Perfluoroorganylxenonium(II) salts from reactions of XeF_2 or $[FXe][SbF_6]$ with selected perfluorinated alk-1-yn-1-yl- and alk-1-en-1-yltrifluoroborate salts in aHF

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ABSTRACT

Xenon difluoride reacted with alkynylborate salts, $K[R_FC{\equiv}CBF_3]$, in anhydrous HF (aHF) to give alkynylxenonium salts, $[R_FC{\equiv}CXe][BF_4]$ ($R_F = CF_3$, C_3F_7, $(CF_3)_2CF$), in 50–55% yield. Both $[FXe][SbF_6]$ and $K[C_3F_7C{\equiv}CBF_3]$ formed the $[C_3F_7C{\equiv}CXe]^+$ salt in aHF. In the reaction of XeF_2 with the alkenylborate salt, $K[CF_2{=}C(CF_3)BF_3]$, the competitive hydrodeboration reaction (formation of $CF_2{=}C(CF_3)H$ in 85% yield) exceeded the xenodeboration reaction (formation of the xenonium salt $[CF_2{=}C(CF_3)Xe][BF_4]$ in 15% yield only). $K[4\text{-}BF_3C_5F_4N]$ did not react with XeF_2 in aHF, but underwent fluorine addition in the presence of AsF_5.

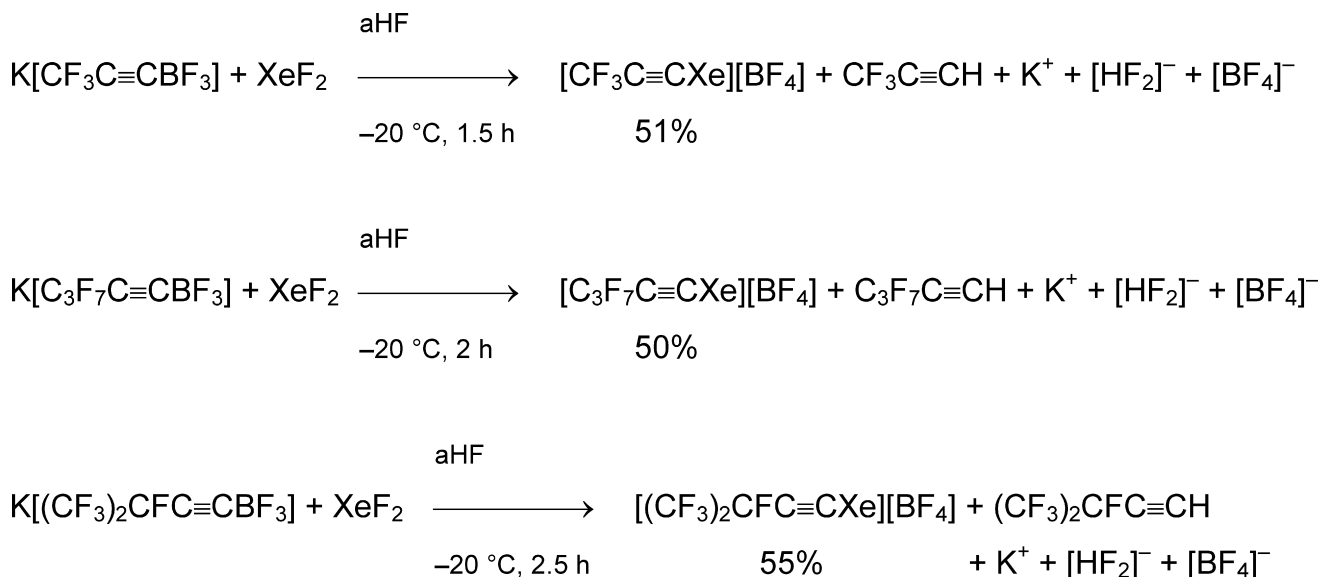© 2012 Elsevier B.V. All rights reserved.

