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# The fluorine-pentafluorophenyl substitution reaction in anhydrous hydrogen fluoride (aHF): a new interesting methodical approach to synthesize pentafluorophenylxenonium salts

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Dedicated to Prof. K.O. Christe on the occasion of his 65th birthday

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**Abstract**

In anhydrous hydrogen fluoride (aHF) (heterogeneous reaction) $B(C_6F_5)_3$ transfers all the three aryl groups to $XeF_2$ forming $[C_6F_5Xe]^+$ salts. Upon addition of KF, the $[C_6F_5Xe]$ $[HF_2]$ salt was isolated in 78.7% yield. $[C_6F_5Xe]$ $[HF_2]$ dissolved in MeCN exhibits significant cation–anion interactions and decomposes within 14 days at 20 °C. The acidity of the aHF solvent determines the nature of the products in the reaction of $XeF_2$ with $B(C_6F_5)_3$. The reaction path of this new methodical approach of fluorine-aryl substitution in aHF is discussed.

*Keywords:* Anhydrous hydrogen fluoride; Fluorine-aryl substitution; Xenon compounds; Arylboranes; Oxidative fluorination

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## 1. Introduction

Two direct routes for the synthesis of arylxenonium salts have been reported so far:

1. the xenodeborylation of boranes like $B(C_6F_5)_3$ [1–3] or $C_6F_5BF_2$ [4] (Eqs. (1a) and (1b)) and
2. the xenodeprotonation [5] of aromatics (R–H) which are relatively stable towards oxidation (Eq. (2)). Both routes proceed in an acidic environment [2–5].

$$XeF_2 + B(C_6F_5)_3 \xrightarrow[-50\,^{\circ}C]{CH_2CL_2} [C_6F_5Xe][(C_6F_5)_2BF_2] \tag{1a}$$

$$XeF_2 + C_6F_5BF_2 \xrightarrow[-50\,^{\circ}C]{CH_2CL_2} [C_6F_5Xe][BF_4] \tag{1b}$$

$$XeF_2 \xrightarrow[-2HF]{+2CF_3CO_2H} Xe(O_2CCF_3)_2 \xrightarrow[-CF_3CO_2H]{+CF_3SO_2H} \langle CF_3CO_2XeO_3SCF_3 \rangle \xrightarrow[-CF_3CO_2H]{R-H} [RXe][O_3SCF_3] \tag{2}$$

Attempts to introduce nucleophilic aryl groups on xenon using organometallic reagents like aryl lithium compounds, aryl Grignard reagents, $Cd(C_6F_5)_2$ or $Me_3SnC_6F_5$ were unsuccessful. Mainly two reasons are responsible for these findings.

1. The high oxidation potential of $XeF_2$ in combination with easily oxidizable carbanionic organometallic reagents.
2. The low electrophilicity of $XeF_2$ (despite the high positive partial charge on the $Xe^{II}$ centre) which is a consequence of the absence of a permanent dipole moment and the presence of three electron lone pairs at xenon.

A Lewis acidic reagent (Eqs. (1a) and (1b)) or two different substituents on xenon (Eq. (2)) are necessary to activate the hypervalent (**3c–4e**) F–Xe–F bond towards nucleophilic attack.

The high solubility of $XeF_2$ in aHF (9.88 mol/kg at 30 °C) [6] compared to that in $CH_2Cl_2$ (0.45 mol/kg at 25 °C) [7], the oxidative stability of aHF towards $XeF_2$ and the short-term stability of the $[C_6F_5BF_3]^-$ anion against protodeborylation in aHF solution [8] encouraged us to investigate the reaction of $XeF_2$ with $B(C_6F_5)_3$ in aHF.

## 2. Results and discussion

The arylborane $B(C_6F_5)_3$ is practically insoluble in aHF between −78 and 20 °C. At 20 °C, slow solvolysis occurs

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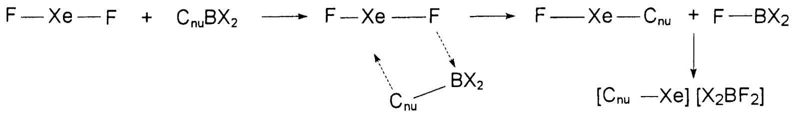

Scheme 1.

