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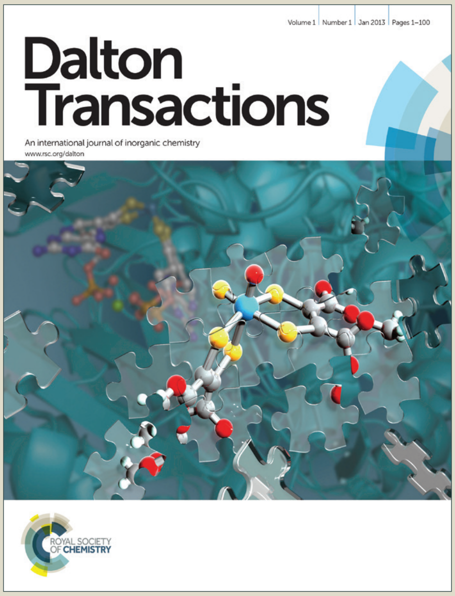

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ARTICLE TYPE

Iron-Catalyzed Electrochemical C-H Perfluoroalkylation of Arenes

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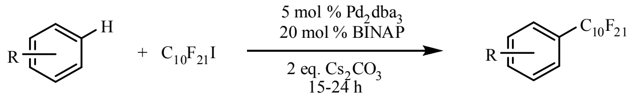
A new iron-catalyzed reaction for the coupling of perfluoroalkyl iodides (R_FI) with aromatic substrates is described. The perfluoroalkylated arene products are obtained in good to excellent yields in the presence of a [(bpy)Fe(II)] catalyst(10%) electrochemically regenerated or generated from [(bpy)Fe(III)] at room temperature. The development, scope, and preliminary mechanistic studies of these transformations are reported.

Introduction

Fluoroalkyl groups can profoundly influence the properties of organic and organometallic molecules, and thus their applicability in pharmaceuticals, agrochemicals, and building blocks for organic materials and catalyst design has grown.[1-8] Despite the importance of this substituent class, more general and reliable methods to incorporate fluoroalkyl groups into complicated molecules are needed.[9-18] Recent reports have demonstrated metal (Cu- or Pd)-catalyzed reactions for the trifluoromethylation of C-H bonds and/or aryl halides using, for example, [(S-trifluoromethyl)dibenzothiophene][BF_4],[17] $TESCF_3$,[10] and $TMSCF_3$,[12] as CF_3 sources. Another interesting report[19] described the perfluoroalkylation of benzene and substituted arenes with perfluoroalkyl halides catalyzed by a Pd^0 complex with phosphine ligands in the presence of a base (Scheme 1) at 80 ºC. The best yields (81%) were achieved by using 20 mol % BINAP and cesium carbonate as the base. The use of other phosphines and potassium carbonate resulted in a maximum product yield of 47%.



Scheme 1

While these transformations represent very exciting advances, they are limited by the high cost of the reagents, the frequent requirement for forcing reaction conditions, and/or modest substrate scope.[14-19] Recently, a simple protocol for the direct C-H perfluoroalkylation of (hetero)arenes with R_FI or R_FBr has been developed using a robust and supported platinum catalyst.[20] The Pt/C catalyst affords exclusive formation of the perfluoroalkylated product under conditions that involve heating at 100 ºC for 20 h in the presence of Cs_2CO_3.[20] Consequently, synthetic methodology to incorporate fluoroalkyl synthons must be improved in order to use more widespread and accessible metals (for example, Fe, Ni) and to prepare sophisticated organofluorine molecules on a practical scale. Iron has long been used in organic synthesis as a catalyst for oxidation and Friedel-Crafts reactions, and until this past decade, its use in homogeneous catalysis has attracted much less attention.[21]

The interest in electrochemical fluoroalkylation reactions is stirred by a number of factors: mild conditions (moderate temperature, ambient pressure), the possibility of closed-loop implementation with a small amount of the catalyst reactant that is repeatedly recycled,[22-28] and the high environmental safety of the synthesis, especially in comparison with traditional organic chemistry techniques. Electrosynthesisis also useful in transition metal catalysis for generating the active form of the catalyst without the need to add external oxidizing or reducing agents.[29,30]

We aimed to develop an iron-based electrocatalytic method for the perfluoroalkylation of both simple and complex arenes. Our goal was to utilize relatively inexpensive perfluoroalkyl iodides as R_F precursors,[19] together with an accessible and nontoxic iron compound[16,21-25] as a catalyst. We report herein that a variety of aromatic substrates undergo facile perfluoroalkylation with R_FI in the presence of a [(bpy)Fe(II)] catalyst electrochemically regenerated or generated from [(bpy)Fe(III)]. The development, optimization, site-selectivity, and mechanism of this transformation are discussed herein.

