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A first methodical approach to salts with unsymmetrical fluorophenyl (pentafluorophenyl)difluoroiodonium(V) cations $[R_f(R_F)IF_2]^+$ (R_f=x-FC_6H_4, x=2, 3, 4; R_F=C_6F_5)

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ABSTRACT

A promising approach to the unknown type of $[Ar'(Ar)IF_2]X$ salts is offered. x-$FC_6H_4IF_4$ (x=2, 3, 4) reacts with $C_6F_5BF_2$ in CH_2Cl_2 and forms $[x\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ salts in good yields. For $[4\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ the fluoro-oxidizer property is shown in reactions with weakly reducing agents like $E(C_6F_5)_3$ (E=P, As, Sb, Bi) and ArI (Ar=4-FC_6H_4, C_6F_5). The fluorine/aryl substitution method is also applied to the synthesis of $[(4\text{-}FC_6H_4)_2IF_2][BF_4]$, an example with two identical aryl groups in the difluoroiodonium(V) moiety.

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1. Introduction

The chemistry of organoderivatives of iodine(V) is far less developed than that of iodine(III). While di(aryl)iodonium salts[1] represent the largest number of polyvalent organoiodine(III) compounds, only few examples of the corresponding di(aryl) iodonium(V) salts are known. This is astonishing because Masson[2] published a fundamental access to this type of compounds already in 1935. He obtained $[(C_6H_5)_2IO]OH$ by 'self-condensation' of $C_6H_5IO_2$ in the presence of $NaOH_{aq}$ (Eq. 1).

$$2C_6H_5IO_2 + OH^- \rightarrow [(C_6H_5)_2IO]OH + [IO_3]^- \tag{1}$$

Beringer[3] used this reaction in 1968 to obtain the first examples of $[(Ar)_2IO]X$ salts by metathesis (Eq. 2).

$$[(Ar)_2IO]OH \xrightarrow{HOAc_F} [(Ar)_2IO]OAc_F \xrightarrow{M^IX} [(Ar)_2IO]X \tag{2}$$

Ar=C_6H_5, 4-FC_6H_4, 4-MeC_6H_4; M^I=Na, K; X=F, Cl, Br.

Based on this results, in 1972 Yagupol'skii[4] published the syntheses of the first di(aryl)difluoroiodonium(V) salts (Eq. 3).

$$[(Ar)_2IO]OAc_F \xrightarrow{SF_4} [(Ar)_2IF_2]OAc_F \xrightarrow{SF_4} [(Ar)_2IF_2]F \tag{3}$$

Ar=C_6H_5, 4-FC_6H_4.

The nature of $[(C_6H_5)_2IF_2]F$ was elucidated first in 2004 by Hoyer.[5] She was able to get the single crystal structure and could prove that no $(C_6H_5)_2IF_3$ was present. Three $[(C_6H_5)_2IF_2]^+$ cations are bridged by fluoride ions in distances of 2.5–2.6 Å. Each $[(C_6H_5)_2IF_2]^+$ cation has in agreement with the VSEPR notation (AB_2C_2E) a ψ-trigonal bipyramidal geometry.

Up to now all approaches to salts with cations of the general type $[(Ar)_2IY_2]X$ were principally based on the 'self-condensation' step by Masson and allowed only symmetrical di(aryl) constitutions. In addition it is worth to mention that Masson's method cannot be applied when a larger number of electron-withdrawing substituents like F or NO_2 are present in the aryl group. In such cases the aryl group is eliminated under basic conditions (formation of Ar–H).[6] In 2008 we have published a new methodical approach. We obtained the symmetrical example, $[(C_6F_5)_2IF_2][BF_4]$, by F/C_6F_5 substitution in $C_6F_5IF_4$ with $C_6F_5BF_2$.[7] In the present paper we show the potential of this approach for the synthesis of unsymmetrical $[R_f(R_F)IF_2][BF_4]$ salts. Furthermore we want to show that $[Ar(Ar')IF_2]^+$ cations are good fluoro-oxidizers. This property may be useful in future to introduce fluorine into an organic moiety.

2. Experimental results

x-$FC_6H_4IF_4$ (x=2, 3, 4) reacted with $C_6F_5BF_2$ in weakly coordinating solvents like CH_2Cl_2 under F/C_6F_5 substitution and the products $[x\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ precipitated and could be easily isolated in good yields (Eq. 4).

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$$x-\mathrm{FC_6H_4IF_4}+\mathrm{C_6F_5BF_2}\xrightarrow[\leq 20\ ^\circ\mathrm{C}/\leq 3\ \mathrm{h}]{\mathrm{CH_2Cl_2}}[x-\mathrm{FC_6H_4(C_6F_5)IF_2}][\mathrm{BF_4}]\downarrow \qquad (4)$$

It is important to mention that few percent of [x-$FC_6H_4(C_6F_5)I$][BF_4] were often included in the product. The different channels, which explain the reduction of [x-$FC_6H_4(C_6F_5)IF_2$][BF_4] are discussed in Ref. 7.

The pair of starting materials with opposite functionalities can also be used, as was demonstrated for [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] (Eq. 5).

$$\mathrm{C_6F_5IF_4}+4-\mathrm{FX_6H_4BF_2}\xrightarrow[\leq 20\ ^\circ\mathrm{C}/\geq 4\ \mathrm{d}]{\mathrm{CH_2Cl_2}}[4-\mathrm{FC_6H_4(C_6F_5)IF_2}][\mathrm{BF_4}]\downarrow \qquad (5)$$

But the reaction proceeded significantly slower and was accompanied by a large amount of reduced product [4-$FC_6H_4(C_6F_5)I$][BF_4] (molar ratio [4-$FC_6H_4(C_6F_5)IF_2$][BF_4]/[4-$FC_6H_4(C_6F_5)I$][BF_4]/C_6F_5I=52:46:3).

In order to evaluate the influence of a low number of fluorine substituents in the aryl group of $ArIF_4$ and $ArBF_2$ on the reaction rate, we have additionally studied the reaction of 4-$C_6H_4IF_4$ and 4-$FC_6H_4BF_2$ (Eq. 6).

$$4-\mathrm{C_6H_4IF_4}+4-\mathrm{FC_6H_4BF_2}\xrightarrow[20\ ^\circ\mathrm{C}/<3\ \mathrm{h}]{\mathrm{CH_2Cl_2}}[(4-\mathrm{FC_6H_4})_2\mathrm{IF_2}][\mathrm{BF_4}]\downarrow \qquad (6)$$

All three [x-$FC_6H_4(C_6F_5)IF_2$][BF_4] salts are colorless solids and decompose exothermically without proceeding melting. The hypervalent IF_2 triad in combination with the high partial positive charge on iodine make these salts attractive as fluoro-oxidizers. We tested this property in reactions of [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] with weakly reducing $E(C_6F_5)_3$ compounds (E=P, As, Sb) (Eq. 7). In case of E=Bi, side-reactions became dominant (see Discussion).

$$[4-\mathrm{FC_6H_4(C_6F_5)IF_2}][\mathrm{BF_4}]+\mathrm{E(C_6F_5)_3}\xrightarrow{\mathrm{MeCN}}_{20\ ^\circ\mathrm{C}}$$
$$[4-\mathrm{FC_6H_4(C_6H_5)I}][\mathrm{BF_4}]+(\mathrm{C_6H_5})_3\mathrm{EF_2} \qquad (7)$$

E=P, As, Sb.