1. Introduction

In 1989 Naumann and Frohn independently reported the first preparation of an organylxenonium(II) salt, namely $[C_6F_5Xe][(C_6F_5)_nBF_{4-n}]$, by reaction of XeF_2 with $(C_6F_5)_3B$ in acetonitrile ($n = 3$) [1] or in dichloromethane ($n = 1$) [2], respectively. A larger number of organylxenonium(II) salts $[RXe]Y$ with different types of organyl groups (R = poly- and perfluorinated aryl, alkenyl, cycloalkenyl, and alkynyl) were subsequently prepared from xenon difluoride and preferentially organyldifluoroboranes in CH_2Cl_2 or 1,1,1,3,3-pentafluoropropane (PFP) or 1,1,1,3,3-pentafluorobutane (PFB). The later solvents are more stable towards XeF_2 in the presence of Lewis acidic fluoroboranes than CH_2Cl_2. This synthetic approach was *formally* described as *xenodeborylation*, e.g., the displacement of BF_2 in the three-coordinated borane precursor R_FBF_2 by Xe^+, and was explained by an acid–base interaction with a subsequent four-center transition state [3]. When reactions of XeF_2 with the pentafluorophenylboranes, $C_6F_5BX_2$ (X = F, C_6F_5), were performed in superacidic aHF, $[C_6F_5Xe]^+$ salts (products of xenodeborylation) were obtained besides products with the anions, $[cyclo\text{-}C_6F_7BF_3]^-$ and $[cyclo\text{-}C_6F_9BF_3]^-$ (fluorine addition to the pentafluorophenyl moiety). Both reaction routes were also realized in reactions of XeF_2 with the pentafluorophenyl(fluoro)borate salts, $K[C_6F_5BF_3]$ and $Cs[(C_6F_5)_3BF]$, in aHF [4,5]. Under similar conditions, perfluoroalkenyldifluoroboranes, $F(CF_2)_nCF{=}CFBF_2$, and potassium perfluoroalkenyltrifluoroborates, $K[F(CF_2)_nCF{=}CFBF_3]$ (n = 0, 1, 2, 4), yielded perfluoroalkyltrifluoroborates (products of fluorine addition across the $C{=}C$ double bond) only. The latter did not subsequently result in xenodeboration (see below for definition) or oxidative C–B bond-cleavage reactions with XeF_2 in aHF [4]. Based on fluorine addition to alkenyltrifluoroborates, we planned to prepare the unknown trifluoroborate salt with the branched perfluoroalkyl group from $K[CF_2{=}C(CF_3)BF_3]$ using XeF_2 in aHF as the fluorinating agent. Surprisingly, the experiment showed the formation of the corresponding alkenylxenonium(II) tetrafluoroborate. This unexpected result and the absence of information about reactions of XeF_2 with $K[R_FC{\equiv}CBF_3]$ salts in aHF prompted us to investigate, in detail, *xenodeboration* reactions (displacement of BF_3 in *four*-coordinated $[R_FBF_3]^-$ by Xe^+) in reactions of XeF_2 with organyltrifluoroborate salts in aHF.

2. Results and discussion

We found that XeF_2 reacted with potassium perfluoroalkynyltrifluoroborate salts, $K[CF_3C{\equiv}CBF_3]$, $K[C_3F_7C{\equiv}CBF_3]$, and $K[(CF_3)_2CFC{\equiv}CBF_3]$, in aHF at $-20\,°C$ within 1.5–2.5 h yielding

$$K[CF_3C\equiv CBF_3] + XeF_2 \xrightarrow[-20\ °C,\ 1.5\ h]{aHF} [CF_3C\equiv CXe][BF_4] + CF_3C\equiv CH + K^+ + [HF_2]^- + [BF_4]^-$$
$$51\%$$

$$K[C_3F_7C\equiv CBF_3] + XeF_2 \xrightarrow[-20\ °C,\ 2\ h]{aHF} [C_3F_7C\equiv CXe][BF_4] + C_3F_7C\equiv CH + K^+ + [HF_2]^- + [BF_4]^-$$
$$50\%$$

$$K[(CF_3)_2CFC\equiv CBF_3] + XeF_2 \xrightarrow[-20\ °C,\ 2.5\ h]{aHF} [(CF_3)_2CFC\equiv CXe][BF_4] + (CF_3)_2CFC\equiv CH$$
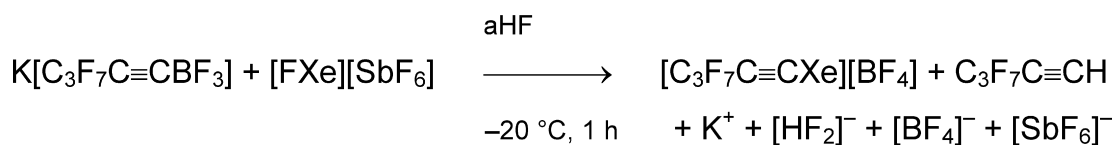$$55\% \qquad + K^+ + [HF_2]^- + [BF_4]^-$$

Scheme 1.

the corresponding perfluoroalkynylxenonium(II) tetrafluoroborates. In all cases, xenodeboration was accompanied by hydrodeboration yielding 1H-perfluoroalkynes in admixture with K[BF$_4$] (Scheme 1).

In contrast to the behavior of K[R$_F$CF=CFBF$_3$], no addition of fluorine across the carbon–carbon multiple bond occurred even for alkynyltrifluoroborate salts under the action of the stronger fluorooxidant [FXe][SbF$_6$] (Scheme 2)
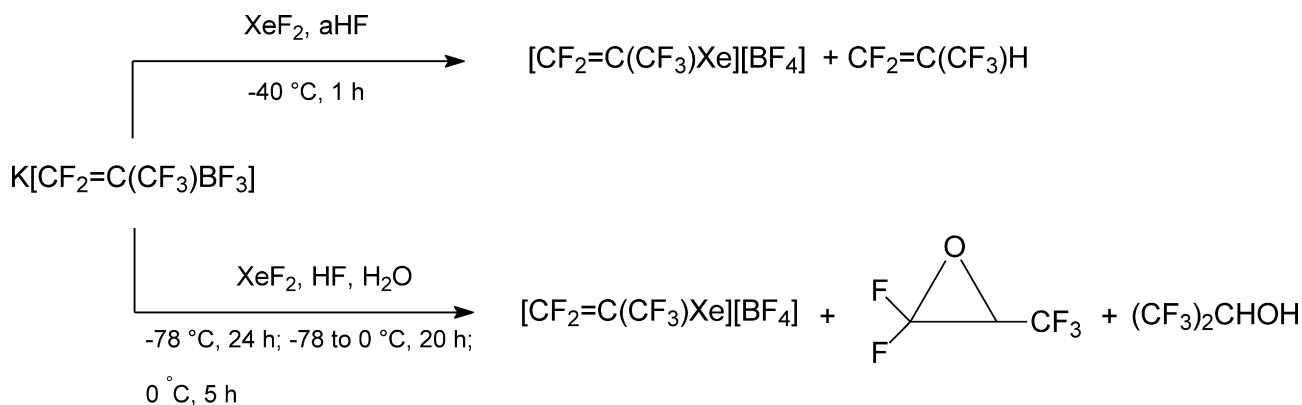
The potassium perfluoroalkenyltrifluoroborate, K[CF$_2$=C(CF$_3$)BF$_3$], is less stable towards aHF than the perfluoroalkynyltrifluoroborates, K[CF$_3$C≡CBF$_3$], K[C$_3$F$_7$C≡CBF$_3$], and K[(CF$_3$)$_2$CFC≡CBF$_3$]. Its hydrodeboration (electrophilic reaction) occurred to a small extent even at −78 °C. At −40 °C xenodeboration proceeded at a lower rate than hydrodeboration. Thus, perfluoro-1-methylethenylxenon(II) tetrafluoroborate, [CF$_2$=C(CF$_3$)Xe][BF$_4$], was formed in only 15% yield besides 85% of 1,1,3,3,3-pentafluoropropene, CF$_2$=C(CF$_3$)H. When XeF$_2$ and K[CF$_2$=C(CF$_3$)BF$_3$] were warmed in aHF from −78 to

