Organometallic Chemistry

Electrochemically activated reaction of nucleophilic substitution in polyfluorovinyl halides under the action of the cyclopentadienylirondicarbonyl anion $[CpFe(CO)_2]^-$

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The reaction of polyfluorovinyl halides RCF=CFX (R = t-C_4F_9, X = F, Cl, or Br; R = Ph, X = F, Cl) with the $[CpFe(CO)_2]^-$ anion has been studied by cyclic voltammetry and preparative-scale electrolysis. The electrochemical activation of vinyl halides made it possible to obtain the products of nucleophilic substitution for all substrates investigated independently of their configuration and the nature of the halogen.

Key words: polyfluorovinyl halides, cyclopentadienylirondicarbonylate anion, cyclic voltammetry, preparative-scale electrolysis.

Nucleophilic substitution in organic halides under the action of carbonylmetallates of transition metals is of interest as one possible method for synthesizing new compounds containing a carbon—metal σ-bond. However, if S_N2-type reactions resulting in the formation of a metal—alkyl σ-bond usually proceed fairly easily,[1,2] the introduction of a metal-containing fragment into the aromatic and vinyl substrates in most cases requires additional external activation of the latter. This can be done, for instance, by metallocomplex catalysis[3–5] as well as by photochemical[6] or electrochemical[7–9] electron transfer.

Carrying out the reaction in an electrochemical cell provides certain advantages. First, stable dimeric metal complexes can be introduced into the reaction mixture, and their reduction allows one to obtain reactive metal containing nucleophiles *in situ*. Second, by carrying out the electrochemical reduction of an organic halide to the corresponding anion radical (which becomes a source of active radicals upon further fragmentation) one can perform the reaction of nucleophilic substitution with substrates that usually do not enter this reaction. Eventually, the pliability of electrochemical methods allows one to perform very fine adjustments to the conditions of the reaction (the potential) as well as to obtain important information about the reaction's mechanism, kinetics *etc.*

Previously,[8–10] using electrochemical methods (cyclic voltammetry (CVA), rotating ring-disk electrode (RRDE), and preparative-scale electrolysis), we have studied the reaction of nucleophilic substitution under the action of Fe, Mo, and W carbonylmetallates for a wide range of aryl halides that did not contain[8,9] (or contained[10]) strong electron acceptor groups in the aromatic ring. We showed that using potential-controlled electrolysis one can obtain σ-aryl derivatives of η^5-cyclo-

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pentadienylirondicarbonyl. In the present work we continued the electrochemical study of the reaction of nucleophilic substitution at the sp^2-hybridized carbon atom. We studied the reaction of the cyclopentadienylirondicarbonyl anion with a number of polyfluorovinyl halides RCF=CFX (R = t-C_4F_9, X = F, Cl, Br; R = Ph, X = F, Cl). Very few examples of electrochemically activated reactions of nucleophilic substitution in vinyl systems are known: the reaction of 1-bromo-2,2-bis(4-chlorophenyl)ethylene with iron(I)porphyrins[11] and nucleophilic substitution in the (*E*)- and (*Z*)-isomers of bromostilbene under the action of $[CpFe(CO)_2]^-$ (**1**) have been described.[12]

By analogy with polyfluoroaryl halides,[10] one could expect that polyfluorovinyl halides would readily enter the reaction of nucleophilic substitution under the action of anion **1**. However, we succeeded in obtaining quantitative yields of the products of the reaction of nucleophilic substitution in RCF=CFX (R = t-C_4F_9, X = F, Cl, Br; R = Ph, X = F, Cl) by the action of **1** only in the case of polyfluorovinyl fluorides $RCF{=}CF_2$ (R = t-C_4F_9, Ph)[13,14] and the (*Z*)-isomer of difluorochlorostyrene PhCF=CFCl.[14] Reactions with chloro and bromo derivatives t-$C_4F_9CF{=}CFX$ (X = Cl, Br)[13] and the (*E*)-isomer of difluorochlorostyrene[14] give no products of nucleophilic substitution or the latter are obtained in low yields ((*E*)-PhCF=CFCl).

In this connection, it was of interest to carry out this reaction using electrochemical techniques, which was just the aim of the present work.