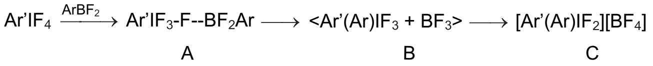
The aryl iodides C_6F_5I and 4-FC_6H_4I were chosen to demonstrate the electronic influence of aryl groups with strongly differing electron-withdrawing character on the reaction rate with [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] (Eq. 8).

$$[4-\mathrm{FC_6H_4(C_6F_5)IF_2}][\mathrm{BF_4}]+\mathrm{ArI}\xrightarrow[20\ ^\circ\mathrm{C}]{\mathrm{MeCN}}$$
$$[4-\mathrm{FC_6H_4(C_6H_5)I}][\mathrm{BF_4}]+\mathrm{ArIF_2} \qquad (8)$$

Ar=C_6F_5I, 4-FC_6H_4I.

3. Discussion

The interaction of hypervalent element–fluoride moieties with fluoroorganyldifluoroboranes is a widely applicable method for F/R substitution. It was well elaborated for aryl-, alkenyl-, and alkynylxenonium[8] and diorganyliodonium(III) salts.[9,10] The hypervalent bond in $Ar'IF_4$ compounds is characterized by significant partial negative charges on fluorine (>-0.5) and strong partial positive charges on iodine(V) (<3.0).[11] As a consequence of interaction of the Lewis acidic aryldifluoroborane with aryliodine tetrafluoride the borane takes over partially borate character and the nucleophilic property of its aryl group increases. Parallel the iodine center becomes more electrophilic. The transition state allows the transfer of the aryl group to iodine(V) and of fluorine to boron and ends with two kinetically independent species: $Ar'(Ar)IF_3$ and BF_3, which form the iodonium(V) tetrafluoroborate, stabilized by lattice energy (Scheme 1).



$$\mathrm{Ar'IF_4}\xrightarrow{\mathrm{ArBF_2}}\underset{\mathrm{A}}{\mathrm{Ar'IF_3\text{-}F\text{--}BF_2Ar}}\longrightarrow\underset{\mathrm{B}}{<\mathrm{Ar'(Ar)IF_3+BF_3}>}\longrightarrow\underset{\mathrm{C}}{[\mathrm{Ar'(Ar)IF_2}][\mathrm{BF_4}]}$$

Scheme 1.

$C_6F_5BF_2$ is a stronger Lewis acid than 4-$FC_6H_4BF_2$ and BF_3, based on the result of gas phase fluoride affinity calculations.[12] Thus the polarization of an I–F bond of the IF_4 group (A in Scheme 1) proceeded better with $C_6F_5BF_2$ (Eq. 4) than with 4-$FC_6H_4BF_2$ (Eq. 5). Furthermore the I–F bond in 4-$FC_6H_4IF_4$ (Eq. 4) can be more easily polarized than in $C_6F_5IF_4$ (Eq. 5). Additionally, the nucleofugality of the C_6F_5 group (Ar in species A, Scheme 1) is higher than that of the 4-FC_6H_4 group. All three arguments explain the higher reaction rate of Eq. 4 in relation to Eq. 5. We have found that in the reaction of $C_6F_5IF_4$ (strong I–F bond) with 4-$FC_6H_4BF_2$ (weak fluoride acceptor) (Eq. 5) the quantity of the by-product [4-$FC_6H_4(C_6F_5)I$][BF_4] was of the same magnitude as [4-$FC_6H_4(C_6F_5)IF_2$][BF_4]. This result is in agreement with more frequent attacks of the strong Lewis acid on chlorine in the solvent CH_2Cl_2 during the slow reaction. Chloride is an effective reducing agent for $[(Ar)_2IF_2]^+$ cations.[7]

All [x-$FC_6H_4(C_6F_5)IF_2$][BF_4] salts were isolated as colorless solids in good yields. We were able to get single crystals of [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] directly from the reaction mixture and to determine the molecular structure. [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] crystallizes in the monoclinic space group $P2_1/n$ (a=13.4487(16) Å, b=12.2497(15) Å, c=19.390(2) Å, α=90°, β=94.056(2)°, γ=90°) with Z=8 and two symmetry independent cations and anions in the asymmetric unit. The cation has a ψ-trigonal bipyramidal geometry with both hypervalently bonded fluorine atoms in the axial positions (Fig. 1). Both C–I (averaged 2.09(3) Å) and F–I distances (averaged 1.92(2) Å) are longer than in the $[(C_6F_5)_2IF_2]^+$ cation (averaged 2.064(5) Å and 1.913(3) Å, respectively), mainly caused by smaller electrostatic contributions in the bonds. For the same reason the I–C_6F_5 distance is shorter than the I–C_6H_4F distance. In [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] the averaged F–I–F angle is slightly increased and the C–I–C angle decreased relative to the $[(C_6F_5)_2IF_2]^+$ cation.[7] The latter phenomena can be deduced to the larger demand of space of C_6F_5 groups.

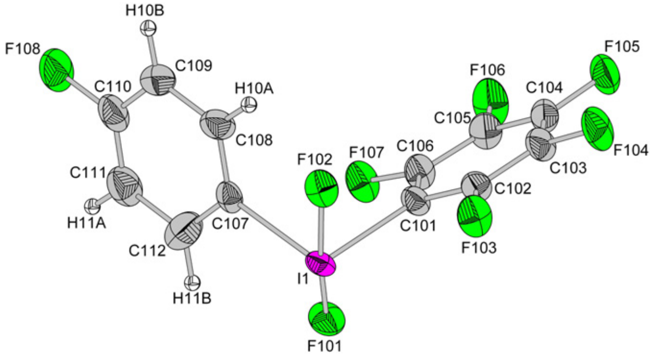


Figure 1. Molecular structure of the [4-$FC_6H_4(C_6F_5)IF_2$]$^+$ cation: selected distances/Å and angles/°: I1–C101 2.072(7), I1–C107 2.113(7), I1–F101 1.919(4), I1–F102 1.932(5), C101–I1–C107 99.6(3), F101–I1–F102 167.24(19).

There are three significant I–F contacts (2.787(5)–2.843(6) Å) between two weakly coordinating $[BF_4]^-$ anions and iodine(V) of the electrophilic cation (Fig. 2): one trans to the 4-FC_6H_4 group and two in a chelating manner trans to the C_6F_5 group. These contacts are ∼18% shorter than the sum of van der Waals radii of 3.45 Å.[13]

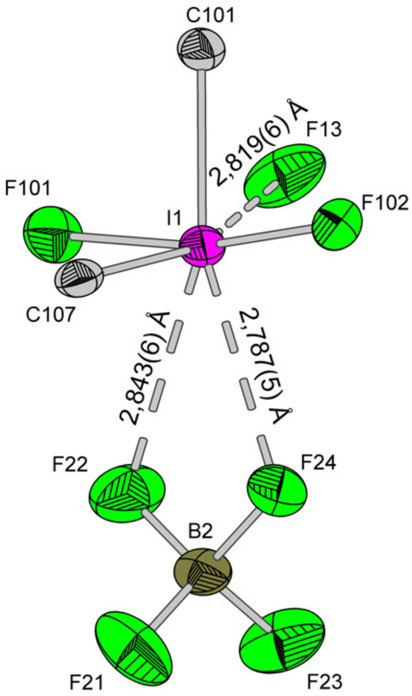


Figure 2. Cation–anion contacts in [4-$FC_6H_4(C_6F_5)IF_2$][BF_4].