which is completed within 72 h upon the formation of $C_6F_5H$ and $[BF_4]^-$ ($^{19}F$ NMR: molar ratio $\sim$ 3:1). One to three equivalents of $XeF_2$ (**1**) react with $B(C_6F_5)_3$ (**2a**) in aHF below $-10\,^\circ C$ under consumption of both the substrates, yielding suspensions with the major part of the products $[C_6F_5Xe]^+$ (**3**) (main product), $[BF_4]^-$ (**4d**) and the (heptafluoro-1,4-cyclohexadien-1-yl)trifluoroborate anion $[c\text{-}C_6F_7BF_3]^-$ (**4e**) dissolved in the mother liquor. Increasing the ratio of **1**:**2a** from 1 to 3, results in a decrease of the amounts of **4d** and **4e**. Polyfluoride anions $[F(HF)_n]^-$ as additional counter anions are not observable by $^{19}F$ NMR spectroscopy in aHF due to fast exchange with aHF solvent. The solid residues contained mixtures of the arylfluoroboranes $(C_6F_5)_{3-n}BF_n$ and their corresponding borates $[(C_6F_5)_{3-n}BF_{n+1}]^-$ and small amounts of the cation **3**. With an increasing amount of the substrate **1**, the number $n$ in the borane/borate mixture increases. It is noteworthy that mixtures of arylfluoroboranes $R_nBF_{3-n}$ and of their corresponding borates $[R_nBF_{4-n}]^-$ in aHF do not appear in the $^{19}F$ NMR spectra as separate signals, but as an exchange averaged signal as a result of fast exchange of the fluorines on boron and HF solvent. The analysis of all the reaction products reveals the following:

1. the fluorine-aryl substitution at **1** is the main reaction;
2. independent of the ratio of **1**:**2a** no fluorine addition on the aryl group of **3** occurs;
3. the solubility of $[C_6F_5Xe]$ $[(C_6F_5)_nBF_{4-n}]$ in aHF decreases with increasing $n$ and
4. **4e** is the only anion where the $C_6F_5$ group is fluorinated by **1**.

To elucidate the reaction path between **1** and **2a**, it is helpful to consider three related reactions between **1** and $C_6F_5$–boron compounds in aHF. Three equivalents of **1** react with $Cs[(C_6F_5)_3BF]$ ($-40$ to $20\,^\circ C$) under formation of $Cs[BF_4]$—which can be separated in $SO_2$—**3**, **4e** and $[HF_2]^-$. In the case of the equimolar reaction of $[C_6F_5Xe]$ $[(C_6F_5)_2BF_2]$ with **1** in aHF ($-50$ to $20\,^\circ C$), a solution of **3**, **4d**, $C_6F_5H$ and $C_6F_6$ (molar ratio 100:23:61:5) is formed. Finally, $[N(CH_3)_4]$ $[(C_6F_5)_4B]$ shows no significant reaction with **1** in aHF at $20\,^\circ C$. After 2 days at $20\,^\circ C$, mainly the solvolysis product of the $[(C_6F_5)_4B]^-$ anion, i. e. $C_6F_5H$ is observed. $XeF_2$ (**1**) having a symmetric hypervalent bond and no permanent dipole moment does not form an adduct with the strongest nucleophile, the fluoride anion, and does not undergo $^{19}F$–$^{18}F$ exchange in neutral medium [9]. However, this exchange proceeds in acidic medium in which a polarized asymmetric $F{-}Xe{-}F\cdots$ Lewis acid adduct is formed [10]. The polarized asymmetric adduct of **1** is the key intermediate in the reaction of **1** with organoboranes under homogeneous conditions in $CH_2Cl_2$ (see Scheme 1) [11].

The electrophilicity of Xe and the nucleophilicity of the organo group are increased upon interaction of the fluorine atom of **1** with the acidic boron centre of **2a**. Additionally, the C(1)–B p–p–π back bond is weakened as the boron environment is pyramidalized. Consequently, the interaction of the nucleophilic C(1) atom with the electrophilic Xe centre is promoted. A Lewis acidic $FBX_2$ abstracts fluoride from the primary product RXeF [12]. In the heterogeneous reaction of **1** and **2a** in aHF solvent **1** is polarized by the Lewis acid HF (Eq. (3)). HF can also react as a Lewis base with the Lewis acid **2a** (Eq. (4)).

