereas the potassium salt shows lower solubility. Suspensions and solutions of fluorosilicates **2** and **3** in MeCN are stable at room temperature at least for one day, but over longer periods pentafluorobenzene is formed. Decomposition of tetrafluorosilicate **2** in

[☆] Dedicated to Prof. Dr. Herbert Schumann on the occasion of his 60th birthday.

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diglyme proceeds more slowly, but also leads to pentafluorobenzene.

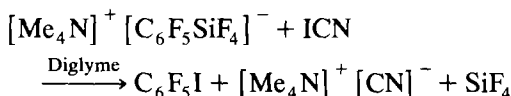
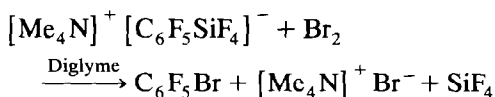
In contrast to pentafluorophenyltrifluorosilane [1], pentafluorophenyltetrafluorosilicates $M^+[C_6F_5SiF_4]^-$ are highly reactive toward electrophiles. They react immediately with ethanol-D or water to form of deuteropentafluorobenzene or pentafluorobenzene:



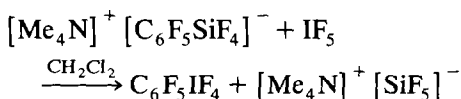
where $M = [Et_4N]$ or $[Bu_4N]$.

The apparent paradox of the fast carbon–silicon bond cleavage in $C_6F_5SiF_3$ with 40% HF_{aq} [5] and the stability of this silane in anhydrous HF (AHF) [1] may now be rationalized within the framework of intermediate formation of fluorosilicate in aqueous HF (the more nucleophilic medium) and its protodesilylation.

Bromine reacts immediately with aryltetrafluorosilicate **2** in diglyme at $-10^\circ C$ to form bromopentafluorobenzene and SiF_4 . The interaction of salt **2** with the less reactive ICN proceeds slowly and the formation of iodopentafluorobenzene indicates unambiguously the electrophilic character of the desilylation.



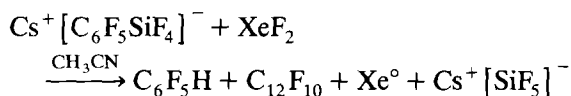
It was known that silane **1** is inert to IF_5 in AHF, CH_2Cl_2 [1] or chlorofluorocarbons [6] but reacts slowly under basic conditions (MeCN, pyridine) to yield $C_6F_5IF_4$ [6]. However, in dichloromethane the reaction of pentafluorophenyltetrafluorosilicate **3** with IF_5 to $C_6F_5IF_4$ was completed within a few minutes.



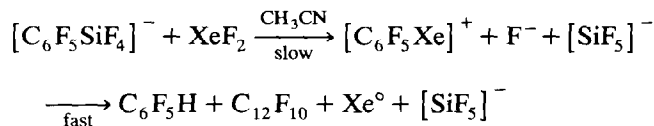
The role of pyridine in the formation of $C_6F_5IF_4$ from $C_6F_5SiF_3$ and IF_5 [6] now may be explained by complex formation of the *N*-base with trifluorosilane **1** followed by desilylation of the complex with IF_5 .

The reaction between $Cs^+[C_6F_5SiF_4]^-$ and xenon difluoride in acetonitrile at room temperature proceeded slowly. Monitoring of the reaction mixture by ^{19}F NMR spectrometry indicated the formation of pentafluorobenzene and decafluorobiphenyl (5.3 : 1, mol) or deuteropentafluorobenzene and $C_{12}F_{10}$ (3.1 : 1, mol) in CD_3CN . No pentafluorophenylxenon(II) cation was observed. However, the latter species is known to react quickly with fluoride ions in CH_3CN or in CD_3CN at -30 to $-10^\circ C$ to give C_6F_5H (C_6F_5D) and $C_{12}F_{10}$ in the same ratio [7]. Therefore, the intermediate formation

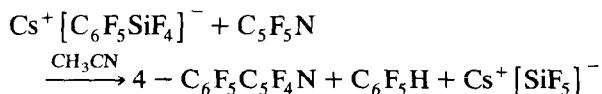
of the $[C_6F_5Xe]^+$ cation from $[C_6F_5SiF_4]^-$ and XeF_2 (slow step) and its fast conversion into C_6F_5H and $C_{12}F_{10}$ cannot be excluded.



