Electrochemical activation of nucleophilic substitution in aryl and vinyl halides with [CpFe(CO)$_2$]$^-$ anion using homogeneous redox-catalysis

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Abstract

The feasibility of indirect electrochemical activation of nucleophilic substitution in several non-active aryl and vinyl halides with [CpFe(CO)$_2$]$^-$ by means of a specially introduced mediator (a reversible redox couple A/A$^-$) has been demonstrated. The efficiency of different mediators for several aryl and vinyl halides as well as the corresponding σ-aryl and σ-vinyl derivatives of (η^5-cyclopentadienyl)irondicarbonyl has been examined. It was shown that by carefully selecting the mediator it becomes possible to perform the electrochemically induced substitution reaction even in those cases where the substitution products are reduced irreversibly and at less cathodic potentials than the initial substrates.

Keywords: Iron; Mediator; Redox catalysis; Electrochemistry

1. Introduction

Nucleophilic substitution in aryl and vinyl halides with metal-containing nucleophiles is one of the important ways for obtaining new compounds with a carbon(sp^2)-metal σ-bond. We have previously studied [1,2] the electrochemically promoted aromatic nucleophilic substitution in low(S$_N$Ar)-active and non-active aryl halides with carbonylmetallates of Fe, Mo and W using cyclic voltammetry (CV), the rotating ring-disc electrode (RRDE) technique and preparative-scale electrolysis. We showed [1,2] that the potential-controlled electrolysis of aryl halides in the presence of the [CpFe(CO)$_2$]$^-$ (electrochemically generated from the dimer complex [CpFe(CO)$_2$]$_2$) is a convenient way to synthesise σ-aryl(η^5-cyclopentadienyl)irondicarbonyl derivatives.

However, the proposed method has some limitations. The electrochemical reduction of the nucleophilic substitution products (σ-aryl derivatives of (η^5-cyclopentadienyl)irondicarbonyl) is irreversible and involves C–M σ-bond breaking [1,2]. Therefore, even if electrochemically promoted, this reaction can be carried out only with substrates that are more readily reduced than the corresponding metallocomplexes.

Several ways can be envisaged to overcome this restriction and to extend the number of substrates that are active in the electrochemically induced nucleophilic substitution. First, it is known that using a mercury, rather than a platinum, electrode [3] can effectively promote the reduction of organic halides, whereas the reduction of σ-aryl (η^5-cyclopentadienyl)irondicarbonyl derivatives is significantly less influenced by the electrode material [1,2]. Therefore, replacing the platinum working electrode with mercury would allow the nucleophilic substitution reaction to be performed even with those substrates for which the electrochemically activated reaction at Pt is impossible [1,2]. However, for a number of aryl halides (e.g. p-iodotoluene [1]) and several vinyl halides [4] changing the electrode material is still insufficient because, even at an Hg electrode, the reduction of corresponding σ-aryl derivatives of (η^5-cyclopentadienyl)irondicarbonyl occurs almost at the same potentials as the reduction of the initial substrates.
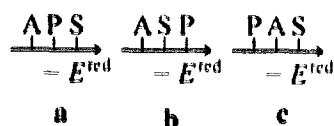
Yet another way of involving a wider range of substrates into electrochemically activated nucleophilic substitution is their indirect electrochemical reduction by the mediator mechanism [5]. Under these conditions, the substrate reduction occurs in an homogeneous redox

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reaction with the components of a specially introduced redox couple A/A⁻ rather than by an ordinary electrochemical mechanism. The use of such mediator reduction can significantly promote the reduction of organic halides and decrease the relative contribution of the competing reactions both at the electrode and in the electrode vicinity, thus increasing the yield of the target products.

In this work we demonstrated the feasibility of the electrochemically promoted nucleophilic substitution reaction in several aryl and vinyl halides with cyclopentadienylirondicarbonyl anion [CpFe(CO)₂]⁻, using homogeneous redox-catalysis even in those cases when direct electrochemical activation of this reaction cannot be performed. A detailed description of the homogeneous redox-catalysis mechanism can be found elsewhere [6]. However, there are some questions that require special consideration.