Results and Discussion

One could expect on the basis of electrochemical reduction data[15] that activated vinyl halides RCF=CFX (R = t-C_4F_9, X = F, Cl, Br; R = Ph, X = F, Cl) would be suitable substrates for the electrochemically activated reaction of nucleophilic substitution with participation of iron carbonylate anions as nucleophiles. Though the reduction of the reaction products, σ-vinyl complexes of η^5-cyclopentadienylirondicarbonyl, is irreversible (with the rupture of the carbon—metal bond), it proceeds at considerably more negative potentials than the reduction of the starting vinyl halides (Table 1). Thus, in the course of the reaction sequence (1)—(4), the $(RCF{=}CFFe(CO)_2Cp)^{\cdot -}$ anion radical rapidly donates its electron to the electrode (Eq. (5)) turning into a neutral molecule.

$$[CpFe(CO)_2]_2 \xrightarrow[\text{electrode}]{+2e} 2\,[CpFe(CO)_2]^- \qquad (E_1) \tag{1}$$

$$RCF{=}CFX + e \overset{\text{electrode}}{\rightleftharpoons} (RCF{=}CFX)^{\cdot -} \qquad (E_2) \tag{2}$$

$$(RCF{=}CFX)^{\cdot -} \xrightarrow[\text{or solution}]{\text{electrode}} RCF{=}\dot{C}F + X^- \tag{3}$$

Table 1. Reduction potentials of polyfluorovinyl halides RCF=CFX, their mixtures with $[CpFe(CO)_2]_2$, and the corresponding products of nucleophilic substitution, $RCF{=}CFFe(CO)_2Cp$ (Pt, n-Bu_4NBF_4, CH_3CN, $Ag^+/AgCl/KCl$, 20 °C)

Compound or reaction mixture	$-E^{Red}$/V
$(CF_3)_3CCF{=}CF_2$	0.99
$(CF_3)_3CCF{=}CF_2+[CpFe(CO)_2]_2$	1.0, 1.60, 1.97
Z-$(CF_3)_3CCF{=}CFCl$	1.04
Z-$(CF_3)_3CCF{=}CFCl+[CpFe(CO)_2]_2$	1.06, 1.58, 1.96
Z-$(CF_3)_3CCF{=}CFBr$	1.17
Z-$(CF_3)_3CCF{=}CFBr+[CpFe(CO)_2]_2$	1.13, 1.63, 1.98
$PhCF{=}CF_2$	1.13
$PhCF{=}CF_2+[CpFe(CO)_2]_2$	1.11, 1.64, 2.06
Z-PhCF=CFCl	1.15
Z-$PhCF{=}CFCl+[CpFe(CO)_2]_2$	1.15, 1.66, 2.10
E-PhCF=CFCl	1.12
E-$PhCF{=}CFCl+[CpFe(CO)_2]_2$	1.10, 1.60, 2.02
Z-$(CF_3)_3CCF{=}CFFe(CO)_2Cp$	1.99
Z-$PhCF{=}CFFe(CO)_2Cp$	2.03
E-$PhCF{=}CFFe(CO)_2Cp$	2.01
$[CpFe(CO)_2]_2$	1.6

$$RCF{=}\dot{C}F + [CpFe(CO)_2]^- \xrightarrow[\text{or solution}]{\text{electrode}} (RCF{=}CFFe(CO)_2Cp)^{\cdot -} \tag{4}$$

$$(RCF{=}CFFe(CO)_2Cp)^{\cdot -} \xrightarrow[\text{electrode}]{-e} (RCF{=}CFFe(CO)_2Cp) \tag{5}$$

$$(RCF{=}CFFe(CO)_2Cp) \underset{\text{electrode}}{\overset{+e}{\rightleftharpoons}} (RCF{=}CFFe(CO)_2Cp)^{\cdot -} \qquad (E_3) \tag{6}$$

$$(RCF{=}CFFe(CO)_2Cp)^{\cdot -} \xrightarrow[\text{solution}]{} RCF{=}\dot{C}F + [CpFe(CO)_2]^- \tag{7}$$

Since step (5) is fast, the contribution of reactions (6) and (7) is very small.

Cyclic voltammograms of solutions of (*Z*)-t-$C_4F_9CF{=}CFCl$ and (*E*)-PhCF=CFCl in the presence of $[CpFe(CO)_2]^-$ are shown in Figs. 1 and 2, respectively. As can be seen from Figs. 1 and 2 and Table 1, for all substrates under study, after the peak of reduction of $[CpFe(CO)_2]_2$ to **1** a new peak arises already at the first potential scan. Its potential coincides with the reduction potential of the corresponding product of nucleophilic substitution (see Table 1).