$$\underset{\mathbf{1}}{F{-}Xe{-}F} + HF \rightleftharpoons F{-}Xe{-}F\cdots HF \qquad (3)$$

$$\underset{\mathbf{2a}}{(C_6F_5)_3B_{(s)}} + 2HF \leftrightarrows \underset{\mathbf{4a}}{[(C_6F_5)_3BF]^-} + [H_2F]^+ \qquad (4)$$

The missing reactivity of $[N(CH_3)_4]$ $[(C_6F_5)_4B]$ towards **1** in aHF reveals that four-coordinated borates like the $[(C_6F_5)_4B]^-$ anion do not transfer an aryl group to **1**. Consequently, arylfluoroborates have to be transformed to the corresponding boranes before a successful reaction like that of $Cs[(C_6F_5)_3BF]$ with **1** is possible (Eq. (5)).

$$\underset{\mathbf{4a}}{[(C_6F_5)_3BF]^-} + HF \rightleftharpoons \underset{\mathbf{2a}}{(C_6F_5)_3B} + [HF_2]^- \qquad (5)$$

In aHF, the substrate **2a** transfers first one aryl group to **1** forming $C_6F_5XeF$ and $(C_6F_5)_2BF$ (**2b**). Subsequently, fluoride is abstracted from $C_6F_5XeF$ by HF or the arylfluoroborane **2a** or **2b** forming a polyfluoride or arylfluoroborate anions, like $[(C_6F_5)_3BF]^-$ (**4a**) or $[(C_6F_5)_2BF_2]^-$ (**4b**), respectively. The latter anions undergo fluoride transfer corresponding to the equilibrium (5) and the resulting diarylfluoroborane continues to react with **1** (Eq. (6)).

$$\begin{aligned}&\underset{\mathbf{2a}}{(C_6F_5)_3B} \xrightarrow[-[RXe]^+]{+XeF_2} \underset{\mathbf{4b}}{[(C_6F_5)_2BF_2]^-} \xrightarrow[-[HF_2]^-]{+HF} \underset{\mathbf{2b}}{(C_6F_5)_2BF}\\ &\xrightarrow[-[RXe]^+]{+XeF_2} \underset{\mathbf{4c}}{[C_6F_5BF_3]^-} \xrightarrow[-[HF_2]^-]{+HF} \underset{\mathbf{2c}}{C_6F_5BF_2} \xrightarrow[-[RXe]^+]{+XeF_2} \underset{\mathbf{4d}}{[BF_4]^-}\end{aligned} \qquad (6)$$

The acidity of the borane, its reactivity towards **1** and the solubility of the corresponding borate anions $[(C_6F_5)_n\text{-}BF_{4-n}]^-$ in aHF increases with decrease in the number of aryl groups in the borane $(C_6F_5)_nBF_{3-n}$. The solubility of the $[C_6F_5BF_3]^-$ anion **4c** in combination with the highest negative charge on the aryl group in the series of $[(C_6F_5)_nBF_{4-n}]^-$ borate anions is responsible for the oxidation of **4c** by **1** to **4e**. It should be mentioned that the formation of **4e** proceeds at the end of the reaction sequence and that the corresponding alkenyldifluoroborane $c$-$C_6F_7BF_2$ (**2e**) is presumably more acidic (weaker C–B back bond) than the aryldifluoroborane $C_6F_5BF_2$ (**2c**). Consequently, the fluoride abstraction from **4e** is hindered. The absence of $c$-$C_6F_7BF_2$ explains why no transfer of the $c$-$C_6F_7$ group to xenon occurs in aHF.

A comparison of the reactions of **1** with **2a** under homogeneous ($CH_2Cl_2$) and heterogeneous (aHF) conditions shows the advantages and disadvantages using aHF as a solvent. In $CH_2Cl_2$ only one-third of the aryl groups of **2a** can be transferred under formation of **3** (Eq. (1a)). In aHF, all three aryl groups are used for the generation of cation **3** (see idealized (Eq. (7)).

$$\underset{\mathbf{1}}{3XeF_2} + \underset{\mathbf{2a}}{(C_6F_5)_3B} + 2HF \rightarrow 3\underset{\mathbf{3}}{[C_6F_5Xe]^+} + \underset{\mathbf{4d}}{[BF_4]^-} + 2\underset{\mathbf{4f}}{[HF_2]^-} \qquad (7)$$