Results and Discussion

Electrosynthesis

Initial studies were focused on achieving the Fe-catalyzed C-H perfluoroalkylation of benzene with $C_6F_{13}I$. We investigated the reaction of R_FI and benzene in the presence of [(bpy)$FeCl_3$] or [(bpy)$FeCl_2$] in DMF without any added electricity. R_FI and benzene fail to react in the presence of [(bpy)$FeCl_3$], but addition of *t*-BuOK to their mixture results in low yield of R_FPh (7% of $C_6H_5C_6F_{13}$ when 10% of Fe(III) catalyst was used). We have found that [(bpy)$FeCl_2$] promotes the benzene perfluoroalkylation more effectively, and this reaction lead to 55% yield of coupling product in the presence of 10% of Fe(II) catalyst (or 79% in the presence of 100% $[(bpy)FeCl_2]$) and stoichiometric quantity of *t*-BuOK (Scheme 2).

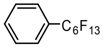
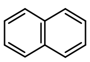
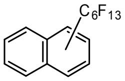
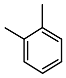
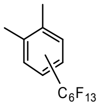
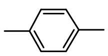
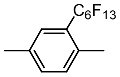
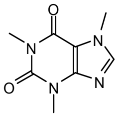
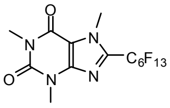
$$R_FI + PhH + KOtBu \xrightarrow{[(bpy)FeCl_2]} Ph\text{-}R_F + KI + HOtBu$$

Scheme 2

Based on these results, we hypothesized that maintaining the electrode potential required for the generation and regeneration of $[(bpy)FeCl_2]$ would render the perfluoroalkylation reaction catalytic. It was found that under room temperature electroreductive conditions, iron could catalyse the perfluoroalkylation of benzene in high yields (Table 1, entry 1). The potential of the electrolysis was -1.0 V vs. Ag/AgCl in DMF.

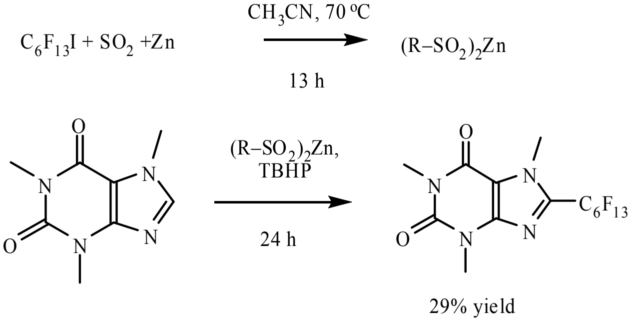
Table 1 Reaction results of [(bpy)Fe]-Catalyzed Perfluoroalkylation

$$Ar\text{-}H + C_6F_{13}I \xrightarrow[tBuOK]{10\%[(bpy)FeCl_3],\ +ne,\ rt} Ar\text{-}C_6F_{13}$$

Entry	Substrate	Product	NMR yield[a] (isolated yield)[b], [%]	Isomer ratio[c]
1			88 (81)	-
2			77 (53)	5:1[d]
3			76 (55)	20:1[e]
4			61 (50)	-
5			100 (83)	-

[a]NMR yields obtained by ^{19}F NMR analysis of the crude reaction mixtures. [b]Isolated yields based on R_FI with 100% conversion by ^{19}F NMR spectroscopy. [c]Selectivity determined by ^{19}F NMR analysis of the crude reaction mixture. [d]Ratio of 1-perfluoroalkyl:2-perfluoroalkyl isomers; [e]Ratio of 4-perfluoroalkyl:3-perfluoroalkyl isomers. General conditions:$[(bpy)FeCl_3]$:R_FI:tBuOK:ArH= 1:9.7: 9.7:9.7 (with one exception:benzene is used in excess). DMF is solvent.

The scope of this transformation was evaluated using the different aromatic substrates described in Table 1. Dimethylated benzenes, naphthalene, and caffeine all reacted to provide perfluoroalkylated products in good to excellent yields (Table 1). The site selectivity of these transformations was dictated by the substitution patterns on the aromatic substrate. The 1,2-disubstituted benzene (*o*-xylene) afforded high selectivity for functionalization at the 4-position. Naphthalene perfluoroalkylation proceeded with modest selectivity for the kinetically preferred *α*-position. Gratifyingly, our technique was also highly effective for the synthesis of a perfluoroalkylated heterocycle, caffeine. The perfluoralkylated caffeine product was obtained in one step at room temperature, with excellent yield (Table 1, line 5) in a short time of three hours, which is a convenient alternative to Baran *et al.* approach.[31] In that report, several time-consuming steps were needed to obtain the product. The first step involved the synthesis of a fluoroalkylated zinc sulphinate reagent (13 hours), and the second step was the fluoroalkylation of caffeine in the presence of *tert*-butyl hydroperoxide (TBHP) (24 hours) (Scheme 3). Baran and co-workers observed the fluoroalkylated caffeine product in 29% yield[31] but Beller isolated this product in 47% yield.[20] In our catalytic system, the use of iron as an electrocatalyst provided faster and more efficient results.