0 °C over 20 h, [CF$_2$=C(CF$_3$)Xe][BF$_4$] was formed in almost the same low yield, but CF$_2$=C(CF$_3$)H was the minor product. In a consecutive reaction, K[CF$_2$=C(CF$_3$)BF$_3$] underwent electrophilic oxygenation with XeF$_2$-H$_2$O to form 1,2-epoxy-1,1,3,3,3-pentafluoroethane (cf. [6]). The long reaction time allowed the penetration of stoichiometric quantities of moisture through the thin FEP walls (≤0.3 mm) of the reaction vessel. Consecutive addition of HF to the epoxide resulted in (CF$_3$)$_2$CHOH (Scheme 3).

It is important to emphasize that XeF$_2$ does not react with solutions of [Bu$_4$N][CF$_3$C≡CBF$_3$] in 1,1,1,3,3-pentafluorobutane (PFB, a weakly coordinating solvent) as well as K[C$_6$F$_5$BF$_3$] in acetonitrile (a coordinating solvent) (Scheme 4). We can essentially consider [R$_F$BF$_3$]$^-$ anions as addition products of [R$_F$]$^-$ carbanions to the Lewis acid, BF$_3$. The aforementioned absence of reactivity with XeF$_2$ in CH$_3$CN indicates that [R$_F$BF$_3$]$^-$ did not undergo a S$_N$2-like transfer of [R$_F$]$^-$ in the presence of CH$_3$CN.

$$K[C_3F_7C\equiv CBF_3] + [FXe][SbF_6] \xrightarrow[-20\ °C,\ 1\ h]{aHF} [C_3F_7C\equiv CXe][BF_4] + C_3F_7C\equiv CH$$
$$+ K^+ + [HF_2]^- + [BF_4]^- + [SbF_6]^-$$

Scheme 2.

Scheme 3.

$$[Bu_4N][CF_3C\equiv CBF_3] + XeF_2 \xrightarrow[\approx 20\ ^\circ C,\ 46\ h]{PFB} \text{No reaction}$$

$$K[C_6F_5BF_3] + XeF_2 \xrightarrow[\approx 20\ ^\circ C,\ 48\ h]{CH_3CN} \text{No reaction}$$
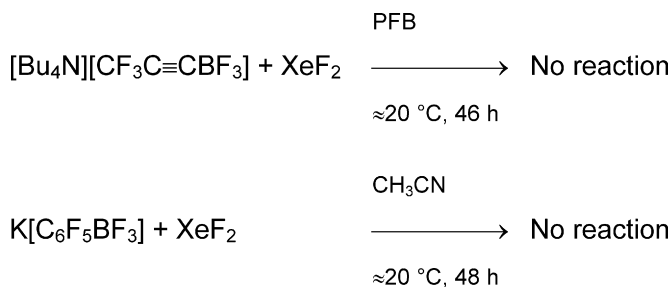
Scheme 4.

The negative results in PFB and CH_3CN compared with the positive result in aHF illustrates the key role of aHF in the formation of organylxenonium salts in reactions of XeF_2 with organylborate salts. The ^{19}F NMR spectroscopic investigation of $K[R_FBF_3]$ ($R_F=C_6F_5$, XCF=CF, C_6F_{13}) in aHF [7] can be interpreted by the following sequence of equilibria (Scheme 5). The equilibrium concentration of R_FBF_2 mainly depends on the fluoride ion donor properties of the individual $[R_FBF_3]^-$ anions.
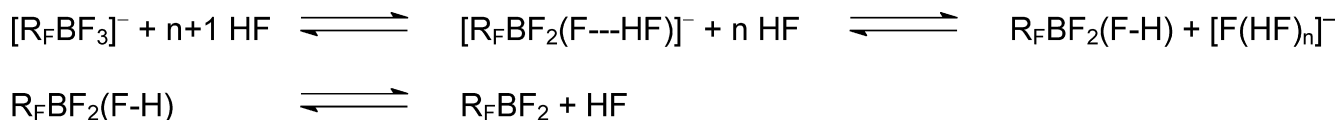
A comparison of the ^{11}B and ^{19}F NMR chemical shift values of the BF_3^- group of perfluoroalkenyl- and perfluoroalkynyltrifluoroborate anions in aHF and CH_3CN exhibits a deshielding trend in aHF ($\Delta\delta(F) \leq 3.7$ ppm). But this deshielding is small when compared with the $\Delta\delta(F)$ values of the individual species $[R_FBF_3]^-$ and R_FBF_2 [8] (see Table S1, Supplementary Data). When the borane, R_FBF_2, results from equilibria with aHF, it should be able to react with XeF_2 (as experimentally proven [4]) to yield the corresponding xenonium salt, $[R_FXe][BF_4]$ (Scheme 6).