Thus, the voltammetric data show that, independently of the configuration of the starting vinyl halide and the nature of the halogen, the reaction of the (RCF=CF) (R = t-C_4F_9, Ph) vinyl radical with

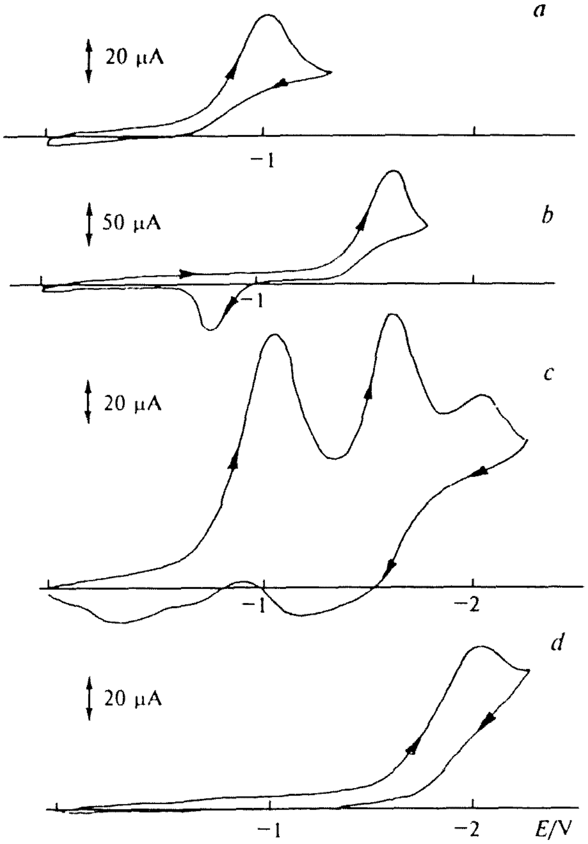


Fig. 1. Cyclic voltammograms of solutions: *a*, (*Z*)-$(CF_3)_3CCF=CFCl$ ($1.2 \cdot 10^{-3}$ mol L^{-1}); *b*, $[CpFe(CO)_2]_2$ ($0.93 \cdot 10^{-3}$ mol L^{-1}); *c*, mixtures of (*Z*)-$(CF_3)_3CCF=CFCl$ ($1 \cdot 10^{-3}$ mol L^{-1}), and $[CpFe(CO)_2]_2$ ($0.42 \cdot 10^{-3}$ mol L^{-1}); *d*, (*Z*)-$(CF_3)_3CCF=CFFe(CO)_2Cp$ ($5.68 \cdot 10^{-4}$ mol L^{-1}) (Pt, CH_3CN, 0.05 mol L^{-1} *n*-Bu_4NBF_4, 200 mV s^{-1}, Ag/AgCl/KCl, 20 °C).

