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Electrochemically induced aromatic nucleophilic substitution in p-diiodobenzene with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ and $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-$-anions

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Abstract

The reactions of p-diiodobenzene with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ and $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-$ were studied using a complex of electrochemical techniques (cyclic voltammetry, rotating ring-disk electrode and preparative scale electrolysis). For $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ it was shown that aromatic nucleophilic substitution of either one or two iodine atoms in p-diiodobenzene for η^5-cyclopentadienylirondicarbonyl can be performed through electrochemical activation of the aryl halide. The ratio of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_4I$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_4Fe(CO)_2(\eta^5\text{-}C_5H_5)$ was shown to depend strongly on the electrolysis conditions: electrode potential, electrolysis duration, etc. The yield of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_4Fe(CO)_2(\eta^5\text{-}C_5H_5)$ can be considerably increased when $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_4I$ is taken as a starting compound. For $[(\eta^5\text{-}C_5H_5)W(CO)_3I^-$ the main product of the reaction with p-diiodobenzene is $(\eta^5\text{-}C_5H_5)W(CO)_3I$.

Keywords: Iron; Tungsten; Electrochemistry; Bond activation

1. Introduction

Aromatic nucleophilic substitution in low $S_N(Ar)$-active and nonactive aryl halides with transition metal carbonylmetallates is of great interest because various new compounds with a carbon–metal σ-bond can be obtained in this way. Earlier [1] we studied electrochemically induced aromatic nucleophilic substitution in mono-substituted iodo- and bromobenzenes with cyclopentadienylcarbonylmetallates of Fe and Mo using cyclic voltammetry (CVA) and rotating ring-disk electrode (RRDE) techniques and showed that electrochemical activation can be performed only with aryl halides that are more readily reduced than the corresponding σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl. With $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$-anion the main product of the electrochemical reaction is $(\eta^5\text{-}C_5H_5)Mo(CO)_3Hal$. To extend the number of aromatic substrates that are active in reaction with transition metal carbonylmetallates under electrochemical activation of aryl halide, we investigated the interaction of $CpFe(CO)_2^-$ and $CpW(CO)_3^-$ ($Cp = (\eta^5\text{-}C_5H_5)$) with p-diiodobenzene. The carbon–halogen bond in this compound can be activated in the metallocomplex catalysis as well (e.g. with $Pd(Ph_3P)_2Cl_2$), but only one iodine atom can be easily substituted in this case and the yield of $CpFe(CO)_2C_6H_4I$ ranges up to 70% [2].

The substitution of the second iodine atom is deferred and the yield of the double substituted product, $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$, is significantly lower.

This work deals with an alternative metallocomplex catalysis reaction: activation of the C–I bond by electrochemical reduction of p-diiodobenzene.

2. Results and discussion

Study of the electrochemical activation of the reaction p-diiodobenzene with $CpFe(CO)_2^-$-anion requires a preliminary investigation of the electrochemical reduction of the starting p-diiodobenzene and the possible products of nucleophilic substitution. The reduction potentials for these compounds at Pt and Hg

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Table 1
Reduction potentials ($-E_{1/2}$,V) of p-IC_6H_4I, p-$CpFe(CO)_2C_6H_4I$, p-$CpFe(CO)_2C_6H_4Fe(CO)_2Cp$ (0.05 M Bu_4NBF_4, vs. Ag/AgCl, 20°C)

	IC_6H_4I	$CpFe(CO)_2$-C_6H_4I	$CpFe(CO)_2$-$C_6H_4Fe(CO)_2Cp$
DMSO (Pt)	1.72	1.80	2.05
CH_3CN (Pt)	1.97	2.00	2.24
CH_3CN (Hg)	1.62	1.78	2.01

electrodes in DMSO and CH_3CN are presented in Table 1.