All three [x-$FC_6H_4(C_6F_5)IF_2$][BF_4] salts can be stored at ambient temperature under an dry atmosphere without decomposition. DSC informed that decomposition proceeded without proceeding melting in the series [3-$FC_6H_4(C_6F_5)IF_2$][BF_4] (134.3 °C)<[4-$FC_6H_4(C_6F_5)IF_2$][BF_4] (142.6 °C)<[2-$FC_6H_4(C_6F_5)IF_2$][BF_4] (197.4 °C) according to their T_{onset} data.

The Raman data were assigned by comparison with the parent compounds x-FC_6H_4I and C_6F_5I and based on DFT-calculations (B3LYP/cc-pVTZ-PP). The characteristic symmetrical IF_2 vibration in [x-$FC_6H_4(C_6F_5)IF_2$][BF_4] salts gave rise to intensive Raman bands at 556 (x=2), 554 (x=3), and 542 cm^{-1} (x=4). The IF_2 deformation mode appeared at 175 (n=2), 154 (n=3), and 163 cm^{-1} (n=4) in the same region as it was found for $C_6F_5IF_2$ (174 cm^{-1}).[14]

[x-$FC_6H_4(C_6F_5)IF_2$][BF_4] salts are well soluble in MeCN. In such solutions we can assume a competition between the neutral base MeCN and the anion to coordinate at iodine(V). The NMR data inform of this process. In the ^{19}F NMR (Table 1) the shielding trend of the IF_2 group from x=2 to 4 and the highest shielding in [(4-$FC_6H_4)_2IF_2$][BF_4] and the lowest in [$(C_6F_5)_2IF_2$][BF_4] are in agreement with the inductive effect of the involved aryl groups and correlate with the individual partial charge on iodine(V). A high partial positive charge on iodine polarizes not only the attached fluorine atoms but also both aryl groups. The C_6F_5 group is a good probe to inform about such a polarization process. The shift value of $F^{3,5}$ reflects preferentially the inductive effect of the iodine center whereas the shift value of F^4 informs about the polarization of the aryl π-system. In the x-FC_6H_4 group $F^{3'}$ and $F^{4'}$ are significantly deshielded with respect to the monovalent x-FC_6H_4I parent compounds. Generally, the shift value $F^{2'}$ is strongly influenced by steric aspects of the iodine environment. We have observed a worth to mention deshielding of the fluorine atoms of $[BF_4]^-$ from $[(C_6F_5)_2IF_2]^+$ via [2- and 3-/4-$FC_6H_4(C_6F_5)IF_2]^+$ to $[(4\text{-}FC_6H_4)_2]^+$.

Table 1

Characteristic ^{19}F NMR shift values[a] δ/ppm of [x-$FC_6H_4(C_6F_5)IF_2$][BF_4] (x=2, 3, 4) and related salts [(4-$FC_6H_4)_2IF_2$][BF_4] and [$(C_6F_5)_2IF_2$][BF_4] in MeCN at 24 °C

Compound	IF_2	$F^{2,6}$	$F^{3,5}$	F^4	x-FC_6H_4	$[BF_4]^-$
[2-$FC_6H_4(C_6F_5)IF_2$][BF_4][b]	−66.6	−125.8	−154.7	−137.6	−98.9	−147.3
[3-$FC_6H_4(C_6F_5)IF_2$][BF_4][c]	−74.2	−127.0	−155.4	−138.5	−103.1	−146.1
[4-$FC_6H_4(C_6F_5)IF_2$][BF_4][d]	−74.0	−127.4	−155.5	−138.7	−99.6	−146.3
[(4-$FC_6H_4)_2IF_2$][BF_4]	−85.3	—	—	—	−100.5	−145.9
[$(C_6F_5)_2IF_2$][BF_4][e]	−58.2	−125.4	−153.7	−136.3	—	−147.7

[a] For ^nJ-coupling constants, see Experimental part.

[b] 2-FC_6H_4I and 2-$FC_6H_4IF_2$ δ/ppm: −93.4 and −97.6, −163.8 (IF_2).

[c] 3-FC_6H_4I and 3-$FC_6H_4IF_2$ δ/ppm: −110.3 and −108.1, −173.0 (IF_2).

[d] 4-FC_6H_4I and 4-$FC_6H_4IF_2$ δ/ppm: −114.2 and −107.9, −171.1 (IF_2).

[e] C_6F_5I and $C_6F_5IF_2$ δ/ppm: −120.2, −160.4, −153.6 and −122.9, −157.0, −144.5, −160.6 (IF_2).

The carbon atom C^1 of the C_6F_5 group in [x-$FC_6H_4(C_6F_5)IF_2]^+$ is slightly more deshielded than in $[(C_6F_5)IF_2]^+$ (Tables 2). Both carbon atoms C^1 and $C^{1'}$ of each [x-$FC_6H_4(C_6F_5)IF_2]^+$ cation are deshielded by 41.2–45.1 ppm with respect to x-FC_6H_4I or C_6F_5I, respectively.

Finally, the fluoro-oxidizer property of [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] in reactions with an excess of $E(C_6F_5)_3$ (E=P, As, Sb, Bi) (Eq. 7) and C_6F_5I or 4-FC_6H_4I (Eq. 8) in MeCN will be discussed. The addition of two fluorine atoms to $E(C_6F_5)_3$ under total consumption of [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] proceeded comparatively fast for E=As (3.5 h) and Sb (0.5 h), whereas the long reaction times for E=P and Bi were accompanied by consecutive reactions. In case of E=P approx. one-third of $(C_6F_5)_3PF_2$ was hydrolyzed by water vapor, which penetrates through the thin FEP-wall of the trap. In case of E=$Bi(C_6F_5)_3$ no $(C_6F_5)_3BiF_2$ was observed and [4-$FC_6H_4(C_6F_5)I$][BF_4] was only a minor product besides the major C_6F_5H, [$(C_6F_5)_2I$][BF_4], and 1,4-$F_2C_6H_4$. The latter two can be explained by elimination of a higher pentafluorophenylated iodonium(V) species like [4-$FC_6H_4(C_6F_5)_2IF$][BF_4]. The F/C_6F_5 substitution in IF_5 by $Bi(C_6F_5)_3$ is well known.[11] It is important to mention that all reactions of [$(C_6F_5)_2IF_2$][BF_4] with $E(C_6F_5)_3$ proceeded significant faster than with [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] and differing with $Bi(C_6F_5)_3$ the desired product $(C_6F_5)_3BiF_2$ was obtained.[7] [4-$FC_6H_4(C_6F_5)IF_2$][BF_4] reacted with 4-FC_6H_4I and C_6F_5I under fluorine addition (Eq. 8). The reaction with 4-FC_6H_4I proceeded approx. four times faster than with C_6F_5I, where 11 d were needed for the total consumption of [4-$FC_6H_4(C_6F_5)IF_2$][BF_4].

