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From hypervalent xenon difluoride and aryliodine(III) difluorides to onium salts: Scope and limitation of acidic fluoroorganic reagents in the synthesis of fluoroorgano xenon(II) and iodine(III) onium salts

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Dedicated to Professor Boris Žemva.

Abstract

Fluorinated organodifluoroboranes R_fBF_2 are in general suitable reagents to transform XeF_2 and RIF_2 into the corresponding onium tetrafluoroborate salts $[R_fXe][BF_4]$ and $[R(R_f)I][BF_4]$, respectively. (4-C_5F_4N)BF_2 and *trans*-$CF_3CF{=}CFBF_2$ which represent boranes of high acidity form no Xe–C onium salts in reactions with XeF_2 but give the desired iodonium salts with RIF_2 (R = C_6F_5, *o*-, *m*-, *p*-C_6FH_4). The reaction of (4-C_5F_4N)BF_2 with XeF_2 ends with a XeF_2–borane adduct. C_6F_5Xe(4-C_5F_4N), the first Xe-(4-C_5F_4N) compound, was obtained when C_6F_5XeF was reacted with Cd(4-$C_5F_4N)_2$. We describe the synthesis of (4-C_5F_4N)IF_2 and reactions of (4-C_5F_4N)IF_2 and $C_6F_5IF_2$ with (4-C_5F_4N)BF_2. Analogous to $[(4\text{-}C_5F_4N)_2I][BF_4]$ and $[C_6F_5(4\text{-}C_5F_4N)I][BF_4]$ aryl(perfluoroalkenyl)iodonium salts $[R(R')I][BF_4]$ were obtained from RIF_2 (R = C_6F_5, *o*-, *m*-, *p*-C_6FH_4) and $R'BF_2$ (R' = *trans*-$CF_3CF{=}CF$, $CF_2{=}CF$). The gas phase fluoride affinities pF^- of selected fluoroorganodifluoroboranes R_fBF_2 and their hydrocarbon analogs are calculated (B3LYP/6-31+G*) and discussed with respect to their potential to introduce R_f-groups into hypervalent EF_2 bonds. Four aspects which influence the transformation of hypervalent EF_2 bonds (E = Xe, R′I) under the action of Lewis acidic reagents RAF_{n-1} (A = B, P; *n* = 3, 5) into the corresponding $[RE][AF_{n+1}]$ salts are presented and the important role of the acidity is emphasized. Fluoride affinities may help to plan the introduction of organo groups into EF_2 moieties and to expand the types of acidic reagents. Thus $C_6H_5PF_4$ with a pF^- value comparable to that of R_fBF_2 compounds is able to introduce the C_6H_5 group into RIF_2 (R = C_6F_5, *p*-C_6FH_4).

Keywords: XeF_2; Xe–C compound; Iodonium salts; Perfluoropyridyldifluoroborane; Perfluoroalk-1-enyldifluoroboranes; Fluoride affinities

1. Introduction

The basic knowledge about Xe–C compounds: preparation, spectroscopic and structural properties, and reactivities, is summarized in reviews [1,2]. Most of the original papers deal with arylxenonium salts. Alk-1-enyl- [3,4] and alk-1-ynyl xenonium salts [5,6] have been investigated to a lesser extent until now. In addition to organylxenonium salts [RXe][Y], with a 2 center – 2 electron Xe–C bond, only few examples of Xe–C molecules of the types R–Xe–Y [7–9] or R–Xe–R′ [7,8,10] with a 3 center – 4 electron bond are presently known. All [RXe][Y] salts were obtained under acidic conditions. Basic or low acidic conditions are applied to obtain the molecules R–Xe–Y or R–Xe–R′. The class of organoiodine difluorides, RIF_2, belongs to the large family of polyvalent iodine compounds [11–13]. XeF_2 and RIF_2 have a hypervalent EF_2 triad in common. Both compounds have a Ψ-trigonal bipyramidal arrangement with three electron pairs (sum of bonding and lone pairs) in the equatorial plane and two fluorine atoms in the apical positions. Generally, hypervalent F–E–F triads are characterized by strong opposite partial charges in the E–F subunits. The Mulliken charges, for example, on E and F can be used to indicate this phenomenon. From RHF calculations (UGBS or LANL2DZ basis sets) of representative molecules in the gas phase we can deduce the influence of the equatorial group R in RIF_2 on the Mulliken charge of I and F (Table 1) Despite a comparable polarity of the E–F bonds

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Table 1
Partial charges in hypervalent XeF_2 and IF_2 triads: Mulliken charges calculated on RHF level using UGBS and LANL2DZ basis sets

Compounds with EF_2 triad	UGBS		LANL2DZ	
	E	F	E	F
XeF_2	0.95	−0.48	1.31	−0.65
IF_3	1.44	−0.50	1.78	−0.64
$C_6F_5IF_2$	1.61	−0.49	1.54	−0.67
$C_6H_5IF_2$	1.10	−0.54	1.38	−0.69
CF_3IF_2	1.14	−0.46	1.46	−0.66
CH_3IF_2	0.98	−0.55	1.30	−0.69

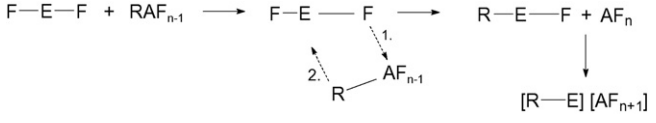
different reactivities of XeF_2 and RIF_2 should not be astonishing because RIF_2 possesses a permanent dipole moment in contrast to XeF_2. Thus XeF_2 [14] and $C_6F_5IF_2$ [15] show distinct intermolecular interactions in their single crystals.

The present work deals with influences, mainly the acidity of the transfer reagent R_fAF_{n-1} (A = B, P; $n = 3$, 5), on the substitution of fluorine in the hypervalent F–E–F triad by one organyl group, preferentially a perfluoroorganyl group. Classical carbon nucleophiles, such as organolithium or Grignard reagents, are no suitable candidates to substitute fluorine in such a EF_2 moiety. The low stability of these reagents towards strong oxidizers and their preferential handling in basic solvents like ethers, which can be attacked by the reactive EF_2 group, militate against these widely applied carbon nucleophiles in reactions with EF_2 compounds. Lewis acidic organoelement fluorides R_fAF_{n-1} present a suitable type of reagents for the introduction of fluoroorgano groups into molecules bearing an EF_2 group. Two aspects are important for such acid-assisted nucleophilic substitutions: (a) the interaction of the acid R_fAF_{n-1} with the EF_2 triad weakens one E–F bond and makes the access of the nucleophilic R_f group to the electrophilic center E more easy and (b) as a consequence of the interaction of the fluoro base with R_fAF_{n-1} the nucleofugality of the R_f group will be increased. In a borderline description we can illustrate this interaction as a transition from the molecule R_fAF_{n-1} to the anion $[R_fAF_n]^-$ (Scheme 1). Aim of the present work is to demonstrate the preparative potential of moderate R_fAF_{n-1} Lewis acids, especially organodifluoroboranes, for the synthesis of fluoroorgano onium salts of Xe(II) and I(III) and to show different reactivities of XeF_2 and R_fIF_2 if the acidity of R_fAF_{n-1} is gradually varied.

2. Results and discussion

2.1. Three different approaches and results in experiments to obtain 2,3,5,6-tetrafluoropyrid-4-ylxenon compounds

A larger number of arylxenonium salts is known. The stability of such Xe–C compounds premises electron-poor aryl groups,



Scheme 1.

e.g. fluorinated phenyl groups, and anions of low nucleophilicity [1]. Surprisingly, till the present work no Xe–C compounds with heteroaryl groups have been known. Thus we were interested to introduce the 2,3,5,6-tetrafluoropyrid-4-yl group into XeF_2.

Our first aim was the synthesis of $[(4\text{-}C_5F_4N)Xe][BF_4]$. In an analogous procedure to the synthesis of $[C_6F_5Xe][BF_4]$ we investigated the reaction of XeF_2 with $(4\text{-}C_5F_4N)BF_2$ in the temperature range from −78 to −36 °C in CH_2Cl_2 and 1,1,1,3,3-pentafluoropropane (PFP). In case of CH_2Cl_2 under markedly acidic conditions (XeF_2 was slowly added to $(4\text{-}C_5F_4N)BF_2$) the solvent was attacked in part as shown by the formation of CH_2ClF, CH_2F_2, and $CHCl_2F$. In CH_2Cl_2 as well as in PFP the precipitation of a green or blue solid proceeded between −78 and −36 °C. After separation, washing and drying the solid became white and was characterized as a XeF_2-$(4\text{-}C_5F_4N)BF_2$ adduct (Eq. (1)). The adduct, even if cooled at ≤ −60 °C, is shock-sensitive. The approximately 1:1 relation of the adduct is based on the stoichiometry and the amount of consumed starting materials. The coloration of the impure adduct arises from a by-product, presumably an oxidation product of a $(4\text{-}C_5F_4N)BF_n$ derivative. In a modified experiment the acid $(4\text{-}C_5F_4N)BF_2$ was added as very diluted CH_2Cl_2 solution in small portions to an excess of XeF_2. In that case the adduct did not exhibit the green color and the solvent was not attacked.

The presence of $[(4\text{-}C_5F_4N)Xe][BF_4]$ in the solid product could be excluded by chemical proofs (see below) and low temperature Raman spectroscopy. The absence of a Xe–C bond is in agreement with the lack of the generally very intensive Xe–C vibration mode nearby the region 198–205 cm^{-1} which is characteristic for $[C_6F_5Xe]^+$ salts [16]. Salts with the $[XeF]^+$ or $[Xe_2F_3]^+$ cation can be excluded because of their instability in CH_2Cl_2 and by the low temperature Raman spectrum (no band in the region 596–619 cm^{-1} ($[XeF]^+$) or at 160 cm^{-1} (Xe–F bend of $[Xe_2F_3]^+$)). The product contains no band ($\nu_s(XeF_2)$) at 496 cm^{-1}, characteristic for non-coordinated XeF_2. Two bands at 536 and 548 cm^{-1} may belong to XeF_2 coordinated at the borane. The intensive band at 517 was attributed to $(4\text{-}C_5F_4N)BF_2$. XeF_2 coordinated at Ca^{2+} or Cd^{2+} in $[M(XeF_2)_5][PF_6]_2$ is characterized by Raman bands at 522 (strong) and 545 (weak) cm^{-1} (Ca^{2+}) [17].

Multi-NMR characterization of the adduct is not possible because the solid could not be dissolved in aHF or EtCN at −78 °C without decomposition.

We attribute the absence of the desired F-$(4\text{-}C_5F_4N)$ substitution in XeF_2 to the cooperation of two influences: (a) the high acidity of $(4\text{-}C_5F_4N)BF_2$ (see Section 2.5) and (b) the lower C-nucleophilicity of the $(4\text{-}C_5F_4N)$ group relative to fluorinated aryl groups.

$$XeF_2 + (4\text{-}C_5F_4N)BF_2 \xrightarrow[-78\ \text{to}\ -36\ ^\circ C]{CH_2Cl_2\ \text{or PFP}} \textit{no}\ \text{formation of}\ [(4\text{-}C_5F_4N)Xe][BF_4] \rightarrow (4\text{-}C_5F_4N)BF_2 \cdot XeF_2 \quad (1)$$

It should be mentioned that $2XeF_2{\cdot}BF_3$ and $XeF_2{\cdot}BF_3$ were reported, but have not been confirmed [18].

The acidic component of the adduct $(4\text{-}C_5F_4N)BF_2{\cdot}XeF_2$ reacted with $[NMe_4]F$ to the corresponding fluoroborate anion

and XeF_2 was released (Eq. (2)). But the recovered amount of XeF_2 was low (≈11%) and varied from experiment to experiment, caused by several side-reactions with the easily oxidizable $[(4\text{-}C_5F_4N)BF_3]^-$ anion under heterogeneous conditions.

$$(4\text{-}C_5F_4N)BF_2 \cdot XeF_2 + [NMe_4]F \xrightarrow[-40\,^\circ C]{CH_2Cl_2} [NMe_4][(4\text{-}C_5F_4N)BF_3] + XeF_2 \quad (2)$$

$$(4\text{-}C_5F_4N)BF_2 \cdot XeF_2 + 2[NBu_4]I \xrightarrow[-50\text{ to }20\,^\circ C]{CH_2Cl_2} [NBu_4][(4\text{-}C_5F_4N)BF_3] + Xe^o + <[NBu_4]F> + I_2 \quad (3)$$

Above −50 °C the reaction of $(4\text{-}C_5F_4N)BF_2{\cdot}XeF_2$ with $[NBu_4]I$ (Eq. (3)) resulted in evolution of Xe° and the formation of 89% $[NBu_4][(4\text{-}C_5F_4N)BF_3]$, 8% $[BF_4]^-$, and 2% $(4\text{-}C_5F_4N)H$, but no $(4\text{-}C_5F_4N)I$ was detected as would be expected in case of a $[(4\text{-}C_5F_4N)Xe]^+$ salt (*cf.* $[C_6F_5Xe][C_6F_5BF_3]$ + $[NMe_4]I$ [19]).