Since mediator A must possess a standard redox potential more positive than the reduction potential of substrate S, there are three possible cases of the reactants' potential arrangement. (A denotes the redox potential of the mediator, S and P are the observed peak potentials of the organic halide and the nucleophilic substitution product respectively):

$$\underset{-E^{\text{red}}}{\underset{a}{\xrightarrow{\hspace{1.5cm}}}}\overset{\text{A P S}}{\underset{\Big\downarrow\Big\downarrow\Big\downarrow}{}} \qquad \underset{-E^{\text{red}}}{\underset{b}{\xrightarrow{\hspace{1.5cm}}}}\overset{\text{A S P}}{\underset{\Big\downarrow\Big\downarrow\Big\downarrow}{}} \qquad \underset{-E^{\text{red}}}{\underset{c}{\xrightarrow{\hspace{1.5cm}}}}\overset{\text{P A S}}{\underset{\Big\downarrow\Big\downarrow\Big\downarrow}{}}$$

In all previous work (e.g. see Ref. [5] and references cited therein) on homogeneous redox-catalysis of S_RN 1-reactions, the reduction of nucleophilic substitution products (P) is one-electron and reversible, so that the radical anions (P⁻) formed are sufficiently stable, and no further fragmentation occurs. P⁻ simply gives back its extra electron to the neutral form of the catalyst (A) and/or the substrate (S) in the solution bulk. This depends on the mutual arrangement of the reagent reduction potentials on the electrochemical scale (cases a and b). However, in our case the reduction of the nucleophilic substitution products (σ-aryl and σ-vinyl derivatives of (η⁵-cyclopentadienyl)irondicarbonyl)) is irreversible [7] and gives rise to their destruction. Therefore, the mediator reduction of the nucleophilic substitution products, which may occur when the reduction potential of the product is less cathodic than the potential of organic halide (case a) or their potentials are close (case b), should be avoided.

However, the efficiency of the catalytic reduction process depends not only on the difference between the redox potentials of the mediator and the substrate (or the product), but also on other factors such as the mediator and substrate structural compatibility, kinetics of the reaction, etc. [8]. Therefore, it should be possible to select a mediator such that it would be efficient in the

catalytic substrate reduction even if the observed potential of the substitution product is less negative than that of the substrate (case a). In particular, this may be the case when the structures of the substrate and the product are considerably different. For instance, the presence of the bulky organometallic fragment CpFe(CO)₂ can be supposed to decrease the efficiency of the catalytic reduction of σ-aryl and σ-vinyl (η⁵-cyclopentadienyl)irondicarbonyl complexes compared with organic halides.

In this work we demonstrate the feasibility of the mediator electrochemical activation of reaction of aryl and vinyl halides with CpFe(CO)₂⁻ accompanied by irreversible reduction of the reaction products. This can be accomplished by carefully selecting the mediator and the reaction conditions.

As for the case c, this arrangement of the reagent reduction potentials results in a high probability of further reductive destruction of the initially formed (if any) radical anions of the substitution products at the electrode. If the substitution product is formed in the solution bulk, its concentration gradually increases as the reaction occurs until its reduction at the electrode dominates over its formation in the solution. Therefore, this case does not seem to be a good prospect and will not be examined here.

2. Results and discussion

The redox potentials of several reversible organic redox couples that can be used as the catalysts (mediators) of aryl and vinyl halides reduction are presented in Table 1. They were measured at Pt and Hg electrodes under the same conditions as the electrochemically in-

Table 1
Reduction potentials of the compounds studied (CH₃CN, 0.05 M n-Bu₄NBF₄, Ag/AgCl/KCl⁻¹, 20 °C); potential values corrected for IR-drop

Compounds	$-E^{\text{Red}}$ (V)	
	Pt	Hg
Substrates		
p-CH₃C₆H₄I	2.60 [b]	1.93
C₆H₅I	2.53 [b]	1.86
(E)-PhCH=C(Ph)Br	2.02	1.82
(Z)-PhCH=C(Ph)Br	1.98	1.77
Products		
p-CH₃C₆H₄Fe(CO)₂Cp	2.15	1.98 [c]
C₆H₅Fe(CO)₂Cp	2.08	1.96 [c]
(E)-PhCH=C(Ph)Fe(CO)₂Cp	2.04	1.82
(Z)-PhCH=C(Ph)Fe(CO)₂Cp	2.10	1.86
Mediators		
Anthracene	1.98	1.94
Benzophenone	1.82	1.79
o-Dicyanobenzene	1.67	1.65