Table 2

Characteristic ^{13}C NMR shift values[a] δ/ppm of [x-$FC_6H_4(C_6F_5)IF_2$][BF_4] (x=2, 3, 4) and related salts [(4-$FC_6H_4)_2IF_2$][BF_4] and [$(C_6F_5)_2IF_2$][BF_4] in MeCN at 24 °C

Compound	C_6F_5 group				x-FC_6H_4 group					
	C^1	$C^{2,6}$	$C^{3,5}$	C^4	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$	$C^{5'}$	$C^{6'}$
[2-$FC_6H_4(C_6F_5)IF_2$][BF_4]	113.5	147.0	140.0	148.5	125.7	159.6	120.8	129.4	132.2	140.5
[3-$FC_6H_4(C_6F_5)IF_2$][BF_4]	114.0	146.8	139.4	147.9	135.8	118.6	164.4	124.5	134.6	127.4
[4-$FC_6H_4(C_6F_5)IF_2$][BF_4]	114.1	146.9	139.6	148.0	129.1	134.4	121.4	167.8	121.4	134.4
[(4-$FC_6H_4)_2IF_2$][BF_4]	—	—	—	—	133.4	133.2	120.9	167.3	120.9	133.2
[$(C_6F_5)_2IF_2$][BF_4]	112.8	146.9	140.0	148.8	—	—	—	—	—	—

[a] For ^nJ-coupling constants, see Experimental part.

4. Conclusion

The Lewis acid assisted substitution of a hypervalently bonded fluorine atom by an aryl group can be applied to aryliodine(V) tetrafluorides and delivers $[Ar'(Ar)IF_2][BF_4]$ iodonium(V) salts with a cation of high electrophilicity. The electrophilic nature of the cation can be deduced from cation–anion interactions in the solid state and from ^{19}F NMR data in MeCN for solutions. This type of salts opens a new application for polyvalent iodine compounds, namely to act as a fluoro-oxidizer. Di(aryl)difluoroiodonium(V) salts as well with a symmetrical as with a unsymmetrical constitution concerning both aryl groups are accessible by the reaction of $ArIF_4$ and $ArBF_2$ in weakly coordinating solvents. There are reasonable arguments that the reported method for di(aryl) difluoroiodonium salts can be even transferred to alkynyl- and alkenyl-iodonium compounds.

5. Experimental part

5.1. General

All moisture sensitive compounds were handled under an atmosphere of dry argon. Reactions were carried out in vessels constructed from FEP tubes (o.d.=4.1 mm, i.d.=3.5 mm or o.d.=9.0 mm, i.d=8.0 mm, FEP is a co-polymer of $(CF_2CF_2)_n$ and $(CF_2C(CF_3)F)_m$). Acetonitrile was refluxed and distilled from $KMnO_4$ and repeatedly refluxed and distilled from P_4O_{10}. Dichloromethane was treated in sequence with concd H_2SO_4, $Na_2CO_{3(aq)}$, and H_2O and finally refluxed and distilled from P_4O_{10}. NMR spectra were recorded on a Bruker spectrometer AVANCE 300 (^{13}C at 75.47 MHz, ^{11}B at 96.29 MHz, ^{19}F at 282.40 MHz), and ^1H at 300.13 MHz. The chemical shifts were referenced to $BF_3\cdot OEt_2/CDCl_3$ 15% v/v (^{11}B), TMS (^{13}C, ^1H), and CCl_3F (^{19}F) (C_6F_6 as a secondary reference, $\delta=-162.9$ ppm). Shift values of overlapping signals are marked by o. The Raman spectra were recorded on a Bruker FT-Raman spectrometer RFS 100/S using the 1064 nm line of a Nd:YAG laser. The backscattered (180°) radiation was sampled and analyzed (Stoke range: 50–4000 cm^{-1}). The powdered sample was measured in a melting point capillary (512 scans and a resolution of 2 cm^{-1}) using a laser power of $\leq$500 mW. X-ray diffraction data were collected using a Bruker AXS SMART APEX diffractometer equipped with a CCD area detector APEXII. For solution and refinement of the crystal structures the programs SHELXTL (version 6.10) and SADABS (version 2.03) were used. CCDC 770539 contains the supplementary crystallographic data for $[4\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ which can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). $C_6F_5BF_2$,[15] x-$FC_6H_4IF_4$,[16] and $C_6F_5IF_4$[11] were synthesized by literature procedures. ($P(C_6F_5)_3$,[17] $As(C_6F_5)_3$,[18] $Sb(C_6F_5)_3$,[18] and $Bi(C_6F_5)_3$[19]) were synthesized analogue to literature by reactions of C_6F_5MgBr with the corresponding element(III) trichlorides in Et_2O.

5.2. $[2\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$

A cold solution (−78 °C) of $C_6F_5BF_2$ (1.10 mmol) in CH_2Cl_2 (1.3 mL) was added in portions to a cold (−40 °C) vigorously stirred suspension of $2\text{-}FC_6H_4IF_4$ (329 mg, 1.10 mmol) in CH_2Cl_2 (3 mL). The suspension was warmed to 20 °C and after 1.5 h the mother liquor was separated and the solid residue washed with 1 mL CH_2Cl_2. The solid was pumped in vacuum at 20 °C and gave 274 mg of a mixture of $[2\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ (0.488 mmol, 44%) and $[2\text{-}FC_6H_4(C_6F_5)I][BF_4]$ (0.040 mmol, 4%), which contained still small quantities of CH_2Cl_2 (^1H NMR).

DSC: $T_{onset}=197.4$ °C (exothermic effect).

^{19}F NMR (MeCN, 24 °C) $[2\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ δ: −66.6 (tdd, $^4J(F^{(IF)},F^{2,6})=14$ Hz, $^4J(F^{(IF)},F^{2'})=14$ Hz, $^6J(F^{(IF)},F^4)=2$ Hz, IF_2, 2F); −98.9 (m, $2\text{-}FC_6H_4$, 1F); −125.8 (br, $\Delta\nu_{½}=55$ Hz, o-C_6F_5, 2F); −137.6 (ttt, $^3J(F^4,F^{3,5})=21$ Hz, $^4J(F^4,F^{2,6})=9$ Hz, $^6J(F^4,F^{(IF)})=2$ Hz, p-C_6F_5, 1F); −154.7 (m, m-C_6F_5, 2F); $[2\text{-}FC_6H_4(C_6F_5)I][BF_4]$ δ: −94.7 (m, $2\text{-}FC_6H_4$, 1F); −121.1 (m, o-C_6F_5, 2F); −142.2 (tt, $^3J(F^4,F^{3,5})=20$ Hz, $^4J(F^4,F^{2,6})=6$ Hz, p-C_6F_5, 1F); −155.8 (m, m-C_6F_5, 2F); $[BF_4]^-$ δ:=−147.3 (s, BF_4, 4F).

