

# Electrochemically induced aromatic nucleophilic substitution with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^-$ anions

T.V. Magdesieva, I.I. Kukhareva, G.A. Artamkina, K.P. Butin and I.P. Beletskaya

Chemistry Department, M.V. Lomonosov Moscow State University, 119899 Moscow (Russian Federation)

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## Abstract

The reaction of low  $S_N(\text{Ar})$ -active and non-active aryl halides  $p\text{-XC}_6\text{H}_4\text{Hal}$  ( $X = \text{CH}_3, \text{H}, \text{Cl}, \text{COCH}_3, \text{CN}$  or  $\text{NO}_2$ ;  $\text{Hal} = \text{I}$  or  $\text{Br}$ ) with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^-$  is studied using a number of electrochemical methods (cyclic voltammetry, rotating-ring-disk-electrode technique and preparative-scale electrolysis). It is shown that the electrode catalysis enables one to carry out aromatic nucleophilic substitution which generally leads to  $\sigma$ -aryl derivatives of ( $\eta^5$ -cyclopentadienyl) ironcarbonyl.

Nevertheless, a detailed study of the mechanism of the reduction and oxidation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{X-p}]$  at a Pt electrode reveals that the irreversibility of their reduction processes imposes certain restrictions on performing electrode-initiated aromatic nucleophilic substitution. This results in the occurrence of the "electrochemical activation window", *i.e.* limitation of the potential region where electrochemically induced aromatic nucleophilic substitution is possible. For the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^-$  anion, we failed to obtain its  $\sigma$ -aryl derivatives using electrochemical activation of aryl halides. The main product of the reaction is  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Hal}$ .

**Key words:** Iron; Molybdenum; Electrochemistry

## 1. Introduction

Carbonylate anions of transition metals  $[\text{M}(\text{CO})_n\text{-L}_m]^-$  are known to be supernucleophiles [1–3]. Nevertheless, they react only with very active aromatic substrates such as hexafluorobenzene and pentafluoropyridine [4,5]. However, obtaining the  $\sigma$ -aryl derivatives of the transition metals is of great interest because the formation of these types of compound is a key step in the carbonylation reactions.

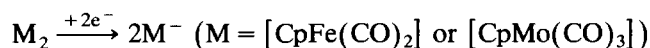
The arylation of the transition metal carbonylate anions is known to be catalysed by electron transfer, *e.g.* photochemically [6]. The application of metallo-complex catalysis is another possible way of activating the carbon-halogen bond [7]. Electrochemical methods can be also useful in this relation, giving rise to the radical anions of aryl halides. The radicals formed by halogen ion elimination are able to react with the nucleophiles. This type of reaction was widely investi-

gated with various nucleophiles that contain no metal atom [8–11]. The possibility of the electrochemically activated reaction of  $p$ -iodonitrobenzene with  $[\text{CpM}(\text{CO})_3]^-$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ), has been reported but with no experimental details presented [12].

The present work deals with the detailed investigation of the possibilities of electrochemical activation of the aromatic nucleophilic substitution in the low active and non-active aryl halides  $p\text{-XC}_6\text{H}_4\text{Hal}$  ( $X = \text{CH}_3, \text{H}, \text{Cl}, \text{COCH}_3, \text{CN}$ , or  $\text{NO}_2$ ;  $\text{Hal} = \text{I}$  or  $\text{Br}$ ) with  $[\text{CpFe}(\text{CO})_2]^-$  and  $[\text{CpMo}(\text{CO})_3]^-$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) anions. (We chose these particular anions because their nucleophilicity is rather different. The nucleophilicity of  $[\text{CpFe}(\text{CO})_2]^-$  is approximately six orders of magnitude greater than that of  $[\text{CpMo}(\text{CO})_3]^-$  [1].) For this purpose, we used a number of electrochemical methods: cyclic voltammetry (CVA), rotating-ring-disk-electrode (RRDE) technique and preparative-scale electrolysis. The application of these electrochemical methods allows us not only to activate aryl halides by producing radical anions but also to generate nucleophilic species, *i.e.* carbonylate anions, directly at the

Correspondence to: K.P. Butin.

electrode as a result of the reduction of corresponding dimer:



This is feasible because these dimers as well as the aryl halides investigated are reduced in the available potential range (see Table 1; see also ref. 13). This approach increases the relative contribution of the substitution reaction at the electrode surface or nearby and therefore enhances the yield of the desired product in competition with various side reactions at the electrode.

## 2. Results and discussion

Studying the possibilities of performing the electrochemical activation of aromatic nucleophilic substitution involves necessarily a preliminary investigation of the electrochemical properties of both the reagent and the products of the reaction.

A detailed study of the electrochemical oxidation and reduction processes of the  $[CpFe(CO)_2]_2$  and  $[CpMo(CO)_3]_2$  binuclear complexes, which are the precursors of the nucleophilic carbonylate anions, was presented earlier (see ref. 13 and references cited therein).

### 2.1. Reduction of the substituted aryl halides

Iodoarenes with various *p* substituents in the aromatic nucleus and *p*-bromobenzonitrile were chosen as the aromatic substrates. These compounds have significantly different reduction potentials and also significantly different stabilities of the corresponding radical anions. Thus the logarithm of the rate constant of their decomposition for *p*-iodonitrobenzene is equal to 0.8 [14] and for *p*-iodobenzonitrile is equal to 10.7 [15].