In addition to the desired cation **3**, a mixture of the anions **4d** and bifluoride is obtained together with a small amount of **4e**. Three different attempts were made to obtain an anion-pure salt of **3**. The addition of three equivalents of $Na[BF_4]$ to the reaction solution according to Eq. (7) did not result in precipitation of $[C_6F_5Xe]\ [BF_4]$ (**3d**) at −78 °C. After the evaporation of aHF and extraction with $SO_2$, salt **3d** with an admixture of **4e** was isolated. Alternatively, precipitation of the $[BF_4]^-$ anion in Eq. (7) was attempted by adding $Ag[NO_3]$, since Clifford and Kongpricha [13] had shown that the introduction of $BF_3$ into the aHF solution of $Ag[NO_3]$ led to the precipitation of $Ag[BF_4]$. In the present case, the precipitation was incomplete and, additionally, a partial decomposition of **3** occurred due to the presence of nitrate ions or its solvolysis products.

Finally, the separation of the $[BF_4]^-$ anion and the isolation of a pure bifluoride salt $[C_6F_5Xe]\ [HF_2]$ (**3f**) was achieved by the addition of KF at the end of the reaction (Eq. (7)). The $[C_6F_5Xe]\ [HF_2]$ salt (**3f**) was obtained after the evaporation of aHF and extraction with $SO_2$ as a slightly yellow waxy product in 79% yield.

The new compound was characterized by multi nuclear NMR spectroscopy. Only the remarkable NMR spectroscopic differences to the salt $[C_6F_5Xe]\ [AsF_6]$ (**3g**) [14] and the two related compounds $C_6F_5XeF$ (**3i**) and $[(C_6F_5Xe)_2F]\ [AsF_6]$ (**3h**) [15,16] will be discussed here (Table 1).

All $^{19}F$ NMR chemical shift values of $[C_6F_5Xe]\ [HF_2]$ (**3f**) (MeCN/−40 °C) appear at lower frequencies compared to $[C_6F_5Xe]\ [AsF_6]$ (**3g**) (MeCN/−40 °C) and at higher frequencies compared to $C_6F_5XeF$ (**3i**) ($CH_2Cl_2$/−78 °C). The values of the $^{19}F$ chemical shifts as well as the $^3J_{F,Xe}$ coupling constants of **3f** are very similar to the values observed for the binuclear cation in $[(C_6F_5Xe)_2F]\ [AsF_6]$ (**3h**). The chemical shift values and coupling constants support the presence of significant $Xe\cdots F$ interactions [14] in the xenon compounds **3f–3i**. The low frequency shifts in **3f** relative to **3g** and the larger $^3J_{F,Xe}$ coupling constant of **3f** relative to **3g** are in agreement with the higher nucleophilicity of the $[HF_2]^-$ anion compared to that of the $[AsF_6]^-$ anion.

In the $^{13}C$ NMR spectra C(1) (83.0 ppm) and C(2,6) (144.4 ppm) of $[C_6F_5Xe]\ [HF_2]$ (**3f**) are shifted to higher frequencies in comparison to **3g** (82.2 and 143.4 ppm, respectively) and the coupling $^1J_{C,Xe}$ of 135.5 Hz is significantly larger than that of **3g** (117.4 Hz).

The interaction of the electrophilic cation **3** with the nucleophilic $[HF_2]^-$ anion renders the $C_6F_5$ group in **3** more anionic (asymmetric hypervalent environment about Xe) and reduces the polarization of its π-system.

The $[C_6F_5Xe]\ [HF_2]$ salt (**3f**) melts at 25 °C, forming a yellow highly viscous liquid. On heating up to 100 °C, gas evolution was observed. After cooling and dissolving the residue in MeCN, the $^{19}F$ NMR spectrum indicates a partial decomposition with the formation of $C_6F_6$ and HF (Eqs. (8a) and (8b)).

$$[C_6F_5Xe][HF_2] \xrightarrow[25\,^{\circ}C<T\leq 100\,^{\circ}C]{} C_6F_6 + Xe + HF \qquad (8a)$$

$$[C_6F_5Xe][HF_2] + nHF \rightarrow [C_6F_5Xe][F(HF)_{n+1}] \qquad (8b)$$

HF reacts with the $[HF_2]^-$ anion of **3f** under formation of less nucleophilic $[F(HF)_{n+1}]^-$ anions. Consequently, the $^{19}F$ chemical shift values of the $[C_6F_5Xe]^+$ cation shift to higher frequencies and the coupling $^3J_{F,Xe}$ decreases.