The base-catalyzed transfer of the perfluoroorgano group – a method introduced by Naumann [8] – did not lead to the desired molecules $(4\text{-}C_5F_4N)XeF$ or $(4\text{-}C_5F_4N)_2Xe$. $(4\text{-}C_5F_4N)_2$ was formed as the main pyridyl species beside traces of $(4\text{-}C_5F_4N)H$ (Eq. (4)).

$$XeF_2 + (4\text{-}C_5F_4N)Me_3Si \xrightarrow[CH_2Cl_2\ -60\,^\circ C/10\,min]{[[NMe_4]F]} \textit{no}\ (4\text{-}C_5F_4N)XeF \text{ or } (4\text{-}C_5F_4N)_2Xe,\ \ \text{mainly}(4\text{-}C_5F_4N)_2 \quad (4)$$

As a third alternative to establish a Xe–$(4\text{-}C_5F_4N)$ bond we investigated the fluoride substitution in C_6F_5XeF [7,10] and used weakly acidic $Cd(4\text{-}C_5F_4N)_2$ as a transfer reagent of the heteroaryl group (Eq. (5)).

$$2C_6F_5XeF + Cd(4\text{-}C_5F_4N)_2 \xrightarrow[-78\text{ to }-50\,^\circ C]{CH_2Cl_2} 2C_6F_5Xe(4\text{-}C_5F_4N) + CdF_2 \quad (5)$$

By this approach the desired pyridylxenon compound $C_6F_5Xe(4\text{-}C_5F_4N)$ could be realized. C_6F_5H, $(4\text{-}C_5F_4N)H$, $C_6F_5(4\text{-}C_5F_4N)$, $(C_6F_5)_2$, and $(4\text{-}C_5F_4N)_2$ were the characteristic by-products or decomposition products of the temperature-sensitive target product. $C_6F_5Xe(4\text{-}C_5F_4N)$ was characterized by ^{19}F and ^{129}Xe NMR spectroscopy in CH_2Cl_2 solution at −80 °C. The ^{19}F NMR displayed two signals (−92.2 and −135.0) for the $(4\text{-}C_5F_4N)$ and three signals (−133.3, −153.1, and −158.6) for the C_6F_5 group in the correct integral ratios 2:2 and 2:1:2. The resonances of the C_6F_5 group appeared at low frequency in relation to that in $[C_6F_5Xe][AsF_6]$ (MeCN, 32 °C, δ −124.7 (*o*-F), −141.4 (*p*-F), −154.4 (*m*-F) [20]) and are similar to that in $(C_6F_5)_2Xe$ (CH_2Cl_2, −78 °C, δ −133.1 (*o*-F), −154.1 (*p*-F), −159.0 (*m*-F) [10]). The ^{129}Xe NMR resonance appeared as an unresolved singlet ($\tau_{1/2}$ = 112 Hz) at −4100 ppm in a comparable position to $(C_6F_5)_2Xe$ (δ −4152 [10]). The constitution of the molecule $C_6F_5Xe(4\text{-}C_5F_4N)$ was proved by solvolysis in aHF (Eq. (6)). The cleavage products $[C_6F_5Xe]^+$ and $(4\text{-}C_5F_4N)H$ underline that in $C_6F_5Xe(4\text{-}C_5F_4N)$ the $(4\text{-}C_5F_4N)$ group possesses a more anionic character than the C_6F_5 group.

$$C_6F_5Xe(4\text{-}C_5F_4N) + aHF \xrightarrow[-78\,^\circ C/1\ h]{} [C_6F_5Xe][F(HF)_n] + (4\text{-}C_5F_4N)H \quad (6)$$

2.2. The substitution of fluorine in hypervalent bonds of organoiodine difluorides using 2,3,5,6-tetrafluoropyrid-4-ylboron difluoride

In order to compare the reactivity of the hypervalent EF_2 triad in R_fIF_2 compounds with that in XeF_2 we discuss reactions of $C_6F_5IF_2$ and $(4\text{-}C_5F_4N)IF_2$ with $(4\text{-}C_5F_4N)BF_2$. The new heteroaryliodine difluoride $(4\text{-}C_5F_4N)IF_2$ – subsequently used as starting material – was obtained by the sequence of reactions ((7a)–(7c)). Recently we have published the formation of $[(C_6F_5)_2I][BF_4]$ [21] (Eq. (8)) and $[C_6F_5(4\text{-}C_5F_4N)I][BF_4]$ but the latter as an admixture with $[C_6F_5(4\text{-}C_5F_4N)I][(4\text{-}C_5F_4N)BF_3]$ [22] (Eq. (9)).

$$(4\text{-}C_5F_4N)H + BuLi \xrightarrow[-78\,^\circ C]{Et_2O} (4\text{-}C_5F_4N)Li + Bu\text{-}H \quad (7a)$$

$$(4\text{-}C_5F_4N)Li + ICl \xrightarrow[\leq -40\,^\circ C]{Et_2O} (4\text{-}C_5F_4N)I + LiCl \quad (7b)$$

$$(4\text{-}C_5F_4N)I + XeF_2 \xrightarrow[20\,^\circ C]{CH_2Cl_2} (4\text{-}C_5F_4N)IF_2 + Xe\ \ (\text{cf. } [23]) \quad (7c)$$

$$C_6F_5IF_2 + C_6F_5BF_2 \xrightarrow[20\,^\circ C/\leq 1\,min]{CH_2Cl_2} [(C_6F_5)_2I][BF_4] \quad (8)$$

$$C_6F_5IF_2 + >1(4\text{-}C_5F_4N)BF_2 \xrightarrow[0\,^\circ C/1\,h]{CH_2Cl_2} [C_6F_5(4\text{-}C_5F_4N)I][BF_4] + [C_6F_5(4\text{-}C_5F_4N)I][(4\text{-}C_5F_4N)BF_3] \quad (9)$$

Now we append to the former investigation [22] the following two reactions with less than 1 equiv. of $(4\text{-}C_5F_4N)BF_2$ (Eqs. (10) and (11)).

$$C_6F_5IF_2 + <1(4\text{-}C_5F_4N)BF_2 \xrightarrow[0\,^\circ C/\text{spontaneously}]{CH_2Cl_2} [C_6F_5(4\text{-}C_5F_4N)I][BF_4] \quad (10)$$

$$(4\text{-}C_5F_4N)IF_2 + <1(4\text{-}C_5F_4N)BF_2 \xrightarrow[0\,^\circ C/\geq 10\,min]{CH_2Cl_2} [(4\text{-}C_5F_4N)_2I][BF_4] \quad (11)$$

Reaction (11) proceeded slower than (10). The important information from Eq. (11) is that fluorine-(2,3,5,6-tetrafluoropyridyl) substitution took place. Even if the IF_2 triad is bonded to the strong electron-withdrawing $(4\text{-}C_5F_4N)$ group it reacts with the highly acidic pyridylboron difluoride and forms the corresponding onium salt. This reactivity is in contrast to that of XeF_2 where $[(4\text{-}C_5F_4N)Xe][BF_4]$ is not formed (see Section 2.1).

It is worth mentioning that in the optimized reaction of $C_6F_5IF_2$ with less than 1 equiv. of $(4\text{-}C_5F_4N)BF_2$ only the pure

$[C_6F_5(4\text{-}C_5F_4N)I][BF_4]$ salt resulted. Thus the presence of the $[(4\text{-}C_5F_4N)BF_3]^-$ anion in Eq. (9) is due to a slow consecutive reaction of very acidic $(4\text{-}C_5F_4N)BF_2$ under abstraction of fluoride from $[BF_4]^-$ (Eq. (12)). Now we have experimentally verified reaction (12). By the absence of $[(4\text{-}C_5F_4N)BF_3]^-$ in Eq. (10) we can exclude that the intermediate R(R′)IF reacts faster with $(4\text{-}C_5F_4N)BF_2$ than with BF_3 (Scheme 1).

$$[R(R')I][BF_4]_{(s)} + (4\text{-}C_5F_4N)BF_2 \xrightarrow{CH_2Cl_2} [R(R')I][(4\text{-}C_5F_4N)BF_3] + BF_3$$
$$R = C_6F_5, R' = (4\text{-}C_5F_4N) \quad (12)$$

Table 2 compiles ^{19}F spectroscopic data of $(4\text{-}C_5F_4N)I^{III}$ compounds in MeCN solution. The step from $(4\text{-}C_5F_4N)IF_2$ to $[(4\text{-}C_5F_4N)_2I]^+$ is associated with a high-frequency shift of $F^{2,6}$ as well as $F^{3,5}$ comparable to that observed for the couple $C_6F_5IF_2$ and $[(C_6F_5)_2I]^+$. The higher deshielding of the *p*- and *m*-F atoms of the C_6F_5 group in $[C_6F_5(4\text{-}C_5F_4N)I]^+$ compared to $[(C_6F_5)_2I]^+$ is in agreement with the stronger electron-withdrawing nature of the $(4\text{-}C_5F_4N)$ group. Thus the strong polarization of the π-system of the C_6F_5 group by I^{III} is consequently compensated by F–C back-bonding.

2.3. The substitution of hypervalently bonded fluorine in fluoroaryliodine difluorides using perfluoroalk-1-enylboron difluorides

In general, aryl(perfluoroalk-1-enyl)iodonium salts are promising electrophilic perfluoroalkenylating agents, because of the high fugality of aryliodides [24]. In addition to the necessity of developing a widely applicable synthesis there was the aspect to compare the introduction of perfluoroalkenyl groups into aryliodine difluorides with that into XeF_2. Recently we introduced a larger variety of fluorinated alk-1-enyl groups into XeF_2 using the corresponding boranes $CF_2{=}CXBF_2$ (X = H, Cl, CF_3) [3] or $XCF{=}CFBF_2$ (X = F, *trans*-H, *cis*- and *trans*-Cl, *cis*-CF_3, *cis*-C_2F_5) [4]. In case that X was a perfluoroalkyl substituent *trans* to the BF_2 group in $XCF{=}CFBF_2$ the reaction failed (Eq. (13)) and mainly addition across the C=C double bond occurred and $C_3F_7BF_2$ and C_3F_8 or $C_6F_{13}BF_2$ and C_6F_{14} beside the olefines $XCF{=}CF_2$ were observed.

$$XeF_2 + \textit{trans}\text{-}XCF{=}CFBF_2 \xrightarrow[-50\,\text{to}\,-40\,^\circ C]{\text{PFB or PFP}} \textit{no}\ \text{formation of}\ [\textit{trans}\text{-}XCF{=}CFXe][BF_4] \quad (13)$$

X = CF_3, C_4F_9 [4]; PFB = 1,1,1,3,3-pentafluorobutane, PFP = 1,1,1,3,3-pentafluoropropane.

In order to compare the reactivity of XeF_2 with that of R_fIF_2 we investigated the reactions of mono-(*o*-, *m*-, *p*-) and perfluorinated phenyliodine difluorides with *trans*-$CF_3CF{=}CFBF_2$ (Eqs. (14) and (15)). Qualitatively we compared the reaction with that of $CF_2{=}CFBF_2$ to study the influence of the CF_3 group (CF_3: $\sigma_I = 0.38$, $\sigma_R = 0.16$; F: $\sigma_I = 0.45$, $\sigma_R = -0.39$ [25]) in *trans* position to BF_2 (Eqs. (16) and (17)).

$$o\text{-}, m\text{-}, p\text{-}C_6FH_4IF_2 + \textit{trans}\text{-}CF_3CF{=}CFBF_2 \xrightarrow[-60\,^\circ C]{CH_2Cl_2} \underset{75-85\%\ \text{yield}}{[o\text{-}, m\text{-}, p\text{-}C_6FH_4(\textit{trans}\text{-}CF_3CF{=}CF)I][BF_4]} \quad (14)$$

$$C_6F_5IF_2 + \textit{trans}\text{-}CF_3CF{=}CFBF_2 \xrightarrow[-60\,^\circ C]{CH_2Cl_2} \underset{92\%\ \text{yield}}{[C_6F_5(\textit{trans}\text{-}CF_3CF{=}CF)I][BF_4]} \quad (15)$$

$$o\text{-}, m\text{-}, p\text{-}C_6FH_4IF_2 + CF_2{=}CFBF_2 \xrightarrow[-60\,^\circ C]{CH_2Cl_2} \underset{79-94\%\ \text{yield}}{[o\text{-}, m\text{-}, p\text{-}C_6FH_4(CF_2{=}CF)I][BF_4]} \quad (16)$$

$$C_6F_5IF_2 + CF_2{=}CFBF_2 \xrightarrow[-60\,^\circ C]{CH_2Cl_2} \underset{91\%\ \text{yield}}{[C_6F_5(CF_2{=}CF)I][BF_4]} \quad (17)$$

The conversion of R_fBF_2 in reactions ((14)–(17)) proceeded quantitatively in less than 30 min at −60 °C. Different to the system XeF_2/*trans*-$CF_3CF{=}CFBF_2$ where no fluorine substitution took place below −40 °C, *o*-, *m*-, *p*-$C_6FH_4IF_2$ as well as $C_6F_5IF_2$ with the strong electron-withdrawing C_6F_5 group underwent successful transformations to the corresponding onium salts.

Table 2
^{19}F NMR shift values δ (ppm) of $(4\text{-}C_5F_4N)I^{III}$ compounds in MeCN

Compounds	T (°C)	MeCN			
		$F^{2,6}$	$F^{3,5}$	IF_2	$[BF_4]^-$
$(4\text{-}C_5F_4N)$ moiety					
$(4\text{-}C_5F_4N)IF_2$[a]	24	−86.1	−125.8	−162.5	
$[C_6F_5(4\text{-}C_5F_4N)I][BF_4]$[b]	24	−84.3	−123.1		−148.9
$[(4\text{-}C_5F_4N)_2I][BF_4]$[b]	24	−83.9	−122.5		−148.8

Compounds	T (°C)	MeCN				
		o-F	*p*-F	*m*-F	IF_2	$[BF_4]^-$
C_6F_5 moiety						
$C_6F_5IF_2$	24	−123.0	−144.6	−157.1	−160.5	
$[C_6F_5(4\text{-}C_5F_4N)I][BF_4]$	24	−119.7	−140.5	−155.0		−148.9
$[(C_6F_5)_2I][BF_4]$[b]	24	−120.2	−141.1	−155.2		−149.4

[a] In CH_2Cl_2: −84.9 −125.3, −160.5.
[b] Insoluble in CH_2Cl_2.