Scheme 3

In order to better understand the perfluoroalkylation reaction mechanism and the role of each component, we performed a series of experiments, changing the catalyst from iron(III) to iron(II), the catalyst amounts, the presence or absence of *t*-BuOK and the type of reaction (chemical or electrochemical). The results indicate that electrochemical fluoroalkylation catalysed by [(bpy)Fe(II)] is efficient both in the presence or absence of *t*-BuOK, while $[(bpy)FeCl_3]$ is less active in the absence of *t*-BuOK (SI).

We observed that the electrochemical synthesis proceeded much faster reaction than the chemical one. Thus, the comparable yields of the coupling products were obtained in electrosynthesis during 2 hours and in the chemical synthesis for 48 hours in the best conditions (SI).

Cyclic voltammetry

Information regarding the electrogeneration of active iron complexes in the presence of perfluoroalkyl halides was obtained by cyclic voltammetry techniques. We have analyzed the CV (cyclic voltammogram) picture of $[(bpy)FeCl_3]$ and $[(bpy)FeCl_2]$ in the absence and presence of other components of reaction system, R_FI, *t*-BuOK, and benzene as the model substrate.

Electrochemical features of $[(bpy)FeCl_3]$ were studied in DMF. Previously, Ocafrain reported that the iron(III) complex of bpy (1:1) undergoes three stepwise quasi-reversible reductions in DMF on a gold electrode,[32] but the CVs for $[(bpy)FeCl_2]$ were recorded only in the presence of excess of Et_4NCl. The peak at near 0 mV (vs. SCE), which is close to our values, was assigned to the redox couple $Fe^{III}(bpy)/Fe^{II}(bpy)$.[32] Our data obtained for the electrochemical reduction of iron(III) complexes have been presented in Table 2. $[(bpy)FeCl_3]$ displays three distinct reversible (or quasi-reversible) reduction waves with a peak-to-peak separation (ΔEp) for each of the waves from 37 to 210 mV in DMF (Table 2, Figure 1). The three waves assigned to Fe(III/II), Fe(II/I) and Fe(I/0) couples at the potential 38, 580 and 1370 mV, respectively were detected. The first peak potential has a value similar to that which was previously reported,[32] but the second and third potentials are different (we have also established that the nature of working electrodes (Au, glassy carbon) does not influence on the shapes of the CVs (Figure 8S, SI)).The differences in between these works may originate either from the formation of iron chlorides through the use of Et_4NCl or from the methods of preparation of $[(bpy)FeCl_2]$.[33-36]

It should also be noted that metal-centered Fe (III/II), Fe (II/I) and Fe (I/0) reductions were described previously for (bpy)Fe complexes.[33,37-43] In the present work, we have traced the reduction processes at every stage by ESR spectroscopy and observed a transition from the paramagnetic particles corresponding to Fe (III) state (before the reduction) to diamagnetic Fe (II) (E_1). The free bpy radical-anion signal appears only at the potentials of E_4 (Table 2), providing a g value of 2.0030.[44,45] No ESR spectra of ligand-centered radicals are observed during the other electrochemical reductions at room temperature.

Plots of the peak current (i_p) versus the square root of the scan rate display linear relationships for third couples indicating that these redox processes are diffusion controlled (Fig. 2).[46]

Table 2 Electrochemical data for 5mM $[(bpy)FeCl_3]$ in DMF (Potentials vs. Ag/AgCl)

	Potential, V	I, mA	ΔE, mV	i_a/i_c
E_1	0.038	0.0550	95	0.50
E_2	-0.570	0.0050	37	1.50
E_3	-1.370	0.0490	210	0.75
E_4	-1.670	0.0150	90	2.30

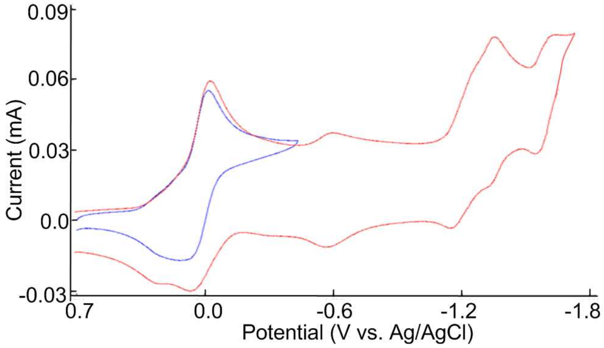


Fig. 1 CVs of 5 mM $[(bpy)FeCl_3]$ in DMF. Conditions: 0.1 V/s scan rate, 0.1 M Bu_4NBF_4, glassy carbon working electrode.