In 1993, Frohn and Bardin [17] have shown that $[C_6F_5Xe]\ [AsF_6]$ (**3g**) is oxidized by **1** in aHF forming stepwise $[c\text{-}C_6F_7Xe]^+$ and $[c\text{-}C_6F_9Xe]^+$ salts. In the reaction of **1** with **2a** (molar ratio 3:1), no comparable oxidation products of **3** were observed despite the high ratio of **1**:**3** in the mother liquor at the beginning of the reaction. The F-$C_6F_5$ substitution on xenon is associated with a decrease of the acidity of aHF (Eqs. (9a) and (9b)).

$$XeF_2 + (C_6F_5)_3B \rightarrow [C_6F_5Xe]^+ + (C_6F_5)_2BF + F^- \qquad (9a)$$

$$F^- + HF \rightleftarrows [HF_2]^- \qquad (9b)$$

Table 1
$^{19}F$ NMR shift values $\delta$ (ppm) and the coupling constant $^3J_{F,Xe}$ (Hz) of some related $C_6F_5Xe$ compounds

| Compound | Solvent ($T$, °C) | $\delta$($o$-F) | $\delta$($p$-F) | $\delta$($m$-F) | $^3J_{F,Xe}$ | Reference |
|---|---|---|---|---|---|---|
| $[C_6F_5Xe]\ [HF_2]$ (**3f**) | $CD_3CN$ (−40) | −127.1 | −144.6 | −156.1 | 72.6 | This study |
| $[C_6F_5Xe]\ [AsF_6]$ (**3g**) | $CD_3CN$ (−40) | −125.4 | −141.7 | −154.8 | 68.9 | [14] |
| $[(C_6F_5Xe)_2F]\ [AsF_6]$ (**3h**) | $CD_3CN$ (−40) | −127.2 | −144.5 | −155.9 | 72.2 | [15] |
| $C_6F_5XeF$ (**3i**) | $CD_2Cl_2$ (−78) | −129.4 | −146.9 | −156.5 | 81.0 | [15,16] |

The oxidation potential of $XeF_2$ depends on the acidity of HF (Eq. (10)).

$$XeF_2 + [H_2F]^+ \rightleftarrows [FXe]^+ + 2HF \qquad (10)$$

Gillespie and Liang [18] have investigated the influence of strong Lewis acids and bases like $SbF_5$ or $F^-$ on the acidity function $H_0$ of HF. They related $H_0$ to the concentration of $[H_2F]^+$ ions by Eq. (11) as follows:

$$-H_0 = \log\{[H_2F]^+\} + 21.1 \qquad (11)$$

The influence of the addition of Lewis acids on the reaction of **1** with **2a** in aHF was investigated by reacting the suspensions of **2a** in aHF with saturated aHF solutions of [FXe] $[SbF_6]$ at −40 °C. Depending on the amount of [FXe] $[SbF_6]$ $[c\text{-}C_6F_7Xe]^+$ and $c\text{-}C_6F_9H$ or $[c\text{-}C_6F_9Xe]^+$ are formed spontaneously.

In the reaction of **2a** with three equivalents of **1** in a 1 M NaF/aHF solution at −30 °C F-$C_6F_5$ substitution on xenon takes place. The products, $[C_6F_5Xe]^+$ (**3**), $[BF_4]^-$ (**4d**), $C_6F_6$ and $[c\text{-}C_6F_7BF_3]^-$ (**4e**) were formed in a molar ratio of 100:17:4:17. No oxidation of the $[C_6F_5Xe]^+$ cation takes place under basic conditions. However, the amount of $C_6F_6$ and **4e** was doubled compared to the experiments in the absence of NaF.