Table 3
The dependence of ^{19}F NMR shift values δ (ppm) of [*x*-C_6FH_4(XCF=CF)I][BF_4] salts on the coordination property of the solvent

x-C_6FH_4(*trans*-XCF=CF)I^+ compounds	T (°C)	MeCN					CH_2Cl_2				
		x-F	F^1	F^2	*trans*-X	$[BF_4]^-$	*x*-F	F^1	F^2	*trans*-X	$[BF_4]^-$
[*o*-C_6FH_4(FCF=CF)I][BF_4]	24	−95.0	−158.2	−98.0	−78.7	−148.5	−94.8	−157.8	−98.0	−79.0	−143.6
[*m*-C_6FH_4(FCF=CF)I][BF_4]	24	−105.0	−158.5	−98.2	−78.8	−148.7	−104.3	−158.1	−98.6	−79.1	−143.2
[*p*-C_6FH_4(FCF=CF)I][BF_4]	24	−102.7	−158.9	−98.7	−79.5	−148.3	−101.7	−157.9	−98.9	−79.0	−143.9
[*o*-C_6FH_4(*trans*-CF_3CF=CF)I][BF_4]	24	−94.1	−140.4	−119.3	−67.4	−148.7	−93.1	−138.2	−119.4	−67.7	−141.8
[*m*-C_6FH_4(*trans*-CF_3CF=CF)I][BF_4]	24	−104.7	−140.7	−119.9	−67.5	−148.4	−103.5	−139.1	−120.1	−68.4	−142.5
[*p*-C_6FH_4(*trans*-CF_3CF=CF)I][BF_4]	24	−101.9	−141.4	−120.2	−67.5	−148.6	−101.4	−140.2	−120.8	−68.6	−142.5

All mentioned aryl(1,2,3,3,3-pentafluoroprop-1-enyl)iodonium and -(trifluorovinyl)-iodonium salts are colorless solids stable at room temperature. In case of the C_6F_5 species the thermal stability was determined in closed melting capillaries and by DSC measurements: [C_6F_5(*trans*-CF_3CF=CF)I][BF_4] 160–162 °C (capillary) and 161.2 °C (T_{onset}, endothermal process); [C_6F_5(CF_2=CF)I][BF_4] 108–110 °C (capillary) and 109.7 °C (T_{onset}, endothermal process). All [C_6FH_4(XCF=CF)I][BF_4] salts are not only soluble in coordinating solvents (MeCN, $MeNO_2$) but also in weakly coordinating, polar solvents (CH_2Cl_2). This property allows to investigate the effect of close contact ion pairing. Such an interaction is responsible for the significant deshielding caused by the change of solvent from MeCN to CH_2Cl_2 (Table 3) of the boron-bonded fluorine atoms ($\Delta\delta(^{19}F)$ = 4.4–4.9 ppm for X = F and 5.9–6.9 ppm for X = *trans*-CF_3). A less expressed deshielding can also be found for the fluorine atom F^1 of the alk-1-enyl group and the single fluorine atom in the phenyl group. This deshielding is stronger for X = *trans*-CF_3 than for X = F.

2.4. A comparison of two reagents of different fluoro acid types, phenylboron difluoride and phenylphosphorous tetrafluoride, in aryl transfer reactions forming iodonium salts

We compared the reaction of *p*-$C_6FH_4IF_2$ with $C_6H_5BF_2$ and $C_6H_5PF_4$ (Eqs. (18) and (19)) to show the influence of the type of fluoro acid and its acidity on the formation of iodonium salts. Additionally we indicated the influence of distinct fluoride donor properties of IF_2 groups and compared the reaction of *p*-$C_6FH_4IF_2$ and $C_6F_5IF_2$ with $C_6H_5BF_2$ (Eqs. (18) and (20)). Finally we showed the reactivity of $C_6H_5BF_2$ and $C_6H_5PF_4$ in their reactions with $C_6F_5IF_2$ (Eqs. (20) and (21)). In the here discussed series, $C_6F_5IF_2$ is the candidate with the lowest fluoride donor property and $C_6H_5PF_4$ the strongest acid.

$$p\text{-}C_6FH_4IF_2 + C_6H_5BF_2 \xrightarrow{CH_2Cl_2/-50\,^\circ C} [p\text{-}C_6FH_4(C_6H_5)I][BF_4] \quad (18)$$

$$p\text{-}C_6FH_4IF_2 + C_6H_5PF_4 \xrightarrow{CH_2Cl_2/-60\,^\circ C} [p\text{-}C_6FH_4(C_6H_5)I][PF_6] \quad (19)$$

$$C_6F_5IF_2 + C_6H_5BF_2 \xrightarrow{CH_2Cl_2/-40\,^\circ C} [C_6F_5(C_6H_5)I][BF_4] \quad (20)$$

$$C_6F_5IF_2 + C_6H_5PF_4 \xrightarrow{CH_2Cl_2/-60\,^\circ C} [C_6F_5(C_6H_5)I][PF_6] \quad (21)$$

The temperature at which the fast reactions ((18)–(21)) started differed and increased parallel to lower acidity in case of identical R_fIF_2 molecules (Eqs. (18) versus (19) and (20) versus (21)). Aryliodine difluorides with electron-withdrawing aryl groups (low fluoride donors) require in case of the less acidic aryltransfer reagent $C_6H_5BF_2$ (Eqs. (20) versus (18)) a higher starting temperature for the reaction.

The iodonium salts [$C_6FH_4(C_6H_5)I$][AF_{n+1}] (E = B, n = 3; E = P, n = 5) are soluble in MeCN but also in weakly coordinating CH_2Cl_2 and show in comparison to [C_6FH_4(XCF=CF)I][BF_4] salts a significantly lower tendency to form close contact ion pairs (Table 4). The deshielding of their $[BF_4]^-$ anion in CH_2Cl_2 is reduced to 2.9–3.4 ppm. We deduce this to a lower positive partial charge on iodine and explain this by the ability of the electron-rich phenyl group to take over positive charge better than perfluoroalkenyl groups.

2.5. Influences on the fluorine–fluoroorgano group substitution in hypervalent EF_2 triads and presentation of gas phase acidities (fluoride affinities pF^-) of organo- and perfluoroorganoelement fluorides

There are four main factors which influence the reaction of the EF_2 triad with Lewis acidic RAF_{n-1} reagents to the corresponding onium salts: the acidity of RAF_{n-1}, the nucleophilicity and nucleofugality of the group R in RAF_{n-1}, the fluoride donor property of the EF_2 triad, and the electrophilicity of E in EF_2. In this paper we want to focus on the acidity of RAF_{n-1} and discuss the other three factors on the basis of the actual results only shortly.

In arylelement compounds a C_6F_5 group takes over more negative partial charge than a C_6H_5 group. The transition of RAF_{n-1} to $[RAF_n]^-$ (R = aryl) is associated with a higher

Table 4
The dependence of ^{19}F NMR shift values δ (ppm) of *x*-$C_6FH_4(C_6H_5)I[BF_4]$ salts on the coordination property of the solvent

x-$C_6FH_4(C_6H_5)I[BF_4]$	T (°C)	MeCN		CH_2Cl_2	
		x-F	$[BF_4]^-$	*x*-F	$[BF_4]^-$
o-$C_6FH_4(C_6H_5)I[BF_4]$	24	−95.7	−149.7	−95.5	−146.6
m-$C_6FH_4(C_6H_5)I[BF_4]$	24	−105.8	−148.9	−105.2	−146.0
p-$C_6FH_4(C_6H_5)I[BF_4]$	24	−104.4	−149.2	−104.6	−145.8

nucleofugality for R = C_6F_5 than for R = C_6H_5 as demonstrated for the introduction of aryl groups into IF_5 under basic conditions [26]. If we compare the nucleophilicity of the C_6F_5 and the (4-C_5F_4N) group we have to consider that in the (4-C_5F_4N) group more negative partial charge is located on nitrogen than on the ipso carbon. Thus C_6F_5 can more easily be introduced into RIF_2 than (4-C_5F_4N). The influence of the fluoride donor property of the EF_2 triad could be proved by varying R in RIF_2. Strong electron-withdrawing groups R increase the positive partial charge on iodine and make the

Table 5
Fluoride affinities pF^- of organodifluoroboranes and related compounds

Lewis acid RAF_{n-1}	pF^- [a]	Reference [b]	Difference in acidity R_FAF_{n-1}/R_HAF_{n-1}	$\Delta(pF^-)$
BF_3	7.88	8.31		
$(CF_3)_3CBF_2$	9.98		$(CF_3)_3CBF_2/(CH_3)_3CBF_2$	3.11
$CF_3CF_2CF_2BF_2$	9.67		$CF_3CF_2CF_2BF_2/CH_3CH_2CH_2BF_2$	3.08
$(CF_3)_2CFBF_2$	9.61		$(CF_3)_2CFBF_2/(CH_3)_2CHBF_2$	2.90
$CF_3CF_2BF_2$	9.58		$CF_3CF_2BF_2/C_2H_5BF_2$	3.05
CF_3BF_2	9.40		CF_3BF_2/CH_3BF_2	2.94
(4-C_5F_4N)BF_2	9.08		(4-C_5F_4N)BF_2/(4-C_5H_4N)BF_2	1.46
cis-$CF_3CF{=}CFBF_2$	9.00		*cis*-$CF_3CF{=}CFBF_2$/*cis*-$CH_3CH{=}CHBF_2$	2.65
trans-$CF_3CF{=}CFBF_2$	8.90		*trans*-$CF_3CF{=}CFBF_2$/*trans*-$CH_3CH{=}CHBF_2$	2.64
$CF_3C{\equiv}CBF_2$	8.90		$CF_3C{\equiv}CBF_2/CH_3C{\equiv}CBF_2$	2.01
$C_6F_5BF_2$	8.51		$C_6F_5BF_2/C_6H_5BF_2$	1.74
$CF_2{=}CFBF_2$	8.03		$CF_2{=}CFBF_2/CH_2{=}CHBF_2$	1.48
(4-C_5H_4N)BF_2	7.62			
$FC{\equiv}CBF_2$	7.53		$FC{\equiv}CBF_2/HC{\equiv}CBF_2$	0.10
$HC{\equiv}CBF_2$	7.43			
m-$FC_6H_4BF_2$	7.25			
o-$FC_6H_4BF_2$	7.16			
p-$FC_6H_4BF_2$	7.10			
$CH_3C{\equiv}CBF_2$	6.89			
$(CH_3)_3CBF_2$	6.87			
$C_6H_5BF_2$	6.77			
$(CH_3)_2CHBF_2$	6.71			
$CH_3CH_2CH_2BF_2$	6.59			
$CH_2{=}CHBF_2$	6.55			
$C_2H_5BF_2$	6.53			
CH_3BF_2	6.46			
cis-$CH_3CH{=}CHBF_2$	6.35			
trans-$CH_3CH{=}CHBF_2$	6.26			
SiF_4	7.18	7.35		
$C_2F_5SiF_3$	8.45		$C_2F_5SiF_3/C_2H_5SiF_3$	3.14
(4-C_5F_4N)SiF_3	7.98		(4-C_5F_4N)SiF_3/(4-C_5H_4N)SiF_3	1.40
$C_6F_5SiF_3$	7.45		$C_6F_5SiF_3/C_6H_5SiF_3$	1.69
(4-C_5H_4N)SiF_3	6.58			
m-$FC_6H_4SiF_3$	6.24			
p-$FC_6H_4SiF_3$	6.12			
o-$FC_6H_4SiF_3$	6.05			
$C_6H_5SiF_3$	5.76			
$C_2H_5SiF_3$	5.31			
$C_6F_5Si(CH_3)_3$	4.92		$C_6F_5Si(CH_3)_3/C_6H_5Si(CH_3)_3$	2.24
$(CH_3)_3SiCN$	3.95			
$(CH_3)_3SiF$	3.03			
$C_6H_5Si(CH_3)_3$	2.68			
PF_5	8.92	9.49		
(4-C_5F_4N)PF_4	9.78		(4-C_5F_4N)PF_4/(4-C_5H_4N)PF_4	0.97
$C_2F_5PF_4$	9.58		$C_2F_5PF_4/C_2H_5PF_4$	2.11
(4-C_5H_4N)PF_4	8.81			
$C_6F_5PF_4$	8.62		$C_6F_5PF_4/C_6H_5PF_4$	0.47
$C_6H_5PF_4$	8.15			
$C_2H_5PF_4$	7.47			
m-$FC_6H_4PF_4$	7.44			
o-$FC_6H_4PF_4$	7.34			
p-$FC_6H_4PF_4$	7.30			

[a] The fluoride affinities pF^- were calculated on the B3LYP level using the 6-31 + G* basis set for the isodesmic reaction $RAF_{n-1} + [COF_3]^- \rightarrow [RAF_n] + COF_2$ and the experimentally known fluoride affinity of COF_2 = 49.9 kcal/mol [27].
[b] pF^- values from Ref. [27].

polarization and finally the cleavage of the I–F bond by Lewis acids more difficult. On the other hand electron-withdrawing groups R in RIF_2 increase the electrophilicity of iodine and favor the interaction with the nucleophile and thereby the onium cation formation.