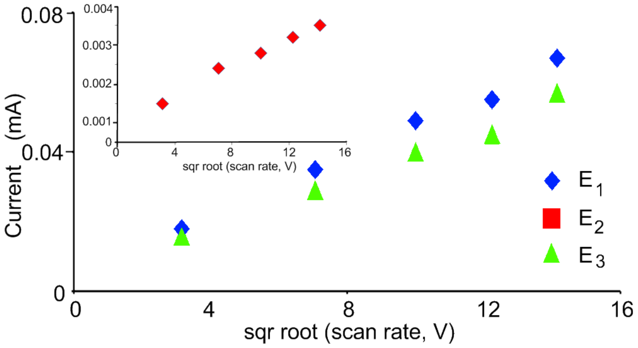


Fig. 2 Plots of i_p vs the square root of the scan rate for the three reduction waves corresponding to the Fe(III/II), Fe(II/I) and Fe(I/0) couples in DMF.

We have confirmed that the first reduction potential of $[(bpy)FeCl_2]$ coincides with the second reduction potential of $[(bpy)FeCl_3]$ (Fig.3). It was found that addition t-BuOK to a solution of $[(bpy)FeCl_3]$ caused the disappearance of the reduction wave for the Fe(III/II) couple. The ESR signal of paramagnetic Fe(III) disappears after addition of t-BuOK. This can be explained by the conversion of [(bpy)Fe(III)] to [(bpy)Fe(II)] in the presence one equivalent of t-BuOK. Also the similarity of the CVs of [(bpy)Fe(III)+t-BuOK] and [(bpy)Fe(II)] solutions in DMF has support this hypothesis (Fig. 3).

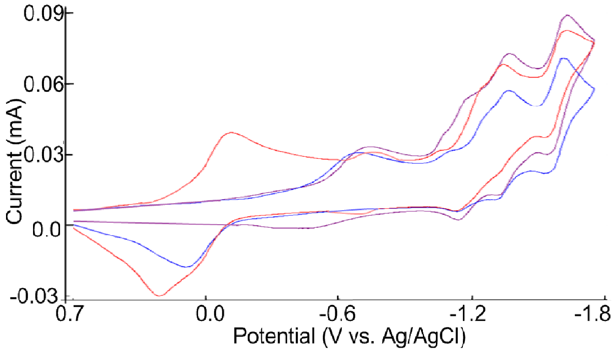


Fig. 3 CVs of 5mM $[(bpy)FeCl_3]$ (red) in the presence of t-BuOK (1:1, blue) and 5mM $[(bpy)FeCl_2]$(purple) for comparison. Conditions: DMF, 0.1 V/s scan rate, 0.1 M Bu_4NBF_4 , glassy carbon working electrode.

t-BuOK is a strong electron donor and is able to form charge-transfer complexes in which there is electron transfer and reduction of certain substrates; for example: Ph_3CCl[47-49] and ferrocene derivatives.[50] That is, t-BuOK often acts as a reducing agent.

The electrocatalytic experiments have been performed using $[(bpy)FeCl_3]$ as a catalyst and R_FI as a substrate. The new catalytic wave at -1.0 V is observed on CVs of $[(bpy)FeCl_3]$ in the presence of increasing amounts of perfluorohexyl iodide (Fig.4). The peak potential of catalytic wave is more than 300 mV positive in comparison to the direct R_FI reduction peak in similar conditions. The potential and current of Fe(III/II) couple remain constant after R_FI addition. At the same time the Fe(II/I) peak current is decreased, possibly indicating the formation of a fluoroalkyl-iron complex.

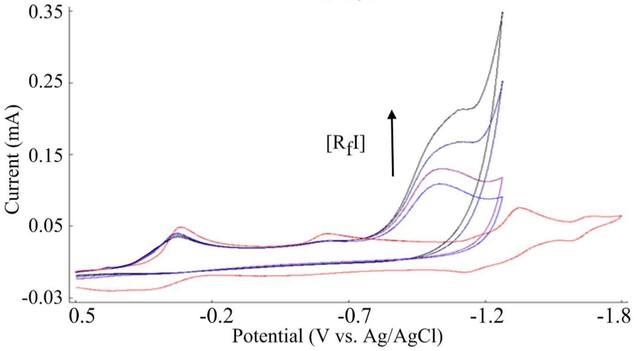


Fig. 4 CVs of 5mM $[(bpy)FeCl_3]$ in the presence of R_FI excess (1:15, 1:20, 1:25, 1:30) in DMF. Conditions: 0.1 V/s scan rate, 0.1 M Bu_4NBF_4, glassy carbon working electrode.