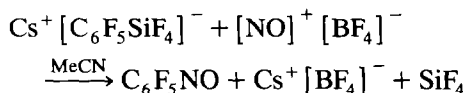
A possible reaction path is:



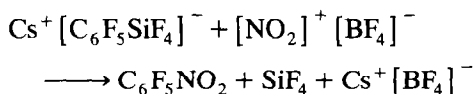
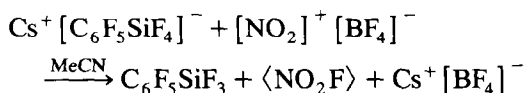
Previously the pentafluorophenylation of some carbon electrophiles with $C_6F_5SiMe_3$ in the presence of CsF was assumed to proceed via the intermediate generation of the fluorosilicate anion $[C_6F_5SiMe_3F]^-$ [2c]. We now show that the individual salt **3** has reacted with pentafluoropyridine to give perfluoro-4-phenylpyridine and pentafluorobenzene (co-product)



Further proof of the strong nucleophilic arylating ability of pentafluorophenyltetrafluorosilicate is given by the interaction of salt **3** with nitrosonium tetrafluoroborate. It is known that the cation $[NO]^+$ is a very weak electrophile and reacts only with electron-rich aromatic compounds like anilines, anisoles, polymethylbenzenes, etc. to yield nitrosoarenes [8]. Nevertheless, nitrosopentafluorobenzene was obtained from pentafluorophenyltetrafluorosilicate and $[NO]^+[BF_4]^-$.

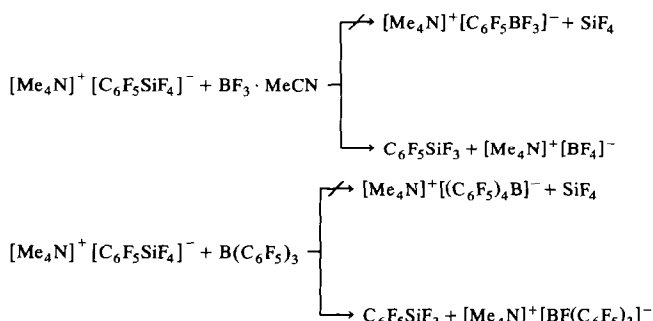


The powerful electrophile nitronium tetrafluoroborate would be expected to give nitropentafluorobenzene. Indeed, this compound was formed in the reaction of cesium pentafluorophenyltetrafluorosilicate with $[NO_2]^+[BF_4]^-$ in acetonitrile. Surprisingly, the main product was pentafluorophenyltrifluorosilane. This means that the $[NO_2]^+$ cation acts mainly as a fluoride acceptor with respect to the $[C_6F_5SiF_4]^-$ anion rather than as an electrophile.

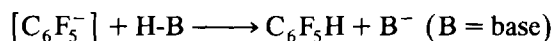
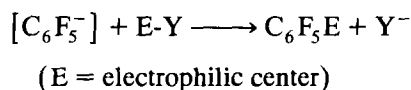
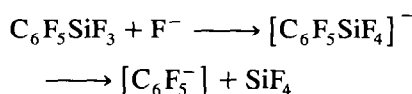


The fluoride-donating ability of $[C_6F_5SiF_4]^-$ may be demonstrated by the reaction with boron trifluoride antris(pentafluorophenyl)borane where the silane $C_6F_5SiF_3$ was formed in addition to the corresponding fluorob

rates. Pentafluorophenylation of the boranes did not occur.



The mechanism of desilylation of pentafluorophenyltetrafluorosilicates can be described as direct attachment of the electrophilic species to the C(1) atom of $[\text{C}_6\text{F}_5\text{SiF}_4]^-$ or by dissociation of the fluorosilicate anion into the $[\text{C}_6\text{F}_5]^-$ anion and SiF_4 . The second path seems more probable. It allows us to explain the formation of pentafluorobenzene in reactions with weak electrophiles in acetonitrile or diglyme (C-H acids). Moreover, the interaction of salt **3** with the stronger C-H acid $\text{CH}_3\text{SO}_2\text{F}$ in diglyme led only to pentafluorobenzene.