^1H NMR (CH_3CN, 24 °C) $[2\text{-}FC_6H_4(C_6F_5)IF_2]^+$ δ: 8.2 (m, $H^{5'}$, 1H); 8.0 (m, $H^{6'}$, 1H); 7.8 (mo, $H^{4'}$, 1H); 7.8 (mo, $H^{3'}$, 1H); $[2\text{-}FC_6H_4(C_6F_5)I]^+$ δ: 8.3 (m, $H^{5'}$, 1H); 7.8 (m, $H^{6'}$, 1H); 7.5 (m, $H^{3'}$, 1H); 7.4 (m, $H^{4'}$, 1H); CH_2Cl_2 δ: 5.4 (s); molar ratio $[(2\text{-}FC_6H_4)_2IF_2]^+ + [(2\text{-}FC_6H_4)_2I]^+/CH_2Cl_2=100:12$.

^{13}C NMR (CH_3CN, 24 °C) $[2\text{-}FC_6H_4(C_6F_5)IF_2]^+$ δ: 159.6 (dm, $^1J(C^{2'},F^{2'})=261$ Hz, $2\text{-}FC_6H_4$, $C^{2'}$), 148.5 (dm, $^1J(C^4,F^4)=265$ Hz, C_6F_5, C^4); 147.0 (dm, $^1J(C^2,F^2)={}^1J(C^6,F^6)=261$ Hz, C_6F_5, $C^{2,6}$); 140.5 (dmo, $^1J(C^{6'},H^{6'})=175$ Hz, $2\text{-}FC_6H_4$, $C^{6'}$); 140.0 (dmo, $^1J(C^3,F^3)={}^1J(C^5,F^5)=253$ Hz, C_6F_5, $C^{3,5}$); 132.2 (dm, $^1J(C^{5'},H^{5'})=173$ Hz, $2\text{-}FC_6H_4$, $C^{5'}$); 129.4 (dm, $^1J(C^{4'},H^{4'})=171$ Hz, $2\text{-}FC_6H_4$, $C^{4'}$); 125.7 (m, $2\text{-}FC_6H_4$, $C^{1'}$); 120.8 (dm, $^1J(C^{3'},H^{3'})=174$ Hz, $2\text{-}FC_6H_4$, $C^{3'}$); 113.5 (m, C_6F_5, C^1).

^{11}B NMR (CH_3CN, 24 °C) $[BF_4]^-$ δ: −1.3 (s, BF_4).

Raman (20 °C) $\bar{\nu}$: 83 (81), 136 (35), 159 (21), 175 (25), 194 (33), 210 (20), 220 (22), 244 (18), 271 (23), 353 (11), 363 (10), 374 (15), 383 (17), 441 (19), 463 (13), 494 (28), 532 (21), 556 (100), 587 (23), 617 (5), 638 (16), 680 (4), 703 (4), 762 (15), 803 (4), 823 (17), 1005 (13), 1041 (14), 1106 (4), 1134 (5), 1167 (6), 1237 (8), 1271 (6), 1297 (5), 1408 (5), 1497 (4), 1522 (3), 1575 (8), 1593 (4), 1636 (9) cm^{-1}.

5.3. $[3\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$

A −78 °C cold solution of $C_6F_5BF_2$ (0.85 mmol) in CH_2Cl_2 (1.2 mL) was added under stirring to a −40 °C cold solution of $3\text{-}FC_6H_4IF_4$ (281 mg, 0.94 mmol) in CH_2Cl_2 (3 mL). Within 2 h the solution was warmed to 2 °C and formed a slightly yellow suspension. The solid was separated and washed with CH_2Cl_2 (3 mL) and pumped in vacuum at 20 °C to yield 305 mg, 0.0555 mmol, 61%. From ^1H NMR resulted that 0.42 CH_2Cl_2 are co-crystallized per $[3\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$.

DSC: $T_{onset}=96.1$ °C (endothermic effect: loss of CH_2Cl_2), $T_{onset}=134.3$ °C (exothermic effect).

^{19}F NMR (CH_3CN, 24 °C) $[3\text{-}FC_6H_4(C_6F_5)IF_2]^+$ δ: −73.6 (t, $^4J(F^{(IF)},F^{2,6})=11$ Hz, IF_2, 2F); −102.9 (m, 1F, $3\text{-}FC_6H_4$); −126.7 (br, $\Delta\nu_{½}=71$ Hz, o-C_6F_5, 2F); −138.4 (ttt, $^3J(F^4,F^{3,5})=20$ Hz, $^4J(F^4,F^{2,6})=8$ Hz, $^6J(F^4,F^{(IF)})=2$ Hz, p-C_6F_5, 1F); −155.1 (m, m-C_6F_5, 2F); $[BF_4]^-$ δ: −147.7 (s, BF_4, 4F).

^1H NMR (CH_3CN, 24 °C) $[3\text{-}FC_6H_4(C_6F_5)IF_2]^+$ δ: 8.0 (mo, $H^{2'}$, $H^{6'}$, $H^{5'}$, 3H); 7.7 (m, $H^{4'}$, 1H): CH_2Cl_2 δ: 5.4 (s); molar ratio $[(3\text{-}FC_6H_4)(C_6F_5)IF_2]^+/CH_2Cl_2=100:42$.

^{13}C NMR (CH_3CN, 24 °C) $[3\text{-}FC_6H_4(C_6F_5)IF_2]^+$ δ: 164.4 (dm, $^1J(C^{3'},F^{3'})=257$ Hz, $3\text{-}FC_6H_4$, $C^{3'}$), 147.9 (dm, $^1J(C^4,F^4)=264$ Hz, C_6F_5, C^4); 146.8 (dm, $^1J(C^2,F^2)={}^1J(C^6,F^6)=261$ Hz, C_6F_5, $C^{2,6}$); 139.4 (dm, $^1J(C^3,F^3)={}^1J(C^5,F^5)=255$ Hz, C_6F_5, $C^{3,5}$); 135.8 (m, $3\text{-}FC_6H_4$, $C^{1'}$); 134.6 (dm, $^1J(C^{5'},H^{5'})=173$ Hz, $3\text{-}FC_6H_4$, $C^{5'}$); 127.4 (dm, $^1J(C^{6'},H^{6'})=178$ Hz, $3\text{-}FC_6H_4$, $C^{6'}$); 124.5 (dm, $^1J(C^{4'},H^{4'})=168$ Hz, $3\text{-}FC_6H_4$, $C^{4'}$); 118.6 (dm, $^1J(C^{2'},H^{2'})=177$ Hz, $3\text{-}FC_6H_4$, $C^{2'}$); 114.0 (m, C_6F_5, C^1).

^{11}B NMR (CH_3CN, 24 °C) $[BF_4]^-$ δ: −1.3 (s, BF_4).

Raman (20 °C) $\bar{\nu}$: 84 (100), 132 (39), 154 (21), 179 (47), 242 (39), 270 (32), 349 (13), 381 (28), 440 (24), 493 (45), 518 (17), 554 (90), 587 (29), 615 (4), 645 (13), 766 (17), 800 (4), 830 (9), 994 (44), 1039 (14), 1071 (6), 1102 (5), 1167 (8), 1226 (8), 1277 (3), 1410 (3), 1476 (2), 1518 (3), 1572 (9), 1596 (5), 1636 (12), 3092 (26) cm^{-1}.

Co-crystallized CH_2Cl_2 could be removed totally from the solid by pumping further 5 h at 20 °C, 30 min at 80 °C, and 5 min at 95 °C in vacuum (3×10^{-2} h Pa). After this treatment no CH_2Cl_2 could be detected by ^1H NMR. The ^{19}F and ^1H NMR spectra of the iodonium (V) salt was not changed after thermal treatment.