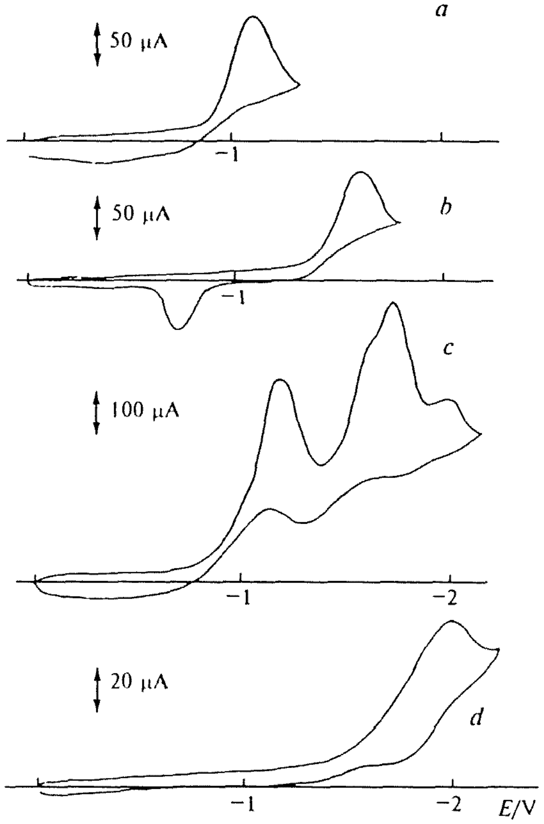


Fig. 2. Cyclic voltammograms of solutions: *a*, (*E*)-PhCF=CFCl ($0.9 \cdot 10^{-3}$ mol L^{-1}); *b*, $[CpFe(CO)_2]_2$ ($0.93 \cdot 10^{-3}$ mol L^{-1}); *c*, mixtures of (*E*)-PhCF=CFCl ($1 \cdot 10^{-3}$ mol L^{-1}) and $[CpFe(CO)_2]_2$ ($0.38 \cdot 10^{-3}$ mol L^{-1}); *d*, (*E*)-$PhCF=CFFe(CO)_2Cp$ ($0.91 \cdot 10^{-3}$ mol L^{-1}) (Pt, CH_3CN, 0.05 mol L^{-1} *n*-Bu_4NBF_4, 200 mV s^{-1}, Ag/AgCl/KCl, 20 °C).

$[CpFe(CO)_2]^-$ (Eq. (4)) proceeds in the vicinity of the electrode surface. The sequence of reactions (4)—(5) results in the formation of the nucleophilic substitution product, $RCF=CFFe(CO)_2Cp$ (R = *t*-C_4F_9, Ph). These results are all the more interesting, since, as noted above, the interaction between RCF=CFX vinyl halides and **1** in the absence of activation of the former by electric current does not always result in the formation of σ-vinyl derivatives of η^5-cyclopentadienylirondicarbonyl.[13,14]

According to CVA data, one could expect that preparative-scale electrolysis of the RCF=CFX (R = *t*-C_4F_9, X = F, Cl, Br; R = Ph, X = F, Cl) vinyl halides in the presence of $[CpFe(CO)_2]^-$ would allow one to also carry out the reaction of nucleophilic substitution for substrates for which one fails to obtain products of nucleophilic substitution by non-electrochemical techniques.

However, in contrast to CVA, the reactants formed at the electrode in the course of preparative-scale electrolysis not only interact with each other in the vicinity of the electrode surface, but also go into the bulk of the solution and can enter side reactions that do not necessarily result in a desired product.

The processes taking place at the electrode, as well as in solution during the electrochemical activation of the reaction of nucleophilic substitution, have been studied in detail in the literature.[16] The central problem in the course of preparative-scale electrolysis of some non-activated aryl[8,9] and vinyl halides[12] in the presence of **1** was the choice of the electrolysis potential. Since the reaction products, σ-aryl and σ-vinyl derivatives of η^5-cyclopentadienylirondicarbonyl, are irreversibly reduced at, as a rule, less cathodic potentials than the starting halides, one had to choose the electrolysis conditions in such a way that the reactants formed at the cathode would be transported into solution in a maximum yield. To this end we used the potential scan technique[8,9] as well as electrochemical homogeneous redox catalysis.[12]

In this work, the choice of the electrolysis potential of vinyl substrates was not a problem for two reasons. First, the reduction potentials of the products of nucleophilic substitution and those of the reactants differed significantly. Second, reaction (5) is fast and can proceed at the electrode. Therefore, one did not fear further destructive reduction of the reaction product at the electrode. In that case, the optimum potential in the electrolysis is the potential of the formation of **1** from the $[CpFe(CO)_2]_2$ dimer (−1.6 V) because of the simultaneous generation of vinyl halide anion radicals.

In this case the following problem arises: in contrast to non-activated aryl halides, which do not enter the reaction of nucleophilic substitution in the absence of external activation of the C−Hal bond, the vinyl halides under study react with $[CpFe(CO)_2]^-$ without any activation. However, as was already mentioned, the reaction between vinyl halides and **1** does not always follow the desired direction, and the composition of the reaction products depends on both the nature of X in RCF=CFX and the configuration of the vinyl halide.[13,14] This means that the $(RCF{=}CFX)^{\cdot -}$ anion radical of the substrate in preparative-scale electrolysis should decompose to form a vinyl radical $(RCF{=}CF)^{\cdot}$ (Eq. (3)); it should be close to the electrode surface and the rate of the reaction of the vinyl radical with nucleophile **1** (Eq. (4)) should be fairly high. Otherwise the anions of **1** formed at the electrode will go into solution and react with unreduced vinyl halide, which, as mentioned above, does not necessarily result in the formation of σ-vinyl complexes of η^5-cyclopentadienylirondicarbonyl.