[a] The potential of the Fc/Fc⁺ couple in our conditions is +0.43 V.
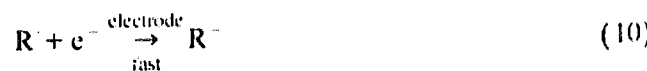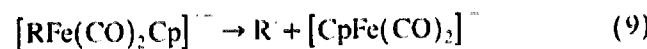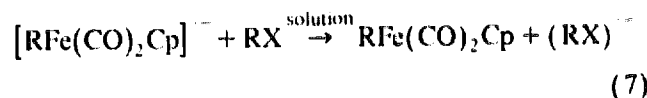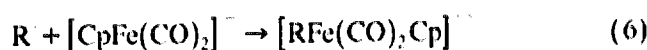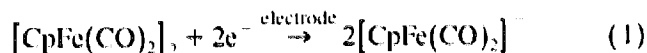[b] Potentials are measured in DMSO; [c] Data taken from Refs. [9,10].

duced nucleophilic substitution reactions. As expected, the potential values of these compounds are independent of the electrode material.

Fig. 1 presents the voltammograms which are typical of the mediator reduction of the substrates (here for iodobenzene). The originally reversible reduction of the mediator becomes irreversible on adding the substrate; the current of the mediator reduction increases. A criterion for the mediator efficiency is the value of the excess of the substrate that must be added to the solution to completely suppress the mediator radical-anion reoxidation (the corresponding peak in the voltammograms disappears). This quantity is designated as C^S/C^A (where C^S and C^A are the concentrations of the substrate and the mediator respectively). The absence of the peak of A^- reoxidation implies that A^- was chemically oxidised in the solution rather than at the electrode. This means that homogeneous redox-catalysis occurs. The higher the efficiency of the homogeneous electron transfer in the solution, the lower the value of C^S/C^A.

The experimental data on the efficiency of different mediators in the reduction of several aryl and vinyl halides and the corresponding σ-aryl and σ-vinyl derivatives of $(\eta^5$-cyclopentadienyl)irondicarbonyl at a Pt electrode are presented in Table 2. As inferred from a comparison of mediator and substrate reduction potentials, the best catalyst for the iodobenzene and p-iodo-

toluene reduction is anthracene. The gap between the anthracene and aryl halide reduction potentials, $\Delta E = E^0_{A/A} - E^{Red}_{RX}$, is smallest at the Pt electrode (Table 2) being 0.55 V and 0.62 V for iodobenzene and p-iodotoluene respectively. The peak of the anthracene radical-anion reoxidation disappears almost completely at only a twofold excess of these aryl halides (Table 2). At the same time, the reduction of σ-phenyl and σ-tolyl derivatives of $(\eta^5$-cyclopentadienyl)irondicarbonyl by anthracene radical-anion is significantly less efficient than in the previous case of aryl halides. This is illustrated by the form of the anthracene cyclic voltammogram: the reoxidation peak of the anthracene radical-anion disappears only at about a fourfold excess of σ-aryl $(\eta^5$-cyclopentadienyl)irondicarbonyl derivatives (Table 2). These observations confirm the hypothesis of the influence of the nature of the substrate (aryl halide or organometallic complex) on the catalytic efficiency. Therefore, it could be expected that using anthracene as a mediator would allow one to perform electrochemical activation of the nucleophilic aromatic substitution in iodobenzene and iodotoluene with $CpFe(CO)_2^-$ anions.

If a nucleophilic substitution reaction does occur, the addition of nucleophile to the aryl halide-mediator system must result in the reappearance in the cyclic voltammograms of the reoxidation peak of the mediator radical-anion A/A^-. The reaction sequence is as follows:

Fig. 1. Cyclic voltammograms obtained at a Pt electrode in CH_3CN with 0.05 M n-Bu$_4$NBF$_4$ as a supporting electrolyte: (a) 5×10^{-4} M anthracene (- - -); (b) a mixture of 5×10^{-4} M anthracene and 1×10^{-3} M iodobenzene (———).

