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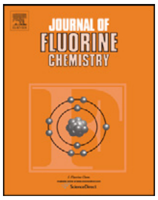

$[Ar(Ar')I][N(CF_3)_2]$, effect of fluorine substituents on aryl groups of iodonium cations and of coordinating bases on the fluoride transfer from the anion to the cation

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ABSTRACT

Three prototypical fluoroaryliodonium salts with the $[N(CF_3)_2]^-$ anion were obtained by metathesis in the corresponding tetrafluoroborate salts $[Ar(Ar')I][BF_4]$ ($Ar/Ar' = C_6H_5/4\text{-}FC_6H_4$, $3\text{-}FC_6H_4/4\text{-}FC_6H_4$, C_6F_5/C_6F_5) with *in situ* generated $Rb[N(CF_3)_2]$. The kinetic lability of the $[N(CF_3)_2]^-$ anion (potential fluoride donor like $[OCF_3]^-$) in combination with the gradual change in fluoride affinity of the three $[Ar(Ar')I]^+$ fluoroaryliodonium cations allowed to distinguish the fluoride acceptor property of the three $[Ar(Ar')I]^+$ fluoroaryliodonium cations. Coordinating solvents or ligands suppressed the fluoride transfer from the $[N(CF_3)_2]^-$ anion to the fluoroaryliodonium cation.

1. Introduction

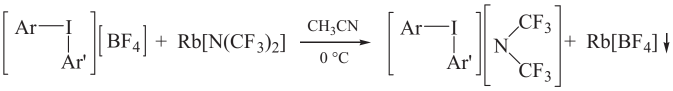
Iodonium salts were first synthesized by Viktor Meyer in 1894, namely phenyl(*p*-iodophenyl)iodonium salts with the anions Cl^-, Br^-, I^-, and NO_3^- [1]. Generally, iodonium salts represent the most common type of iodine(III) compounds and have found numerous applications, *e.g.* as cationic photoinitiators or reagents in organic chemistry [2–4]. The starting materials for the present investigation, symmetric and asymmetric fluoroaryliodonium tetrafluoroborates, were accessible in good yields by a common procedure, the reaction of $ArIF_2$ with $Ar'BF_2$ in weakly coordinating solvents like CH_2Cl_2 or other halocarbons [5,6].

With the present paper we continue our investigations of as well fluoroaryliodonium salts as $[N(CF_3)_2]^-$ anion chemistry [7,8].

2. Results and discussion

2.1. Syntheses of the fluoroaryliodonium bis(trifluoromethyl)imides

The $[N(CF_3)_2]^-$ anion was *in situ* generated by the reaction of $CF_3SO_2N(CF_3)_2$ with RbF [9] and was used for the anion metathesis in fluoroaryliodonium tetrafluoroborates $[Ar(Ar')I][BF_4]$. Fluoroaryliodonium bis(trifluoromethyl)imides $[Ar(Ar')I][N(CF_3)_2]$ were prepared in the coordinating solvent CH_3CN (1). The co-product $Rb[BF_4]$ precipitated quantitatively and was characterized by Raman spectroscopy.



$$[Ar{-}I(Ar')][BF_4] + Rb[N(CF_3)_2] \xrightarrow[0\,^{\circ}C]{CH_3CN} [Ar{-}I(Ar')][N(CF_3)_2] + Rb[BF_4]\downarrow$$

($Ar/Ar' = C_6H_5/4\text{-}FC_6H_4$, $3\text{-}FC_6H_4/4\text{-}FC_6H_4$, C_6F_5/C_6F_5) (1)

2.2. How N-base coordination to the fluoroaryliodonium cation influences the fluoride transfer from the $[N(CF_3)_2]^-$ anion to the fluoroaryliodonium cation?

While at 20 °C solutions of $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$ and $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$ in CH_3CN showed no products of

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fluoride transfer, namely ArAr′IF and $CF_3{-}N{=}C(F){-}N(CF_3)_2$, under comparable conditions the solution of $[(C_6F_5)_2I][N(CF_3)_2]$ contained a significant admixture of $(C_6F_5)_2IF$ after degassing in vacuum besides the iodonium bis(trifluoromethyl)imide. In the series Ar/Ar′ = C_6H_5/4-FC_6H_4, 3-FC_6H_4/4-FC_6H_4, C_6F_5/C_6F_5, the electrophilicity – or to be more precise, the fluoride affinity – of the fluoroaryliodonium cation increased parallel to the instability of $[Ar(Ar')I][N(CF_3)_2]$ in CH_3CN solution.