In order to determine the correct electrode potentials giving rise to electrochemically induced aromatic nucleophilic substitution in solution as well as at the electrode, it was necessary to measure the reduction potentials of the chosen aryl halides at Pt and Hg electrodes under the same reaction conditions. The potential values obtained experimentally are presented in Table 1. All the aryl halides investigated in the

TABLE 2. The reduction potential  $E_d^{\text{Red}}$  and oxidation potentials  $E_d^{\text{Ox}}$  for the  $CpFe(CO)_2C_6H_4X-p$  complexes, the reoxidation potentials  $E_r^{\text{Ox}}$  at the ring of the products of the  $CpFe(CO)_2C_6H_4X-p$  reduction at the disk and the corresponding ring current efficiencies  $N_r$  (dimethylsulphoxide; 0.05 M  $n\text{-Bu}_4\text{NBF}_4$ ; Ag/AgCl;  $\omega = 1500 \text{ min}^{-1}$ ; 20°C)

X	$-E_d^{\text{Red}}$ (V)	$-E_r^{\text{Ox}}$ (V)	$N_r$	$E_d^{\text{Ox}}$ (V)
CH <sub>3</sub>	1.98	0.79	0.43	1.01
H	1.95	0.79	0.40	1.15
Cl	1.92	0.79	0.46	1.18
COCH <sub>3</sub>	1.90	0.79	0.46	1.35
CN	1.88	0.79	0.43	1.3 <sup>a</sup>
NO <sub>2</sub>	1.15	0.95	0.42	1.35 <sup>a</sup>

<sup>a</sup> The potentials were measured in CH<sub>3</sub>CN.

present work, except *p*-iodonitroarenes and *p*-iodoacetylarenes, are reduced in a two-electron step.

### 2.2. Reduction and oxidation of $\sigma$ -aryl derivatives of ( $\eta^5$ -cyclopentadienyl)irondicarbonyl

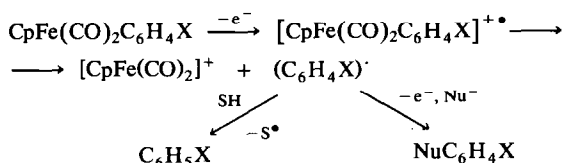
Whereas the reduction of some  $\sigma$ -aryl and  $\sigma$ -alkyl derivatives of transition metal carbonylate anions at a dropping-mercury electrode was studied earlier [17,18], their oxidation and reduction at platinum have not been investigated yet.

We studied the oxidation and reduction at a Pt electrode of a number of  $\sigma$ -aryl derivatives of ( $\eta^5$ -cyclopentadienyl)irondicarbonyl with various substituents in the aromatic nucleus:  $CpFe(CO)_2C_6H_4X-p$  (X = CH<sub>3</sub>, H, Cl, COCH<sub>3</sub>, CN or NO<sub>2</sub>). The results obtained are presented in Table 2.

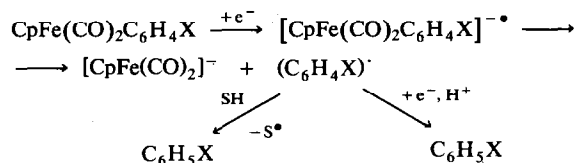
As follows from the CVA data the reduction and oxidation processes of all the  $\sigma$ -aryl complexes of iron, except the *p*-iodonitro derivative, are electrochemically and chemically irreversible. The particles produced by the decomposition of the initially formed  $[CpFe(CO)_2C_6H_4X]^{*-}$  and  $[CpFe(CO)_2C_6H_4X]^{*+}$  are  $[CpFe(CO)_2]^-$  and  $[CpFe(CO)_2]^+$  respectively. That was confirmed by the occurrence in the cyclic voltammograms of the peaks, whose potentials correspond to the potentials of  $[CpFe(CO)_2]^-$  oxidation ( $E = -0.79 \text{ V}$ ) and  $[CpFe(CO)_2]^+$  reduction ( $E = -0.56 \text{ V}$ ) (these values are in agreement with those in ref. 13).

TABLE 1. The reduction potentials of the substituted aryl halides ( $5 \times 10^{-4} \text{ M}$ ) at Pt (dimethylsulphoxide) and Hg (CH<sub>3</sub>CN [16]) electrodes (0.05 M  $n\text{-Bu}_4\text{NBF}_4$ ; Ag/AgCl; 20°C)

	Value for <i>p</i> -IC <sub>6</sub> H <sub>4</sub> X with the following X					Value for <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CN	
	CH <sub>3</sub>	H	Cl	COCH <sub>3</sub>	CN		NO <sub>2</sub>
$-E_{1/2}^{\text{Red}}$ (Pt)	2.60	2.53	2.13	1.77	1.73	1.02	2.05
$-E_{1/2}^{\text{Red}}$ (Hg)	1.93	1.86	1.73	1.64	1.56	1.08	1.89



Scheme 1.



Scheme 2.

This conclusion was also confirmed by the RRDE technique. When the disk potential which corresponds to the limiting current of the  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{X}$  reduction is maintained constant and the dependence of the ring current on the ring potential ( $i_r = f(E_r)$ ) is recorded, one can observe the oxidation of  $[\text{CpFe}(\text{CO})_2]^-$  at the ring. The current efficiency of this process is very close to the theoretical value (0.43), which is determined only by the geometric parameters of the system. This means that the whole amount of the compound that is reduced at the disk completely decomposes. Both oxidation and reduction of  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{X}$ -*p* are two-electron processes for all the compounds presented in Table 2, except for *p*- $\text{IC}_6\text{H}_4\text{NO}_2$ .

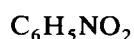
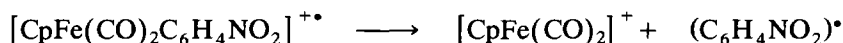
The results obtained indicate that the oxidation (Scheme 1) as well as the reduction (Scheme 2) processes for  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{X}$ -*p* at a Pt electrode follow the same mechanism (ECE).