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

$$A + e^- \xrightleftharpoons{electrode} A^- \qquad (2)$$

$$A^- + RX \rightleftharpoons (RX)^- + A \qquad (3)$$

$$(RX)^- \rightarrow R^- + X^- \qquad (4)$$

$$R^- + A^- \xrightarrow{solution} R^- + A \qquad (5)$$

$$R^- + [CpFe(CO)_2]^- \rightarrow [RFe(CO)_2Cp]^- \qquad (6)$$

$$[RFe(CO)_2Cp]^- + RX \xrightarrow{solution} RFe(CO)_2Cp + (RX)^- \qquad (7)$$

$$[RFe(CO)_2Cp]^- + A \rightleftharpoons RFe(CO)_2Cp + A^- \qquad (8)$$

$$[RFe(CO)_2Cp]^- \rightarrow R^- + [CpFe(CO)_2]^- \qquad (9)$$

$$R^- + e^- \xrightarrow[fast]{electrode} R^- \qquad (10)$$

(R = aryl, vinyl)

A^- can be found in the solution only if the equilibrium in Eq. (8) is shifted to the right, i.e. if A^- does not reduce the nucleophilic substitution product. Therefore, the observations of the peak of A^- reoxidation in the

Table 2

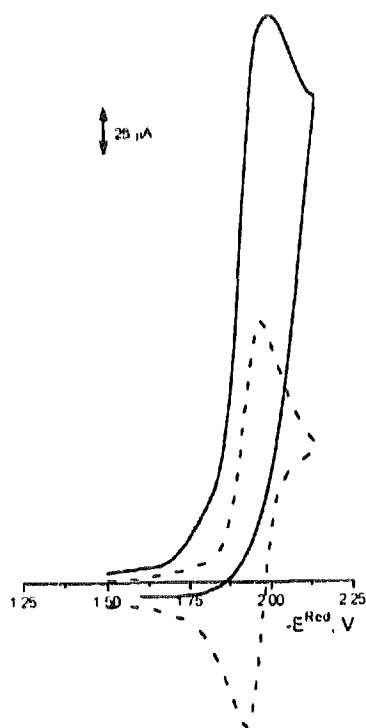Data on homogeneous redox catalysis of the reduction of aryl and vinyl halides and corresponding σ-aryl and σ-vinyl derivatives of (η^5-cyclopentadienyl)irondicarbonyl (Pt, 0.05 M n-Bu$_4$NBF$_4$, Ag/AgCl/KCl, 20 °C, $C^A = 5 \times 10^{-4}$ M); potential values corrected for IR-drop

Substrate, S or Product, P	Mediator, A	$\Delta E = E^\circ(A/A^-) - E^{Red}(S)$ (V)	C^S/C^A	I^a/I^c
p-Iodotoluene	Anthracene	0.62	0	0.34
			1	0.09
			2	0.05
	Benzophenone	0.78	0	0.23
			1.2	0.13
			2.5	0.07
			3.8	0.03
	o-Dicyanobenzene	0.93	0	0.33
			2	0.24
			4	0.13
			11	0.07
			13	0
Iodobenzene	Anthracene	0.55	0	0.34
			1	0.09
			2	0
	Benzophenone	0.71	0	0.20
			1.25	0.06
			2	0.02
			2.5	0
	o-Dicyanobenzene	0.88	0	0.33
			2.4	0.25
			5	0.04
			7	0
(E)-Bromostylbene	o-Dicyanobenzene	0.35	0	0.37
			2	0
(Z)-Bromostylbene	o-Dicyanobenzene	0.31	0	0.40
			1	0.20
			2	0.08
			4	0
σ-Phenyl-η^5-cyclopentadienyl-irondicarbonyl C$_6$H$_5$Fp	Anthracene	0.10	0	0.30
			1	0.15
			2	0.08
			4	0
	Benzophenone	0.26	0	0.20
			1	0.11
			2	0.10
			3	0.09
			4	0.08
	o-Dicyanobenzene	0.41	0	0.30
			2	0.27
			3	0.27
			5	0.27
σ-Tolyl-η^5-cyclopentadinyl-irondicarbonyl p-CH$_3$-C$_6$H$_4$Fp	Anthracene	0.17	0	0.27
			1	0.20
			2	0.10
			4	0.05
	Benzophenone	0.33	0	0.20
			1	0.15
			2	0.12
			4	0.10
	o-Dicyanobenzene	0.48	0	0.27
			2	0.27
			4	0.27
			5	0.27