In general, a coordinating solvent like CH_3CN is essential for the stability of $[Ar(Ar')I][N(CF_3)_2]$ since coordination reduces the electrophilicity at the iodine(III) atom. The removal of CH_3CN led to the transfer of fluoride from the $[N(CF_3)_2]^-$ anion to the iodonium cation and Ar(Ar′)IF [10] and $CF_3{-}N{=}C(F){-}N(CF_3)_2$ [11] were obtained (2).

$$[N(CF_3)_2]^- \xrightarrow[-ArAr'IF]{+[Ar(Ar')I]^+} CF_3{-}N{=}CF_2 \xrightarrow{+[N(CF_3)_2]^-} CF_3N{=}C(F){-}N(CF_3)_2 + F^- \qquad (2)$$

In case of the CH_3CN solution of $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$ we demonstrated the influence of N-base coordination to the iodine center. After addition of one equivalent of 1,10-phenanthroline the removal of CH_3CN in vacuum was possible without decomposition (fluoride transfer) of the $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$ entity. 1,10-phenanthroline is a stronger coordinating base in comparison to CH_3CN. The ^{19}F and ^{1}H resonances of the base-coordinated cation were slightly shifted to lower frequencies. N-base coordination to the cation reduced the electrophilicity of the iodonium cation and prevented the fluoride transfer from the anion to the cation.

$CF_2{=}NCF_3$ is the fluoride acceptor form which corresponds to the $[N(CF_3)_2]^-$ anion. The gas-phase fluoride affinity (B3LYP method, 6-31+G* basis set) of $CF_2{=}NCF_3$ was calculated to be 60.2 kcal/mol and is larger than that of $C(O)F_2$ (49.9 kcal/mol), the corresponding fluoride acceptor form to the $[OCF_3]^-$ anion, and of the moderate Lewis acid $(CH_3)_3SiCl$ (53.7 kcal/mol), but smaller than that of SiF_4 (71.8 kcal/mol). The gas-phase fluoride affinity of fluoroaryliodonium cations is larger by order of magnitude than the afore given values.

It is worth mentioning that our earlier attempts to synthesize $[Ar(Ar')I][OCF_3]$ salts were not successful. Fluoride transfer proceeded from the labile $[OCF_3]^-$ anion to the electrophilic $[Ar(Ar')I]^+$ cations. That property was in agreement with the lower gas-phase fluoride affinity of $C(O)F_2$ relative to $CF_2{=}NCF_3$. The pronounced fluoride acceptor property of fluoroaryliodonium cations in $[Ar(Ar')I][N(CF_3)_2]$ reduces their application potential to generate $Ar{-}N(CF_3)_2$ or $Ar'{-}N(CF_3)_2$ molecules on a thermal route.

2.3. *$C_6H_5(4\text{-}FC_6H_4)IF$ – an effective fluoride donor – able to convert $CF_3SO_2N(CF_3)_2$ into the $[N(CF_3)_2]^-$ anion*

The fluoride donor property of $C_6H_5(4\text{-}FC_6H_4)IF$ offered an interesting new route to the corresponding $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$ salt, alternatively to the afore discussed metathesis.

$C_6H_5(4\text{-}FC_6H_4)IF$ acted in the coordinating solvent CH_3CN as a source of fluoride. Fluoride attacked the electrophilic sulfur center of the reagent $CF_3SO_2N(CF_3)_2$ [12]. As shown in (3), the bis(trifluoromethyl)imide anion was eliminated and the co-product trifluoromethylsulfonylfluoride was formed.

$$C_6H_5(4\text{-}FC_6H_4)IF + CF_3SO_2N(CF_3)_2 \xrightarrow[0\,^\circ C]{CH_3CN} [C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2] + CF_3SO_2F \qquad (3)$$

2.4. *Multinuclear magnetic resonance spectra of the fluoroaryliodonium bis(trifluoromethyl)imides*