But the route via RBF_2, formed by fluoride abstraction from $[RBF_3]^-$ with HF, does not satisfactorily account for all known experimental results. $CF_3C\equiv CBF_2$ and cis-$CF_3CF=CFBF_2$ form organylxenonium salts when reacted with XeF_2 in PFB [9]. Their gas-phase fluoride affinities are nearly equal (89.0 and 90.0 kcal/mol, respectively [10]). If we assume comparable relative fluoride affinities in solution, the equilibrium concentration of the corresponding boranes in aHF solutions of $K[CF_3C\equiv CBF_3]$ and $K[cis$-$CF_3CF=CFBF_3]$ should be of the same magnitude. But the reactions of both borates with XeF_2 in aHF proceeded via different routes. The first borate formed the alkynylxenonium salt whereas $K[cis$-$CF_3CF=CFBF_3]$ underwent only fluorine addition across the C≡C double bond yielding $K[CF_3CF_2CF_2BF_3]$ [4]. If we further include the result obtained with $K[CF_2=CFBF_3]$ (no xenodeboration, only fluorine addition, see Introduction) and take into account its significantly higher fluoride ion donor properties (gas-phase fluoride affinity of $CF_2=CFBF_2$, 80.3 kcal/mol), then it becomes obvious that the equilibrium concentration of R_FBF_2 alone in the system $[R_FBF_3]^-$/aHF does not determine the success of xenodeboration.
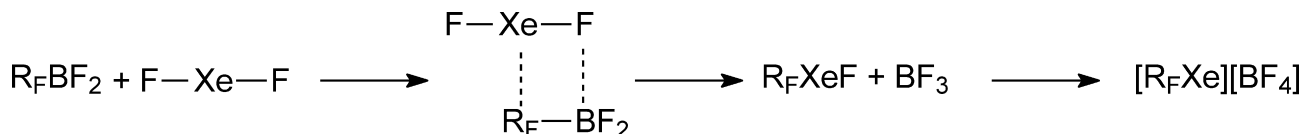
We have found a second plausible factor, which influences xenodeboration when we analyzed the Natural Population Analysis charges on the $ipso$-carbon atoms C^1 or C^4 of the perfluoroorganyltrifluoroborate anions (see Table 1). The borate anions, ($[R_FC\equiv CBF_3]^-$, $[CF_2=C(CF_3)]^-$, and $[C_6F_5BF_3]^-$), which underwent xenodeboration with XeF_2 in aHF, carry a significant partial negative charge on the carbon atom C^1 in contrast to the $[CF_2=CFBF_3]^-$ and $[cis$-$CF_3CF=CFBF_3]^-$ anions, which have a partial positive charge on the carbon atom C^1. In case of the borates, with a significant partial negative charge on C^1, it seems reasonable to assume an "electrophilic" route for xenodeboration, e.g., attack of xenon difluoride, with an increased partial positive charge in form of $[FXe$-$F\cdots HF]$, on C^1 of the corresponding borate (Scheme 7). Such an interaction is electrostatically not favored for alkenylborates, $[F(CF_2)_nCF=CFBF_3]^-$ ($n \geq 0$), which possess a partial positive charge on C^1. In the latter case, the alternative process of oxidative fluorination of the polar C=C double bond occurred. It is important to underscore that the partial negative charge on C^1 in $[C_6F_5BF_3]^-$(1–3 HF becomes successively more negative (Table 1) when HF forms adducts with the three fluorine atoms of the BF_3^- group. The borate anion, $[CF_2=C(CF_3)BF_3]^-$, which also underwent xenodeboration shows a similar property in the 1:1 adduct with HF, whereas in the 1:1 adduct of $[CF_2=CFBF_3]^-$ with HF (no xenodeboration!) the partial charge on C^1 is still positive.

The remarkable partial negative charge on C^1 in the $[CF_2=C(CF_3)BF_3]^-$ anion principally explains also the hydroboration route, which competes with xenodeboration. It should be noted that the rate of hydrodeboration (electrophilic replacement of BF_3 in $[R_FBF_3]^-$ by H^+ in acidic medium) decreases in the order $K[CF_2=C(CF_3)BF_3] > K[C_6F_5BF_3] > K[R_FC\equiv CBF_3] \gg K[F(CF_2)_n CF = CFBF_3]$ ($n \geq 0$) [7,11].