Table 2 (continued)

Substrate, S or Product P	Mediator, A	$\Delta E = E^\circ(A/A^-) - E^{Red}(S)$ (V)	C^S/C^A	I^a/I^c
σ-(E)-1,2-diphenylvinylcyclopentadienylirondicarbonyl, PhCH=CH(Ph)Fp	o-Dicyanobenzene	0.37	0	0.40
			1	0.20
			2	0.08
			4	0

Notes: C^S/C^A (C^P/C^A) are the ratios of the substrate (product) and mediator concentrations; I^a/I^c is the ratio of the currents of mediator anion-radical oxidation and mediator reduction in the CV experiments.

cyclic voltammograms can serve as an indicator that the target reaction (Eq. (6), Eq. (7)) does occur.

However, in the case of anthracene, when the nucleophile — (η^5-cyclopentadienyl)irondicarbonyl anion — is added to the reaction mixture, the peak of the anthracene radical-anion reoxidation does not appear in the voltammograms. This implies that the equilibrium in Eq. (8) in this case is shifted to the left, and the relative contributions of reactions in Eq. (9) and Eq. (10) are quite significant in preventing the formation of an aromatic nucleophilic substitution product. In other words, even though anthracene seems to be an efficient mediator of this reaction according to the redox potentials data, the electrochemical activation of nucleophilic substitution with it is impossible. The same behaviour was also observed for p-iodotoluene.

However, the nucleophilic substitution can be performed when less effective mediators (e.g. o-dicyanobenzene) are used. Thus, a fivefold excess of iodobenzene and an elevenfold excess of p-iodotoluene with respect to the mediator are required to completely suppress the o-dicyanobenzene radical-anion reoxidation (Table 2). The lower efficiency of this mediator originates from a higher gap between the reduction potentials of the mediator and the substrate, which results in less effective electron transfer from the mediator (o-dicyanobenzene radical anion) to the substrate (Eq. (3)). At the same time, the lower efficiency of the mediator in the electrochemical activation of organic halide implies a lower reactivity towards the substitution product because the potential gap between the mediator and the product also increases (except for case c (see above), which is not considered here). Furthermore, the lower rate of the electron transfer from the mediator to the substrate results in the reaction zone moving into the bulk of the solution. This will decrease the relative contribution of the side reactions in Eq. (9) and Eq. (10), which occur at the electrode, thus increasing the yield of the target reactions in Eq. (6) and Eq. (7).

The above considerations are illustrated in Fig. 2. Fig. 2 presents cyclic voltammograms of o-dicyanobenzene taken in presence of iodobenzene and CpFe(CO)$_2^-$. A distinct peak for the o-dicyanobenzene

radical-anion reoxidation is observed. This indicates that the target reaction (Eq. (6)) does occur, resulting in formation of the nucleophilic substitution products. The same behaviour is observed when p-iodotoluene is used as a substrate. In both cases the CV curves were taken at the mercury rather than the platinum electrode. The reason is that at platinum the reduction of o-dicyanobenzene and the nucleophile — [CpFe(CO)$_2$]$^-$ — formation from [CpFe(CO)$_2$]$_2$ occur almost simultaneously ($E^{Red} = -1.67$ V and -1.65 V respectively), and the
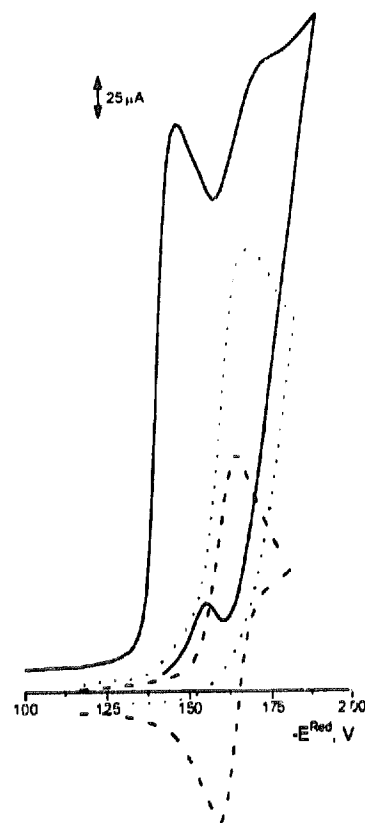