The ^{19}F NMR spectra of $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$ and $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$ in CH_3CN solution displayed the signal of the $[N(CF_3)_2]^-$ anion at −39 ppm as a singlet. This shift value is akin to that of $Rb[N(CF_3)_2]_{in\ situ}$ ($\delta(^{19}F) = -36$ ppm) or to that of aryldiazonium bis(trifluoromethyl)imides ($\delta(^{19}F) = -37$ ppm) in CH_3CN at 24 °C [7] and proved the separation of the cations and the $[N(CF_3)_2]^-$ anion by solvent molecules. Surprisingly and in contrast to the above examples, the chemical shift of the $[N(CF_3)_2]^-$ anion in $[(C_6F_5)_2I][N(CF_3)_2]$ occurred at −49.6 ppm. This shift is in between the shift of $N(CF_3)_2$ groups in ionic and covalent vicinity. In 4-$FC_6H_4N(CF_3)_2$ the resonance of the $N(CF_3)_2$ group in the solvent CCl_3F was observed at −56.4 ppm [13]. In 4-$F_2IC_6H_4N(CF_3)_2$ in the presence of the strong σ-electron withdrawing substituent IF_2 the resonance in CH_2Cl_2 solution was found at −55.9 ppm [8]. The shift value at −49.6 ppm in $[(C_6F_5)_2I][N(CF_3)_2]/CH_3CN$ solution is a strong hint for a cation–anion interaction, even in the well coordinating solvent CH_3CN.

The ^{13}C NMR spectroscopic information for the $[N(CF_3)_2]^-$ anion of $[Ar(Ar')I][N(CF_3)_2]$ (Ar/Ar′ = C_6H_5/4-FC_6H_4, 3-FC_6H_4/4-FC_6H_4) in CH_3CN solution depended on temperature. The resonance of $[N(CF_3)_2]^-$ was detected at 24 °C in 0.8 molar solutions only in the $^{13}C\{^{19}F^*\}$ mode (S/N ≈ 400), but not in the ^{13}C or $^{13}C\{^{1}H\}$ mode, whereas at −30 °C a singlet ($^{13}C\{^{19}F^*\}$) or a quartet of quartets (^{13}C or $^{13}C\{^{1}H\}$, $^{1}J_{C,F} = 247$ Hz and $^{3}J_{C,F} = 10$ Hz) was observed at 125 ppm, ($^*N(CF_3)_2$ selectively decoupled). Both coupling constants are akin to those in diazonium bis(trifluoromethyl)imide salts [7].

3. Conclusions

$[Ar(Ar')I][N(CF_3)_2]$ salts (Ar/Ar′ = C_6H_5/4-FC_6H_4, 3-FC_6H_4/4-FC_6H_4, C_6F_5/C_6F_5) were prepared by anion metathesis and could be stabilized in solution by the solvent CH_3CN (Ar/Ar′ = C_6H_5/4-FC_6H_4, 3-FC_6H_4/4-FC_6H_4) or in the solid state by coordination of 1,10-phenanthroline (Ar/Ar′ = 3-FC_6H_4/4-FC_6H_4). N-base stabilization avoided fluoride transfer from the labile anion to the electrophilic cation. The extend of the fluoride transfer depended on the degree of fluorine substituents on the aryl groups in the $[Ar(Ar')I]^+$ cation. Fluoride transfer – the intrinsic reactivity of $[Ar(Ar')I][N(CF_3)_2]$ salts – reduces an alternative potential reactivity of the $[Ar(Ar')I]^+$ cation, namely to phenylate the $[N(CF_3)_2]^-$ anion on a non-catalyzed route and to form arylbis(trifluoromethyl)anilines. Despite of the perfluorinated moiety of the $[N(CF_3)_2]^-$ anion and its low charge, it does not belong to the class of weakly coordinating anions. It possesses a pronounced kinetic lability and is an effective source of fluoride.

4. Experimental part

Moisture sensitive compounds were handled under an atmosphere of dry argon. Reactions were carried out in standard glass equipment or in traps made from FEP tubes (o.d. = 4.1 mm, i.d. = 3.5 mm or o.d. = 9.0 mm, i.d = 8.0 mm). CH_3CN (KMF) was purified by reflux and distillation in sequence over $KMnO_4$ and P_4O_{10}, respectively.

NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (^{13}C at 75.47 MHz, ^{19}F at 282.40 MHz, and ^{1}H at 300.13 MHz). The chemical shifts were referenced to TMS (^{13}C, ^{1}H), CCl_3F (^{19}F, with C_6F_6 as secondary reference, $\delta = -162.9$ ppm). The ratio of ^{19}F and ^{1}H nuclei in the products was determined by NMR spectroscopy after the addition of the internal standards 1,3,5-trifluorobenzene or benzotrifluoride, respectively. Raman spectra were recorded on the Bruker FT-Raman spectrometer RFS 100/S using the 1064 nm line of a Nd/YAG laser. The back-scattered

(180°) radiation was sampled and analyzed (Stoke range: 50–4000 cm^{-1}). The samples were placed in glass capillaries.