A fast interaction of $[(bpy)FeCl_2]$ and R_FI was observed to take place on the CV time scale (Fig.5). The $[(bpy)FeCl_2]$ reduction peak (in the presence of R_FI) disappears and a new peak at -1.0 V appears, the current of which is constant with the increase in the concentration of organic halide, unlike the case with $[(bpy)FeCl_3]$

as initial form of the catalyst (Fig.4). The activity of electrochemically generated iron(II) from [(bpy)FeCl$_3$] versus [(bpy)FeCl$_2$] prepared chemically, are somewhat different as shown by the CVs in Figs.4-6. The catalytic current at -1.0V is higher in the case of [(bpy)FeCl$_2$], other conditions being equal (Fig.6). Addition of benzene to the reaction mixtures before the reduction in any of the cases does not yield a change in CVs. Probably at this stage the reaction with benzene coupling partner is too slow to be observed on the time scale of cyclic voltammetry experiment.

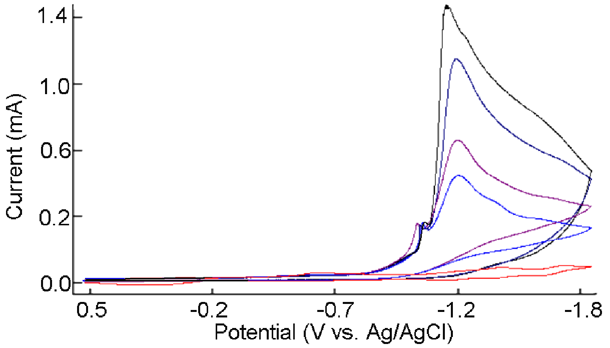


Fig. 5 CVs of 5mM [(bpy)FeCl$_2$] (red) in the presence of increasing amounts of R$_F$I (1:6 (blue), 1:8 (purple)), 1:15 (dark blue), 1:30 (black) in DMF. Conditions: 0.1 V/s scan rate, 0.1 M Bu$_4$NBF$_4$, glassy carbon working electrode.

ESR Spectroelectrochemistry

In order to establish the character of the intermediate reduced complex and the character of the Fe−R$_F$ bond scission (ionic or radical type), we carried out a number of ESR experiments under anaerobic conditions.

It is known that [(bpy)FeCl$_3$] is high spin d^5.[51] The ESR spectrum of [(bpy)FeCl$_3$] powder (Fig.9S) is typical for strong interactions between paramagnetic high-spin iron (III) centers in the polynuclear species.[52] The ESR spectrum of the [(bpy)FeCl$_3$] complex solution in DMF at room temperature is a homogeneously broadened line (Fig.7, left), g= 2.014, $\Delta H_{\text{pk-pk}}$ = 60 G. The line width of the ESR spectrum in DMF is too small for a high-spin-mononuclear Fe complex. Perhaps in DMF solution, an octahedral [(bpy)FeCl$_3$(DMF)] is in equilibrium with a dimer [(bpy)Fe(Cl)$_2$(DMF)(μ-Cl$_2$)Fe(Cl)$_2$(bpy)(DMF)], and the observed spectrum belongs to the dimer with two high-spin Fe(III) centers (Scheme 4).

$$2[\mathrm{Fe(bpy)Cl_3(DMF)}] \rightleftharpoons [\mathrm{Fe(bpy)(Cl)_2(DMF)(\mu\text{-}Cl_2)Fe(Cl)_2(bpy)(DMF)}]$$

Scheme 4

The line width and g-factor of the observed spectrum are characteristic for Fe(III) dimers.[53] The temperature dependence of the spectrum in DMF and acetonitrile (Fig.10S,11S, SI) is in agreement with this assignment. The dimer is diamagnetic at low temperatures, but at higher temperatures the paramagnetic states may be accessible. Therefore, the spectrum intensity decreases with drop of temperature.

Joint reduction of [(bpy)FeCl$_3$] and C$_6$F$_{13}$I at -1.0 V (vs Ag/AgCl) in DMF in the presence of the spin trap PBN (PBN = N-tert-butyl-α-phenylnitrone) is concurrent with the decreasing of [Fe(III)bpy] signal and the advent the signal of the PBN bound radical species of C$_6$F$_{13}$ adduct (Fig.7, right, and Scheme 5). In the absence of PBN there is no ESR signal after reduction of the [(bpy)FeCl$_3$] and C$_6$F$_{13}$I mixture under the same conditions.