## 3. Experimental

All reactions and NMR measurements were performed in FEP (tetrafluoroethylene hexafluoropropylene copolymer) traps under a dry argon atmosphere. Hydrogen fluoride was dried by electrolysis (stainless steel cell, Ni electrode). The reaction products and their ratios were determined by NMR spectroscopy using the Bruker spectrometers WP 80 SY (80 MHz) or AVANCE-DRX (500 MHz). The $^{129}$Xe, $^{19}$F, $^{13}$C and $^{1}$H chemical shift values are measured relative to the standards $XeOF_4$ (external standard, neat, 24 °C; using $XeF_2$/MeCN/24 °C ($c \to 0$) as secondary external reference with $\delta(XeF_2) = -1813.28$ ppm), $CCl_3F$ ($C_6F_6$ as secondary external reference with $\delta(C_6F_6) = -162.9$ ppm in the corresponding solvent ($c \to 0$) at the measurement temperature) and TMS (as external reference in the corresponding solvent at the measurement temperature). The absolute values of the coupling constants $J$ are given in hertz.

### 3.1. Reaction of **2a** with $n = 1$, 2 and 3 equivalents of **1** in aHF (general procedure)

The compound **2a** (0.1–0.3 mmol scale) was suspended in 0.2–2.5 ml aHF at −50 °C. Under stirring the corresponding solution of **1** in aHF (≤0.5 ml) was added and warmed to −10 °C ($n = 1$ and 2) or −30 °C ($n = 3$). NMR spectra after 4 h showed that both the substrates were consumed. The slightly yellow mother liquor was separated at −78 °C from minor amounts of solid. The latter was washed twice with $CCl_3F$, dried and dissolved in $CD_3CN$.

Molar ratio of products in the mother liquors is given as follows:

($n$=1) **3** : **4d** : **4e** : $C_6F_5H$ : $C_6F_6$ = 100 : 71 : 16 : 56 : n.d.

($n$=2) **3** : **4d** : **4e** : $C_6F_5H$ : $C_6F_6$ = 100 : 37 : 11 : 0 : 6

($n$=3) **3** : **4d** : **4e** : $C_6F_5H$ : $C_6F_6$ = 100 : 28 : 9 : 0 : 2

Molar ratio of products in the solid residues is given as follows:

($n$ = 1) **3** : **2a**/**4a** : **2b**/**4b** : **2c**/**4c** : **2d**/**4d** : **2e**/**4e**
= 40 : 100 : 21 : 73 : 10 : 0

($n$ = 2) **3** : **2a**/**4a** : **2b**/**4b** : **2c**/**4c** : **2d**/**4d** : **2e**/**4e**
= 31 : 12 : 18 : 100 : 7 : 0

($n$ = 3) **3** : **2a**/**4a** : **2b**/**4b** : **2c**/**4c** : **2d**/**4d** : **2e**/**4e**
= 100 : 0 : 88 : 0 : 5 : 8

### 3.2. Solvolytical stability of **2a** in aHF

The compound **2a** (60 mg, 0.117 mmol) was suspended in 0.2 ml aHF at −50 °C. While monitored by $^{19}$F NMR spectroscopy, the temperature was raised in five steps of 10 °C/h to 0 °C. After 15 h at 0 °C (suspension, molar ratio $C_6F_5H$:**4d** in the mother liquor 100:36) the sample was stirred at 20 °C for further 72 h until complete dissolution. The molar ratio of the solvolysis products did not change.

### 3.3. Reaction of Cs[$(C_6F_5)_3BF$] (Cs-**4a**) with 3 equivalents of **1** in aHF

Cs-**4a** (49 mg, 0.074 mmol) was suspended in 1.5 ml aHF at −40 °C and vigorously stirred. The compound **1** (38 mg, 0.225 mmol) was added and the suspension was warmed to 20 °C. After 15 min, a yellow solution was obtained. aHF was removed in vacuum and the residue was pumped at 20 °C/$10^{-2}$ h Pa for 15 h. After extraction with $SO_2$ (0.4 ml, −78 °C) Cs[$BF_4$] (14.2 mg, 87%) remained as colorless solid. The $SO_2$ phase contained **3**, $[HF_2]^-$ and **4e** (molar ratio 100:96:47).

### 3.4. Reaction of [$C_6F_5Xe$] [$(C_6F_5)_2BF_2$] (**3b**) with **1** in aHF

To a suspension of **3b** (50 mg, 0.073 mmol) in 0.07 ml aHF at −50 °C, a solution of **1** (12.6 mg, 0.074 mmol) in 0.15 ml aHF was added. Upon stirring, the suspension was warmed in steps of 10 °C/h to 20 °C. After 1 h, a yellow solution resulted, which contained **3**, **4d**, $C_6F_6$ and $C_6F_5H$ (molar ratio 100:23:61:5).