In contrast, the anion $[4$-$BF_3C_5F_4N]^-$ of potassium tetrafluoro-pyrid-4-yltrifluoroborate, which carries a partial negative charge on the $ipso$-C-atom C^4 (Table 1), is inert to attack by aHF ($\approx 20\ ^\circ C$, 74 h) and did not react with XeF_2 (2 equiv.) in aHF (0–15 $^\circ C$) (Scheme 8). Adduct formation of the trifluoroborate group with HF increased the partial negative charge on C^4 (see FH–$[4$-$BF_3C_5F_4N]^-$, Table 1). Even the N-protonated form of the anion, the zwitterion, $^{(-)}4$-$BF_3C_5F_4N$-$H^{(+)}$, and the N–HF adduct, $[4$-$BF_3C_5F_4N$-$HF]^-$, carry a partial negative charge on the C^4 atom even though of a reduced magnitude (Table 1). It is noteworthy that after addition of AsF_5 (excess) at $-55\ ^\circ C$ and warming to $\approx 10\ ^\circ C$, a reaction commenced with gas evolution. When the reaction ceased, the solution contained, besides unreacted $[4$-$BF_3C_5F_4N]^-$, a new compound whose ^{19}F NMR spectrum could be attributed to the 1-azaper-fluorocyclohexa-1,3-dien-4-yltrifluoroborate anion (molar ratio 10:6) (Scheme 8). Obviously, the electrophilicity of $[FXe]^+$, which increased in the presence of the strong Lewis acid, AsF_5, presumably led to the $[4$-$BF_3C_5F_4N$-$XeF]$ adduct (kinetically controlled reaction at low temperature). A closely related reaction,

$$[R_FBF_3]^- + n+1\ HF \rightleftharpoons [R_FBF_2(F\text{---}HF)]^- + n\ HF \rightleftharpoons R_FBF_2(F\text{-}H) + [F(HF)_n]^-$$

$$R_FBF_2(F\text{-}H) \rightleftharpoons R_FBF_2 + HF$$

Scheme 5.

$$R_FBF_2 + F\text{—}Xe\text{—}F \longrightarrow \begin{matrix} F\text{—}Xe\text{—}F \\ \vdots \quad\ \vdots \\ R_F\text{—}BF_2 \end{matrix} \longrightarrow R_FXeF + BF_3 \longrightarrow [R_FXe][BF_4]$$

Scheme 6.

Table 1
Natural population analysis charges[a] of C^1 and C^2 in C^2–C^1–BF_3 fragments of $[R_FBF_3]^-$ anions, $[R_FBF_3]^-$–nHF adducts, and C^2–C^1–BF_2 fragments of related boranes R_FBF_2.

	Borate		Borane	
	C^2	C^1	C^2	C^1
$[R_FBF_3]^-$				
$[CF_2=CFBF_3]^-$	0.760	0.070	0.916	−0.081
$[cis\text{-}CF_3CF=CFBF_3]^-$	0.187	0.237	0.359	0.061
$[CF_2=C(CF_3)BF_3]^-$	0.922	−0.570	1.044	−0.698
$[CF_3\text{-}C≡CBF_3]^-$	−0.318	−0.098	−0.054	−0.315
$[C_6F_5BF_3]^-$	0.415	−0.384	0.479	−0.557
	0.424		0.479	
$[R_FBF_3]^-$(nHF adducts				
$[CF_2=CFBF_3]^-$–HF adduct	0.775	0.060		
$[CF_2=C(CF_3)BF_3]^-$–HF adduct	0.931	−0.576		
$[C_6F_5BF_3]^-$–HF adduct	0.420	−0.394		
	0.427			
$[C_6F_5BF_3]^-$–2 HF adduct	0.425	−0.406		
	0.431			
$[C_6F_5BF_3]^-$–3 HF adduct	0.429	−0.418		
	0.435			

$[4\text{-}BF_3C_5F_4N]^-$ anion, HF-adducts, and N-protonated derivative	Borate		Borane	
	C^3	C^4	C^3	C^4
$[4\text{-}BF_3C_5F_4N]^-$	0.356	−0.321[b]	0.412	−0.496[c]
	0.348		0.412	
$[4\text{-}BF_3C_5F_4N\text{-}HF]^-$	0.359	−0.283[d]	0.411	−0.477[e]
	0.350			
$^{(-)}4\text{-}BF_3C_5F_4N\text{-}H^{(+)}$	0.338	−0.162[f]	0.395	−0.339[g]
	0.349			
$FH\text{-}[4\text{-}BF_3C_5F_4N]^-$ adduct	0.361	−0.334[h]		
	0.354			

[a] Natural population analysis charges; RHF level, LANL2DZ basis set.
[b] N −0.585.
[c] N −0.509; BF_2 group is in-plane with the C_5F_4N ring.
[d] N −0.663; N–H 1.773 Å.
[e] N −0.580; N–H 1.900 Å; BF_2 group is in-plane with the C_5F_4N ring.
[f] N −0.634; N–H 1.004 Å.
[g] N −0.596; N–H 1.012 Å; dihedral angle between BF_2 group and C_5F_4N ring: 28.9°.
[h] N −0.578; B–F–H–F 1.628 Å; H–F 0.936 Å; −14.103 kJ/mol lower in energy (ΔHF) than $[4\text{-}BF_3C_5F_4N\text{-}HF]^-$.

the formation of the $[C_5F_5N\text{-}XeF]^+$ adduct in aHF solution by the interaction of C_5F_5N, XeF_2, and AsF_5 at −30 °C, was studied by Schrobilgen [12]. The aforementioned adduct explains why, despite of the strengthened electrophilicity of $[FXe]^+$, it remained insufficient to perform xenodeboration. Finally, at ≥10 °C the fluorination to $[4\text{-}BF_3\text{-}cyclo\text{-}1,3\text{-}C_5F_6N]^-$ (thermodynamically controlled reaction) occurred as a competitive reaction (Scheme 8).