The reduction and the oxidation of *p*- $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{NO}_2$  are one-electron processes, but the latter is irreversible. In the CVA curve corresponding to the reduction of  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{NO}_2$ -*p* one can observe a reversible peak of radical-anion reoxidation. The ring current efficiency measured by the RRDE technique for the oxidation of  $[\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{NO}_2]^{-\bullet}$  generated at the disk is equal to 0.42. This indicates that the  $\text{NO}_2$  group unlike the others stabilizes the radical anion of the  $\sigma$ -aryl complex of ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl.

Unlike the radical anion, the radical cation  $[\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{NO}_2]^{+\bullet}$  produced initially decomposes immediately (Scheme 3).

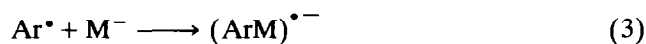
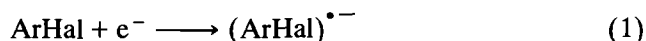
### 2.3. Electrochemical activation of nucleophilic substitution

Because the chosen aryl halides as well as the binuclear Fe and Mo complexes are reduced at a Pt elec-



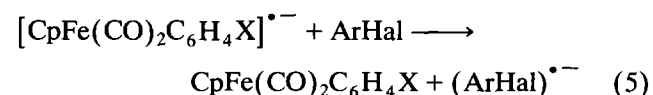
Scheme 3.

trode in an accessible potential range, one can perform simultaneous generation of nucleophiles (carbonylate anions) and radical anions of aryl halides followed by their reaction at the electrode surface:



However, the irreversibility of the reduction of nucleophilic substitution products, which is accompanied by carbon-metal bond cleavage, imposes a restriction on the electrochemically induced aromatic nucleophilic substitution. This is illustrated in Fig. 1, which presents experimental linear dependences of the reduction potentials of aryl halides and  $\sigma$ -aryl derivatives of ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl on the Hammett constants  $\sigma_p$  for the different substituents. The value of  $\rho$  for the aryl halides is 1.25 V and for the reaction products is equal to 0.13 V. This indicates that the  $\sigma$ -aryl complexes are less sensitive to the nature of the substituent in the aromatic nucleus.

It is obvious that electrochemical activation of nucleophilic aromatic substitution will be effective only for substrates that are reduced at more positive potentials than the corresponding products are. The origin of this is the following. The sequence of reactions (1)–(3) yields the formation of radical anions of the substitution product and should be followed by its oxidation either at the electrode (eqn. (4)) or in solution:



If the potential of the aryl halide radical anion formation is more negative than the reduction potential of

their interaction product, the latter, which is being produced at the electrode, immediately decomposes in accordance with the ECE mechanism (Scheme 2) because oxidation processes (4) and (5) at the electrode will be impossible. The relative contribution of the substitution that occurs in the solution will depend on the stability of the radical anion of the aryl halide. Thus, instead of the desired reaction of aromatic nucleophilic substitution, ArHal will be transformed into ArH (Scheme 2) and the concentration of  $[\text{CpFe}(\text{CO})_2]^-$  in solution will be almost invariant. The potential area where electrochemical activation of the aromatic nucleophilic substitution will be effective ("the electrochemical activation window") is indicated in Fig. 1.

The combination of the CVA and RRDE techniques appears to be rather convenient for verification of this assumption. We applied these methods for investigating the possibilities of electrochemical initiation of aromatic nucleophilic substitution which involves the chosen aryl halides and carbonylate anions of iron and molybdenum.

#### 2.4. The reactions of *p*-iodobenzonitrile and *p*-iodoacetophenone with $[\text{CpFe}(\text{CO})_2]^-$

Figure 2, curve c, is a cyclic voltammogram of the reaction mixture containing *p*-iodobenzonitrile and

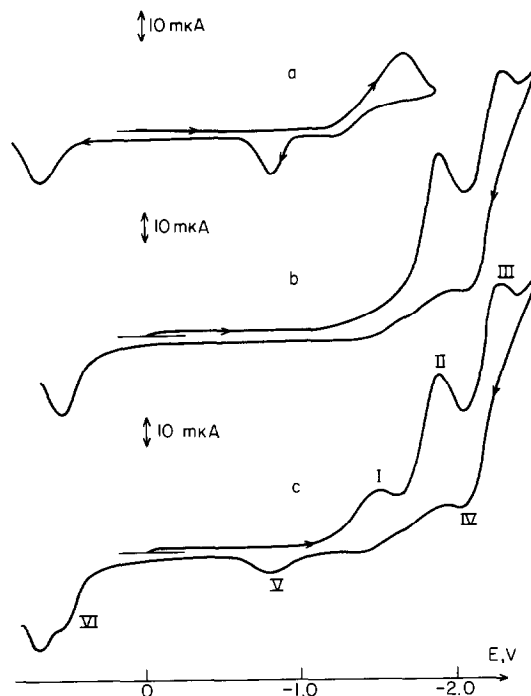


Fig. 2. Cyclic voltammograms of  $[\text{CpFe}(\text{CO})_2]_2$  ( $5 \times 10^{-4}$  M) (curve a), *p*- $\text{IC}_6\text{H}_4\text{CN}$  ( $1 \times 10^{-3}$  M) (curve b) and  $[\text{CpFe}(\text{CO})_2]_2$  ( $5 \times 10^{-4}$  M) and *p*- $\text{IC}_6\text{H}_4\text{CN}$  ( $1 \times 10^{-3}$  M) (curve c) (DMSO; 0.05 M *n*- $\text{Bu}_4\text{NBF}_4$ ; Ag/AgCl; 20°C;  $V = 200 \text{ mV s}^{-1}$ ). For reference to peaks I–VI see the text.