2.2. NMR spectra of pentafluorophenyltetrafluorosilicates

The NMR spectra of organyltetrafluorosilicates $[\text{RSiF}_4]^-$ have been thoroughly investigated [3]. For instance, addition of F^- to $\text{C}_6\text{H}_5\text{SiF}_3$ is accompanied by a high-frequency shift of the ^{19}F resonance and an opposite shift of the ^{29}Si resonance (Table 1). Similar changes were observed for the couples $\text{BzSiF}_3-[\text{BzSiF}_4]^-$ and $\text{CF}_3\text{SiF}_3-[\text{CF}_3\text{SiF}_4]^-$. Coordination of the fluoride anion at $\text{C}_6\text{F}_5\text{SiF}_3$ displayed analogous shifts of ^{19}F and ^{29}Si resonances of the SiF fragment. In all cases the resonance of the SiF_4 group in $[\text{C}_6\text{F}_5\text{SiF}_4]^-$ displayed a broad singlet and variation of temperature in the range -20 to $+35$ °C did not affect the position and structure of the C_6F_5 and SiF_4 signals. (The low solubility at low temperatures did not allow us to perform measurements at temperatures significantly lower than -25 °C.) A comparison of ^{19}F NMR spectra of trifluorosilane **1** and tetrafluorosilicates **2** and **3** in the region of aromatically bonded fluorine atoms showed unambiguously a significant delocalization of negative charge at the pentafluorophenyl group in salts **2** and **3**.

Table 1
The ^{19}F and ^{29}Si nuclear magnetic resonances of Si-F fragments in RSiF_3 and $\text{M}^+ [\text{RSiF}_4]^-$ compounds

Compound	$\delta(^{19}\text{F})$ ppm	$^1J(\text{F-Si})$ Hz	$\delta(^{29}\text{Si})$ ppm	$^1J(\text{Si-F})$ Hz	Ref.
$\text{C}_6\text{H}_5\text{SiF}_3$	-143.0	266	-72.9	268	[11]
$[\text{C}_6\text{H}_5\text{SiF}_4]^-$ ^a	-119.2	206			[11]
$[\text{C}_6\text{H}_5\text{SiF}_4]^-$ ^b	-114.3	209	-125.9	210	[11]
$\text{C}_6\text{H}_5\text{CH}_2\text{SiF}_3$	-138.9	281	-64.1	282	[11]
$[\text{C}_6\text{H}_5\text{CH}_2\text{SiF}_4]^-$ ^c	-117.3	215	-116.4	218	[11]
CF_3SiF_3	-150.0	271			[12]
$[\text{CF}_3\text{SiF}_4]^-$	-133.1				[12]
$\text{C}_6\text{F}_5\text{SiF}_3$ ^d	-132.8				[1]
$\text{C}_6\text{F}_5\text{SiF}_3$ ^e	-134.2	248	-77.8	248	[1]
$\text{Cs}^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ ^d	-109.9				
$[\text{Me}_4\text{N}]^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ ^d	-104.2		-131.0		
$[\text{Me}_4\text{N}]^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ ^e	-104.2				

^a At 35°C.

^b At -18.2 °C (^{19}F), -58.2 °C (^{29}Si).

^c At -98 °C.

^d In CH_3CN or $\text{CD}_3\text{CN-EtCN}$.

^e In diglyme.

^f In CD_2Cl_2 .

$\text{C}_6\text{F}_5\text{SiF}_3$ (^{19}F , CD_2Cl_2) [1]: -124.82 (F2,6), -143.03 (F4), -159.04 (F3,5) ppm. $\text{C}_6\text{F}_5\text{SiF}_3$ (^{19}F , $\text{CD}_3\text{CN-EtCN}$) [1]: -125.93 (F2,6), -143.84 (F4), -159.52 (F3,5) ppm. $\text{Cs}^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ (^{19}F , CH_3CN): -129.9 (F2,6), -156.6 (F4), -162.6 (F3,5) ppm. $[\text{Me}_4\text{N}]^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ (^{19}F , CH_3CN): -130.6 (F2,6), -158.8 (F4), -163.1 (F3,5) ppm. $[\text{Me}_4\text{N}]^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ (^{19}F , diglyme): -129.2 (F2,6), -159.9 (F4), -164.2 (F3,5) ppm.

The differences between the ^{19}F and ^{29}Si NMR spectra of $\text{C}_6\text{F}_5\text{SiF}_3$ in neutral (CD_2Cl_2) and basic ($\text{CD}_3\text{CN-EtCN}$) solvents can be rationalized by formation of the neutral adduct $[\text{C}_6\text{F}_5\text{SiF}_3 \cdot \text{NCR}]$.

3. Experimental details

The ^1H and ^{19}F NMR spectra were recorded on Varian EM 360 L (^1H at 60.0 MHz and ^{19}F at 56.4 MHz), 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 (^{29}Si at 79.5 MHz) spectrometers (with TMS and C_6F_6 as internal references). The chemical shifts ^{19}F were assigned to CFCl_3 using $\delta(\text{F}) = -162.9$ ppm for C_6F_6 .