The results of preparative-scale electrolysis of the RCF=CFX (R = t-C_4F_9, X = F, Cl, Br; R = Ph, X = F, Cl) and $[CpFe(CO)_2]_2$ mixtures are listed in Table 2.* As can be seen from Table 2, electrochemical activation allows one to obtain the products of nucleophilic substitution for chloro- and bromo- derivatives of t-$C_4F_9CF{=}CFX$ (X = Cl, Br) as well as for the (*E*)-isomer of difluorochlorostyrene. It should be noted that in some cases preparative-scale electrolysis gives higher yields of the above-mentioned products (for the same substrates) than non-electrochemical techniques (see Table 2).

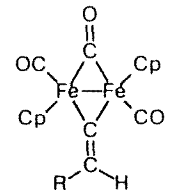
Apart from the products of nucleophilic substitution indicated in Table 2 and obtained by the reaction in the electrochemical cell, side products were observed, which were the same as those obtained in non-electrochemical reactions: dimeric  complexes (**2**) (R = t-C_4F_9, Ph), ferrocene, $CpFe(CO)_2Br$ (in the case of t-$C_4F_9CF{=}CFBr$).

Table 2. Results of preparative-scale electrolysis of the mixtures of vinyl halides RCF=CFX and $[CpFe(CO)_2]_2$ (Hg, 0.25 *M* n-Bu_4NBF_4, CH_3CN, $Ag^+/AgCl/KCl$, 20 °C)

R	X	Configuration	Product of nucleophilic substitution	Configuration	Preparative yield (%)[a]
$(CF_3)_3C$	F		$(CF_3)_3C$ CF=CFFp[b]	*Z*	40
				E	Traces
	Cl	*Z*	«	*Z*	15
				E	Traces
	Br	*Z*	«	*Z*	14
				E	Traces
Ph	F		PhCF=CFFp	*Z*	42
				E	5
	Cl	*Z*	«	*Z*	32
				E	3
		E	«	*Z*	10
				E	5

[a] The products were isolated by TLC. [b] Fp = $Fe(CO)_2Cp$.

Thus, the results of preparative-scale electrolysis confirm the conclusion based on CVA data that the product of nucleophilic substitution is formed only in the vicinity of the electrode surface by an $S_{RN}1$-type reaction (Eqs. (1)—(5)).

This conclusion is also confirmed by the stereochemistry of the products of nucleophilic substitution. If the reaction with participation of RCF=CFX is carried out by non-electrochemical techniques, then, at the formation of substitution products, the configuration of the starting vinyl halide completely remains unchanged. Unlike this, the electrochemically activated reaction of nucleophilic substitution with these substrates is not a stereoselective reaction, and a mixture of (*E*)- and (*Z*)-isomers of the nucleophilic substitution products forms in the course of preparative-scale electrolysis (see Table 2). The (*Z*)-isomer dominates among the reaction products regardless of the configuration of the starting vinyl halide (see Table 2). This fact is in good agreement with the scheme of electrochemical transformations of RCF=CFX (R = t-C_4F_9, X = F, Cl, Br; R = Ph, X = F, Cl) vinyl halides we suggested.[15] This is likely associated with the fact that the anion radical of the substitution product (Eq. (4)) formed in the course of the reaction adopts the least sterically hindered conformation. That is just the conformation providing the minimum repulsion between the bulky phenyl and *tert*-perfluorobutyl groups and the organometallic — $Fe(CO)_2Cp$ fragment with the resulting formation of the (*Z*)-isomer of the substitution product.

Experimental

The electrochemical measurements were carried out using an SVA-1B-M voltammetric system at both stationary and rotating platinum and mercury electrodes with a working

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* Although the preparative yields of the products of nucleophilic substitution are low even for $RCF{=}CF_2$ (R = t-C_4F_9, Ph) and (*E*)-PhCF=CFCl, the only spot corresponding to the t-$C_4F_9CF{=}CFFe(CO)_2Cp$ nucleophilic substitution product or traces of starting reactants were observed on the thin layer chromatogram of the t-$C_4F_9CF{=}CF_2$ and $[CpFe(CO)_2]_2$ reaction mixture. Nevertheless, the yield of the product of preparative-scale electrolysis reached only 40 % of the theoretical yield.

surface of 11.8 mm^2 in acetonitrile with n-Bu_4NBF_4 as the supporting electrolyte at 20 °C. Platinum served as the auxiliary electrode; potentials were measured with reference to Ag/AgCl/KCl. The potential scan rate was varied from 20 to 500 mV s^{-1}.