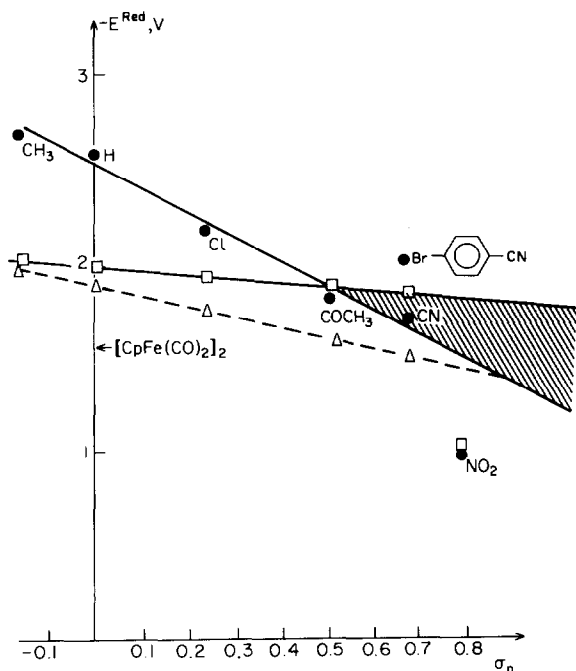


Fig. 1. Dependences of the reduction potentials  $E^{\text{Red}}$  of *p*- $\text{IC}_6\text{H}_4\text{X}$  (●, Pt electrode; △, Hg electrode) and of  $[\text{CpFe}(\text{CO})_2]_2\text{C}_6\text{H}_4\text{X-p}$  (□, Pt electrode) on Hammett constants  $\sigma_p$  for the different substituents. The highlighted area between the two crossed lines corresponds to the electrochemical activation window.

$[\text{CpFe}(\text{CO})_2]_2$ . When scanning the potential in the cathodic direction, one can observe the reduction of  $[\text{CpFe}(\text{CO})_2]_2$  (peak I), *p*- $\text{IC}_6\text{H}_4\text{CN}$  (peak II) and  $\text{C}_6\text{H}_4\text{CN}$  (peak III) as well as the reoxidation of  $(\text{C}_6\text{H}_4\text{CN})^{\bullet-}$  (peak IV),  $[\text{CpFe}(\text{CO})_2]^-$  (peak V) and  $\text{I}^-$  (peak VI) at a reverse scan. Applying the RRDE technique to this reaction mixture, we simultaneously registered the dependence of the disk current on the disk potential ( $i_d = f(E_d)$ ) together with a set of dependences of the ring current on the disk potential ( $i_r = f(E_d)$ ) at a number of constant values of the ring potential. The latter were chosen in order to register consequently at the ring different particles that were generated at the disk. For the mixture containing *p*-iodobenzonitrile and  $[\text{CpFe}(\text{CO})_2]_2$  it is reasonable to choose the following ring potentials.

(a)  $-1.1 \text{ V}$ : only the oxidation of  $(\text{C}_6\text{H}_4\text{CN})^{\bullet-}$  will be registered at the ring.

(b)  $-0.6 \text{ V}$ : together with  $(\text{C}_6\text{H}_4\text{CN})^{\bullet-}$  specified above, the oxidation of  $[\text{CpFe}(\text{CO})_2]^-$  anions will be recorded (they arise when the disk potential reaches the value of  $[\text{CpFe}(\text{CO})_2]_2$  reduction).

(c)  $0.45 \text{ V}$ : together with the particles observed in cases (a) and (b), one will observe oxidation of  $\text{I}^-$  at a disk potential corresponding to the *p*- $\text{IC}_6\text{H}_4\text{CN}$  reduction.

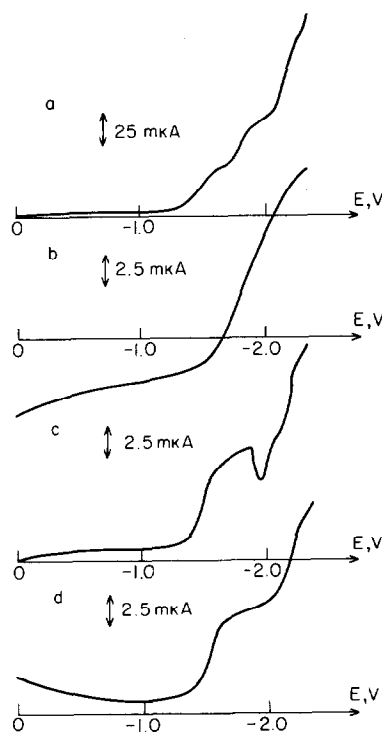


Fig. 3. Voltammograms of *p*-iodobenzonitrile ( $8.9 \times 10^{-4}$  M) in the presence of  $[\text{CpFe}(\text{CO})_2]^-$  ( $3.5 \times 10^{-4}$  M), which were taken at the disk ( $i_d = f_d(E)$ ) (curve a) and at the ring ( $i_r = f_r(E)$ ) (curves b–d), where the ring potentials are as follows: curve b,  $-1.1$  V; curve c,  $-0.6$  V; curve d,  $0.45$  V (DMSO;  $0.05$  M *n*-Bu<sub>4</sub>NBF<sub>4</sub>; Ag/AgCl;  $20^\circ\text{C}$ ;  $V = 20$  mV s<sup>-1</sup>;  $\omega = 1850$  rev min<sup>-1</sup>).