3. Experimental part

3.1. General

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (^{19}F at 282.40 MHz; ^{11}B at 96.29 MHz, and ^{129}Xe at 83.02 MHz). The chemical shifts were referenced to CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), $BF_3\cdots OEt_2/CDCl_3$ (15% v/v) (^{11}B), and $XeOF_4$ (^{129}Xe, with XeF_2 in CH_3CN (extrapolated to zero concentration) as secondary external reference (−1818.3 ppm) [13], respectively. The composition of reaction mixtures and the yields of products were determined by ^{19}F NMR spectroscopy using $(CF_3)_2CHOH$ as an internal standard for integration.

Acetonitrile was purified and dried as described in Ref. [14]. 1,1,1,3,3-pentafluorobutane (PFB) (Solvay Fluor und Derivate GmbH) was stored over molecular sieves 3 Å before use. The salts, $K[CF_2=C(CF_3)BF_3]$ [15], $K[CF_3C≡CBF_3]$, $K[C_3F_7C≡CBF_3]$, $K[(CF_3)_2CFC≡CBF_3]$ [16], $[Bu_4N][CF_3C≡CBF_3]$ [17], $K[C_6F_5BF_3]$ [18], and $K[4\text{-}BF_3C_5F_4N]$ [19], were prepared as described. Anhydrous hydrogen fluoride (aHF) was obtained by electrolysis (stainless steel cell, Ni-electrodes). CAUTION: Adequate precautions are necessary when handling aHF [20].

All manipulations with aHF were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) or PFA (block copolymer of tetrafluoroethylene and perfluoroalkoxytrifluoroethylene) equipment under an atmosphere of dry argon.

3.2. Reaction of $K[CF_3C≡CBF_3]$ with XeF_2 in aHF

Cold (−20 °C) aHF (0.6 mL) was added to cold (−20 °C) $K[CF_3C≡CBF_3]$ (82 mg, 0.41 mmol). After stirring the solution for

$$XeF_2 + HF \rightleftharpoons \overset{\delta^+}{F}\text{—}Xe\text{—}\overset{\delta^-}{F}\text{---}HF$$
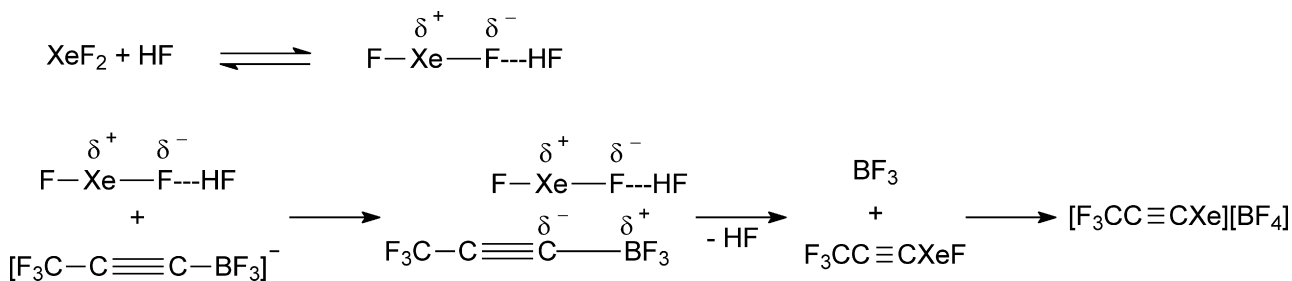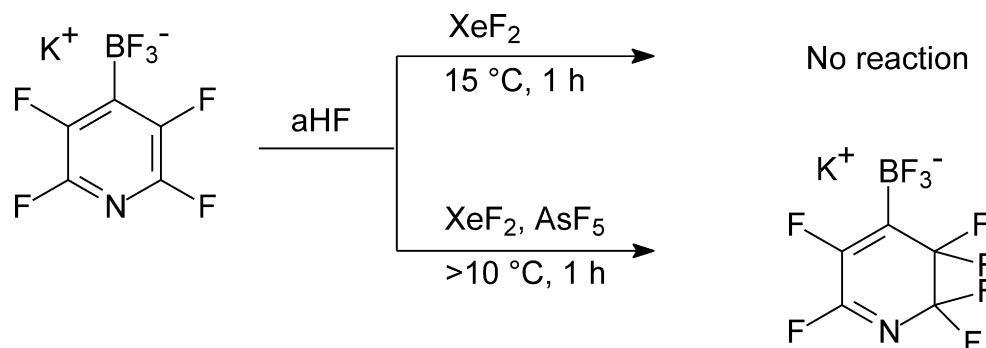
Scheme 7.

Scheme 8.

5 min, XeF$_2$ (79 mg, 0.46 mmol) was added in one portion. Subsequently, the mixture was stirred for 1.5 h at −20 °C before analyzed by NMR spectroscopy. The ^{19}F and ^{129}Xe NMR spectra showed the formation of [CF$_3$C≡CXe][BF$_4$] [21] in 51% yield (^{19}F NMR) besides <3% of CF$_3$C≡CH and minor amounts of unknown perfluorinated products.