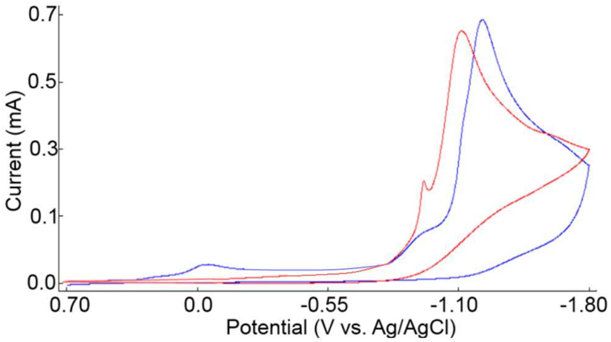


Fig. 6 CVs of 5mM [(bpy)FeCl$_2$] (red) and [(bpy)FeCl$_3$] (blue) in the presence of 6 equiv. of R$_F$I in DMF. Conditions: 0.1 V/s scan rate, 0.1 M Bu$_4$NBF$_4$, glassy carbon working electrode.

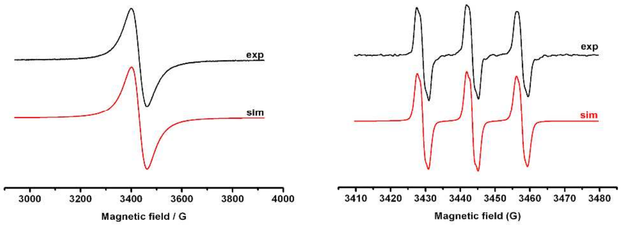
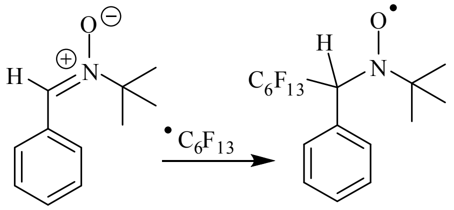


Fig. 7 ESR spectra of [(bpy)FeCl$_3$]solution (left) and obtained during cathodic joint electrolysis of [(bpy)FeCl$_3$]and C$_6$F$_{13}$I at –0.9-1.0 V (vs Ag/AgCl) in DMF in the presence of PBN (right) in DMF/Bu$_4$NBF$_4$, recorded at 293 K with simulations.



Scheme 5

The ESR spectrum of the PBN adduct is a poorly resolved triplet (N) of doublet (H) of triplets (2F) with magnetic resonance parameters obtained as a result of the simulation: g = 2.0061, a$_N$= 14.2 G, a$_H$≤ 0.5 G, 2:a$_F$ = 1.2 G, ΔH = 0.7 G. This observed g values at around g = 2.006 indicate the formation of PBN bound radical species and fluoroalkyl radical species in particular.[54-59]

We can thus conclude that •C$_6$F$_{13}$ reacts readily with the spin trap and the spin adduct is quite stable. The relatively broad lines of the fluoroalkylated spin trap spectrum is not uncommon. For example, for PBN-C$_2$F$_5$, Janzen et al. found the following magnetic resonance parameters: a$_N$ = 14.05, a$_H$ <1.2 G, 2: a$_F$ = 1.46 G. At the same time, for almost all other spin adducts reported, the exact value of the hyperfine coupling constants for the hydrogen nucleus was given.[60] This suggests that just as in our case, contributions only from two nuclei with spin ½ to the super hyperfine splitting patterns are appreciable, and splitting from the third nucleus is indistinguishable because of the relatively large line width of the ESR spectrum.

The calculation of the reaction order for each partner of the catalytic process (on the substrate R$_F$I and iron-bpy catalyst was performed by standard conventional approaches developed for homogeneous catalytic processes electrochemically induced and applied previously in numerous publications.[61-69] A plot catalytic current enhancement in the R_FI presence vs. substrate (R_FI) concentration shows linear dependence indicating the rate of reaction is second order with respect to the perfluoroalkyl substrate (Fig.8).[61-69]

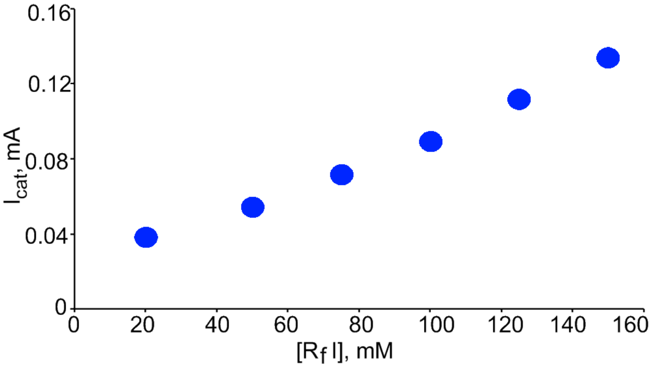


Fig. 8. Plot i_{cat} vs. [R_FI] (E_p^{cat} = -1.0V vs Ag/AgCl) at constant catalyst concentration ([(bpy)Fe(III)]$_2$]=2.5 mM).