If no reaction between the nucleophile and aryl iodide occurs, the sum of the oxidation currents of all the possible particles should be registered at the ring. A similar pattern will be observed when the reaction product is immediately reduced at the reaction starting potential according to Scheme 2 (the reaction starting potential corresponds to the potential at which both the reagents, nucleophile and  $(\text{ArHal})^{\bullet-}$ , are simultaneously generated at the electrode). Figure 3 presents the experimental dependences of the ring current on the disk potential. A decrease in the current of  $[\text{CpFe}(\text{CO})_2]^-$  oxidation at the ring at the potential when *p*-IC<sub>6</sub>H<sub>4</sub>CN starts to be reduced (Fig. 3, curve b) indicates partial consumption of the carbonylate ions that were formed at the disk and therefore the occurrence of the reaction. As soon as the disk potential becomes equal to the potential of  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{CN-}p$  reduction, the latter decomposes in accordance with Scheme 2 and the ring current of the carbonylate anion oxidation returns to its initial value, when the reaction was impossible owing to absence of the second reagent (compare Fig. 3, curves a and c).

The experimental data obtained for *p*-IC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub> were similar to those for *p*-IC<sub>6</sub>H<sub>4</sub>CN. However,

in the case of *p*-IC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub> the potential region where the substitution reaction product exists (*i.e.* the interval  $\Delta E = E_{\text{ArHal}}^{\text{Red}} - E_{\text{CpFe}(\text{CO})_2\text{Ar}}^{\text{Red}}$ ) is smaller.

This results in narrowing of the interval of potentials where electrochemically induced aromatic nucleophilic substitution is possible.

### 2.5 The reaction of iodobenzene with $[\text{CpFe}(\text{CO})_2]^-$

As follows from Fig. 1, iodobenzene does not fall within the electrochemical activation window because its reduction potential is more cathodic than that for  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_5$ . Hence, the  $(\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_5)^{\bullet-}$  formed should immediately decompose to produce benzene and  $[\text{CpFe}(\text{CO})_2]^-$  (see Scheme 2), the amount of the latter thus being unaltered.

The voltammetric curves obtained by the RRDE technique completely confirm this suggestion. No decrease in the current of  $[\text{CpFe}(\text{CO})_2]^-$  oxidation at the ring was observed at the reaction starting potential.

A similar behaviour was observed for other aryl halides investigated which do not fall within the electrochemical activation window (*e.g.* for *p*-IC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> and *p*-BrC<sub>6</sub>H<sub>4</sub>CN).

### 2.6 Broadening of the electrochemical activation window

As follows from Fig. 1, the number of aromatic halides that react with  $[\text{CpFe}(\text{CO})_2]^-$  under electrochemical activation is small, so that the broadening of the electrochemical activation window is of great importance. One possible way to solve this problem is to use a mercury electrode instead of a platinum electrode because the reduction potentials of aryl halides are significantly more positive than at a platinum electrode (see Table 1). This is also illustrated by the broken line in Fig. 1. In comparison with aryl halides the reduction potentials of  $\sigma$ -aryl derivatives of  $(\eta^5\text{-cyclopentadienyl})\text{irondicarbonyl}$  are significantly less influenced by the electrode material. This is confirmed by the reduction of the following two compounds at Pt and Hg electrodes: for  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{X-}p$  (X = NO<sub>2</sub>),  $-E_{1/2}^{\text{Red}}(\text{Pt}) = 1.15$  V and  $-E_{1/2}^{\text{Red}}(\text{Hg}) = 1.15$  V; for  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{X-}p$  (X = CN),  $-E_{1/2}^{\text{Red}}(\text{Pt}) = 1.88$  V and  $-E_{1/2}^{\text{Red}}(\text{Hg}) = 1.78$  V.

Therefore the application of a mercury electrode allows one to broaden the electrochemical activation window with  $[\text{CpFe}(\text{CO})_2]^-$  as the nucleophile. It becomes possible for iodobenzene, *p*-bromobenzonitrile and some other compounds, for which electrochemical activation at a Pt electrode was impossible.

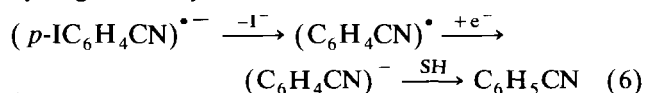
## 3. Preparative-scale electrolysis

In order to confirm our conclusion, we carried out preparative-scale electrolysis and demonstrated that

the  $\sigma$ -aryl derivatives of ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl can be really isolated as a result of the electrochemically induced aromatic nucleophilic substitution. *p*-Iodobenzonitrile and *p*-bromobenzonitrile, as well as *p*-iodonitrobenzene were chosen as model compounds. The working electrode was a mercury pool. The electrolysis was interrupted when the residual current was less than one fifth of its initial value. Usually, it takes nearly 2 h. The reaction mixture was separated by thin layer chromatography and the obtained products analysed using mass spectroscopy.

### 3.1. *p*-Iodobenzonitrile and *p*-bromobenzonitrile with $[\text{CpFe}(\text{CO})_2]^-$

Our experimental data showed that preparative electrolysis of *p*-iodobenzonitrile in the presence of  $[\text{CpFe}(\text{CO})_2]^-$  gives  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{CN-}p$ , although with a poor yield (10%). The major product of the electrolysis was benzonitrile. This has a simple explanation. The radical anion  $(\text{NCC}_6\text{H}_4\text{I})^{\bullet-}$  is rather unstable; its decomposition ( $\log k = 10.7$  [15]) leads to the aryl radical  $(\text{NCC}_6\text{H}_4)^{\bullet}$ , which is then reduced at the electrode or in solution, ultimately yielding the hydrogenated hydrocarbon:

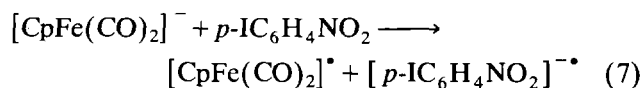


This process proceeds concurrently to nucleophilic substitution (see reactions (1)–(3)), yielding the desired product. This competition is confirmed by numerous data in the literature [15,19–21]. In our experiments, the simultaneous generation of the nucleophile and the radical anion of the substrate at the electrode increases the relative contribution of the substitution product. Nevertheless, the ECE process (6) dominates. The concurrent reduction of  $(\text{C}_6\text{H}_4\text{CN})^{\bullet}$  at the electrode depends upon the rate of  $(\text{ArHal})^{\bullet-}$  decomposition; so one can decrease its contribution using *p*- $\text{NCC}_6\text{H}_4\text{Br}$ , whose radical anion is more stable ( $\log k = 10$  [15]) than that for the corresponding iodide. However, in the case of *p*- $\text{NCC}_6\text{H}_4\text{Br}$ , we met with another difficulty. The value of the reduction potentials for the initial aryl halide and for the desired product  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{CN-}p$  are very close to each other ( $-1.75$  V and  $-1.78$  V respectively). Hence the electrolysis should be performed at a controlled potential where the substrate starts to be reduced whereas the product is not yet reduced. Because the high value of the *IR* drops are rather significant and time dependent (the current varies with time), determination of the optimal potential is rather difficult. So we have to perform scanning electrolysis with the potential being changed in the forward and reverse directions from  $-1.6$  to  $-1.8$  V with a sweep rate of  $500 \text{ mV s}^{-1}$ .

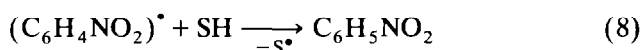
When the average current per period becomes half its initial value, the potential range was changed to between  $-1.5$  and  $-1.75$  V. Scanning electrolysis was performed to decrease the probability of a created product to be reduced at the electrode; so it would be able to diffuse into the bulk of the solution. The procedure described above allowed us to increase the yield of the nucleophilic substitution product  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{CN-}p$  up to 44.7%. Among other products from the reaction mixture,  $\text{CpFe}(\text{CO})_2\text{Br}$  (72.7%), benzonitrile (55%) and some initial *p*-bromobenzonitrile were isolated. When optimizing the experimental conditions of the preparative electrolysis, we demonstrated that the yield of the substitution product can be further increased if a certain amount of the carbonylate ions are preliminarily generated electrochemically in the solution. Then aryl halide should be added to the mixture obtained and the electrolysis should be carried out at a potential where both the nucleophile and the substrate are generated at the electrode. In this case, nucleophilic substitution can occur in solution as well as at the electrode, thus decreasing the contribution of various concurrent processes.

### 3.2. *p*-Iodonitrobenzene with $[\text{CpFe}(\text{CO})_2]^-$

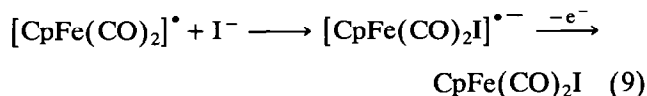
*p*-Iodonitrobenzene forms rather a stable radical anion and thus differs from the other aryl halides considered in the present work. This results in a decrease in the relative contribution of the reactions that take place at the electrode, and the main contribution to the product formation is from the reactions occurring in the solution. Another distinctive feature of this substrate is that the reduction potential ( $-1.02$  V) of *p*- $\text{IC}_6\text{H}_4\text{NO}_2$  and the potential ( $-0.79$  V [13]) of iron carbonylate anion reoxidation are close to each other. This accounts for the rapid redox reaction occurring in the solution:



That is why the preparative-scale electrolysis with preliminary accumulation of the nucleophile in solution turned out to be unsuitable in this case, and the yield of the desired product, namely the  $\sigma$ -aryl derivative of ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl, significantly decreases, being equal to about 3%. The reaction of  $[\text{CpFe}(\text{CO})_2]^-$  with  $(\text{C}_6\text{H}_4\text{NO}_2)^{\bullet}$  cannot occur at the electrode (because the latter is produced only in the solution) and the main contribution seems to be from the reaction with the solvent, which is in a large excess:



Thus the electrolysis results in converting almost the whole amount of iodobenzene into nitrobenzene, whereas the dimer  $[\text{CpFe}(\text{CO})_2]^-$  is not consumed. The electrolysis also yields nearly 20% of  $\text{CpFe}(\text{CO})_2\text{I}$  which seems to originate from the following reaction in solution:



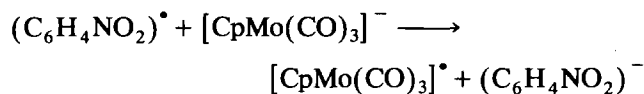
### 3.3. *p*-Iodobenzonitrile and *p*-bromobenzonitrile with $[\text{CpMo}(\text{CO})_3]^-$

Therefore we investigated in detail the possibilities of electrochemical activation of aromatic nucleophilic substitution involving iron carbonylate anions, but similar results may be expected for carbonylate anions of other transition metals, e.g. molybdenum and tungsten. However, the electrochemical activation window for Mo and W seems to be narrower than for Fe. This originates from the fact that Mo and W dimers  $[\text{CpM}(\text{CO})_3]_2$  ( $\text{M} \equiv \text{Mo}$  or  $\text{W}$ ), as well as their  $\sigma$ -aryl derivatives, are reduced at a more positive potential than their iron analogues. For example, in our experimental conditions, the reduction potential of  $\text{CpW}(\text{CO})_3\text{C}_6\text{H}_4\text{CH}_3\text{-}p$  is  $-1.79$  V. This is more positive than the  $\text{CpFe}(\text{CO})_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$  reduction potential by  $0.19$  V (see Table 2). Hence, for a wide number of substituents in the aromatic ring, the reduction potential of aryl halides is more negative than the reduction potential of the product of nucleophilic substitution. Narrowing the electrochemical activation window of the nucleophilic substitution for Mo is confirmed by the preparative electrolysis data. Thus the reactions of *p*-bromobenzonitrile and *p*-iodobenzonitrile with  $[\text{CpMo}(\text{CO})_3]^-$  fail to yield the nucleophilic substitution product. Benzonitrile and almost all initial amount of  $[\text{CpMo}(\text{CO})_3]_2$  were isolated from the reaction mixtures. This result can be explained as follows: (i) the low nucleophilicity of  $[\text{CpMo}(\text{CO})_3]^-$  (i.e. the rate constant of reaction (3) is small); and (ii) even if a certain amount of  $[\text{p-NCC}_6\text{H}_4\text{Mo}(\text{CO})_3]^-$  is created at the electrode, at the reaction starting potential it will immediately decompose in accordance with Scheme 2.