Fig. 2. Cyclic voltammograms obtained at an Hg electrode in CH$_3$CN with 0.05 M n-Bu$_4$NBF$_4$ as a supporting electrolyte: (a) 5×10^{-4} M o-dicyanobenzene (– – –); (b) a mixture of 3×10^{-3} M iodobenzene and 5×10^{-4} M o-dicyanobenzene (· · ·); (c) the same as (b) on addition of 3×10^{-3} M [CpFe(CO)$_2$]$_2$ (———). The reference electrode was aqueous Ag/AgCl/KCl, the scan rate was 200 mV s^{-1}.

interference of these two processes distorts the real pattern of the mediator behaviour. At a mercury electrode, the two processes are separated because, while the mediator reduction potential remains constant (Table 1), the nucleophile formation potential becomes less negative (− 1.50 V). The results obtained indicate that, despite the lower efficiency of o-dicyanobenzene in the reduction of iodobenzene and p-iodotoluene, the former is a better catalyst for the nucleophilic substitution in these substrates with [CpFe(CO)₂]⁻ than anthracene.

The electrochemical activation of the nucleophilic substitution reaction can also be performed for some non-active vinyl halides such as E- and Z-isomers of bromostylbene. This was confirmed by the cyclic voltammograms of o-dicyanobenzene in the presence of E- or Z-isomers of bromostylbene and [CpFe(CO)₂]₂, which were very similar to those obtained for o-di-cyanobenzene in the presence of iodobenzene and [CpFe(CO)₂]₂ (Fig. 2). It should be noted that there are only a few instances of electrochemically activated nucleophilic substitution in vinyl halides [11,12]. The first reaction of this type was the interaction of iron(I)porphyrine with $HBrC=CH(C_6H_4-Cl-p)$ [11]. Recently, we have demonstrated [12] the electrochemically promoted nucleophilic substitution in several polyfluorovinyl halides with [CpFe(CO)₂]⁻ anion.

The feasibility of an electrochemically induced mediator nucleophilic substitution reaction in the above aryl and vinyl systems was also confirmed by preparative-scale electrolysis. The results are presented in Table 3. It can be seen that the use of mediators enables one to carry out the nucleophilic substitution reaction with [CpFe(CO)₂]⁻ for those substrates, where the reaction

without mediator does not occur both at Pt and Hg electrodes (e.g. for p-iodotoluene and E-bromostylbene). The preparative-scale electrolysis of p-iodotoluene in the presence of [CpFe(CO)₂]₂ yields only traces of the σ-p-tolyl derivative of (η⁵-cyclopentadienyl)irondicarbonyl. Performing this reaction in the presence of o-dicyanobenzene leads to a substantial increase in the yield of the substitution product, $CpFe(CO)_2C_6H_4CH_3-p$ (Table 3).

The other substrates investigated can, in principle, enter into direct electrochemically activated reactions because, in this case (at least on mercury), the reduction potential of the product is more cathodic than that of the substrate [1]. However, even at the Hg electrode this potential separation is small and results in extremely low yields of the target products in the direct electrochemically activated reaction. The application of mediator redox catalysis allows us to dramatically increase the reaction yield. For instance, the maximal yield of the substitution product for iodobenzene was 15%, even when the potential scanning electrolysis technique was used [1]. With o-dicyanobenzene, the yield of the substitution product increased to 45%.

Interestingly, the electrochemically induced mediator nucleophilic substitution in vinyl halides with [CpFe(CO)₂]⁻ is not stereoselective. The nucleophilic substitution in either E- or Z-isomers of vinyl halides yields a mixture of E- and Z-isomers of $CpFe(CO)_2C(Ph)=C(Ph)H$ with the E-isomer dominating, regardless of the initial vinyl halide configuration. This suggests that the reaction involves the formation of a radical-anion species that can undergo isomerisation. This species can be either RHal⁻ or [RFe(CO)₂Cp]⁻

Table 3

The results of the preparative-scale electrolysis of aryl and vinyl halides in the presence of [CpFe(CO)₂]₂ (Hg, 0.25 M n-Bu₄NBF₄, CH₃CN, Ag/AgCl/KCl, 20 °C)