4.1. Syntheses of fluoroaryliodonium bis(trifluoromethyl)imides

4.1.1. Synthesis of $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$

$CF_3SO_2N(CF_3)_2$ (0.288 g, 1.010 mmol) was added to a cold suspension (0 °C) of RbF (0.089 g, 0.852 mmol) in CH_3CN (0.5 mL). After 30 min the suspension turned into a solution which was subsequently added to a cold solution (0 °C) of $[C_6H_5(4\text{-}FC_6H_4)I][BF_4]$ (0.302 g, 0.783 mmol) in CH_3CN (0.5 mL). The reaction mixture was stirred for 15 min. The supernatant was separated and degassed in vacuum (0.05 hPa, −35 °C, 15 min). Based on ^{19}F NMR, 98% $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$ were present besides 2% $CF_3SO_2N(CF_3)_2$. The solid (99% yield) consisted of $Rb[BF_4]$ and was characterized by Raman spectroscopy $\overline{\nu}/cm^{-1}$: 770 (100), 526 (18), 356 (21) [14].

4.1.2. $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$

^{19}F NMR (CH_3CN, 24 °C) δ, ppm: −39.0 (s, 6F, $N(CF_3)_2$), −106.6 (m, 1F, $4\text{-}FC_6H_4$). **^1H NMR** (CH_3CN, 24 °C) δ, ppm: 8.00 (m, 4H, $H^{2,6}$, $4\text{-}FC_6H_4$ and C_6H_5), 7.57 (m, 1H, H^4, C_6H_5), 7.42 (m, 2H, $H^{3,5}$, C_6H_5), 7.15 (m, 2H, $H^{3,5}$, $4\text{-}FC_6H_4$). **$^{13}C\{^{19}F^*\}$ NMR** (CH_3CN, 24 °C) δ, ppm: 165.1 (dm, $^1J_{C,F} = 249$ Hz, C^4, $4\text{-}FC_6H_4$), 138.4 (dm, $^1J_{C,H} = 171$ Hz, $C^{2,6}$, $4\text{-}FC_6H_4$), 135.6 (dm, $^1J_{C,H} = 169$ Hz, $C^{2,6}$, C_6H_5), 132.5 (dm, $^1J_{C,H} = 164$ Hz, C^4, C_6H_5), 132.3 (dm, $^1J_{C,H} = 166$ Hz, $C^{3,5}$, C_6H_5), 125.3 (s, $N(CF_3)_2$), 119.6 (dd, $^2J_{C,F} = 15$ Hz, $^2J_{C,H} = 4$ Hz, $C^{3,5}$, $4\text{-}FC_6H_4$), 118.5 (m, C^1, C_6H_5), 112.0 (m, C^1, $4\text{-}FC_6H_4$), ($^*N(CF_3)_2$ selectively decoupled).

$[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$ and $[(C_6F_5)_2I][N(CF_3)_2]$ were prepared in an analogous manner.

4.1.3. $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$

^{19}F NMR (CH_3CN, 24 °C) δ, ppm: −39.5 (s, 6F, $N(CF_3)_2$), −106.3 (m, 1F, $4\text{-}FC_6H_4$), −107.3 (m, 1F, $3\text{-}FC_6H_4$). **^1H NMR** (CH_3CN, 24 °C) δ, ppm: 8.01 (m, 2H, $H^{2,6}$, $4\text{-}FC_6H_4$), 7.77 (m, 2H, $H^{2,6}$, $3\text{-}FC_6H_4$), 7.44 (m, 1H, H^5, $3\text{-}FC_6H_4$), 7.31 (m, 1H, H^4, $3\text{-}FC_6H_4$), 7.17 (m, 2H, $H^{3,5}$, $4\text{-}FC_6H_4$). **$^{13}C\{^{19}F^*\}$ NMR** (CH_3CN, 24 °C) δ, ppm: 165.3 (d, $^1J_{C,F} = 252$ Hz, C^4, $4\text{-}FC_6H_4$), 163.2 (d, $^1J_{C,F} = 253$ Hz, C^3, $3\text{-}FC_6H_4$), 138.6 (dm, $^1J_{C,H} = 172$ Hz, $C^{2,6}$, $4\text{-}FC_6H_4$), 133.9 (dm, $^1J_{C,H} = 168$ Hz, C^5, $3\text{-}FC_6H_4$), 131.6 (dm, $^1J_{C,H} = 171$ Hz, C^6, $3\text{-}FC_6H_4$), 125.2 (s, $N(CF_3)_2$), 122.7 (dm, $^1J_{C,H} = 172$ Hz, C^2, $3\text{-}FC_6H_4$), 119.9 (dm, $^1J_{C,H} = 168$ Hz, C^4, $3\text{-}FC_6H_4$), 119.8 (dm, $^1J_{C,H} = 173$ Hz, $C^{3,5}$, $4\text{-}FC_6H_4$), 117.9 (m, C^1, $3\text{-}FC_6H_4$), 112.4 (t, $^2J_{C,H} = 10$ Hz, C^1, $4\text{-}FC_6H_4$), ($^*N(CF_3)_2$ selectively decoupled).