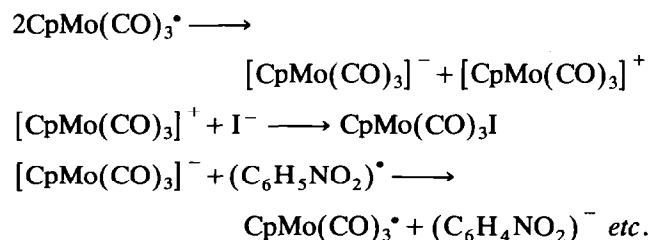
### 3.4. *p*-Iodonitrobenzene with $[\text{CpMo}(\text{CO})_3]^-$

One can significantly lower the reaction starting potential when using more readily reduced aryl halide, e.g. *p*-iodobenzene. The reoxidation potential of  $[\text{CpMo}(\text{CO})_3]^-$  is equal to  $-0.08$  V [13]; hence the redox reaction that is analogous to (7) in this case is impossible. However, for *p*- $\text{IC}_6\text{H}_4\text{NO}_2$ , unlike in ref. 12, we did not succeed in obtaining a significant amount

of  $\sigma$ -aryl derivative of ( $\eta^5$ -cyclopentadienyl)molybdenumtricarbonyl. The main preparative electrolysis products were  $\text{CpMo}(\text{CO})_3\text{I}$  (70.6%) and nitrobenzene (68.3%), regardless of whether the electrolysis was carried out with preliminary accumulation of the nucleophile or not. We suggest the following explanation for the set of the products obtained. The nitrobenzene radical, which originated from  $[\text{p-IC}_6\text{H}_4\text{NO}_2]^\bullet$  in solution can react either with the solvent to yield nitrobenzene (8) or with the nucleophile (3). The nucleophilicity of  $[\text{CpMo}(\text{CO})_3]^-$  is significantly lower than that of  $[\text{CpFe}(\text{CO})_2]^-$  [1]. Hence the contribution of reaction (3) will be rather small and  $[\text{CpMo}(\text{CO})_3]^-$  is likely to act as a reducing agent:



The formation of the  $[\text{CpMo}(\text{CO})_3]^\bullet$  radicals in the solution results in the creation of  $\text{CpMo}(\text{CO})_3\text{I}$ . The latter can be obtained as a result of reaction that is analogous to (9). However, the yield of  $\text{CpMo}(\text{CO})_3\text{I}$  is significantly higher than that for the reaction of  $[\text{CpFe}(\text{CO})_2]^-$  with *p*-iodobenzene. In our opinion, this originates from the tendency of  $[\text{CpMo}(\text{CO})_3]^\bullet$  radicals to disproportionate:



## 4. Experimental details

The electrochemical measurements were performed using an SVA-1B-M voltammetric system at stationary and rotating platinum and mercury film electrodes with an exposed surface area of  $11.8 \text{ mm}^2$  in anhydrous dimethyl sulphoxide and acetonitrile at  $20^\circ\text{C}$  with  $0.05 \text{ M } n\text{-Bu}_4\text{NBF}_4$  as a supporting electrolyte in an argon atmosphere. The geometric parameters of the rotating-ring-disk electrode were the following: the disc radius  $r_1 = 2.57 \text{ mm}^2$ ; the inside ring radius  $r_2 = 2.65 \text{ mm}^2$ ; the outside ring radius  $r_3 = 3.68 \text{ mm}^2$ .

Determination of the current efficiency of the ring-disk system has been described previously [13]. The counter electrode in all experiments was platinum and the reference electrode was aqueous  $\text{Ag}/\text{AgCl}/\text{KCl}$  electrode. Cyclic voltammograms were recorded with scan rates of  $50$ ,  $100$ ,  $200$  and  $500 \text{ mV s}^{-1}$ , as well as at a rotating electrode at a scan rate of  $20 \text{ mV s}^{-1}$ . The

electrode rotation speed varied from 480 to 3450 rev min<sup>-1</sup>. The ohmic drops were considered.

A Pt electrode surface was covered with a mercury film by means of electrolysis of  $5 \times 10^{-4}$  M solution of HgBr<sub>2</sub> in dimethylsulphoxide (DMSO) or CH<sub>3</sub>CN for 2–3 min at a potential of –0.5 V. Mass spectra were obtained with the aid of MX 1321 A instrument at 70 eV.

#### 4.1. Solvents and chemicals

DMSO of pure grade was stirred first over NaOH (anhydrous) and then over CaH<sub>2</sub> (for 12 h in each case). This procedure was followed by distillation at a reduced pressure (2–4 Torr; boiling point (b.p.), 50–61°C) over CaH<sub>2</sub> in argon flow. The purified DMSO was stored over 4A molecular sieves in an argon atmosphere.