Substrate	Electrolysis potential (V) [a]	Electrolysis duration, (h)	Nucleophilic substitution product	Preparative yield (%)
p-CH₃C₆H₄I	potential [b] cycled from − 1.95 to − 1.55	3–4	p-CH₃C₆H₄Fp [c]	traces
p-CH₃C₆H₄I in the presence of 5 × 10⁻⁴ M o-dicyanobenzene	− 1.80	3	p-CH₃C₆H₄Fp [c]	43
C₆H₅I	potential cycled from − 1.90 to − 1.55	3–4	C₆H₅Fp	15
C₆H₅I in the presence of 5 × 10⁻⁴ M o-dicyanobenzene	− 1.75	3	C₆H₅Fp	45
E-PhCH=C(Ph)Br in the presence of 5 × 10⁻⁴ M o-dicyanobenzene	− 1.75	3–4	E-PhCH=C(Ph)Fp	41
Z-PhCH=C(Ph)Br in the presence of 5 × 10⁻⁴ M o-dicyanobenzene	− 1.75	3–4	Z-PhCH=C(Ph)Fp E-PhCH=C(Ph)Fp	20 32
			Z-PhCH=C(Ph)Fp	13

[a] No IR correction made. [b] Rate of potential cycling $v = 500$ mV s⁻¹. [c] Fp = Fe(CO)₂Cp.
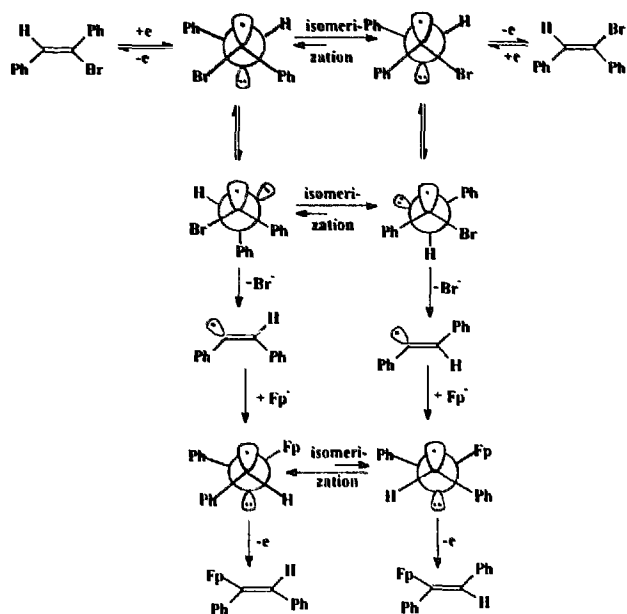
Scheme 1.

(Eq. (3) and Eq. (6)). It is known [13,14] that the reduction of vinyl halides results in their isomerisation. For example, the electrochemical reduction of monobromomomaleic acid yields the mixture of maleic and fumaric acids [13]. In this case, a likely explanation of the preferential formation of the E-isomer is the sterically less hindered conformation of the radical-anion of the substitution product which minimises the repulsion of the phenyl group and the bulky organometallic fragment CpFe(CO)₂ (Scheme 1).

Therefore, we have demonstrated that homogeneous redox-catalysis makes it possible to considerably extend the range of the substrates entering the electrochemically induced nucleophilic substitution at the sp²-hybridised carbon atom with metal-containing nucleophiles. By carefully selecting the mediator one can perform the substitution reaction even in the case when the substitution products are irreversibly reduced at less cathodic potentials than the initial substrates. This approach seems to be rather general and, in our opinion, can be applied not only to nucleophilic substitution, but also to a wider range of electrochemically activated processes involving organic and organometallic compounds.

3. Experimental details

Instrumentation, purification of solvents and general procedures of electrochemical measurements and preparative electrolysis were the same as previously described [1].

3.1. C_6H_5I and $[CpFe(CO)_2]_2$

0.035 g $(1 \times 10^{-4}$ mol) of $[CpFe(CO)_2]_2$ was dissolved in 10 ml of CH_3CN in an electrochemical cell and potentiostatically controlled electrolysis was performed at a potential of -1.85 V until the current decreased to 20% of its initial value.