Mass spectra (EI) were registered on a Varian MAT-442 mass spectrometer at 70 eV ionizing voltage.

Acetonitrile of "pure" grade was stirred for 24 h over CaH_2 and filtered, then KNO_3 (5 g) and conc. H_2SO_4 (10 mL) were added. The mixture was boiled for 3 h, distilled, boiled again for 2 h over P_2O_5, and distilled; b.p. 81—82 °C.

The binuclear $[CpFe(CO)_2]_2$ iron complex was purified according to the known procedure.[13] The $RCF{=}CFFe(CO)_2Cp$ (R = t-C_4F_9, Ph) complexes were obtained using the procedures published previously.[13,14]

Electrochemical activation of the nucleophilic substitution reaction in polyfluorovinyl halides under the action of anion 1. A solution of substrate of a calculated concentration (10 mL) was placed in an electrochemical cell, and the polarization curves on a disk in CVA mode were recorded at various potential scan rates. Then, a calculated amount of a binuclear transition metal complex was put into the cell, and the polarization curves were recorded again in the same mode in order to determine the redox potentials of the forming particles and changes in the peak currents.

General procedure of preparative-scale electrolysis of polyfluorovinyl halides in the presence of $[CpFe(CO)_2]_2$. Potentiostatically controlled electrolysis was carried out in a 10 mL electrochemical cell in acetonitrile with a 0.25 *M* solution of n-Bu_4NBF_4 as the supporting electrolyte. A mercury pool served as the working electrode; the auxiliary platinum anode was separated from the working electrode by a porous membrane. The potential was measured relative to a saturated AgCl electrode. The experiments were carried out at 20 °C; the mixture was stirred by a rotating disk electrode. A cell with calculated quantities of $[CpFe(CO)_2]_2$ and polyfluorovinyl halide was blown with argon for 10 min. Then the working electrode potential corresponding to the limiting reduction current plateau of the binuclear complex (−1.65 V) was set, and the electrolysis started. The course of electrolysis was monitored by a digital voltmeter in accordance with the change in the electrolysis current. When the residual current was not more than 20 % of its initial value, the electrolysis was stopped. The reaction mixture was isolated from the mercury metal, the solution was evaporated to 1—1.5 mL, and anhydrous benzene (10 mL) was added to separate the reaction products from the supporting electrolyte. The benzene solution was evaporated to ~1 mL, and the reaction products obtained were isolated by TLC (Silpearl UV-254, petroleum ether—CH_2Cl_2 = 2 : 1 mixture as eluent).

The structures of all compounds obtained were confirmed by mass spectrometry.

Reaction of perfluoro(*tert*-butyl)ethylene with 1. After electrolysis of $[CpFe(CO)_2]_2$ (0.035 g, $0.99 \cdot 10^{-4}$ mole) and (Z)-t-$C_4F_9CF{=}CF_2$ (0.130 g, $4.3 \cdot 10^{-4}$ mole), (Z)-t-$C_4F_9CF{=}CFFe(CO)_2Cp$ (0.037 g, 40 %, $R_f = 0.65$) was isolated from the reaction mixture. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 458 $[M]^+$ (9.4), 430 $[M-CO]^+$ (3.8), 402 $[M-2CO]^+$ (9), 219 $[C_4F_9C]^+$ (26), 140 $[CpFeF]^+$ (100), 121 $[CpFe]^+$ (24.5), and also traces of a substance (R_f = 0.49) with mass spectrum identical to that of (Z)-t-$C_4F_9CF{=}CFFe(CO)_2Cp$.

Reaction of (*Z*)-2-perfluoro(*tert*-butyl)-1,2-difluoro-1-chloroethylene with 1. After electrolysis of $[CpFe(CO)_2]_2$ (0.0350 g, $0.99 \cdot 10^{-4}$ mole) and (Z)-t-$C_4F_9CF{=}CFCl$ (0.1264 g, $4 \cdot 10^{-4}$ mole), (Z)-t-$C_4F_9CF{=}CFFe(CO)_2Cp$ (0.0136 g, 15 %) and traces of (E)-t-$C_4F_9CF{=}CFFe(CO)_2Cp$ were isolated from the reaction mixture. MS (EI, 70 eV), *m/z* of both compounds are identical: 458 $[M]^+$, 430 $[M-CO]^+$, 402 $[M-2CO]^+$, 219 $[C_4F_9C]^+$, 140 $[CpFeF]^+$, 121 $[CpFe]^+$.