An important parameter which influences the formation of onium ions from the corresponding EF_2 compounds is the acidity of the Lewis acid RAF_{n-1} which acts as transfer reagent of the organo group R. To have a quantitative basis for argumentation we decided to calculate gas phase acidities (fluoride affinities pF^-) on the B3LYP level using the 6-31+G* basis set. Fluoride affinities for most common inorganic Lewis acidic fluorides have been calculated at the correlated MP2/PDZ level of theory by Christe. [27] The difference in pF^- values of BF_3, SiF_4, and PF_5 obtained from B3LYP/6-31+G* calculations shows, compared to MP2/PDZ calculations (higher level of theory), the same tendency of deviation in all three Lewis acids which is minimized in case of the highly symmetric SiF_4 molecule (2.3%), relative to BF_3 (5.2%) and PF_5 (6.0%).

Table 5 includes the Lewis acids BF_3, SiF_4, and PF_5 and selected organo derivatives RBF_2, $RSiX_3$, RPF_4. It is worth to remember the sequence of gas phase acidity of the inorganic fluorides considered here: $SiF_4 < BF_3 < PF_5$. The class (alkyl, alk-1-enyl, phenyl, heteroaryl, alk-1-ynyl) and the type (hydrocarbon and perfluorinated one) of the organo group present in boranes RBF_2, which are in the focus of this work, were varied. In case of the R_fBF_2 compounds we find both properties: more and less acidic molecules than BF_3 itself. For R_fBF_2 with $R_f = (CF_3)_3C$, $CF_3CF_2CF_2$, $(CF_3)_2CF$, CF_3CF_2, CF_3, (4-C_5F_4N), *cis*- and *trans*-$CF_3CF{=}CF$, $CF_3C{\equiv}C$, C_6F_5, and $CF_2{=}CF$ higher pF^- values were calculated than for the parent molecule BF_3, whereas a lower one for $FC{\equiv}CBF_2$. The C_6F_5 derivatives of SiF_4 and PF_5 show a different behavior: $C_6F_5SiF_3$ is more acidic than SiF_4, but $C_6F_5PF_4$ less acidic than PF_5. As expected, in all cases the perfluorinated organo difluoroboranes are more acidic than their hydrocarbon analogs. Caused by their σ_i values [25] the series of acidity is headed by perfluoro species of the alkyl class followed by the ones of the pyridyl, alk-1-enyl, alk-1-ynyl and aryl class. In the right column of Table 5 the increase of acidity caused by perfluorination of the organo group is displayed. It is worth mentioning that the influence of perfluorination of the phenyl group has a significantly stronger implication on acidity in case of the fluoroborane than of the fluorosilane or fluorophosphorane. The high acidity of (4-C_5F_4N)BF_2 which played an important role in the distinct reactivity of (4-C_5F_4N)BF_2 and $C_6F_5BF_2$ towards XeF_2 (see Section 2.1) is supported by the pF^- values in the gas phase. The higher acidity of (4-C_5F_4N)BF_2 in comparison to that of $C_6F_5BF_2$ is also in agreement with the experimental finding that for the abstraction of fluoride from K[(4-C_5F_4N)BF_3] the strong Lewis acid AsF_5 is needed [22] whereas less strong BF_3 is sufficient in case of K[$C_6F_5BF_3$] [28]. Based on our present knowledge about the interaction of the EF_2 triad with Lewis acids RAF_{n-1} we can principally discuss three simplified cases: (a) abstraction of fluoride and formation of [EF][RAF_n] (contact ion pairs or solvent separated ions), (b) adduct formation, mainly stabilized by insolubility, and (c) weak interaction under polarization of one E–F bond, followed by the migration of the nucleophilic group R to the electrophilic center E.

But it should be pointed out that the transformation of hypervalent EF_2 triads into the corresponding organoonium cations cannot only be predicted on the basis of the acidity of the RAF_{n-1} reagent.

3. Conclusion

In reactions with XeF_2, (4-C_5F_4N)BF_2 behaves differently to the related fluorophenyldifluoroboranes. Instead of fluorine-(4-C_5F_4N) substitution adduct formation proceeded. A Xe-(4-C_5F_4N) compound can principally be synthesized but on a different route using the reaction of C_6F_5XeF with Cd(4-$C_5F_4N)_2$. Generally, the hypervalent IF_2 moiety in RIF_2 is more reactive to Lewis acidic transfer reagents than XeF_2. Thus (4-C_5F_4N)BF_2 and *trans*-$CF_3CF{=}CFBF_2$ did not successfully transfer their organo group into XeF_2 but enable the synthesis of the corresponding iodonium salts [C_6F_5(4-C_5F_4N)I][BF_4], [(4-$C_5F_4N)_2$I][BF_4], and [R(*trans*-$CF_3CF{=}CF$)I][BF_4] (R = C_6F_5, *o*-, *m*-, *p*-C_6FH_4). The same approach can be applied to synthesize [R(R′)I][BF_4] salts (R = C_6F_5, *o*-, *m*-, *p*- C_6FH_4, R′ = $CF_2{=}CF$ and C_6H_5) and can be expanded to reagents of the RPF_4 type. The acidity of RAF_{n-1} is an important but not the only factor which determines the result of such fluorine-organyl substitution reactions. Fluoride affinities of organodifluoroboranes and related moderate Lewis acids are helpful tools for planning the transformation of hypervalent triads EF_2 into the corresponding $[RE]^+$ onium salts.

4. Experimental details

NMR spectra were recorded on the Bruker spectrometer AVANCE 300 (^{1}H at 300.13 MHz, ^{11}B at 96.29 MHz, ^{13}C at 75.47 MHz, ^{19}F at 282.40 MHz, and ^{129}Xe at 83.46 MHz). The chemical shifts are referenced to TMS (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$/$CDCl_3$ 15% v/v (^{11}B), CCl_3F (^{19}F) (C_6F_6 as a secondary reference, $\delta = -162.9$), and $XeOF_4$ (XeF_2 as a secondary reference, XeF_2/MeCN/297 K ($c \rightarrow 0$), δ −1813.28 ppm [29]). Low temperature (−60 °C) Raman spectra were recorded on the Bruker FT-Raman spektrometer RFS 100/S. DSC measurements were made with a Netzsch 204/1/g Phoenix instrument. The samples were placed in aluminium pans with a pierced lid and measured under an atmosphere of dry N_2 (heating rate 10 °C/min). Standard quantum chemical calculations were performed with the GAUSSIAN 03 program package [30]. DFT calculations were carried out using the B3LYP method with the basis set 6-31+G* to obtain fluoride affinities pF^-. Optimized geometries were obtained at the RHF/LANL2DZ and RHF/UGBS level. Standard geometries were used as starting points for the structure optimizations, which were performed without any symmetry restrictions.

2,3,5,6-tetrafluoropyridine (4-C_5F_4N)H and (4-C_5F_4N)BF_2 were synthesized according to Refs. [31,22]. Cd(4-$C_5F_4N)_2$ was obtained by decarboxylation of Cd[(4-C_5F_4N)$CO_2]_2$ [32]. *Trans*-$CF_3CF{=}CFBF_2$ was prepared in four steps from $CF_3CF{=}CF_2$ via

trans-$CF_3CF{=}CFH$ [33], Li[*trans*-$CF_3CF{=}CFB(OMe)_3$] [34], and K[*trans*-$CF_3CF{=}CFBF_3$] [34]. $CF_2{=}CFBF_2$ was synthesized according [35], $C_6H_5BF_2$ was obtained from the reaction of $K[C_6H_5BF_3]$ with BF_3 in CH_2Cl_2 analog [28]. *Cis*/*trans*-configuration in olefinic products resulting from the corresponding boranes is related to the position of the B-containing substituent in the parent compound. $C_6H_5PF_4$ was prepared from $C_6H_5PF_2$ and SbF_3 [36]. $C_6F_5IF_2$ was produced by low-temperature fluorination [37] and *x*-$C_6FH_4IF_2$ (*x* = *o*-, *m*-, *p*-) by oxygen–fluorine substitution [34].

4.1. Attempts to prepare 2,3,5,6-tetrafluoropyridin-4-ylxenon compounds

4.1.1. Reaction of 2,3,5,6-tetrafluoropyridin-4-yldifluoroborane with xenon difluoride in methylene chloride under formation of the adduct (4-C_5F_4N)BF_2·XeF_2

A cold solution (−36 °C) of XeF_2 (40 mg, 0.236 mmol) in CH_2Cl_2 (1 ml) was added to a colorless suspension of (4-C_5F_4N)BF_2 (48 mg, 0.235 mmol) in CH_2Cl_2 (3.5 ml, −36 °C). After 10 min of stirring a green–blue solid was formed beside a colorless mother liquor which contained only by-products deriving from attacks on the solvent: CH_2ClF, CCl_2HF, CH_2F_2, (^{19}F NMR, −40 °C). After 1 h at −40 °C the suspension was subdivided into two approximately equal portions. Each was centrifuged (−78 °C). The mother liquors were separated and the solid products were washed with 1 ml CH_2Cl_2 (−50 °C) and dried (HV, 40 min, −50 °C). Two white solids (A and B) resulted.

Caution: The solid product is shock sensitive. Furthermore cooled (≤− 60 °C) samples in FEP tubes (d_i = 3.5 mm) exploded several times during the alignment in the Raman spectrometer.

Raman spectrum of the adduct in FEP (−60 °C): 127 (19), 187 (14), 205 (16), 221 (16), 440 (62), 460 (63), 517 (98), 536.1 (24, ν(Xe–$F_{bridging}$), 548 (12, ν(Xe–$F_{terminal}$), 593 (55), 638 (54), 679 (11), 704 (16), 749 (100), 908 (22), 1169 (10), 1256 (16), 1427 (19), 1508 (22), 1567 (17), 1674 (16) cm^{-1}.

Solid A (∼0.1 mmol) was stored at −78 °C before CH_2Cl_2 (−50 °C, 0.5 ml) was added. The suspension turned green–blue. After addition of a cold $[NBu_4]I$ solution (43 mg, 0.117 mmol) in CH_2Cl_2 (0.77 ml, −50 °C) a light orange solution resulted. After 10 min at −50 °C the temperature was raised to 20 °C. During warming gas bubbles escaped. When the evolution of gas was finished a second portion of $[NBu_4]I$ was added. No further gas evolution could be observed. The ^{19}F NMR spectrum of the solution (−40 °C) showed the presence of $[(4\text{-}C_5F_4N)BF_3]^-$ (89 mol%), $[BF_4]^-$ (9 mol%), and (4-C_5F_4N)H (2 mol%).

Solid B (∼0.1 mmol) was suspended in cold CH_2Cl_2 (1 ml, −48 °C) and turned green–blue. A solution of $[NMe_4]F$ (43 mg, 0.117 mmol) in CH_2Cl_2 (1 ml, −40 °C) was added. ^{19}F monitoring of the suspension at −40 °C indicated only traces of non-reacted $[NMe_4]F$ beside traces of XeF_2. Warming of the suspension to 20 °C within 18 h showed that XeF_2 (11 mol%) was present beside an unknown (4-C_5F_4N) product (δ −83.3 and −123.9, 23 mol%).

In an alternative procedure a cold solution of (4-C_5F_4N)BF_2 (31.6 mg, 0.159 mmol) in CH_2Cl_2 (13,3 ml, −30 °C) was added slowly in five portions to an intensively stirred XeF_2 (33.5 mg, 0.198 mmol) solution in CH_2Cl_2 (5 ml, −45 °C). Within 20 min precipitation proceeded. After 75 min at −40 °C the mother liquor was separated, the solid product washed with CH_2Cl_2 (2 × 3 ml, −40 °C) and dried in vacuum (−40 °C, 2 h). The white product suspended in CH_2Cl_2 at < −40 °C gave the same reaction with $[NBu_4]I$ as described above. The excess of XeF_2 was proved in the mother liquor.

4.1.2. Reaction of 2,3,5,6-tetrafluoropyridin-4-yltrimethylsilan with xenon difluoride in the presence of tetramethylammonium fluoride

(4-C_5F_4N)$Si(CH_3)_3$ (678 mg, 3.04 mmol) was added to a stirred suspension of XeF_2 (333 mg, 1.97 mmol) in CH_2Cl_2 (10 ml, −60 °C). No reaction took place within 15 min (^{19}F NMR). After addition of $[N(CH_3)_3]F$ (51 mg, 0.55 mmol) the mixture turned black immediately. After 10 min (4-C_5F_4N)$Si(CH_3)_3$ had been consumed and the ^{19}F NMR spectrum displayed a mixture (δ (ppm); molar ratio) of Me_3SiF (−158.2, dec, ^3J(F, H) = 7 Hz, ^1J(F, Si) = 274; 100), (4-C_5F_4N)$_2$ (−87.6, m, 4F, $F^{2,6}$ −138.5, m, 4F, $F^{3,5}$; 67) [38], XeF_2 (−175.9, s, ^1J(F, Xe) = 5594 Hz; 22), (4-C_5F_4N)H (−92.3, m, 2F, $F^{2,6}$, −141.0, m, 2F, $F^{3,5}$; 3) [39], C_5F_5N (−87.6, m, 2F, $F^{2,6}$, −133.2m, 1F, F^4, −162.0 m, 2F, $F^{3,5}$; 2), and unknown (4-C_5F_4N)X compounds; 6). After 20 h at −40 °C the distribution of products did not change.