DSC T_{onset}: 132.7 °C (exothermic effect).

5.4. $[4-FC_6H_4(C_6F_5)IF_2][BF_4]$

A cold (−30 °C) solution of $C_6F_5BF_2$ (2.59 mmol) in CH_2Cl_2 (3.5 mL) was added to a stirred $4-FC_6H_4IF_4$ solution (0.75 g, 2.52 mmol) in CH_2Cl_2 (3 mL, −30 °C). A suspension resulted when warmed to 10 °C within 3 h. The solid product was isolated and washed four times with CH_2Cl_2 (each 1 mL). Colorless $[4-FC_6H_4(C_6F_5)IF_2][BF_4]$ was pumped in vacuum at 20 °C for 2 h. Yield 0.75 g, 1.45 mmol, 58%. Single crystals were obtained directly from the reaction mixture.

DSC: T_{onset}=142.6 °C (exothermic effect).

^{19}F NMR (CH_3CN, 24 °C) $[4-FC_6H_4(C_6F_5)IF_2]^+$ δ: −74.0 (t, $^4J(F^{(IF)},F^{2,6})$=11 Hz, IF_2, 2F); −99.6 (m, 4-FC_6H_4, 1F); −127.4 (br, $\Delta\nu_{1/2}$=84 Hz, o-C_6F_5, 2F); −138.7 (ttt, $^3J(F^4,F^{3,5})$=20 Hz, $^4J(F^4,F^{2,6})$=9 Hz, $^6J(F^4,F^{(IF)})$=2 Hz, p-C_6F_5, 1F); −155.5 (m, m-C_6F_5, 2F); $[BF_4]^-$ δ: −146.3 (s, 4F, BF_4).

^{1}H NMR (CH_3CN, 24 °C) $[4-FC_6H_4(C_6F_5)IF_2]^+$ δ: 8.3 (dd, $^3J(H^{2'},H^{3'})={}^3J(H^{6'},H^{5'})$=10 Hz, $^4J(H^{2',6'},F^4)$=4 Hz, $H^{2',6'}$, 2H); 7.7 (dd, $^3J(H^{3'},H^{2'})={}^3J(H^{5'},H^{6'})$=10 Hz, $^3J(H^{3',5'},F^4)$=8 Hz, $H^{3',5'}$, 2H).

^{13}C NMR (CH_3CN, 24 °C) $[4-FC_6H_4(C_6F_5)IF_2]^+$ δ: 167.8 (dtt, $^1J(C^{4'},F^{4'})$=259 Hz, $^2J(C^{4'},H^{3',5'})$=10 Hz, $^3J(C^{4'},H^{2',6'})$=4 Hz, 4-FC_6H_4, $C^{4'}$), 148.0 (dm, $^1J(C^4,F^4)$=265 Hz, C_6F_5, C^4); 146.9 (dm, $^1J(C^2,F^2)={}^1J(C^6,F^6)$=260 Hz, C_6F_5, $C^{2,6}$); 139.6 (dm, $^1J(C^3,F^3)={}^1J(C^5,F^5)$=258 Hz, C_6F_5, $C^{3,5}$); 134.4 (dm, $^1J(C^{2'},H^{2'})={}^1J(C^{6'},H^{6'})$=177 Hz, 4-$FC_6H_4$, $C^{2',6'}$); 129.1 (m, 4-FC_6H_4, $C^{1'}$); 121.4 (ddd, $^1J(C^{3'},H^{3'})={}^1J(C^{5'},H^{5'})$=173 Hz, $^2J(C^{3',5'},F^{4'})$=25 Hz, $^2J(C^{3'},H^{2'})={}^2J(C^{5'},H^{6'})$=4 Hz, 4-$FC_6H_4$, $C^{3',5'}$); 114.1 (m, C_6F_5, C^1).

^{11}B NMR (CH_3CN, 24 °C) $[BF_4]^-$ δ: −1.5 (s, $\Delta\nu_{1/2}$=2 Hz).

Raman (20 °C) $\bar{\nu}$: 84 (100), 141 (39), 163 (27), 189 (67), 237 (52), 255 (16), 269 (17), 314 (7), 335 (10), 355 (18), 374 (23), 441 (25), 495 (50), 542 (83), 565 (39), 588 (28), 621 (18), 763 (14), 807 (16), 821 (11), 986 (15), 997 (14), 1026 (20), 1104 (5), 1163 (17), 1254 (8), 1297 (3), 1407 (5), 1475 (7), 1523 (4), 1577 (11), 1593 (8), 1637 (11), 3090 (26), 3118 (10) cm^{-1}.

5.5. Reaction of $C_6F_5IF_4$ with $4-FC_6H_4BF_2$

When a cold (−45 °C) solution of $4-FC_6H_4BF_2$ (0.13 mmol) in CH_2Cl_2 (700 μL) was mixed with $C_6F_5IF_4$ (43 mg, 0.12 mmol) in CH_2Cl_2 (200 μL, −45 °C), immediately a black suspension resulted, which was warmed to 15 °C within 7 h. After 101 h at 20 °C CH_2Cl_2 was removed in vacuum and the composition of the black residue was characterized by ^{19}F NMR in MeCN solution.

^{19}F NMR (MeCN, 24 °C) $[4-FC_6H_4(C_6F_5)IF_2]^+$ see above, $[4-FC_6H_4(C_6F_5)I]^+$ δ: −102.8 (m, 4-FC_6H_4, 1F); −121.1 (m, o-C_6F_5, 2F); −142.4 (tt, $^3J(F^4,F^{3,5})$=20 Hz, $^4J(F^4,F^{2,6})$=6 Hz, p-C_6F_5, 1F); −155.8 (m, m-C_6F_5, 2F); C_6F_5I δ: −120.1 (m, o-C_6F_5, 2F); −153.3 (tt, $^3J(F^4,F^{3,5})$=19 Hz, $^4J(F^4,F^{2,6})$=2 Hz, p-C_6F_5, 1F); −160.1 (m, m-C_6F_5, 2F); $[BF_4]^-$ δ: −147.3 (s, BF_4, 4F); molar ratio $[4-FC_6H_4(C_6F_5)IF_2]^+$/$[4-FC_6H_4(C_6F_5)I]^+$/$C_6F_5I$/$[BF_4]^-$=52:46:3:97.

5.6. $[(4-FC_6H_4)_2IF_2][BF_4]$

A cold (−78 °C) solution of $4-FC_6H_4BF_2$ (1.4 mmol) in CH_2Cl_2 (3 mL) was added in three portions to a cold (−45 °C) suspension of $4-FC_6H_4IF_4$ (410 mg, 1.38 mmol) in CH_2Cl_2 (3.5 mL). Spontaneously a black suspension was formed, which was warmed to 20 °C. After 170 min the black solid was separated from the mother liquor, washed with CH_2Cl_2 (100 μL), and pumped in vacuum at 20 °C for 60 min. The solid (270 mg) contained $[(4-FC_6H_4)_2IF_2][BF_4]$ (244 mg, 0.54 mmol, 39%), $[(4-FC_6H_4)_2I][BF_4]$ (26 mg, 0.06 mmol, 5%), and still small quantities of CH_2Cl_2.