3.3. Reaction of K[C$_3$F$_7$C≡CBF$_3$] with XeF$_2$ in aHF

Similarly, the reaction of XeF$_2$ (44 mg, 0.26 mmol) with K[C$_3$F$_7$C≡CBF$_3$] (71 mg, 0.23 mmol) in aHF (0.5 mL) at −20 °C led, after 1 h, to the formation of [C$_3$F$_7$C≡CXe][BF$_4$] [21] in 50% yield (^{19}F NMR) besides <5% of C$_3$F$_7$C≡CH and minor amounts of unknown perfluorinated products.

3.4. Reaction of K[C$_3$F$_7$C≡CBF$_3$] with [FXe][SbF$_6$] in aHF

A cold (0 °C) solution of K[C$_3$F$_7$C≡CBF$_3$] (81 mg, 0.27 mmol) in aHF (0.7 mL) was added in portions to a cold (−20 °C) solution of [FXe][SbF$_6$] (119 mg, 0.30 mmol) in aHF (2 mL). The fine suspension was stirred at −20 °C for an additional 1 h. The ^{19}F NMR spectrum showed the resonances of [C$_3$F$_7$C≡CXe]$^+$, [BF$_4$]$^-$, [C$_3$F$_7$C≡CBF$_3$]$^-$, and C$_3$F$_7$C≡CH (molar ratio = 100:608:16:76) besides minor amounts of unknown perfluorinated products.

3.5. Reaction of K[(CF$_3$)$_2$CFC≡CBF$_3$] with XeF$_2$ in aHF

Similarly, the reaction of XeF$_2$ (55 mg, 0.32 mmol) with K[(CF$_3$)$_2$CFC≡CBF$_3$] (81 mg, 0.27 mmol) in aHF (0.6 mL) at −20 °C led, after 2.5 h, to the formation of [(CF$_3$)$_2$CFC≡CXe][BF$_4$] [21] in 55% yield (^{19}F NMR) besides <5% of (CF$_3$)$_2$CFC≡CH and minor quantities of unknown perfluorinated products.

3.6. Reaction of K[CF$_2$=C(CF$_3$)BF$_3$] with XeF$_2$ in aHF

(A) K[CF$_2$=C(CF$_3$)BF$_3$] (133 mg, 0.55 mmol) was added in one portion to a cold (−60 °C) stirred solution of XeF$_2$ (99 mg, 0.58 mmol) in aHF (1.5 mL). The reaction mixture was stirred at −60 °C for 30 min and at −40 °C for 1 h. The ^{19}F NMR spectrum showed the resonances of [CF$_2$=C(CF$_3$)Xe][BF$_4$] (0.08 mmol) [15], CF$_2$=CHCF$_3$ (0.47 mmol), [BF$_4$]$^-$ (0.45 mmol), besides unreacted XeF$_2$ (0.38 mmol) and a trace of [CF$_2$=C(CF$_3$)BF$_3$]$^-$.

(B) A 3.5-mm i.d. FEP-inliner was charged with K[CF$_2$=C(CF$_3$)BF$_3$] (42 mg, 0.17 mmol) and XeF$_2$ (29 mg, 0.17 mmol) and cooled to −78 °C. Cold (−78 °C) aHF (0.4 mL) was added. After shaking, the white suspension was kept at −78 °C for 24 h. The ^{19}F NMR spectrum of the suspension at −50 °C showed resonances for [CF$_2$=C(CF$_3$)BF$_3$]$^-$, CF$_2$=C(CF$_3$)H, XeF$_2$ (molar ratio = 100:50:150) and a trace of [CF$_2$=C(CF$_3$)Xe][BF$_4$]. The suspension was warmed to 0 °C within 20 h and kept at 0 °C for 5 h. The solution contained [CF$_2$=C(CF$_3$)Xe][BF$_4$] (0.02 mmol, 11%), CF$_2$=C(CF$_3$)H (trace), (CF$_3$)$_2$CHOH (0.05 mmol), 1,2-epoxy-1,1,3,3,3-pentafluoroethane (0.03 mmol), and [BF$_4$]$^-$ (0.15 mmol) (^{19}F NMR).

1,2-Epoxy-1,1,3,3,3-pentafluoroethane. ^{19}F NMR (aHF, 0 °C): δ −70.5 (ddd, $^4J(F^3, F^{1cis})$ = 12 Hz, $^4J(F^3, F^{1trans})$ = 2.5 Hz, $^3J(F^3, H^2)$ = 4.5 Hz, 3F, F^3), −104.8 (ddq, $^2J(F^{1trans}, F^{1cis})$ = 52 Hz, $^3J(F^{1trans}, H^2)$ = 4.5 Hz, $^4J(F^{1trans}, F^3)$ = 2.5 Hz, 1F, F^{1trans}), −115.7 (ddq, $^2J(F^{1cis}, F^{1trans})$ = 52 Hz, $^3J(F^{1cis}, H^2)$ = 3.3 Hz, $^4J(F^{1cis}, F^3)$ = 12 Hz, 1F, F^{1cis}).