Pentafluorophenyltrifluorosilane [1] was treated with calcinated NaF before use. Bromine (Merck), $[\text{NO}]^+ [\text{BF}_4]^-$, $[\text{NO}_2]^+ [\text{BF}_4]^-$, $[\text{Et}_4\text{N}]^+ \text{F}^- \cdot 2 \text{H}_2\text{O}$ (Fluka), $[\text{Bu}_4\text{N}]^+ \text{F}^- \cdot 3 \text{H}_2\text{O}$ (Riedel de Haen) were used without further purification. Methods for the preparation of anhydrous $[\text{Me}_4\text{N}]^+ \text{F}^-$, CsF and the purification of MeCN are given in Ref. [7]. Iodine pentafluoride and $\text{CH}_3\text{SO}_2\text{F}$ were distilled before use and diglyme was distilled under vacuum over CaH_2 . All manipulations

with $C_6F_5SiF_3$ and $M^+ [C_6F_5SiF_4]^-$ were carried out in FEP tube-reactors under dry argon.

3.1. Preparation of $[Me_4N]^+ [C_6F_5SiF_4]^-$ **2**

A solution of $C_6F_5SiF_3$ (69 mg, 0.27 mmol) in MeCN (0.1 ml) was added to a solution of $[Me_4N]^+ F^-$ (14 mg, 0.15 mmol) in MeCN (0.4 ml) at $-30^\circ C$. The resulting suspension was shaken at room temperature for 10–15 min, the volatile products were removed under high vacuum and the residue was washed with dichloromethane (2×0.6 ml). The solid was dried in vacuum at room temperature for 30 min to yield salt **2** (38 mg, 76%). Found: C 34.1, H 3.68, F 49.0, N 3.98. $C_{10}H_{12}F_9NSi$. Required: C 34.8, H 3.48, F 49.6, N 4.06.

3.2. Preparation of $Cs^+ [C_6F_5SiF_4]^-$ **3** and $K^+ [C_6F_5SiF_4]^-$ **4**

Salts **3** and **4** were prepared in a similar manner from KF (spray-dried) or CsF (1 equiv.) and $C_6F_5SiF_3$ (1.2–1.4 equiv.) in 67%–72% yield. Pentafluorobenzene was formed as by-product. $Cs^+ [C_6F_5SiF_4]^-$. Found: C 17.3, F 42.9. C_6F_9CsSi . Required: C 17.8, F 42.3. $K^+ [C_6F_5SiF_4]^-$. Found: C 23.2, F 56.0. C_6F_9KSi . Required: C 23.2, F 55.2.

3.3. Reactions of $M^+ [C_6F_5SiF_4]^-$

With alcohol and water

(A) Deuteropentafluorobenzene was obtained by addition of EtOD (0.5 mmol) to a suspension of tetrafluorosilicate **2** (0.3 mmol) in $CD_3CN-C_2H_5CN$ (0.7 ml). (B) A solution of $C_6F_5SiF_3$ (1 equiv.) in MeCN was added dropwise to the solution of $[Et_4N]^+ F^- \cdot 2 H_2O$ or $[Bu_4N]^+ F^- \cdot 3 H_2O$ (1–1.5 equiv.) in MeCN at room temperature. Within a few minutes trifluorosilane **1** had been converted into pentafluorobenzene (quantitative yield, ^{19}F NMR spectra).

With bromine

A suspension of $[Me_4N]^+ [C_6F_5SiF_4]^-$ in diglyme (0.2 ml) derived from $C_6F_5SiF_3$ (76 mg, 0.30 mmol) and $[Me_4N]^+ F^-$ (29 mg, 0.31 mmol) was treated with bromine (100 mg, 0.63 mmol) at $10^\circ C$. Immediately SiF_4 was evolved and after 3–5 min salt **2** was converted completely into bromopentafluorobenzene.

With ICN

A suspension of $[Me_4N]^+ [C_6F_5SiF_4]^-$ in diglyme (0.2 ml) derived from $C_6F_5SiF_3$ (99 mg, 0.39 mmol) and $[Me_4N]^+ F^-$ (47 mg, 0.50 mmol) was treated with a solution of ICN (62 mg, 0.41 mmol) in diglyme (0.2 ml) at $-30^\circ C$. The resulting suspension was kept at

room temperature until the ^{19}F resonances of salt **2** had disappeared (12 h). The precipitate was removed after centrifugation to give a solution of C_6F_5I (quantitative conversion).

With IF_5

A solution of IF_5 (28 mg, 0.13 mmol) in CH_2Cl_2 (0.1 ml) was added to a suspension of salt **2** (41 mg, 0.12 mmol) in CH_2Cl_2 (0.2 ml) at $-30^\circ C$. The reaction mixture was shaken at room temperature for 10–15 min to complete the formation of $C_6F_5IF_4$ (quantitative yield, ^{19}F NMR).