The different reaction mixtures of [(bpy)FeCl$_3$] were prepared with a constant R_FI concentration of 30 mM, while varying catalyst concentration (0.75, 1.25, 2.50, 3.00, 3.75 mM calculated for dimer [(bpy)Fe(III)]$_2$). A plot of i_{cat} vs. [catalyst] (where catalyst is Fe dimer) shows a linear dependence indicating the rate of reaction is first order with respect to the iron catalyst [(bpy)Fe(III)]$_2$ (Fig.9). The catalytic current in all cases was measured at -1.0 V. This gives an overall rate law for the R_FI catalytic reduction rate=k[R_FI]^2[(bpy)Fe(III)]$_2$].[61-69] Figure S7 confirms, that the order of the reaction with respect to substrate (R_FI) twice as much as the reaction order in catalyst [(bpy)Fe]. Possibly, this result shows that two moles of substrate (R_FI) is necessary for each mole of iron dimer. Since the catalytic reaction is first order with respect to the dimer and the second order with respect to the substrate, the rate determining step of the catalytic cycle contains two iron center and two R_F fragments.

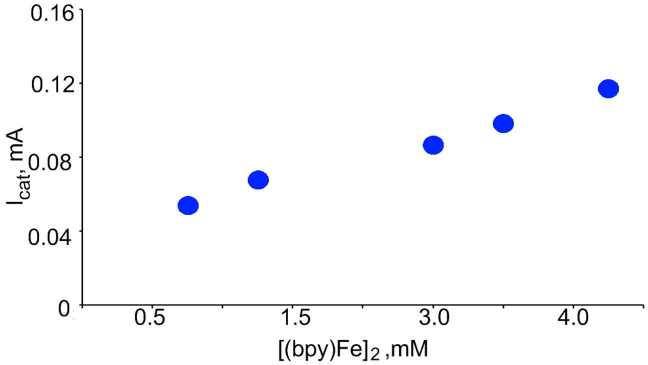


Fig. 9 Plot i_{cat} vs. [[(bpy)Fe(III)]$_2$] at constant R_FI concentration (C(R_FI)= 30 mM). Catalyst concentration is calculated for dimer

A σ-Fe-perfluoroalkyl complex is proposed to form in the course of a catalytic cycle based on the CVA data, however the degree to which the iron center is oxidized was not clear. We observed that reaction of [(bpy)Fe(II)] with R_FI produced peaks that were also found on CVs of [(bpy)FeCl$_3$] (Fig.4). Moreover, when [(bpy)FeCl$_2$] (Fig.6) was generated in the presence of R_FI, the peak at -0.57 V corresponding to the Fe(II) reduction vanishes. σ-Complex Fe(III)-R_FI formation is confirmed firstly, by the disappearance of the reduction peak Fe(II/I) at a potential of -0.57 V (vs.Ag/AgCl) on CVA of [(bpy)Fe(III)] and [(bpy)Fe(II)] complexes in the presence of R_FI due to oxidative addition of R_FI to Fe(II). The generation of the latter is also confirmed by the ESR spectroscopy. Thus, when R_FI was added to a [(bpy)Fe(II)] DMF solution in the 1: 1 ratio, the appearance of steady signal (Fig.13S) with a g-factor of 2.014, corresponding to dimeric Fe (III) derivative was detected ($\Delta H_{pk\text{-}pk}$ = 60 G).