4.1.3. Synthesis of pentafluorophenyl(2,3,5,6-tetrafluoropyridin-4-yl)xenon

Solid Cd(4-C_5F_4N)$_2$ (116 mg, 0.28 mmol) was added to C_6F_5XeF (125 mg, 0.39 mmol) dissolved in CH_2Cl_2 (1 ml, −78 °C). The mixture was diluted with CH_2Cl_2 (1 ml, −78 °C) and after 10 min at −78 °C the suspension (gray solid with a clear mother liquor) was warmed to −50 °C and stirred for 45 min. After sedimentation of the solid at −78 °C the mother liquor was separated. The solid was washed with CH_2Cl_2 (−78 °C, 3 × 0.5 ml). All CH_2Cl_2-phases were combined and evaporated to dryness (HV, −50 °C, 2 h). The white solid residue was washed with pentane (−78 °C, 3 × 1 ml) and dried (HV, −50 °C, 1 h). About 62 mg (<0.14 mmol) of C_6F_5Xe(4-C_5F_4N), still contaminated with decomposition products (see below), were obtained.

C_6F_5Xe(4-C_5F_4N): ^{19}F NMR (CH_2Cl_2, −80 °C) δ −92.2 (m, 2F, $F^{2,6}$, (4-C_5F_4N)), −133.3 (m, 2F, $F^{2,6}$, C_6F_5), −135.0 (m, 2F, $F^{3,5}$, (4-C_5F_4N)), −153.1 (t, ^3J(F^4, $F^{3,5}$) = 21 Hz, 1F, F^4, C_6F_5), −158.6 (m, 2F, $F^{3,5}$, C_6F_5), C_6F_5Xe(4-C_5F_4N) 64.1 mol%, (4-C_5F_4N)Cl (−90.6, m, 2F, $F^{2,6}$, −141.4 m, 2F, $F^{3,5}$; 16 mol%) [40], (4-C_5F_4N)H (7 mol%) [39], C_6F_5(4-C_5F_4N) (4 mol%) [38], C_6F_5H (3 mol%), (C_6F_5)$_2$ (2 mol%), C_6F_6 (2 mol%), (4-C_5F_4N)$_2$ (1 mol%), ^{129}Xe NMR (CH_2Cl_2, −80 °C) δ −4099.8; $\tau_{1/2}$ = 112 Hz).

Solvolysis of C_6F_5Xe(4-C_5F_4N) in aHF: In a 3.5 mm i.d. FEP trap C_6F_5Xe(4-C_5F_4N) (28.3 mg, < 0.063 mmol) was cooled to −78 °C before cold aHF (0.4 ml, −78 °C) was added. After 1 h at −78 °C the ^{19}F NMR spectrum (−80 °C) confirmed the conversion of C_6F_5Xe(4-C_5F_4N) under formation of $[C_6F_5Xe]^+$ (−123.6, m, 2F, $F^{2,6}$, −138.3, m, 2F, F^4, −151.7,

m, 2F, $F^{3,5}$) and (4-C_5F_4N)H in the molar ratio 1.0:0.9. The ^{129}Xe NMR (−80 °C) corroborated the presence of $[C_6F_5Xe]^+$ δ −3917.6 (t, ^3J(Xe, F) = 61 Hz) [20].

4.2. Preparation of 2,3,5,6-tetrafluoropyridin-4-yliodine compounds

4.2.1. 2,3,5,6-tetrafluoropyridin-4-yliodine (4-C_5F_4N)I as starting material

Within 2.5 h a *n*-BuLi solution (80.15 mmol in 32 ml hexane) was added under intensive stirring to a −78 °C cold solution of 2,3,5,6-tetrafluoropyridine (11.532 g, 76.34 mmol) in diethylether (40 ml). The suspension was stirred for 1 h at −78 °C before a solution of ICl (13.01 g, 80.15 mmol) in diethylether (40 ml) was added within 30 min. The crimson solution was warmed to −40 °C and stirred for 2 h before HCl_{aq} (10%, 50 ml) was added. The crimson ether phase was separated and treated with a saturated aqueous solution (50 ml) of Na_2SO_3 till discoloration. The aqueous phase was extracted with diethylether (2 × 25 ml). The combined ether phases were dried over $MgSO_4$. Ether was distilled and the residue treated at 0 °C and 23 h Pa for 10 min till a brown solid resulted which was dissolved in diethylether (10 ml) and evaporated at 20 °C and 23 h Pa. The purification was repeated and the nearly colorless solid was finally sublimed (≤48 °C, 23 hPa). Transparent square shaped prisms were obtained. ^{19}F NMR (CH_3CN, 24 °C) δ −91.3 (m, ^1J(F, C) ≈248 Hz, 2F, $F^{2,6}$) −123.6 (m, ^1J(F, C) = 253 Hz, 2F, $F^{3,5}$), ^{19}F NMR (CH_2Cl_2, 24 °C) δ −90.7 (m, 2F, $F^{2,6}$, −123.7 m, 2F, $F^{3,5}$), ^{13}C{^{1}H} NMR (CH_3CN, 24 °C) δ 144.8 (dm, ^1J(C, F) = 253 Hz, $C^{3,5}$), 143.5 (dm, ^1J(C, F) = 245 Hz, $C^{2,6}$); 114.2 (tt, ^2J(C, F) = 26 Hz, ^3J(C, F) = 2 Hz, C^4) [41]

4.2.2. 2,3,5,6-tetrafluoropyridin-4-yliodine difluoride (4-C_5F_4N)IF_2

XeF_2 (1.208 g, 7.13 mmol) was added to (4-C_5F_4N)I (1.885 g, 6.81 mmol) which was suspended in CH_2Cl_2 (20 ml) at −78 °C. The temperature was raised to ca. 20 °C and after 4 h a solution resulted. Within 20 h transparent crystals were formed. The mother liquor was separated and checked by ^{19}F NMR (CH_2Cl_2, 24 °C) δ −84.9 (m, 2F, $F^{2,6}$ −125.3, m, 2F, $F^{3,5}$, −160.5, s, 2F, IF_2). It still contained (4-C_5F_4N)IF_2, (4-C_5F_4N)I, and XeF_2 in the molar ratio 69:21:10. The crystals were washed (CH_2Cl_2, 1 ml) and dried in vacuum and yielded 1.802 g (84%) (4-C_5F_4N)IF_2. ^{19}F NMR (CH_3CN, 24 °C) δ −86.1 (m, 2F, $F^{2,6}$), −125.8 (m, 2F, $F^{3,5}$), −162.5 (s, 2F, IF_2) ^{13}C{^{1}H} NMR (CH_3CN, 24 °C) δ 144.0 (dm, ^1J(C, F) = 235 Hz, $C^{2,6}$), 140.8 (dm, ^1J(C, F) = 264 Hz, $C^{3,5}$), 118.9 (t, ^2J(C, F) = 24 Hz, C^4).

4.2.3. Pentafluorophenyl(2,3,5,6-tetrafluoropyridyliodonium tetrafluoroborate) [C_6F_5(4-C_5F_4N)I][BF_4]

A cold solution of (4-C_5F_4N)BF_2 (26 mg, 0.131 mmol) in CH_2Cl_2 (6 ml, 0 °C) was added within 30 min to a cold solution of $C_6F_5IF_2$ (65 mg, 0.196 mmol). Immediately a slightly yellow precipitate was formed. After 20 h at 0 °C the mother liquor was separated and the solid product was washed (2 × 4 ml CH_2Cl_2) and dried in vacuum. [C_6F_5(4-C_5F_4N)I][BF_4] was yielded quantitatively.

^{19}F NMR (24 °C, CH_3CN) δ −84.3 (m, 2F, $F^{2,6}$, (4-C_5F_4N)), −119.7 (m, 2F, $F^{2,6}$, C_6F_5), −123.1 (m, 2F, $F^{3,5}$, (4-C_5F_4N)), −140.5 (tt, ^3J(F^4, $F^{3,5}$) = 20 Hz, ^4J(F^4, $F^{2,6}$) = 7 Hz, F^4, C_6F_5), −155.0 (m, 1F, $F^{3,5}$, C_6F_5), −148.8/−148.9 (s, 4F, [$^{10}BF_4$]$^-$/[$^{11}BF_4$]$^-$).

4.2.4. Reaction of pentafluorophenyl(2,3,5,6-tetrafluoropyridyl)iodonium tetrafluoroborate with (2,3,5,6-tetrafluoropyridyl)difluoroborane

A cold solution of (4-C_5F_4N)BF_2 (67 mg, 34 mmol) in CH_2Cl_2 (1 ml, 0 °C) was added to a suspension of [C_6F_5(4-C_5F_4N)I][BF_4] (216 mg, 0.42 mmol) in CH_2Cl_2 (1 ml). The suspension was vigorously stirred in a closed FEP trap. After 5 min the temperature was raised to 20 °C and stirring was continued for 1.5 h. Fuming of BF_3 was observed when a first sample for ^{19}F NMR monitoring was taken. A second sample was taken after 18 h (fuming of BF_3) before the mother liquor was separated. Subsequently, the solid residue was washed and dried in vacuum. The white powder (235 mg) was dissolved in MeCN (0.7 ml) and its composition was determined by ^{19}F NMR.

^{19}F NMR (CH_3CN, 0 °C) δ −85.1 (m, 2F, $F^{2,6}$, [(4-C_5F_4N)RI]$^+$), −123.7 (m, 2F, $F^{3,5}$, [(4-C_5F_4N)RI]$^+$), −120.4 (m, 2F, $F^{2,6}$, [C_6F_5(R′)I]$^+$), −141.2 (t, 1F, F^4, [C_6F_5(R′)I]$^+$), −155.7 (m, 2F, $F^{3,5}$, [C_6F_5(R′)I]$^+$), −149.2 (br, 4F, [BF_4]$^-$), −97.3 (m, 2F, $F^{2,6}$, [(4-C_5F_4N)BF_3]$^-$), −137.7 (m, 2F, $F^{3,5}$, [(4-C_5F_4N)BF_3]$^-$), −134.1 (br, 3F, [(4-C_5F_4N)BF_3]$^-$), molar ratio [C_6F_5(4-C_5F_4N)I]$^+$:[BF_4]$^-$:[(4-C_5F_4N)BF_3]$^-$ = 1:0.63:0.41. [C_6F_5(4-C_5F_4N)I][BF_4] 129 mg, 0.243 mmol, 58% yield, [C_6F_5(4-C_5F_4N)I][(4-C_5F_4N)BF_3] 105 mg, 0.159 mmol, 38% yield.

^{19}F NMR (CH_2C_{12} mother liquor after 1.5 h, 24 °C) δ −81.7 (m, 2F, $F^{2,6}$, [(4-C_5F_4N)RI]$^+$), −122.1 (m, 2F, $F^{3,5}$, [(4-C_5F_4N)RI]$^+$), −118.1 (m, 2F, $F^{2,6}$, [C_6F_5(R′)I]$^+$), −136.2 (t, ^3J(F^4, $F^{3,5}$) = 20 Hz, 1F, F^4, [C_6F_5(R′)I]$^+$), −153.0 (m, 2F, $F^{3,5}$, [C_6F_5(R′)I]$^+$), −92.6 (br, 2F, $F^{2,6}$, [((4-C_5F_4N)BF_2)$_n$F]$^-$), −134.6 (br, 2F, $F^{3,5}$, [((4-C_5F_4N)BF_2)$_n$F]$^-$), −96.3 (br, [((4-C_5F_4N)BF_2)$_n$F]$^-$), molar ratio of (4-C_5F_4N) groups cation: anion = 1:2.6.

^{19}F NMR (CH_2Cl_2 mother liquor after 18 h, 24 °C) δ −81.4 (m, 2F, $F^{2,6}$, [(4-C_5F_4N)RI]$^+$), −122.7 (m, 2F, $F^{3,5}$, [(4-C_5F_4N)RI]$^+$), −117.8 (m, 2F, $F^{2,6}$, [C_6F_5(R′)I]$^+$), −136.0 (t, ^3J(F^4, $F^{3,5}$) = 20 Hz, 1F, F^4, [C_6F_5(R′)I]$^+$), −153.0 (m, 2F, $F^{3,5}$, [C_6F_5(R′)I]$^+$), −95.5 (br, 2F, $F^{2,6}$, [((4-C_5F_4N)BF_2)$_n$F]$^-$), −139.4 (br, 2F, $F^{3,5}$, [((4-C_5F_4N)BF_2)$_n$F]$^-$), −122.9 (br, [((4-C_5F_4N)BF_2)$_n$F]$^-$), molar ratio of (4-C_5F_4N) groups cation:anion ≈ 1:1, content of [C_6F_5(4-C_5F_4N)I][(4-C_5F_4N)BF_3] (determined by the internal quantitative standard $C_6H_5CF_3$) 0.01 mmol, 3%.

4.2.5. Synthesis of bis(2,3,5,6-tetrafluoropyridin-4-yl)iodonium tetrafluoroborate [(4-C_5F_4N)$_2$I][BF_4]

Over a period of 30 min a cold solution of (4-C_5F_4N)BF_2 (105.8 mg, 0.53 mmol) in CH_2Cl_2 (15 ml, 0 °C) was added in five portions to a stirred solution of (4-C_5F_4N)IF_2 (244 mg, 0.78 mmol) in CH_2Cl_2 (5 ml, 0 °C) in a 23 mm i.d. FEP trap.

After 10 min a white tarnish appeared. ^{19}F NMR monitoring proceeded after 90 min at 0 °C. The content of the mother liquor ((4-C_5F_4N)IF_2 (59.0 mg, 0.19 mmol) and (4-C_5F_4N)I (0.016 mg, 0.057 mmol)) was determined using the quantitative internal standard benzotrifluoride. Following the temperature was raised to 20 °C and kept for 1.5 h. The suspension was centrifuged, the mother liquor separated, and the solid residue washed three times with CH_2Cl_2 (3, 2, and finally 1 ml). The yield after drying (HV, 20 °C, 45 min) was 240 mg (0.47 mmol, 88%).