With XeF_2

A solution of $C_6F_5SiF_3$ (60 mg, 0.24 mmol) in MeCN (0.2 ml) was added to the suspension of XeF_2 (47 mg, 0.28 mmol) and CsF (59 mg, 0.39 mmol) in MeCN (0.2 ml) cooled to $-30^\circ C$. The ^{19}F NMR spectrum displayed the presence of $Cs^+ [C_6F_5SiF_4]^-$, XeF_2 , C_6F_5H and $C_{12}F_{10}$ (traces). After 3–4 d salt **3** was converted completely into C_6F_5H and $C_{12}F_{10}$ (5.3:1, mol). In CD_3CN deuteropentafluorobenzene and decafluorobiphenyl were formed (3.1:1, mol). Traces of unreacted XeF_2 were observed in both cases (^{19}F NMR).

With $[NO]^+ [BF_4]^-$

A suspension of $Cs^+ [C_6F_5SiF_4]^-$ in MeCN (0.5 ml) derived from $C_6F_5SiF_3$ (100 mg, 0.40 mmol) and CsF (67 mg, 0.44 mmol) was treated with solid $[NO]^+ [BF_4]^-$ (67 mg, 0.57 mmol). The blue suspension was shaken at room temperature for 3 h until the ^{19}F NMR signals of salt **3** had disappeared. Nitrosopentafluorobenzene was obtained (quantitative conversion).

With $[NO_2]^+ [BF_4]^-$

A suspension of $Cs^+ [C_6F_5SiF_4]^-$ in MeCN (0.2 ml) derived from $C_6F_5SiF_3$ (56 mg, 0.22 mmol) and CsF (45 mg, 0.30 mmol) was treated with solid $[NO_2]^+ [BF_4]^-$ (40 mg, 0.30 mmol) at $-20^\circ C$. The reaction mixture was kept at room temperature for 1 h and delivered nitropentafluorobenzene and pentafluorophenyltrifluorosilane (1:2, mol; ^{19}F NMR).

With $BF_3 \cdot MeCN$

A suspension of $[Me_4N]^+ [C_6F_5SiF_4]^-$ in MeCN (0.3 ml) derived from $C_6F_5SiF_3$ (50 mg, 0.20 mmol) and $[Me_4N]^+ F^-$ (24 mg, 0.26 mmol) was treated with a solution of $BF_3 \cdot MeCN$ (22 mg, 0.20 mmol) in MeCN (0.1 ml) at $-15^\circ C$. After a few minutes the obtained white precipitate was separated and the solution contained $C_6F_5SiF_3$ (quantitative yield) along with minor amounts of $[Me_4N]^+ [BF_4]^-$ (^{19}F NMR).

With $B(C_6F_5)_3$

A suspension of $[Me_4N]^+ [C_6F_5SiF_4]^-$ (38 mg, 0.1 mmol) in CH_2Cl_2 (0.3 ml) was treated with a solution

of $\text{B}(\text{C}_6\text{F}_5)_3$ (66 mg, 0.13 mmol) in CH_2Cl_2 (0.1 ml). After few minutes $\text{C}_6\text{F}_5\text{SiF}_3$ and $[\text{Me}_4\text{N}]^+ [\text{B}(\text{C}_6\text{F}_5)_3\text{F}]^-$ [9] were formed (quantitative yield, ^{19}F NMR).

With pentafluoropyridine

A suspension of $\text{Cs}^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ in MeCN (0.1 ml) derived from $\text{C}_6\text{F}_5\text{SiF}_3$ (82 mg, 0.33 mmol) and CsF (53 mg, 0.34 mmol) was treated with a solution of pentafluoropyridine (62 mg, 0.37 mmol) in MeCN (0.4 ml) under stirring at room temperature and kept at 60–65 °C for 2 h and at room temperature overnight. The volatile products were distilled off in vacuum. The white solid was extracted with CH_2Cl_2 and the solvent removed in vacuum to yield perfluoro-4-phenylpyridine (34 mg, 33%) [10]. The distillate contained pentafluorobenzene (37% yield) and pentafluoropyridine in excess.

With $\text{CH}_3\text{SO}_2\text{F}$

A suspension of $\text{Cs}^+ [\text{C}_6\text{F}_5\text{SiF}_4]^-$ (32 mg, 0.79 mmol) and $\text{CH}_3\text{SO}_2\text{F}$ (98 mg, 1.0 mmol) in diglyme (0.2 ml) was stirred at 50 °C for 3 h. Pentafluorobenzene (95%) was obtained (^{19}F NMR).

Acknowledgments

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