DSC: T_{onset}=187.9 °C (exothermic effect).

^{19}F NMR (CH_3CN, 24 °C) $[(4-FC_6H_4)_2IF_2]^+$ δ: −85.3 (m, IF_2, 2F); −100.5 (m, 4-FC_6H_4, 2F); $[(4-FC_6H_4)_2I]^+$ δ: −104.4 (m, 4-FC_6H_4, 2F); $[BF_4]^-$ δ: −145.9 (s, BF_4, 4F); molar ratio of the products: $[(4-FC_6H_4)_2IF_2]^+$/$[(4-FC_6H_4)_2I]^+$/$[BF_4]^-$=91:9:104.

^{1}H NMR (CH_3CN, 24 °C) $[(4-FC_6H_4)_2IF_2]^+$ δ: 8.1 (dd, $^3J(H^2,H^3)={}^3J(H^6,H^5)$=9 Hz, $^4J(H^{2,6},F^4)$=4 Hz, $H^{2,6}$, 4H); 7.6 (dd, $^3J(H^3,H^2)={}^3J(H^5,H^6)$=9 Hz, $^3J(H^{3,5},F^4)$=8 Hz, $H^{3,5}$, 4H); $[(4-FC_6H_4)_2I]^+$ δ: 8.1 (dd, $^3J(H^2,H^3)={}^3J(H^6,H^5)$=9 Hz, $^4J(H^{2,6},F^4)$=5 Hz, $H^{2,6}$, 4H); 7.3 (dd, $^3J(H^3,H^2)={}^3J(H^5,H^6)$=9 Hz, $^3J(H^{3,5},F^4)$=9 Hz, $H^{3,5}$, 4H); CH_2Cl_2 δ: 5.4 (s, 2H); molar ratio $[(4-FC_6H_4)_2IF_2]^+$+$[(4-FC_6H_4)_2I]^+$/CH_2Cl_2=100:8.

^{13}C NMR (CH_3CN, 24 °C) $[(4-FC_6H_4)_2IF_2]^+$ δ: 167.3 (dm, $^1J(C^4,F^4)$=258 Hz, C^4); 133.4 (m, C^1); 133.2 (dm, $^1J(C^2,H^2)={}^1J(C^6,H^6)$=176 Hz, $C^{2,6}$); 120.9 (ddd, $^1J(C^3,H^3)={}^1J(C^5,H^5)$=172 Hz, $^2J(C^{3,5},F^4)$=24 Hz, $^2J(C^3,H^2)={}^2J(C^5,H^6)$=4 Hz, $C^{3,5}$).

^{11}B NMR (CH_3CN, 24 °C) $[BF_4]^-$ δ: −1.4 (s, BF_4).

5.7. Testing of the fluoro-oxidizer potential of $[4-FC_6H_4(C_6F_5)IF_2][BF_4]$

5.7.1. Reactions of $[4-FC_6H_4(C_6F_5)IF_2][BF_4]$ with $E(C_6F_5)_3$ (E=P, As, Sb, Bi) in MeCN at 20 °C. The following MeCN solutions of $E(C_6F_5)_3$ were prepared in FEP-inliners: (a) $P(C_6F_5)_3$ (89 mg, 0.17 mmol)/600 μL, (b) $As(C_6F_5)_3$ (75 mg, 0.13 mmol)/500 μL, (c) $Sb(C_6F_5)_3$ (96 mg, 0.15 mmol)/500 μL, (d) $Bi(C_6F_5)_3$ (106 mg, 0.149 mmol)/500 μL. Separately the corresponding $[4-FC_6H_4(C_6F_5)IF_2][BF_4]$ solutions were prepared each in 300 μL: (a) 40 mg, 0.078 mmol, (b) 42 mg, 0.082 mmol, (c) 38 mg, 0.075 mmol, (d) 40 mg, 0.077 mmol. After mixing of the four combinations the reaction progress was monitored by ^{19}F NMR till all $[4-FC_6H_4(C_6F_5)IF_2][BF_4]$ was consumed.

(a) ^{19}F NMR (CH_3CN, 24 °C, after 9 d)

$(C_6F_5)_3PF_2$ δ: 2.5 (dhep, $^1J(F^{(PF)},P)$=690 Hz, $^4J(F^{(PF)},F^{2,6})$=16 Hz, PF_2, 2F); −132.8 (m, o-C_6F_5, 6F); −146.2 (t, $^3J(F^4,F^{3,5})$=20 Hz, p-C_6F_5, 3F); −159.3 (m, m-C_6F_5, 6F); $(C_6F_5)_3P$ δ: −130.2 (m, o-C_6F_5, 6F); −149.0 (mo, p-C_6F_5, 3F);−160.8 (m, m-C_6F_5, 6F); $(C_6F_5)_3PO$ δ: −132.1 (m, o-C_6F_5, 6F); −143.4 (m, p-C_6F_5, 3F); −159.0 (m, m-C_6F_5, 6F); $[4-FC_6H_4(C_6F_5)I]^+$ δ: −102.8 (m, 4-FC_6H_4, 1F); −121.3 (m, o-C_6F_5, 2F); −142.5 (tt, $^3J(F^4,F^{3,5})$=20 Hz, $^4J(F^4,F^{2,6})$=6 Hz, p-C_6F_5, 1F); −155.9 (m, m-C_6F_5, 2F); $[BF_4]^-$ δ: −149.0 (so, BF_4, 4F); HF δ: −182.2 (d, ^1J(F,H)=484 Hz); molar ratio of products: $(C_6F_5)_3PF_2$/$(C_6F_5)_3P$/$(C_6F_5)_3PO$/$[4-FC_6H_4(C_6F_5)I]^+$/HF/$[BF_4]^-$=20:40:10:30:27:31.

(b) ^{19}F NMR (CH_3CN, 24 °C, after 3.5 h)

$(C_6F_5)_3AsF_2$ δ: −22.1 (hep, $^4J(F^{(AsF)},F^{2,6})$=13 Hz, AsF_2, 2F); −131.7 (m, o-C_6F_5, 6F); −144.7 (t, $^3J(F^4,F^{3,5})$=20 Hz, p-C_6F_5, 3F);−157.9 (m, m-C_6F_5, 6F); $(C_6F_5)_3As$ δ: −128.1 (m, o-C_6F_5, 6F); −149.8 (t, $^3J(F^4,F^{3,5})$=20 Hz, p-C_6F_5, 3F); −160.3 (m, m-C_6F_5, 6F); $[4-FC_6H_4(C_6F_5)I]^+$ δ: −102.6 (m, 4-FC_6H_4, 1F); −121.0 (m, o-C_6F_5, 2F);−142.3 (tt, $^3J(F^4,F^{3,5})$=20 Hz, $^4J(F^4,F^{2,6})$=6 Hz, p-C_6F_5, 1F); −155.6 (m, m-C_6F_5, 2F); $[BF_4]^-$ δ: −148.5 (s, $\Delta\delta$ (^{10}BF_4–^{11}BF_4)=0.053, BF_4, 4F); molar ratio of products: $(C_6F_5)_3AsF_2$/$(C_6F_5)_3As$/$[4-FC_6H_4(C_6F_5)I]^+$/$[BF_4]^-$=37:24:39:39.