Reaction of (*Z*)-2-perfluoro(*tert*-butyl)-1,2-difluoro-1-bromoethylene with 1. After electrolysis of $[CpFe(CO)_2]_2$ (0.035 g, $0.99 \cdot 10^{-4}$ mole) and (Z)-t-$C_4F_9CF{=}CFBr$ (0.076 g, $2.1 \cdot 10^{-4}$ mole), (Z)-t-$C_4F_9CF{=}CFFe(CO)_2Cp$ (R_f = 0.64), (E)-t-$C_4F_9CF{=}CFFe(CO)_2Cp$ (R_f = 0.49), and $CpFe(CO)_2Br$ (R_f = 0.25) were observed on the chromatogram of the reaction mixture. After chromatography, (Z)-t-$C_4F_9CF{=}CFFe(CO)_2Cp$ (0.013 g, 14 %) was isolated. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 458 $[M]^+$ (8.9.), 430 $[M-CO]^+$ (4.4), 402 $[M-2CO]^+$ (9.5), 219 $[C_4F_9C]^+$ (28), 140 $[CpFeF]^+$ (100), 121 $[CpFe]^+$ (25)).

Reaction of trifluorostyrene with 1. After electrolysis of $[CpFe(CO)_2]_2$ (0.035 g, $1 \cdot 10^{-4}$ mole) and $PhCF{=}CF_2$ (0.040 g, $2.5 \cdot 10^{-4}$ mole), (Z)-$PhCF{=}CFFe(CO)_2Cp$ (0.027 g, 42 %, R_f = 0.45) and (E)-$PhCF{=}CFFe(CO)_2Cp$ (0.003 g, 5 %, R_f = 0.3) were isolated from the reaction mixture. The R_f values of the compounds obtained coincide with those of the pure (E)- and (Z)-isomers of $PhCF{=}CFFe(CO)_2Cp$. MS (EI, 70 eV), *m/z* of both isomers are identical: 316 $[M]^+$, 288 $[M-CO]^+$, 260 $[M-2CO]^+$, 165 $[C_{13}H_9]^+$, 140 $[CpFeF]^+$.

Reaction of (*Z*)-difluorochlorostyrene with 1. After electrolysis of $[CpFe(CO)_2]_2$ (0.035 g, $1 \cdot 10^{-4}$ mole) and (Z)-$PhCF{=}CFCl$ (0.041 g, $2.4 \cdot 10^{-4}$ mole), (Z)-$PhCF{=}CFFe(CO)_2Cp$ (R_f = 0.45), $PhCCHFe_2Cp_2(CO)_3$ (R_f = 0.35), and (E)-$PhCF{=}CFFe(CO)_2Cp$ (R_f = 0.3) were observed on the chromatogram of the reaction mixture. After chromatography, (Z)-$PhCF{=}CFFe(CO)_2Cp$ (0.027 g, 42 %, R_f = 0.45) and (E)-$PhCF{=}CFFe(CO)_2Cp$ (0.003 g, 3 %, R_f = 0.3) were isolated. MS (EI, 70 eV), *m/z* of both isomers are identical: 316 $[M]^+$, 288 $[M-CO]^+$, 260 $[M-2CO]^+$, 165 $[C_{13}H_9]^+$, 140 $[CpFeF]^+$.

Reaction of (*E*)-difluorochlorostyrene with 1. After electrolysis of $[CpFe(CO)_2]_2$ (0.035 g, $0.99 \cdot 10^{-4}$ mole) and (E)-$PhCF{=}CFCl$ (0.040 g, $2.2 \cdot 10^{-4}$ mole), (Z)-$PhCF{=}CFFe(CO)_2Cp$ (0.006 g, 10 %, R_f = 0.45) and (E)-$PhCF{=}CFFe(CO)_2Cp$ (0.003 g, 5 %, R_f = 0.3) were isolated. MS (EI, 70 eV), *m/z* of both isomers are identical: 316 $[M]^+$, 288 $[M-CO]^+$, 260 $[M-2CO]^+$, 165 $[C_{13}H_9]^+$, 140 $[CpFeF]^+$.

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