^{19}F NMR (CH_3CN, 24 °C) δ −83.9 (m, 2F, $F^{2,6}$) −122.5 (m, 2F, $F^{3,5}$), −148.8 (s, 4F, $[BF_4]^-$), minor impurities: (4-C_5F_4N)IF_2 (0.8 mol%), (4-C_5F_4N)I (1.1 mol%), $[AsF_6]^-$ (1.7 mol%); ^{13}C{^{1}H} NMR (CH_3CN, 24 °C) δ 144.3 (dm, ^1J(C, F) = 250 Hz, $C^{2,6}$), 142.7 (dm, ^1J(C, F) = 267 Hz, $C^{3,5}$), 106.8 (t, ^2J(C, F) = 25 Hz, C^4).

4.3. Preparation of pentafluorophenyl(trans-1,2,3,3,3-pentafluoroprop-1-enyl)- and pentafluorophenyl(trifluorovinyl)iodonium tetrafluoroborate

4.3.1. Pentafluorophenyl(trans-1,2,3,3,3-pentafluoroprop-1-enyl)iodonium tetrafluoroborate

A solution of *trans*-1,2,3,3,3-pentafluoroprop-1-enyldifluoroborane (2.44 mmol) in CH_2Cl_2 (20 ml; −78 °C) was added in eight equal portions over a period of 0.5 h to the cold stirred solution of $C_6F_5IF_2$ (863 mg, 2.60 mmol) in CH_2Cl_2 (10 ml, −60 °C) in a 23 mm i.d. FEP trap. The resulting suspension was stirred for further 0.5 h at −50 °C and then warmed to 20 °C within 1 h. The mother liquor was separated and the white solid residue washed with CH_2Cl_2 (4 × 10 ml) to remove the slight excess of $C_6F_5IF_2$. After drying in HV at 20 °C the iodonium salt was stored in a FEP vessel under an atmosphere of dry argon at 20 °C. Yield of $[C_6F_5$(*trans*-$CF_3CF{=}CF)I][BF_4]$ 1.1 g (2.25 mmol, 92%), melting point (sealed capillary) 160–162 °C, DSC: T_{onset} 161.2 °C (endothermal process).

[C_6F_5(trans-CF_3CF=CF)I][BF_4] ^{19}F NMR (CD_3CN, 24 °C) δ −67.4 (dd, 3F, $^3J(F^3, F^2)$ = 19 Hz, $^4J(F^3, F^1)$ = 10 Hz, F^3, alkenyl), −117.8 (dqt, 1F, $^3J(F^2, F^1)$ = 139 Hz, $^3J(F^2, F^3)$ = 19 Hz, $^6J(F^2, F^{2,6})$ = 4 Hz, F^2, alkenyl), −119.6 (m, 2F, $F^{2,6}$, C_6F_5), −138.2 (dqt, 1F, $^3J(F^1, F^2)$ = 139 Hz, $^4J(F^1, F^3)$ = 10 Hz, $^5J(F^1, F^{2,6})$ = 5 Hz, F^1, alkenyl), −140.0 (tt, 1F, $^3J(F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, F^4, C_6F_5), −147.9.0 (s, 4F, BF_4), −154.9 (m, 2F, $F^{3,5}$, C_6F_5); ^{19}F NMR (CD_3NO_2, 24 °C) δ −66.9 (dd, 3F, $^3J(F^3, F^2)$ = 19 Hz, $^4J(F^3, F^1)$ = 10 Hz, F^3, alkenyl), −117.6 (dqt, 1F, $^3J(F^2, F^1)$ = 139 Hz, $^3J(F^2, F^3)$ = 19 Hz, $^6J(F^2, F^{2,6})$ = 4 Hz, F^2, alkenyl), −119.3 (m, 2F, $F^{2,6}$, C_6F_5), −138.2 (dqt, 1F, $^3J(F^1, F^2)$ = 139 Hz, $^4J(F^1, F^3)$ = 10 Hz, $^5J(F^1, F^{2,6})$ = 5 Hz, F^1, alkenyl), −139.8 (tt, 1F, $^3J(F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, F^4, C_6F_5), −147.4 (s, 4F, BF_4), −154.6 (m, 2F, $F^{3,5}$, C_6F_5); ^{11}B NMR (CD_3CN, 24 °C) δ −1.4 (s, BF_4); ^{13}C NMR (CD_3NO_2, 24 °C) δ 147.8 (dm, $^1J(C^4, F^4)$ = 264 Hz, C^4, C_6F_5), 147.6 (dm, $^1J(C^{2,6}, F^{2,6})$ = 256 Hz, $C^{2,6}$, C_6F_5), 145.1 (dqd, $^1J(C^2, F^2)$ = 268 Hz, $^2J(C^2, F^3)$ = 44 Hz, $^2J(C^2, F^1)$ = 30 Hz, C^2, alkenyl), 138.6 (dm, $^1J(C^{3,5}, F^{3,5})$ = 257 Hz, $C^{3,5}$, C_6F_5), 127.5 (ddm, $^1J(C^1, F^1)$ = 354 Hz, $^2J(C^1, F^2)$ = 63 Hz, C^1, alkenyl), 116.2 (qdd, $^1J(C^3, F^3)$ = 277 Hz, $^2J(C^3, F^2)$ = 36 Hz, $^3J(C^3, F^1)$ = 5 Hz, C^3, alkenyl), 84.6 (tm, $^2J(C^1, F^{2,6})$ = 26 Hz, C^1, C_6F_5).

4.3.2. Pentafluorophenyl(trifluorovinyl)iodonium tetrafluoroborate

The preparation proceeded analog to that of $[C_6F_5$(*trans*-$CF_3CF{=}CF)I][BF_4]$ starting from pentafluoro(difluoroiodo)-benzene (664 mg, 2.00 mmol) in CH_2Cl_2 (10 ml) at −60 °C and trifluorovinylborane $CF_2{=}CFBF_2$ (1.82 mmol) as CH_2Cl_2 solution (20 ml; −78 °C). Yield of $[C_6F_5(CF_2{=}CF)I][BF_4]$ 760 mg (1.65 mmol, 91%), melting point (sealed capillary) 108–110 °C, DSC: T_{onset} 109.7 °C (endothermal process).

[$C_6F_5(CF_2{=}CF)I][BF_4$] ^{19}F NMR (CH_3CN, 24 °C) δ −77.2 (dd, 1F, $^3J(F^{2(trans)}, F^1)$ = 61 Hz, $^2J(F^{2(trans)}, F^{2(cis)})$ = 27 Hz, $F^{2(trans)}$, alkenyl), −95.7 (ddt, 1F, $^3J(F^{2(cis)}, F^1)$ = 125 Hz, $^2J(F^{2(cis)}, F^{2(trans)})$ = 27 Hz, $^6J(F^{2(cis)}, F^{2,6})$ = 5 Hz, $F^{2(cis)}$, alkenyl), −120.5 (m, 2F, $F^{2,6}$, C_6F_5), −140.9 (tt, 1F, $^3J(F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, F^4, C_6F_5), −148.1 (s, $\tau_{1/2}$ = 4 Hz, 4F, BF_4), −155.3 (m, 2F, $F^{3,5}$, C_6F_5), −157.0 (ddt, 1F, $^3J(F^1, F^{2(cis)})$ = 125 Hz, $^3J(F^1, F^{2(trans)})$ = 61 Hz, $^5J(F^1, F^{2,6})$ = 3 Hz, F^1, alkenyl); ^{19}F NMR (CH_2Cl_2, 24 °C) δ −75.3 (dd, 1F, $^3J(F^{2(trans)}, F^1)$ = 63 Hz, $^2J(F^{2(trans)}, F^{2(cis)})$ = 17 Hz, $F^{2(trans)}$, alkenyl), −94.9 (ddt, 1F, $^3J(F^{2(cis)}, F^1)$ = 127 Hz, $^2J(F^{2(cis)}, F^{2(trans)})$ = 17 Hz, $^6J(F^{2(cis)}, F^{2,6})$ = 4 Hz, $F^{2(cis)}$, alkenyl), −119.5 (m, 2F, $F^{2,6}$, C_6F_5), −137.8 (tt, 1F, $^3J(F^4, F^{3,5})$ = 21 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, F^4, C_6F_5), −142.0 (s, $\tau_{1/2}$ = 4 Hz, 4F, BF_4), −153.8 (m, 2F, $F^{3,5}$, C_6F_5), −156.5 (ddt, 1F, $^3J(F^1, F^{2(cis)})$ = 127 Hz, $^3J(F^1, F^{2(trans)})$ = 63 Hz, $^5J(F^1, F^{2,6})$ = 3 Hz, F^1, alkenyl); ^{11}B NMR (CH_3CN, 24 °C); δ −1.4 (s, $\tau_{1/2}$ = 2 Hz, BF_4); ^{11}B NMR (CD_3NO_2, 24 °C) δ −1.4 (s, $\tau_{1/2}$ = 5 Hz, BF_4); ^{13}C NMR (CD_3NO_2, 24 °C) δ 156.3 (ddd, $^1J(C^2, F^{2(cis)})$ = 313 Hz, $^1J(C^2, F^{2(trans)})$ = 290 Hz, $^2J(C^2, F^1$ = 31 Hz, C^2, alkenyl), 147.4 (dm, $^1J(C^4, F^4)$ = 263 Hz, C^4, C_6F_5), 147.3 (dm, $^1J(C^2, F^2)$ = 258 Hz, $C^{2,6}$, C_6F_5), 138.5 (dm, $^1J(C^3, F^{3,5})$ = 257 Hz, $C^{3,5}$, C_6F_5), 103.2 (ddd, $^1J(C^1, F^1)$ = 327 Hz, $^2J(C^1, F^{2(trans)})$ = 64 Hz, $^2J(C^1, F^{2(cis)})$ = 31 Hz, C^1, alkenyl), 85.8 (tm, $^2J(C^1, F^{2,6})$ = 26 Hz, C^1, C_6F_5).

4.3.3. The preparation of monofluorophenyl(trans-1,2,3,3,3-pentafluoroprop-1-enyl)iodonium and monofluorophenyl (perfluorovinyl)iodonium tetrafluoroborates, [o-, m-, and p-C_6H_4F(trans-$CF_3CF{=}CF)I][BF_4$] and [o-, m-, and p-$C_6H_4F(CF_2{=}CF)I][BF_4$], general procedure

Monofluoro(difluoroiodo)benzenes (3–4 mmol) were dissolved in CH_2Cl_2 (approximately 12–15 ml) at −60 °C in a 23 mm i.d. FEP trap provided with a suitable stirring bar. Under intensive stirring the appropriate quantity (93–98%) of *trans*-1,2,3,3,3-pentafluoroprop-1-enylborane, *trans*-$CF_3CF{=}CFBF_2$, or perfluorovinyldifluorborane, $CF_2{=}CFBF_2$, was added as CH_2Cl_2 solution (conc. approximately 0.20 mmol/ml, −78 °C) in 8–10 equal portions over a period of 30 min. The resulting suspension was stirred for further 0.5 h. The mother liquor was separated from the light yellowish solid. The solid was washed with CH_2Cl_2 (2 × 5 ml) at −50 °C to remove the slight excess of monofluorodifluoroiodobenzenes. The salt was dried at ≥ −78 °C in high vacuum. The mother liquor and the CH_2Cl_2 washing solutions were combined, evaporated (HV, ≥ −78 °C),

and the solid residue was washed with *n*-pentane (3 × 5 ml) to remove non-reacted monofluoro(difluoroiodo)benzenes. The reaction products were characterized by ^{19}F, ^{13}C, ^{1}H, and ^{11}B spectroscopy. The salts can be stored over months under dry argon at −70 °C.

o-Fuorophenyl(trans-1,2,3,3,3-pentafluoroprop-1-enyl)iodonium tetrafluoroborate prepared from 453.4 mg (1.74 mmol) *o*-$C_6H_4FIF_2$ and 309.6 mg (1.72 mmol) *trans*-$CF_3CF{=}CFBF_2$ in 15 ml CH_2Cl_2; yield 527 mg (1.2 mmol) isolated from the primary precipitation and 50 mg (0.11 mmol, 6.4%) from the mother liquor; overall yield 577 mg (1.31 mmol, 76%).