(c) ^{19}F NMR (CH_3CN, 24 °C, after 0.5 h)

$(C_6F_5)_3SbF_2$ δ: −79.1 (br, $\Delta\nu_{1/2}$=95 Hz, SbF_2, 2F); −126.1 (br, $\Delta\nu_{1/2}$=45 Hz, o-C_6F_5, 6F); −144.2 (br, $\Delta\nu_{1/2}$=111 Hz, p-C_6F_5, 3F); −157.1 (br, $\Delta\nu_{1/2}$=59 Hz, m-C_6F_5, 6F); $(C_6F_5)_3Sb$ δ: −121.8 (m, o-C_6F_5, 6F); −150.5 (tt, $^3J(F^4,F^{3,5})$=19 Hz, $^4J(F^4,F^{2,6})$=3 Hz, p-C_6F_5, 3F); −160.4 (m, m-C_6F_5, 6F); $[4-FC_6H_4(C_6F_5)I]^+$ δ: −102.8 (m, 4-FC_6H_4, 1F); −120.3 (m, o-C_6F_5, 2F); −142.5 (tt, $^3J(F^4,F^{3,5})$=20 Hz, $^4J(F^4,F^{2,6})$=6 Hz, p-C_6F_5, 1F); −155.9 (m, m-C_6F_5, 2F); $[BF_4]^-$ δ: −149.0 (s, BF_4, 4F); molar ratio of products: $(C_6F_5)_3SbF_2$/$(C_6F_5)_3Sb$/$[4-FC_6H_4(C_6F_5)I]^+$/$[BF_4]^-$=22:53:25:23.

(d) ^{19}F NMR (CH_3CN, 24 °C, after 70 h)

$(C_6F_5)_3Bi$ δ: −117.1 (m, *o*-C_6F_5, 6F); −152.1 (t, $^3J(F^4,F^{3,5})$=19 Hz, *p*-C_6F_5, 3F); −160.0 (m, *m*-C_6F_5, 6F); $[4\text{-}FC_6H_4(C_6F_5)I]^+$ δ: −102.8 (m, 4-FC_6H_4, 1F); −121.3 (m, *o*-C_6F_5, 2F);−142.5 (tt, $^3J(F^4,F^{3,5})$= 20 Hz, $^4J(F^4,F^{2,6})$=6 Hz, *p*-C_6F_5, 1F); −155.9 (m, *m*-C_6F_5, 2F); $[(C_6F_5)_2I]^+$ δ: −120.4 (m, *o*-C_6F_5, 4F); −141.3 (tt, $^3J(F^4,F^{3,5})$=20 Hz, $^4J(F^4,F^{2,6})$=6 Hz, *p*-C_6F_5, 2F); −155.5 (m, *m*-C_6F_5, 4F); C_6F_5H δ: −139.2 (m, *o*-C_6F_5, 2F); −154.8 (t, $^3J(F^4,F^{3,5})$=19 Hz, *p*-C_6F_5, 1F); −162.7 (m, *m*-C_6F_5, 2F); 1,4-$F_2C_6H_4$ δ: −119.6 (tt, $^3J(F,H)$=6 Hz, $^4J(F,H)$=6 Hz, 2F); $[BF_4]^-$ δ: −148.8 (s, $\Delta\delta$ ($^{10}BF_4$−$^{11}BF_4$)=0.054, BF_4, 4F); molar ratio of products: $(C_6F_5)_3Bi/[4\text{-}FC_6H_4(C_6F_5)I]^+/[(C_6F_5)_2I]^+/C_6F_5H/1,4\text{-}F_2C_6H_4\ /[BF_4]^-$=46:7:22:24:13:31.

5.7.2. Reactions of $[4\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ with ArI (Ar=C_6F_5I, (a) or 4-FC_6H_4 (b)) in MeCN at 20 °C. 16 µL, 0.12 mmol C_6F_5I (a) or 14 µL, 0.12 mmol 4-FC_6H_4I (b) was added to solutions of $[4\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ in MeCN: (a) 31 mg, 0.060 mmol in 300 µL (a) or 26 mg, 0.051 mmol in 300 µL (b). After mixing of the two combinations the reaction progress was monitored by ^{19}F NMR till all $[4\text{-}FC_6H_4(C_6F_5)IF_2][BF_4]$ was consumed.

(a) ^{19}F NMR (CH_3CN, 24 °C, after 11 d)

$C_6F_5IF_2$ δ: −122.1 (m, *o*-C_6F_5, 2F); −143.7 (m, *p*-C_6F_5, 1F); −156.2 (m, *m*-C_6F_5, 2F); −159.4 (so, IF_2, 2F); $[4\text{-}FC_6H_4(C_6F_5)I]^+$ δ: −102.0 (mo, 4-FC_6H_4, 1F); −120.4 (m, *o*-C_6F_5, 2F); −141.7 (m, *p*-C_6F_5, 1F); −155.1 (m, *m*-C_6F_5, 2F); $[4\text{-}FC_6H_4(C_6F_5)IO]^+$ δ: −102.1 (mo, 4-FC_6H_4, 1F); −128.1 (m, *o*-C_6F_5, 2F); −140.5 (m, *p*-C_6F_5, 1F); −155.7 (m, *m*-C_6F_5, 2F); C_6F_5I δ: −119.3 (m, *o*-C_6F_5, 2F); −152.6 (t, $^3J(F^4,F^{3,5})$=20 Hz, *p*-C_6F_5, 1F); −159.4 (mo, *m*-C_6F_5, 2F); $[BF_4]^-$ δ: −147.3 (s, BF_4, 4F); molar ratio of products: $C_6F_5IF_2/[4\text{-}FC_6H_4(C_6F_5)I]^+/[4\text{-}FC_6H_4(C_6F_5)IO]^+/C_6F_5I/[BF_4]^-$=13:22:12:53:34.

(b) ^{19}F NMR (CH_3CN, 24 °C, after 71 h)

4-$FC_6H_4IF_2$ δ: −107.8 (m, 4-FC_6H_4, 1F); −171.2 (s, IF_2, 2F); $[4\text{-}FC_6H_4(C_6F_5)I]^+$ δ: −102.7 (tt, $^3J(F^4,H^{3,5})$=9 Hz, $^4J(F^4,H^{2,6})$=4 Hz, 4-FC_6H_4, 1F); −121.2 (m, *o*-C_6F_5, 2F); −142.4 (tt, $^3J(F^4,F^{3,5})$=20 Hz, $^4J(F^4,F^{2,6})$=6 Hz, *p*-C_6F_5, 1F); −155.7 (m, *m*-C_6F_5, 2F); 4-FC_6H_4I δ: −114.5 (tt, $^3J(F^4,H^{3,5})$=9 Hz, $^4J(F^4,H^{2,6})$=5 Hz, 4-FC_6H_4, 1F); 4-$FC_6H_4IOF_2$ δ: −27.0 (s, IOF_2, 2F); −103.7 (m, 4-FC_6H_4, 1F); $[BF_4]^-$ δ: −148.4 (s, BF_4, 4F); molar ratio of products: $4\text{-}FC_6H_4IF_2/[4\text{-}FC_6H_4(C_6F_5)I]^+/4\text{-}FC_6H_4I/4\text{-}FC_6H_4IOF_2/[BF_4]^-$=21:29:48:2:29.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.04.047.

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