4.1.4. Mixture of $[(C_6F_5)_2I][N(CF_3)_2]$ with 18 mol-% $(C_6F_5)_2IF$

$[(C_6F_5)_2I][N(CF_3)_2]$: **^{19}F NMR** (CH_3CN, 24 °C) δ, ppm: −49.6 (s, 6F, $N(CF_3)_2$), −124.2 (m, 4F, $o\text{-}C_6F_5$), −148.0 (t, $^3J_{F,F} = 20$ Hz, 2F, $p\text{-}C_6F_5$), −158.1 (m, 4F, $m\text{-}C_6F_5$); $(C_6F_5)_2IF$: **^{19}F NMR** (CH_3CN, 24 °C) δ, ppm: −18.5 (br, 1F, IF), −124.2 (m, 4F, $o\text{-}C_6F_5$), −148.0 (t, $^3J_{F,F} = 20$ Hz, 2F, $p\text{-}C_6F_5$), −158.1 (m, 4F, $m\text{-}C_6F_5$).

4.2. Fluoride transfer from the anion to the cation in fluoroaryliodonium bis(trifluoromethyl)imides in the absence of an N-base

4.2.1. Removal of the solvent from a $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$/$CH_3CN$ solution

The solvent was distilled off from a $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$/$CH_3CN$ solution which contained 5% $[C_6H_5(4\text{-}FC_6H_4)I][BF_4]$ (non-reacted starting material from the metathesis) in vacuum (0.05 hPa) at −40 to −20 °C over 7 h. A white fibered solid resulted. After dissolution in CH_3CN at −30 °C the composition was determined by ^{19}F NMR: 63% $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$, 32% $C_6H_5(4\text{-}FC_6H_4)IF$, besides 5% $[C_6H_5(4\text{-}FC_6H_4)I][BF_4]$.

$C_6H_5(4\text{-}FC_6H_4)IF$: ^{19}F NMR (CH_3CN, −30 °C) δ, ppm: 11.0 (br, 1F, IF), −107.8 (m, 1F, $4\text{-}FC_6H_4$).

4.2.2. Removal of the solvent from a $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$/$CH_3CN$ solution

A $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$/$CH_3CN$ solution which contained 2% $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][BF_4]$ was evacuated (0.05 hPa) at 20 °C for 10 min and formed a white foamy solid which consisted of 56% $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$, 42% $3\text{-}FC_6H_4(4\text{-}FC_6H_4)IF$, besides 2% $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][BF_4]$ (^{19}F NMR in CH_3CN at 24 °C).

$3\text{-}FC_6H_4(4\text{-}FC_6H_4)IF$: ^{19}F NMR (CH_3CN, 24 °C) δ, ppm: 8.9 (br, 1F, IF) −107.3 (m, 1F, $4\text{-}FC_6H_4$), −107.8 (m, 1F, $3\text{-}FC_6H_4$).

4.2.3. Removal of the solvent from the CH_3CN solution of a $[(C_6F_5)_2I][N(CF_3)_2]$ metathesis

The CH_3CN solution of the metathesis reaction contained 82% $[(C_6F_5)_2I][N(CF_3)_2]$ and 18% $(C_6F_5)_2IF$ besides the co-product $CF_3\text{–}N{=}C(F)\text{–}N(CF_3)_2$ (^{19}F NMR δ, ppm: −53.8 (d, $^4J(F,F) = 15$ Hz, 3F, CF_3–N), −20.8 (m, 1F, CF), −54.5 (d, $^4J(F,F) = 15$ Hz, 6F, $N(CF_3)_2$). After degassing and removal of CH_3CN from the solution in vacuum (0.05 hPa) at 20 °C over 10 min a white foamy residue resulted which showed in CH_3CN solution the presence of $(C_6F_5)_2IF$ exclusively.