0.034 g $(1.67 \times 10^{-4}$ mol) of C_6H_5I was added to the solution of $[CpFe(CO)_2]^-$ obtained and cycling electrolysis was carried out, the potential being swept from -1.90 to -1.55 V at a scan rate of 500 mV s⁻¹. After separation of the reaction mixture the following compounds were obtained: the initial iodobenzene (0.022 g) $CpFe(CO)_2C_6H_5$ (0.003 g, 15%) (MS, m/z (I, %): 254 [M]⁺ (15.5), 226 [M − CO]⁺ (40), 198 [M − 2CO]⁺ (70), 56 [Fe]⁺ (100)), and $CpFe(CO)_2I$ (0.015 g, 79%) (MS, m/z (I, %): 304 [M]⁺ (73), 276 [M − CO]⁺ (19.5), 248 [M − 2CO]⁺ (63), 183 [M − 2CO − Cp]⁺ (100)).

3.2. C_6H_5I and $[CpFe(CO)_2]_2$ in the presence of o-dicyanobenzene

After preparative electrolysis of 0.035 g $(1 \times 10^{-4}$ mol) of $[CpFe(CO)_2]_2$ and 0.041 g $(2 \times 10^{-4}$ mol) of C_6H_5I in the presence of 0.007 g $(5 \times 10^{-5}$ mol) of o-dicyanobenzene at a potential of -1.75 V, the following compounds were isolated: $CpFe(CO)_2C_6H_5$ (0.008 g, 45%), $CpFe(CO)_2I$ (0.006 g, 30%) and initial iodobenzene (0.027 g).

3.3. $p-IC_6H_4CH_3$ and $[CpFe(CO)_2]_2$ in the presence of o-dicyanobenzene

After electrolysis of 0.035 g $(1 \times 10^{-4}$ mol) of $[CpFe(CO)_2]_2$, 0.044 g $(2 \times 10^{-4}$ mol) of $p-IC_6H_4CH_3$ and 0.006 g $(5 \times 10^{-5}$ mol) of o-dicyanobenzene were added to the solution of $[CpFe(CO)_2]$ and potentiostatically controlled electrolysis was performed at a potential of -1.80 V. From the reaction mixture, the following compounds were isolated: $CpFe(CO)_2C_6H_4CH_3$-p (0.009 g, 43%) (MS, m/z (I, %): 268 [M]⁺ (20), 240 [M − CO]⁺ (44), 212[M − 2CO]⁺ (100)), $CpFe(CO)_2I$ (0.010 g, 35%) and initial p-iodotoluene (0.023 g).

3.4. (E)-PhCH = C(Ph)Br and $[CpFe(CO)_2]_2$ in the presence of o-dicyanobenzene

After preparative electrolysis of 0.035 g $(1 \times 10^{-4}$ mol) of $[CpFe(CO)_2]_2$ and 0.059 g $(2 \times 10^{-4}$ mol) of (E)-PhCH=C(Ph)Br in the presence of 0.006 g (0.5 $\times 10^{-4}$ mol) of o-dicyanobenzene at a potential -1.75 V, the following compounds were isolated: (E)-$CpFe(CO)_2C(Ph)=C(Ph)H$ (0.015 g, 41%) $(R_f = 0.67$, benzene/hexane = 1/5) and (Z)-$CpFe(CO)_2$-$C(Ph)=C(Ph)H$ (0.007 g, 20%) $(R_f = 0.78$, benzene/hexane = 1/5) (mass-spectra of both isomers are identical, m/z: 356 [M]⁺, 328 [M − CO]⁺, 300 [M − 2CO]⁺, 179 [M − Fe(CO)₂Cp]⁺, 121 [CpFe]⁺).

3.5. (Z)-PhCH = C(Ph)Br and [CpFe(CO)₂]₂ in the presence of o-dicyanobenzene

After preparative electrolysis of 0.035 g (1 × 10^{-4} mol) of [CpFe(CO)₂]₂ and 0.051 g (2 × 10^{-4} mol) of (Z)-PhCH=C(Ph)Br in the presence of 0.006 g (0.5 × 10^{-4} mol) of o-dicyanobenzene at a potential − 1.75 V, the following compounds were isolated: (E)-CpFe(CO)₂C(Ph)=C(Ph)H (0.007 g, 32%) and (Z)-CpFe(CO)₂C(Ph)=C(Ph)H (0.003 g, 13%).

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