### 3.5. Attempted reaction of [$NMe_4$] [$(C_6F_5)_4B$] with 4 equivalents of **1** in aHF

A solution of **1** (19.8 mg, 0.117 mmol) in 0.3 ml aHF (−78 °C) was added to [$NMe_4$] [$(C_6F_5)_4B$] (22 mg, 0.029 mmol). The suspension was immediately warmed to 20 °C and stirred for 2 days. The main product was $C_6F_5H$. Only traces of **3** were detected.

### *3.6. Preparation of [$C_6F_5Xe$] [$HF_2$] (3f)*

The compound **2a** (1090 mg, 2.129 mmol) was added to a solution of **1** (1189 mg, 7.026 mmol) in 25 ml aHF at −78 °C. The stirred suspension was warmed to 20 °C. After 4 h the amount of solid decreased significantly and the mother liquor became yellow. KF (124 mg, 2.134 mmol) was added and the amount of precipitation increased. The suspension was stored at −78 °C for 16 h, the mother liquor separated, the solid residue suspended in $CCl_3F$ (4 ml, −78 °C) and all the volatile components pumped off at −40 °C/$10^{-2}$ h Pa. The solid was dissolved in $CD_3CN$ (0.2 ml, −40 °C) and a $^1H$ and $^{19}F$ NMR spectra were recorded. **3** (−125.6, m, *o*-F, with $^{129}Xe$ satellites: $^3J_{F,Xe} = 68.1$ Hz; −142.7, t, *p*-F, $^3J_{F,F} = 20.3$ Hz; −155.3, m, *m*-F), **4d** (−149.1, s, BF), **4b** (−136.4, m, *o*-F; −144.7, m, b, $BF_2$; −160.2, t, *p*-F, $^3J_{F,F} = 19.8$ Hz; −165.1 m, *m*-F); molar ratio: **3**:**4d**:**4b** = 64:100:75. The mother liquor was evaporated at ≤−10 °C/10 h Pa, the yellow viscous residue suspended in $CCl_3F$ (−78 °C, 15 ml) and stirred for 16 h. The solid was separated and pumped at −40 °C/$10^{-2}$ h Pa for 2 h. Afterwards, the solid was suspended in 10 ml $SO_2$ at −70 °C. The mother liquor was separated from the solid residue (306.9 mg, mainly K[$BF_4$]), $SO_2$ was distilled off and the residue pumped at −60 °C/$10^{-2}$ h Pa. The viscous residue was stirred in 15 ml $CCl_3F$ at −78 °C for 16 h, the solid was separated, washed three times with 10 ml $CCl_3F$ (−78 °C) and pumped at −40 °C/$10^{-2}$ h Pa for 6 h. **3f** (1696 mg, 5.028 mmol, 78.7% yield) was obtained as slightly yellow solid which became waxy when warmed to 20 °C.

$^1H$ NMR ($CD_3CN$, −40 °C): 9.9 (s, [$HF_2$]$^-$); $^{13}C$ NMR ($CD_3CN$, −40 °C): 83.0 (t, with $^{129}Xe$-satellites, $^1J_{C,Xe} = 135.5$ Hz, $^2J_{C,F} = 26.2$ Hz, C-1), 138.3 (d, m, $^1J_{C,F} = 255.4$ Hz, C-3,5), 144.4 (d, m, $^1J_{C,F} = 253.0$ Hz, C-2,6), 144.9 (d, t, t, $^1J_{C,F} = 258.8$ Hz, $^2J_{C,F} = 13.5$ Hz, $^3J_{C,F} = 4.5$ Hz, C-4); $^{19}F$ NMR ($CD_3CN$, −40 °C): −127.1 (m, with $^{129}Xe$-satellites, $^3J_{F,Xe} = 72.6$ Hz, *o*-F) −142.4 (s, $\tau_{1/2} = 200$ Hz, [$HF_2$]$^-$), −144.6 (t, t, $^3J_{F,F} = 20.1$ Hz, $^4J_{F,F} = 4.6$ Hz, *p*-F), −156.1 (m, *m*-F); $^{129}Xe$ NMR ($CD_3CN$, −40 °C): −3780 (t, m, $\tau_{1/2} = 49$ Hz, $^3J_{Xe,F} = 71$ Hz).