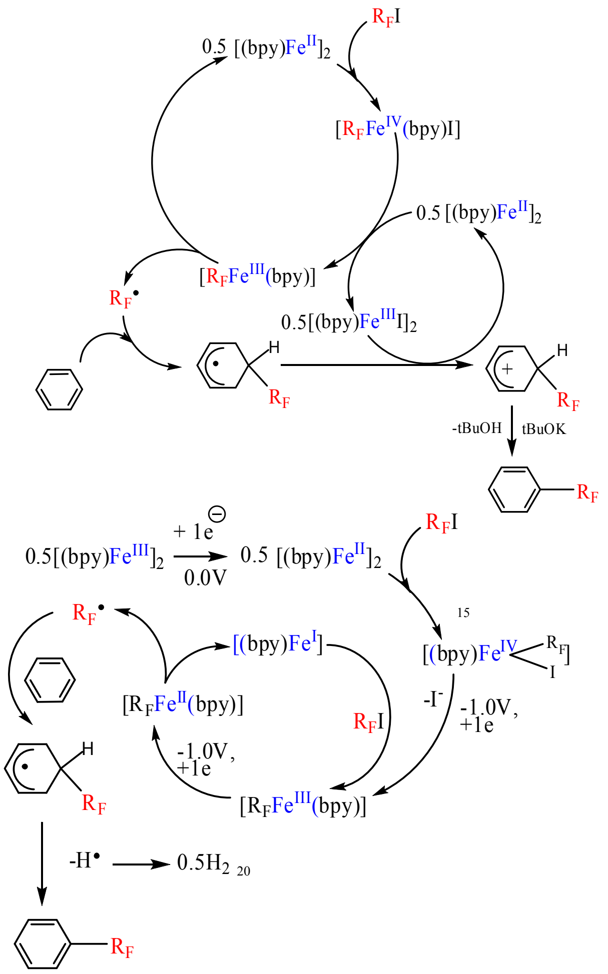
Oxidation peaks corresponding to I^-/ I_2 transition is not observed on the CVs of this [FeR_F] complex oxidation, which suggests the absence of free iodide ions in solution. We can assume that in our conditions perfluoroalkyl-iron species are obtained, but it was not possible to isolate them. When PBN is added to a R_f-Fe sigma complex solution, the spectrum of spin-adduct is not observed, which confirms the relative stability of this σ- complex and its unreactiveness with respect to the arene substrate without electrolysis. -1.0V is the electrode potential for both catalysis and PBN adduct observation. Interestingly, for the radical $R_F^{\cdot}$ formation in chemical synthesis without electricity to be successful, the addition of t-BuOK to the mixture of [(bpy)Fe(II)] +R_FI+PBN is essential.

So, the cyclic voltammetry, ESR, and preparative electrolysis data give experimental support to the reactions highlighted in Scheme 6. Taking into account that the reaction time scales in the chemical and electrochemical conditions are different, we present our observations in two possible free radical pathways for iron-catalysed perfluoroalkylation (Scheme 6). We omitted the stages with t-BuOK in electrochemical scheme for convenience, because the reaction can be carried out and without it. The proposed chemical mechanism of the processes involves the oxidative addition of R_FI to [(bpy)Fe(II)] yielding to fluoroalkylated iron complexes.

Reduction to a Fe(III) species, followed by reductive homolysis generates a perfluoroalkyl radical that could attack an arene (Scheme 6, top). t-Butoxide may assist in reducing any off-cycle formation of Fe(III) back to Fe(II). The electrochemical catalytic generation of perfluoroalkyl radical is achieved in the result of fluoroalkylated iron complexes reduction at -1.0V. Total electrochemical reaction of perfluoroalkylation of arenes can be represented as follows:

$$\text{Ar-H} + C_6F_{13}I \xrightarrow{10\%[(bpy)FeCl_3],\ +\ e} \text{Ar-}C_6F_{13} + 1/_2\, H_2 + I^-$$

Hydrogen evolution is observed visually. The last electrochemical approach is more effective, because the reaction time is reduced and yield of products are higher. Further mechanistic studies are required to verify these proposed mechanisms and are currently underway.



Scheme 6. Possible Free Radical Pathways for Iron-Catalysed Perfluoroalkylation. Chemical (top) and electrochemical (bottom) cycles

Conclusions

Perfluoroalkylation of aromatic and hetero-aromatic compounds by $C_6F_{13}I$ catalyzed by $[(bpy)FeCl_3]$ or $[(bpy)FeCl_2]$ under electrochemical conditions was investigated. Fluoroalkylation of benzene derivatives, naphthalene, and caffeine was obtained under mild reaction conditions with high product yields. The mechanism of electrochemical transformation was proposed to be a radical process based on ESR and CV studies.

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† Electronic Supplementary Information (ESI) available: text, synthesis and electrosynthesis conditions, physico-chemical characteristics of catalysts and products (IR, Raman, X-ray powder diffraction, elemental analysis,^{1}H, ^{13}C, and ^{19}F NMR and ESR spectra), CVs on Au and GC electrodes, and other experimental details. See DOI: 10.1039/b000000x/

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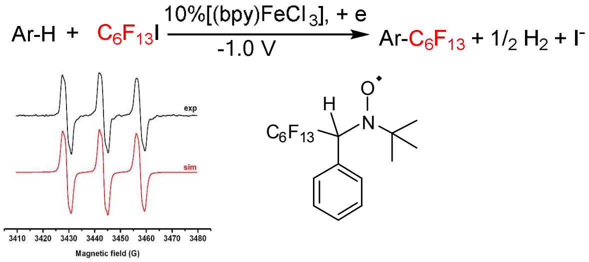

$$\text{Ar-H} + C_6F_{13}I \xrightarrow[-1.0\ V]{10\%[(bpy)FeCl_3],\ +\ e} \text{Ar-}C_6F_{13} + 1/_2\ H_2 + I^-$$

A new iron-catalyzed reaction for the coupling of perfluoroalkyl iodides with aromatic substrates is described.