[o-C_6H_4F(trans-CF_3CF=CF)I][BF_4] ^{19}F NMR (CH_2Cl_2, −40 °C) δ −67.7 (dd, 3F, $^3J(F^3, F^2)$ = 19 Hz, $^4J(F^3, F^1)$ = 11 Hz, F^3, alkenyl), −93.1 (dtdd, 1F, $^3J(F, H^3)$ = 10 Hz, $^4J(F, H^4)$ = 9 Hz, $^5J(F, F^1)$ = 5 Hz, $^6J(F, F^2)$ = 5 Hz, *o*-C_6H_4F), −119.4 (dqd, 1F, $^3J(F^2, F^1)$ = 141 Hz, $^3J(F^2, F^3)$ = 19 Hz, $^6J(F^2, F^{2,6})$ = 4 Hz, F^2, alkenyl), −138.2 (dqd, 1F, $^3J(F^1, F^2)$ = 141 Hz, $^4J(F^1, F^3)$ = 11 Hz, $^5J(F^1, F^{2,6})$ = 6 Hz, F^1, alkenyl), −141.8 (s, 4F, BF_4); ^1H NMR (CH_2Cl_2, 24 °C) δ 8.4 (ddd, $^3J(H^6, H^5)$ = 8 Hz, $^4J(H^6, F)$ = 6 Hz, $^6J(H^6, H^4)$ = 2 Hz, H^6), 8.0 (ddd, $^3J(H^3, F)$ = 9 Hz, $^3J(H^3, H^4)$ = 7 Hz, $^4J(H^3, H^5)$ = 2 Hz, H^3), 7.7 (ddd, $^3J(H^5, H^6)$ = 8 Hz, $^3J(H^5, H^4)$ = 8 Hz, $^4J(H^5, H^3)$ = 1 Hz, H^5), 7.6 (ddd, $^3J(H^4, H^3)$ = 8 Hz, $^3J(H^4, H^5)$ = 8 Hz, $^4J(H^4, H^6)$ = 1 Hz, H^4); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −1.3 (s, BF_4); $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ 160.8 (d, $^1J(C^2, F^2)$ = 257 Hz, C^2, aryl), 145.2 (ddq, $^1J(C^2, F^2)$ = 267 Hz, $^2J(C^2, F^1)$ = 44 Hz, $^2J(C^2, F^3)$ = 31 Hz, C^2, alkenyl), 138.8 (d, $^3J(C^4, F)$ = 8 Hz, C^4), 138.4 (s, C^5), 129.3 (d, $^3J(C^6, F)$ = 3 Hz, C^6), 125.4 (ddq, $^1J(C^1, F^1)$ = 351 Hz, $^2J(C^1, F^2)$ = 62 Hz, $^3J(C^1, F^3)$ = 3 Hz, C^1, alkenyl), 118.7 (d, $^2J(C^3, F)$ = 21 Hz, C^3), 116.5 (qdd, $^1J(C^3, F^3)$ = 277 Hz, $^2J(C^3, F^2)$ = 36 Hz, $^3J(C^3, F^1)$ = 5 Hz, C^3, alkenyl), 98.1 (d, $^2J(C^1, F)$ = 23 Hz, C^1).

m-Fluorophenyl(trans-1,2,3,3,3-pentafluoroprop-1-enyl)iodonium tetrafluoroborate prepared from 824 mg (3.17 mmol) *m*-$C_6H_4FIF_2$ and 606 mg (3.37 mmol) *trans*-$CF_3CF{=}CFBF_2$ in 15 ml CH_2Cl_2; yield 672 mg (1.53 mmol, 45.4%) isolated from the primary precipitation and 374 mg (0.85 mmol, 25.2%) from the mother liquor; overall yield 1046 mg (2.37 mmol, 70.6%).

[m-C_6H_4F(trans-CF_3CF=CF)I][BF_4] ^{19}F NMR (CH_2Cl_2, 24 °C) δ −68.4 (dd, 3F, $^3J(F^3, F^2)$ = 19 Hz, $^4J(F^3, F^1)$ = 11 Hz, F^3, alkenyl), −103.5 (ddd, 1F, $^3J(F, H^{2,4})$ = 8 Hz, $^4J(F, H^5)$ = 7 Hz, *m*-C_6H_4F), −120.1 (dq, 1F, $^3J(F^2, F^1)$ = 142 Hz, $^3J(F^2, F^3)$ = 19 Hz, F^2, alkenyl), −139.1 (dq, 1F, $^3J(F^1, F^2)$ = 142 Hz, $^4J(F^1, F^3)$ = 11 Hz, F^1, alkenyl), −142.5 (s, 4F, BF_4); ^1H NMR (CH_2Cl_2, 24 °C) δ 8.2 (d, $^3J(H^2, F)$ = 9 Hz, H^2), 8.1 (d, $^3J(H^6, H^5)$ = 8 Hz, H^6), 7.9 (ddd, $^3J(H^5, H^6)$ = 8 Hz, $^3J(H^5, H^4)$ = 8 Hz, $^4J(H^5, F)$ = 6 Hz, H^5), 7.7 (ddd, $^3J(H^4, H^5)$ = 8 Hz, $^3J(H^4, F)$ = 8 Hz, $^4J(H^4, H^6)$ = 2 Hz, H^4); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.1 (s, BF_4); $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ 163.6 (d, $^1J(C^3, F^3)$ = 259 Hz, C^3, aryl), 144.9 (ddq, $^1J(C^2, F^2)$ = 267 Hz, $^2J(C^2, F^3)$ = 44 Hz, $^2J(C^2, F^1)$ = 30 Hz, C^2, alkenyl), 134.9 (d, $^3J(C^5, F)$ = 8 Hz, C^5), 133.3 (d, $^4J(C^6, F)$ = 4 Hz, C^6), 125.5 (ddq, $^1J(C^1, F^1)$ = 352 Hz, $^2J(C^1, F^2)$ = 62 Hz, $^3J(C^1, F^3)$ = 3 Hz, C^1, alkenyl), 124.7 (d, $^2J(C^2, F)$ = 26 Hz, C^2), 122.8 (d, $^2J(C^4, F)$ = 21 Hz, C^4), 116.4 (ddd, $^1J(C^3, F^3)$ = 277 Hz, $^2J(C^3, F^2)$ = 36 Hz, $^3J(C^3, F^1)$ = 5 Hz, C^3, alkenyl), 110.2 (d, $^3J(C^1, F)$ = 9 Hz, C^1).

p-Fluorophenyl(*trans*-1,2,3,3,3-pentafluoroprop-1-enyl)iodonium tetrafluoroborate prepared from 796.55 mg (3.063 mmol) *p*-$C_6H_4FIF_2$ and 532 mg (2.96 mmol) *trans*-$CF_3CF{=}CFBF_2$ in 15 ml CH_2Cl_2; yield 500 mg (1.14 mmol, 38.5%) isolated from the primary precipitation and 602 mg (1.37 mmol, 46.3%) from the mother liquor; overall yield 1102 mg (2.51 mmol, 84.8%).

[p-C_6H_4F(trans-CF_3CF=CF)I][BF_4] ^{19}F NMR (CH_2Cl_2, 24 °C) δ −68.6 (dd, 3F, $^3J(F^3, F^2)$ = 19 Hz, $^4J(F^3, F^1)$ = 11 Hz, F^3, alkenyl), −101.4 (tt, 1F, $^3J(F, H^{5,3})$ = 8 Hz, $^4J(F, H^{2,6})$ = 4 Hz, *p*-C_6H_4F), −120.8 (dq, 1F, $^3J(F^2, F^1)$ = 142 Hz, $^3J(F^2, F^3)$ = 19 Hz, F^2, alkenyl), −140.2 (dq, 1F, $^3J(F^1, F^2)$ = 142 Hz, $^4J(F^1, F^3)$ = 11 Hz, F^1, alkenyl), −142.5 (s, 4F, BF_4); ^1H NMR (CH_2Cl_2, 24 °C) δ 8.4 (dd, 2H, $^3J(H^2, H^3)$ = 9 Hz, $^4J(H^2, F)$ = 5 Hz, $H^{2,6}$), 7.5 (dd, 2H, $^3J(H^3, H^2)$ = 9 Hz, $^3J(H^2, F)$ = 8 Hz, $H^{3,5}$); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.2 (s, BF_4); $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ 166.3 (d, $^1J(C^4, F^4)$ = 259 Hz, C^4, aryl), 144.2 (dqd, $^1J(C^2, F^2)$ = 266 Hz, $^2J(C^2, F^3)$ = 43 Hz, $^2J(C^2, F^1)$ = 31 Hz, C^2, alkenyl), 139.9 (d, $^3J(C^{2,6}, F)$ = 10 Hz, $C^{2,6}$), 125.0 (ddq, $^1J(C^1, F^1)$ = 350 Hz, $^2J(C^1, F^2)$ = 63 Hz, $^3J(C^1, F^3)$ = 3 Hz, C^1, alkenyl), 121.0 (d, $^2J(C^{3,5}, F)$ = 23.4, $C^{3,5}$), 116.0 (qdd, $^1J(C^3, F^3)$ = 277 Hz, $^2J(C^3, F^2)$ = 36 Hz, $^3J(C^3, F^1)$ = 5 Hz, C^3), 104.4 (s, C^1).

o-Fluorophenyl(perfluorovinyl)iodonium tetrafluoroborate prepared from 1000 mg (3.85 mmol) *o*-$C_6H_4FIF_2$ and 480 mg (3.69 mmol) $CF_2{=}CFBF_2$ in 15 ml CH_2Cl_2; yield 745 mg (1.91 mmol, 51.8%) isolated from the primary precipitate and 496 mg (1.27 mmol, 34.4%) from the mother liquor; overall yield 1241 mg (3.18 mmol, 86.2%).

[o-$C_6H_4F(CF_2{=}CF)$I][BF_4] ^{19}F NMR (CH_2Cl_2, 24 °C) δ −79.0 (dd, 1F, $^3J(F^{2(trans)}, F^1)$ = 61 Hz, $^2J(F^{2(trans)}, F^{2(cis)})$ = 25 Hz, $F^{2(trans)}$), −94.8 (m, 1F, *o*-C_6H_4F), −98.0 (ddd, 1F, $^3J(F^{2(cis)}, F^1)$ = 127 Hz, $^2J(F^{2(cis)}, F^{2(trans)})$ = 25 Hz, $^6J(F^{2(cis)}, F^2))$ = 6 Hz, $F^{2(cis)}$), −143.6 (s, 4F, BF_4) −157.8 (ddd, 1F, $^3J(F^1, F^{2(cis)})$ = 127 Hz, $^3J(F^1, F^{2(trans)})$ = 61 Hz, $^5J(F^1, F^2)$ = 4 Hz, F^1); ^1H NMR (CH_2Cl_2, 24 °C) δ 8.3 (dd, 1H, $^3J(H^3, F)$ = 7 Hz, $^3J(H^3, H^4)$ = 7 Hz, 1H, H^3), 7.9 (dd, 1H, $^4J(H^6, F)$ = 7 Hz, $^3J(H^6, H^5)$ = 7 Hz, H^6), 7.6 (dd, 1H, $^3J(H^4, H^5)$ = 8 Hz, $^3J(H^4, H^3)$ = 8 Hz, H^4); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.3 (s, BF_4); $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ 160.1 (d, $^1J(C^2, F^2)$ = 256 Hz, C^2, aryl), 155.3 (ddd, $^1J(C^2, F^{2(cis)})$ = 312, $^1J(C^2, F^{2(trans)})$ = 290 Hz, $^2J(C^2, F^1)$ = 32 Hz, C^2, alkenyl), 137.8 (d, $^3J(C^4, F)$ = 8 Hz, C^4), 137.9 (s, C^5), 128.4 (d, $^3J(C^6, F)$ = 3 Hz, C^6), 117.9 (d, $^2J(C^3, F)$ = 21 Hz, C^3), 100.5 (ddd, $^1J(C^1, F^1)$ = 325 Hz, $^2J(C^1, F^{2(trans)})$ = 63.3, $^2J(C^1, F^{2(cis)})$ = 30 Hz, C^1, alkenyl), 98.7 (d, $^2J(C^1, F)$ = 23 Hz, C^1).

m-Fluorophenyl(perfluorovinyl)iodonium tetrafluoroborate prepared from 1040.3 mg (4.00 mmol) *m*-$C_6H_4FIF_2$ and 486.2 mg (3.74 mmol) $CF_2{=}CFBF_2$ in 15 ml CH_2Cl_2; yield 650 mg (1.66 mmol, 44.9%) isolated from the primary precipitate and 496 mg (1.27 mmol, 34%) from the mother liquor; overall yield 1146 mg (2.93 mmol, 78.9%).

[m-$C_6H_4F(CF_2{=}CF)$I][BF_4] ^{19}F NMR (CH_2Cl_2, 24 °C) δ −79.1 (dd, 1F, $^2J(F^{2(trans)}, F^1)$ = 60 Hz, $^2J(F^{2(trans)}, F^{2(cis)})$ = 26 Hz, $F^{2(trans)}$, alkenyl), −98.6 (ddm, 1F, $^3J(F^{2(cis)}, F^1)$ = 127 Hz, $^2J(F^{2(cis)}, F^{2(trans)})$ = 26 Hz, $F^{2(cis)}$, alkenyl),

−104.3 (dd, 1F, ^{3}J(F, H^{2}) = 8 Hz, ^{3}J(F, H^{4}) = 7 Hz, *m*-C_6H_4F), −143.2 (s, 4F, BF_4). −158.1 (dd, 1F, ^{3}J(F^{1}, F$^{2(cis)}$) = 127 Hz, ^{3}J(F^{1}, F$^{2(trans)}$) = 60 Hz, F^{1}, alkenyl); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.2 (s, *B*F_4); ^{1}H NMR (CH_2Cl_2, 24 °C) δ 8.8 (m, 1H), 8.0 (m, 1H), 7.8 (m, 1H), 7.6 (m, 1H); ^{13}C{^{1}H} NMR (CH_2Cl_2, 24 °C) δ 163.0 (d, ^{1}J(C^{3}, F^{3}) = 258 Hz, C^{3}, aryl), 155.3 (ddd, ^{1}J(C^{2}, F$^{2(cis)}$) = 312.4 Hz, ^{1}J(C^{2}, F$^{2(trans)}$) = 289 Hz, ^{2}J(C^{2}, F^{1}) = 32 Hz, C^{2}, alkenyl), 134.2 (d, ^{3}J(C^{5}, F) = 8 Hz, C^{5}), 132.2 (d, ^{4}J(C^{6}, F) = 4 Hz, C^{6}), 123.4 (d, ^{2}J(C^{2}, F) = 26 Hz, C^{2}), 121.8 (d, ^{2}J(C^{4}, F) = 21 Hz, C^{4}), 111.2 (d, ^{3}J(C^{1}, F) = 8 Hz, C^{1}), 100.5 (ddd, ^{1}J(C^{1}, F^{1}) = 324 Hz, ^{2}J(C^{1}, F$^{2(trans)}$) = 63 Hz, ^{2}J(C^{1}, F$^{2(cis)}$) = 30 Hz, C^{1}, alkenyl).

p-Fluorophenyl(perfluorovinyl)iodonium tetrafluoroborate prepared from 1050 mg (4.04 mmol) *p*-$C_6H_4FIF_2$ 479.7 mg (3.69 mmol) and CF_2=CFBF_2 in 15 ml CH_2Cl_2; yield 940 mg (2.41 mmol, 65.3%) isolated from the primary precipitate and 410 mg (1.05 mmol, 28.5%) from the mother liquor; overall yield 1350 mg (3.46 mmol, 93.8%).