Acetonitrile of pure grade was stirred over CaH<sub>2</sub> for 24 h and filtered. Then 5 g of KNO<sub>2</sub> and 10 ml of H<sub>2</sub>SO<sub>4</sub> (98%) were added to 1 l of filtrate. The distillate was refluxed over P<sub>2</sub>O<sub>5</sub> for 2 h and distilled again, obtaining the fraction with a b.p. of 81–82°C at 760 Torr. The dimers  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  were purified according to refs. 22 and 23.  $\sigma$ -Aryl derivatives of ( $\eta^5$ -cyclopentadienyl)iron-dicarbonyl,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{X-}p$  (X  $\equiv$  CH<sub>3</sub>, H, Cl, COCH<sub>3</sub>, CN, or NO<sub>2</sub>) were prepared using the procedure described in ref. 24.

#### 4.2. Electrochemical measurement: a general procedure

10 ml of aryl halide solution ( $0.5 \times 10^{-4}$  M) was placed in an electrochemical cell and then voltammetric curves were recorded in different regimes, by varying the potential scan rate and the electrode rotation speed. Next a calculated amount of binuclear iron or molybdenum complex was added. The voltammetric curves of the mixtures were recorded in the same regimes as for pure aryl halide. In this way one can determine the redox potentials of the particles forming and the variation in the peak current that corresponds to initial reagents. Further investigations were carried out by the RRDE technique in the following regimes: (a)  $i_r = f(E_d)$ ,  $E_r = \text{constant}$ ; (b)  $i_r = f(E_r)$ ,  $E_d = \text{constant}$ .

#### 4.3. Preparative-scale electrolysis: a general procedure

Potentiostatically controlled electrolysis was carried out in a 10 ml electrochemical cell in a CH<sub>3</sub>CN solution containing 0.5 M Bu<sub>4</sub>NBF<sub>4</sub> in an argon flow at 20°C. A mercury pool, which operates as a working electrode, was separated from the anodic compartment with a porous membrane. The course of the electrolysis was controlled with a digital voltmeter. The electrolysis was interrupted when the residual current was less

than 20% of its initial value. The reaction mixture was isolated from the mercury and the solution obtained was reduced by vacuum distillation to about 1–2 ml and diluted with 10 ml of benzene for precipitation of the supporting electrolyte. The solution was again reduced to 1 ml volume and the products obtained were isolated using thin layer chromatography (Silpearl UV-254; benzene served as the eluent). The structures of all substances obtained were confirmed by mass spectroscopy (MS).

##### 4.3.1. *p*-BrC<sub>6</sub>H<sub>4</sub>CN and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$

0.0496 g ( $1.4 \times 10^{-4}$  mol) of  $[(\eta^5\text{-C}_6\text{H}_5)\text{Fe}(\text{CO})_2]_2$  was dissolved in 10 ml of CH<sub>3</sub>CN in an electrochemical cell and potentiostatically controlled electrolysis performed at a potential of –1.88 V until the current value was decreased to 0.038 A. 0.0127 g ( $6.99 \times 10^{-5}$  mol) of *p*-BrC<sub>6</sub>H<sub>4</sub>CN was added to the solution of  $[\text{CpFe}(\text{CO})_2]^-$  obtained and scanning electrolysis was carried out at the potential being swept from –1.5 to –1.75 V at a scan rate of 500 mV s<sup>-1</sup>. After separation of the reaction mixture the following compounds were obtained: benzonitrile, 0.0008 g (55%); initial *p*-bromobenzonitrile, 0.01 g; *p*-NCC<sub>6</sub>H<sub>4</sub>Fe(CO)<sub>2</sub> ( $\eta^5\text{-C}_5\text{H}_5$ ), 0.0016 g (44.7%) (MS:  $m/z$  279 ( $[\text{M}]^+$ , 15.4%), 251 ( $[\text{M} - \text{CO}]^+$ , 42.3%), 223 ( $[\text{M} - 2\text{CO}]^+$  100%)) and  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ , 0.0024 g (72.7%) (MS:  $m/z$  257 ( $[\text{M}]^+$ , 27%), 229 ( $[\text{M} - \text{CO}]^+$ , 38%), 201 ( $[\text{M} - 2\text{CO}]^+$ , 100%)).

##### 4.3.2. *p*-IC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$

0.0496 g ( $1.4 \times 10^{-4}$  mol) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and 0.0174 g ( $6.99 \times 10^{-5}$  mol) of *p*-IC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> underwent electrolysis at a potential of –1.5 V. From the reaction mixture the following compounds were isolated: nitrobenzene, 0.0021 g (80%); initial *p*-iodonitrobenzene, 0.0122 g;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , 0.0013 g (20%) (MS:  $m/z$  304 ( $[\text{M}]^+$ , 30.7%), 276 ( $[\text{M} - \text{CO}]^+$ , 44.1%), 248 ( $[\text{M} - 2\text{CO}]^+$ , 100%)).

##### 4.3.3. *p*-IC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^-$

0.0069 g ( $1.4 \times 10^{-4}$  mol) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  and 0.00174 g ( $6.99 \times 10^{-5}$  mol) of *p*-IC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> underwent electrolysis at a potential of –1.0 V. From the reaction mixture the following compounds were isolated: nitrobenzene, 0.0059 g (68.3%);  $[(\eta^5\text{-C}_5\text{H}_5)\text{-Mo}(\text{CO})_3]_2$ , 0.0018 g (70.6%) (MS:  $m/z$  374 ( $[\text{M}]^+$ , 39%), 346, ( $[\text{M} - \text{CO}]^+$ , 66%), 318 ( $[\text{M} - 2\text{CO}]^+$ , 35%), 290 ( $[\text{M} - 3\text{CO}]^+$ , 100%)).

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