$(C_6F_5)_2IF$: ^{19}F NMR (CH_3CN, 24 °C) δ, ppm: −124.3 (m, 4F, $o\text{-}C_6F_5$) −147.9 (t, $^3J(F^4,F^{3,5}) = 20$ Hz, 2F, $p\text{-}C_6F_5$) −157.9 (m, 4F, $m\text{-}C_6F_5$), the IF-signal was too broad to determine a reliable maximum.

4.3. Suppression of the fluoride transfer from the anion to the cation in $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$ by N-base coordination

An equimolar amount of 1,10-phenanthroline (0.144 mmol) was added to a $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I][N(CF_3)_2]$/$CH_3CN$ solution. CH_3CN was distilled off in vacuum (0.05 hPa) at 0 °C over 1 h and at 20 °C over 10 min. The primary oily product turned to a foamy solid. After dissolution in CH_3CN the ^{19}F NMR confirmed that $3\text{-}FC_6H_4(4\text{-}FC_6H_4)IF$ was absent and that the ratio of $[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I \cdot phen]^+$ to $[N(CF_3)_2]^-$ was 1:1.

$[3\text{-}FC_6H_4(4\text{-}FC_6H_4)I \cdot phen][N(CF_3)_2]$: **$^{19}F$ NMR** (CH_3CN, 24 °C) δ, ppm: −38.6 (s, 6F, $N(CF_3)_2$), −107.0 (m, 1F, $4\text{-}FC_6H_4$), −107.8 (m, 1F, $3\text{-}FC_6H_4$). **^1H NMR** (CH_3CN, 24 °C) δ, ppm: 8.95 (dd, $^3J(H^{2,9},H^{3,8}) = 4$ Hz, $^4J(H^{2,9},H^{4,7}) = 2$ Hz, 2H, $H^{2,9}$), 8.20 (dd, $^3J(H^{4,7},H^{3,8}) = 8$ Hz, $^4J(H^{4,7},H^{2,9}) = 2$ Hz, 2H, $H^{4,7}$), 7.99 (m, 2H, $H^{2,6}$, $4\text{-}FC_6H_4$), 7.72 (m, 2H, $H^{2,6}$, $3\text{-}FC_6H_4$), 7.69 (s, 2H, $H^{5,6}$), 7.55 (dd, $^3J(H^{3,8},H^{4,7}) = 8$ Hz, $^3J(H^{3,8},H^{2,9}) = 4$ Hz, 2H, $H^{3,8}$), 7.33 (m, H^5, 1H, $3\text{-}FC_6H_4$), 7.20 (m, H^4, 1H, $3\text{-}FC_6H_4$), 7.06 (m, 2H, $H^{3,5}$, $4\text{-}FC_6H_4$).

4.4. $C_6H_5(4\text{-}FC_6H_4)IF$, an effective fluoride donor able to convert $CF_3SO_2N(CF_3)_2$ into the $[N(CF_3)_2]^-$ anion

The above mentioned mixture in CH_3CN which contained 32% $C_6H_5(4\text{-}FC_6H_4)IF$, 63% $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$, besides 5% $[C_6H_5(4\text{-}FC_6H_4)I][BF_4]$ was treated with 1.3 equiv. of $CF_3SO_2N(CF_3)_2$ (referred to $C_6H_5(4\text{-}FC_6H_4)IF$) and stirred for 1 h at 0 °C. Iodonium imide was formed besides CF_3SO_2F (^{19}F NMR δ, ppm: 39.2 (q, $^3J(F,F) = 18$ Hz, 1F), −71.2 (d, $^3J(F,F) = 18$ Hz, 3F). The mixture was degassed in vacuum (0.05 hPa) at −40 °C for 2 min and at −35 °C for 10 min and finally analyzed by ^{19}F NMR. 95% $[C_6H_5(4\text{-}FC_6H_4)I][N(CF_3)_2]$ were present besides 5% $[C_6H_5(4\text{-}FC_6H_4)I][BF_4]$.

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