[p-$C_6H_4F(CF_2$=$CF)I][BF_4] ^{19}F NMR ($CH_2Cl_2$, 24 °C) δ −79.0 (dd, 1F, ^{3}J(F$^{2(trans)}$, F^{1}) = 60 Hz, ^{2}J(F$^{2(trans)}$, F$^{2(cis)}$) = 27 Hz, F$^{2(trans)}$, alkenyl), 98.9 (dd, 1F, ^{3}J(F$^{2(cis)}$, F^{1}) = 127 Hz, ^{2}J(F$^{2(cis)}$, F$^{2(trans)}$) = 27 Hz, F$^{2(cis)}$, alkenyl), −101.7 (m, 1F, *p*-C_6H_4F), −143.9 (s, 4F, BF_4) −157.9 (dd, 1F, ^{3}J(F^{1}, F$^{2(cis)}$) = 127 Hz, ^{3}J(F^{1}, F$^{2(trans)}$) = 60 Hz, F^{1}, alkenyl); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.1 (s, *B*F_4); ^{1}H NMR (CH_2Cl_2, 24 °C) δ 8.3 (m, 2H, H^{3,5}), 7.5 (m, 2H, H^{2,6}); ^{13}C{^{1}H} NMR (CH_2Cl_2, 24 °C) δ 166.1 (d, ^{1}J(C^{4}, F^{4}) = 258 Hz, C^{4}, aryl), 155.1 (ddd, ^{1}J(C^{2}, F$^{2(cis)}$) = 312.2, ^{1}J(C^{2}, F$^{2(trans)}$) = 289 Hz, ^{2}J(C^{2}, F^{1}) = 32 Hz, C^{2}, alkenyl), 139.1 (d, ^{3}J(C^{2,6}, F) = 10 Hz, C^{2,6}), 120.7 (d, ^{2}J(C^{3,5}, F) = 23 Hz, C^{3,5}), 105.8 (s, C^{1}), 100.6 (ddd, ^{1}J(C^{1}, F^{1}) = 324 Hz, ^{2}J(C^{1}, F$^{2(trans)}$) = 63 Hz, ^{2}J(C^{1}, F$^{2(cis)}$) = 29 Hz, C^{1}, alkenyl).

4.3.4. Preparation of monofluorophenyl(phenyl)iodonium tetrafluoroborates, [o-, m-, and p-$C_6H_4F(C_6H_5)I][BF_4]$, general procedure

Monofluoro(difluoroiodo)benzenes (2–3 mmol) were dissolved in CH_2Cl_2 (12 ml) at 20 °C in a 23 mm i.d. FEP trap. Under intensive stirring 90–95% of the equimolar quantity of phenyldifluoroborane was added as CH_2Cl_2 solution (concentration approximately 0.24 mmol/ml) in five equal portions within 20 min. The resulting suspension was stirred for additional 0.5 h. The mother liquor was separated from the light yellowish solid. The solid was washed with CH_2Cl_2 at −50 °C (2 × 5 ml) and dried in vacuum at ≤ 20 °C. The products were characterized by ^{19}F, ^{13}C, ^{1}H, and ^{11}B spectroscopy. The melting points of the products were determined in sealed glass capillaries under argon. The salts were stored under a dry atmosphere of argon at ambient temperature.

o-Fluorophenyl(phenyl)iodonium tetrafluoroborate prepared from 710 mg (2.73 mmol) *o*-$C_6H_4FIF_2$ and 340 mg (2.70 mmol) $C_6H_5BF_2$ in 15 ml CH_2Cl_2; yield 520 mg (1.35 mmol, 49.9%) isolated from the primary precipitation and 416 mg (1.08 mmol, 40.0%) from the mother liquor; overall yield 936 mg, 89.9%; melting point: 140–142 °C.

[o-$C_6H_4F(C_6H_5)I][BF_4]$ ^{19}F NMR (CH_2Cl_2, 24 °C) δ −95.5 (ddd, 1F, ^{3}J(F, H^{3}) = 8 Hz, ^{4}J(F, H^{4}) = 6 Hz, ^{4}J(F, H^{6}) = 6 Hz, *o*-C_6H_4F), −146.6 (s, 4F, BF_4); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.1 (s, *B*F_4, $\tau_{1/2}$ = 4 Hz); ^{1}H NMR (CH_2Cl_2, 24 °C) δ 8.3 (dd, 1H, ^{3}J(H^{3}, F) = 7 Hz, ^{3}J(H^{3}, H^{4}) = 7 Hz, H^{3}(*o*-C_6H_4F)), 8.2 (m, 2H), 7.9–7.8 (m, 2H), 7.7 (m, 2H), 7.6 (m, 2H); ^{13}C{^{1}H} NMR (CH_2Cl_2, 24 °C) δ 160.5 (d, ^{1}J(C^{2}, F^{2}) = 254 Hz, C^{2}), 137.9 (s, C^{5}), 136.4 (d, ^{3}J(C^{6}, F) = 8 Hz, C^{6}), 135.9 (s, C$^{3',5'}$, phenyl), 133.5(s, C$^{4'}$, phenyl), 132.9 (s, C$^{2',6'}$, phenyl), 127.8 (d, ^{3}J(C^{4}, F) = 3 Hz, C^{4}), 117.3 (d, ^{2}J(C^{3}, F) = 22 Hz, C^{3}), 112.7 (s, C$^{1'}$, phenyl), 98.5 (d, ^{2}J(C^{1}, F) = 23 Hz, C^{1}).

m-Fluorophenyl(phenyl)iodonium tetrafluoroborate prepared from 800 mg (3.076 mmol) *m*-$C_6H_4FIF_2$ and 370 mg (2.93 mmol) $C_6H_5BF_2$ in 15 ml CH_2Cl_2; yield 750 mg (66.2%) isolated from the primary precipitation and 297 mg (0.77 mmol, 26.3%) from the mother liquor; overall yield 1047 mg, 92.5%; melting point 125–127 °C.

[m-$C_6H_4F(C_6H_5)I][BF_4]$ ^{19}F NMR (CH_2Cl_2, 24 °C) δ −105.2 (ddd, 1F, ^{3}J(F, H^{2}) = 8 Hz, ^{3}J(F, H^{4}) = 7 Hz, ^{4}J(F, H^{5}) = 6 Hz, *m*-C_6H_4F), −146.0 (q, 4F, ^{1}J(BF_4, *B*F_4) = 2 Hz, BF_4); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.1 (q, ^{1}J(*B*F_4, BF_4) = 1 Hz, *B*F_4); ^{1}H NMR (CH_2Cl_2, 24 °C) δ 8.2 (m, 1H), 8.2 (m, 1H), 8.0 (m, 1H), 7.9 (m, 1H), 7.9 (m, 1H), 7.7–7.6 (m, 3H), 7.5 (m, 1H); ^{13}C{^{1}H} NMR (CH_2Cl_2, 24 °C) δ 163.5 (d, ^{1}J(C^{3}, F^{3}) = 257 Hz, C^{3}), 136.3 (s, C$^{2',6'}$, phenyl), 134.2 (d, ^{4}J(C^{5}, F) = 8 Hz, C^{5}), 133.9 (s, C$^{4'}$, phenyl), 133.2(s, C$^{3',5'}$, phenyl), 131.8 (d, ^{4}J(C^{6}, F) = 3 Hz, C^{6}), 123.1 (d, ^{2}J(C^{2}, F) = 26 Hz, C^{2}), 121.0 (d, ^{2}J(C^{4}, F) = 21 Hz, C^{4}), 112.8 (s, C$^{1'}$, phenyl), 111.3 (d, ^{3}J(C^{1}, F) = 8 Hz, C^{1}).

p-Fluorophenyl(phenyl)iodonium tetrafluoroborate prepared from 710 mg (2.73 mmol) *p*-$C_6H_4FIF_2$ and 342 mg (2.72 mmol) $C_6H_5BF_2$ in 15 ml CH_2Cl_2; yield 520 mg (1.35 mmol, 49.5%) isolated from the primary precipitation and 430 mg (1.11 mmol, 41.0%) from the mother liquor; overall yield 950 mg, 90.5%; melting point 134–136 °C.

[p-$C_6H_4F(C_6H_5)I][BF_4]$ ^{19}F NMR (CH_2Cl_2, 24 °C) δ −104.6 (tt, 1F, ^{3}J(F, H^{3,5}) = 8 Hz, ^{4}J(F, H^{2,6}) = 5 Hz, *p*-C_6H_4F), −145.8 (q, 4F, ^{1}J(BF_4, *B*F_4) = 2 Hz, BF_4); ^{11}B NMR (CH_2Cl_2, 24 °C) δ −2.0 (q, ^{1}J(*B*F_4, BF_4) = 2 Hz, BF_4); ^{1}H NMR (CH_2Cl_2, 24 °C) δ 8.3–8.1 (m, 4H), 7.8 (m, 1H), 7.7 (m, 2H), 7.4 (m, 2H); ^{13}C{^{1}H} NMR (CH_2Cl_2, 24 °C) δ 165.1 (d, ^{1}J(C^{4}, F^{4}) = 256 Hz, C^{4}), 138.1 (d, ^{3}J(C^{2,6}, F) = 9 Hz, C^{2,6}), 135.9 (s, C$^{2',6'}$, phenyl), 133.7 (s, C$^{4'}$, phenyl), 133.1 (s, C$^{3',5'}$, phenyl), 119.9 (d, ^{2}J(C^{3,5}, F) = 23 Hz, C^{3,5}), 113.2 (s, C$^{1'}$, phenyl), 105.8 (s, C^{1}).

4.3.5. The reaction of p-$C_6H_4FIF_2$ with $C_6H_5PF_4$

A solution of freshly prepared $C_6H_5PF_4$ (187.7 mg, 1.020 mmol) in CH_2Cl_2 (1 ml; −78 °C) was added to a stirred cold solution of *p*-$C_6H_4FIF_2$ (263.7 mg, 1.014 mmol) in CH_2Cl_2 (2 ml, −60 °C). Immediately a blue colored solution resulted which turned colorless when intensively stirred for some minutes at −60 °C. Following the solvent was removed in HV (≥ −78 °C) and the solid was dried in HV at 20 °C for 2 h. Yield of [*p*-$C_6H_4F(C_6H_5)I$][PF_6] 420 mg (0.946 mmol, 93.3%); melting point 125–126 °C.

[p-$C_6H_4F(C_6H_5)I][PF_6]$ ^{19}F NMR (CH_2Cl_2; 24 °C) δ −69.8 (d, 6F, ^{1}J(PF_6, PF_6) = 714 Hz, PF_6), −103.5 (m, 1F, *p*-C_6H_4F); ^{1}H NMR (CH_2Cl_2, 24 °C); δ 8.2–8.1 (m, 4H), 7.8 (m, 1H), 7.6

(m, 2H), 7.3 (m, 2H); ^{31}P NMR (CH_2Cl_2, 24 °C) δ −144.4 (sep, 1P, $^1J(PF_6, PF_6)$ = 715 Hz, PF_6).

4.3.6. The reaction of $C_6F_5IF_2$ with $C_6H_5PF_4$

In a similar way $C_6H_5PF_4$ (0.288 mmol) in CH_2Cl_2 (0.3 ml, −60 °C) was added slowly to $C_6F_5IF_2$ (47.9 mg, 0.144 mmol) in CH_2Cl_2 (0.3 ml, −60 °C). After 2 h the ^{19}F NMR spectrum of the resulting solution showed that $C_6F_5IF_2$ was quantitatively consumed. The solvent was removed in vacuum and the solid residue was washed five times with *n*-pentane (each 0.5–1 ml). $[C_6F_5(C_6H_5)I][PF_6]$ (69.3 mg, 0.135 mmol) was isolated in 94% yield. The melting point was determined by DSC: T_{onset} 118 °C (endothermal process).

$[C_6F_5(C_6H_5)I][PF_6]$ ^{19}F NMR (CH_2Cl_2; 24 °C) δ −69.3 (d, 6F, ^1J(F, P) = 715 Hz, PF_6), −120.4 (m, 2F, $F^{2,6}$, C_6F_5), −139.9 (tt, 1F, $^3J(F^4, F^{3,5})$ = 21 Hz, $^4J(F^4, F^{2,6})$ = 6 Hz, F^4, C_6F_5), −154.7 (m, 2F, $F^{3,5}$, C_6F_5); ^{1}H NMR (CH_2Cl_2; 24 °C) δ 8.1 (m, 2H, $H^{2,6}$, C_6H_5), 7.8 (m, 1H, H^4, C_6H_5), 7.6 (m, 2H, $H^{3,5}$, C_6H_5).

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