3.7. Attempted hydrodeboration of K[4-BF$_3$C$_5$F$_4$N] with aHF

A solution of K[4-BF$_3$C$_5$F$_4$N] (30 mg, 0.11 mmol) in aHF (0.4 mL) was kept at ≈20 °C for 74 h. No reaction was detected (^{19}F NMR). K[4-BF$_3$C$_5$F$_4$N]. ^{11}B NMR (aHF, 0 °C): δ 0.8 (q, ^1J(B, F) = 36 Hz). ^{19}F NMR (aHF, 0 °C): δ −103.2 (m, 2F, F^{2,6}), −129.6 (m, 2F, F^{3,5}), −135.2 (q (1:1:1:1), ^1J(F, B) = 35 Hz, 3F, BF$_3$).

3.8. Attempted reaction of K[4-BF$_3$C$_5$F$_4$N] with XeF$_2$ in aHF

Xenon difluoride (40 mg, 0.23 mmol) was added in one portion to a cold (≈0 °C) solution of K[4-BF$_3$C$_5$F$_4$N] (26 mg, 0.10 mmol) in aHF (0.6 mL). The colorless solution was stirred for 1 h at ≈0 °C and for 1 h at 15 °C. No reaction was detected (^{19}F NMR).

3.9. Reaction of K[4-BF$_3$C$_5$F$_4$N] with XeF$_2$ in aHF acidified with AsF$_5$

The above solution was cooled to −55 °C. After condensation of AsF$_5$ (≈0.4 mmol) a precipitation resulted. The ^{19}F NMR spectrum of the yellow liquid phase showed resonances of [4-BF$_3$C$_5$F$_4$N]$^-$ at (102.8 (2F), (129.0 (2F), and (135.0 (3F) ppm besides the signal of HF. Warming to −10 °C within 30 min did not change the ^{19}F NMR spectrum. Further keeping at −10 °C for 1 h was accompanied by discoloration, gas evolution, and dissolution of the precipitate. The ^{19}F NMR spectrum contained resonances of [4-BF$_3$C$_5$F$_4$N]$^-$ and presumably, 1-azaperfluorocyclohexa-1,3-dien-4-yltrifluorobo-rate (^{19}F NMR (aHF, −10 °C): δ −26.8 (td, $^4J(F^2, F^6)$ = 10 Hz, $^3J(F^2, F^3)$ = 18 Hz, 1F, F^2), −99.7 (br, 2F, F^{6,6}), −110.8 (td, $^3J(F^5, F^6)$ = 4 Hz, $^4J(F^5, F^3)$ = 15 Hz, 2F, F^{5,5}), −121.9 (td, $^4J(F^3, F^5)$ = 15 Hz, $^3J(F^3, F^2)$ = 18 Hz, 1F, F^3); the signal of −BF$_3$ was too broad to be allocated) (molar ratio 10:6) besides HF and minor quantities of unknown unsaturated fluorinated organics. Signals of 2,3,5,6-tetrafluoro-pyridine, XeF$_2$, [BF$_4$]$^-$, or [AsF$_6$]$^-$ were not found. No changes occurred in the spectrum when the solution was kept at ≈20 °C for further 12 h.

3.10. Attempted reaction of K[C$_6$F$_5$BF$_3$] with XeF$_2$ in CH$_3$CN

A solution of K[C$_6$F$_5$BF$_3$] (31 mg, 0.14 mmol) and XeF$_2$ (58 mg, 0.14 mmol) in CH$_3$CN (1.3 mL) was stirred at ≈20 °C for 48 h. No reaction occurred (^{19}F NMR).

3.11. Attempted reaction of [Bu$_4$N][CF$_3$C≡CBF$_3$] with XeF$_2$ in PFB

A solution of [Bu$_4$N][CF$_3$C≡CBF$_3$] (0.14 mmol), XeF$_2$ (32 mg, 0.19 mmol), and [Bu$_4$N][BF$_4$] (0.02 mmol, internal standard for integration) in PFB (1 mL) was stirred at ≈20 °C for 46 h. No reaction proceeded (^{19}F NMR).

4. Conclusions

A new synthetic methodology (xenodeboration) is presented, which allowed the syntheses of perfluoroorganylxenonium tetrafluoroborate salts (organyl = aryl, alkenyl, alkynyl) from the corresponding organyltrifluoroborate salts and XeF$_2$ in aHF. This method is less general than xenodeborylation (reaction of organyldifluoroboranes and XeF$_2$ in polar halocarbons and strongly limited in aHF). Especially, alkenyltrifluoroborate salts show in reactions with XeF$_2$ in aHF alternative routes of fluorine addition across the C=C double bond or competing routes of hydrodeborylation. It was shown that (a) a preceding fluoride abstraction from the perfluoroorganyltrifluoroborate anion by the Lewis acid, aHF, can be excluded and (b) xenodeboration did not proceed in the absence of aHF, e.g., in polar halocarbons or coordinating CH$_3$CN. Xenodeboration in aHF is successful when the ipso-carbon of the C–B bond of the organyltrifluoroborate anion carries a remarkable partial negative charge (Natural Population Analysis) – a necessary, but not a sufficient precondition. Our present experience allows the conclusion that xenodeboration resulted from electrophilic attack by FXe–F–HF (increased electrophilicity of XeF$_2$ by interaction with the Lewis acid HF) on the nucleophilic ipso-carbon of the organyltrifluoroborate anion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2012.03.014.

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