### *3.7. Thermolysis of (3f)*

The compound **3f** (25 mg) was heated (1–2 °C/min) in a FEP-inliner. At 25 °C a high viscous melt resulted. Further heating was accompanied by evolution of gas. The sample was maintained at 100 °C for 15 min and then cooled to −78 °C forming a glassy yellow material which was dissolved in $CD_3CN$ at −40 °C and characterized by $^1H$ and $^{19}F$ NMR spectroscopy: **3** (−125.7, m, *o*-F, with $^{129}Xe$ satellites, $^3J_{F,Xe} = 69.1$ Hz; −142.9, t, *p*-F, $^3J_{F,F} = 19.7$ Hz; −155.1, m, *m*-F), [$F(HF)_n$]$^-$ (−142.9, s) $C_6F_6$ (−162.9, s); molar ratio: 34:100/*n*+1:48. In addition, several unidentified species of minor concentration with $^{19}F$ NMR shift values from −99.2 to −167.1 ppm were observed.

The thermal stability of **3f** in solution was tested at a 30 mg sample in 0.2 ml $CD_3CN$ at 20 °C. After 7 days one-third of **3** was still present besides $C_6F_6$ and [$F(HF)_n$]$^-$ and after 14 days the decomposition was complete. The $^{19}F$ NMR resonance of [$F(HF)_n$]$^-$ had shifted to −182.9 ppm.

### *3.8. Reaction of **2a** with [FXe] [$SbF_6$] in aHF*

Two samples of **2a**, each with 20 mg in 0.2 ml aHF at −78 °C, were reacted with different quantities of a saturated aHF solution of [FXe] [$SbF_6$] and warmed to −40 °C. Sample "a" a suspension with a minor quantity of [FXe] [$SbF_6$] was directly characterized by $^{19}F$ NMR spectroscopy: [*c*-$C_6F_7Xe$]$^+$ (−90.7, F-2; −93.7, F-6, 6; −108,8 F-3, 3; −147.3 F-5; −151.4, F-4); [*c*-$C_6F_9Xe$]$^+$ (−83.0, F-2; −99.1 F-6, 6; −115.4, F-3, 3; −127.7, F-5, 5; −131.3, F-4, 4); and *c*-$C_6F_9H$ (−103.8, F-6,6; −119.4, F-3,3; ∼−120, F-2, −133.2, F-4, 4 and F-5, 5) were formed in the molar ratio of 100:18:56. Sample "b" was treated with [FXe] [$SbF_6$] as long as a solution resulted. $^{19}F$ NMR spectra showed [*c*-$C_6F_9Xe$]$^+$ as the only product.

### *3.9. Reaction of **2a** with 3 equivalents of **1** in a 1 M NaF/aHF solution*

The compound **2a** (500 mg, 0.977 mmol) was added to a solution of NaF (514 mg, 12.24 mmol) in 12 ml aHF (−78 °C). The suspension was warmed to −50 °C, **1** (496 mg, 2.930 mmol) was added and was stirred for 5 h at −50 °C and 20 min at −30 °C until a yellow solution was formed. $^{19}F$ NMR spectra at −40 °C showed **3** (−122.9, m, *o*-F, with $^{129}Xe$-satellites; −137.2, t, *p*-F; −150.9, m, *m*-F), **4d** (−149.0, q(1:1:1:1), BF), **4e** (−99.0, m, F-6, 6; −111.9, m, F-3, 3; −130.8, m, F-2; −133.5, m, b, $BF_3$; −152.0, m, F-5; −159.1, m, F-4) and $C_6F_6$ (−162.9, s) in a molar ratio of 100:17:17:4.

## 4. Conclusion

Fluorine-aryl substitution on $XeF_2$ can be achieved successfully with $(C_6F_5)_3B$ in aHF. The presence of a three-coordinated boron species is required for the fast transfer of an aryl group from the borane to **1**. All the aryl groups bonded to boron can be transferred. The reaction proceeds even when the base $F^-$ is added in a large stoichiometric excess. In the presence of the strong Lewis acid $SbF_5$ oxidation of the $C_6F_5$ group occurred and cycloalkenylxenonium cations were formed. It seems reasonable to suspect that this new methodical approach of aryl transfer can also be adopted to other strongly oxidizing element fluorides with a hypervalent fluorine–element–fluorine bond.

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