The electrochemical reduction of $[CpFe(CO)_2]_2$ and $[CpW(CO)_3]_2$ complexes, which are the precursors of the nucleophilic carbonylmetallates were studied earlier [3]. As in our previous work [1] nucleophilic species were generated directly at the electrode:

$$M_2 \xrightarrow{+2e^-} 2M^-$$

($E_{1/2} = -1.55$ V (DMSO) for M = $CpFe(CO)_2$ and $E_{1/2} = -1.14$ V (DMSO) for M = $CpW(CO)_3$).
One can see that two binuclear complexes are reduced at less cathodic potentials than p-diiodobenzene. Hence, in the vicinity of the peak of the p-diiodobenzene reduction (-1.72 V) both the nucleophilic species and $(IC_6H_4I)^{\overline{\cdot}}$ are generated at the electrode. The simultaneous generation of both reactants at the electrode increases the probability of their entering the substitution reaction at the electrode surface or near it rather than side processes such as the further reduction of $(IC_6H_4)^{\cdot}$ radicals. However, the irreversibility of the reduction of the nucleophilic substitution products, which is accompanied by their destruction, imposes a restriction on the potential at which the electrochemically induced reaction can be carried out. The potential, optimal for performing the electrochemically induced aromatic nucleophilic substitution, must be sufficiently cathodic for initial p-diiodobenzene and binuclear complexes to be reduced, but less than the reduction potential of the products. Otherwise, they will immediately decompose.

Fig. 1 presents the dependencies on the disk potential of the current at the disk and at the ring ($i_d = f(E_d)$) and ($i_r = f(E_d)$). The ring potential was fixed at -0.65 V, which corresponds to the oxidation of $CpFe(CO)_2^-$-anions. In Fig. 1 one can see a decrease in the current of $CpFe(CO)_2^-$ oxidation at the ring when the disk potential reaches the region of p-diiodobenzene reduction. This indicates that a portion of the carbonylmetallate enters a reaction and does not contribute to the ring current. A similar, though less pronounced decrease in the current was observed for the reaction of $CpFe(CO)_2C_6H_4I$ with $CpFe(CO)_2^-$ at the potential that corresponds to the reduction of $CpFe(CO)_2C_6H_4I$. This behaviour originates from a lower rate of reaction of $CpFe(CO)_2^-$ with $CpFe(CO)_2C_6H_4I$ as compared with p-diiodobenzene. These regularities correlate with the results of the experiments on the activation of p-diiodobenzene by means of metallo-complex catalysis.

From our experimental results we infer the following scheme for the process:

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

$$IC_6H_4I \xrightarrow{+1e^-} [IC_6H_4I]^{\overline{\cdot}} \qquad (2)$$

$$[IC_6H_4I]^{\overline{\cdot}} \longrightarrow [C_6H_4I]^{\cdot} + I^- \qquad (3)$$

$$[IC_6H_4]^{\cdot} + [CpFe(CO)_2]^- \longrightarrow [IC_6H_4Fe(CO)_2Cp]^{\overline{\cdot}} \qquad (4)$$

$$[IC_6H_4Fe(CO)_2Cp]^{\overline{\cdot}} \xrightarrow{-e^-} IC_6H_4Fe(CO)_2Cp \qquad (5)$$

$$[IC_6H_4Fe(CO)_2Cp]^{\overline{\cdot}} \longrightarrow [C_6H_4Fe(CO)_2Cp]^{\cdot} + I^- \qquad (6)$$

$$[C_6H_4Fe(CO)_2Cp]^{\cdot} + [CpFe(CO)_2]^- \longrightarrow [CpFe(CO)_2C_6H_4Fe(CO)_2Cp]^{\overline{\cdot}} \qquad (7)$$

$$[CpFe(CO)_2C_6H_4Fe(CO)_2Cp]^{\overline{\cdot}} \xrightarrow{-e^-} CpFe(CO)_2C_6H_4Fe(CO)_2Cp \qquad (8)$$

Preparative-scale electrolysis showed the yield of σ-aryl derivatives of (η^5-cyclopentadienyl)irondicarbonyl to depend strongly on the electrolysis conditions (see Table 2). The working electrode was a mercury pool. When the electrolysis was performed at a

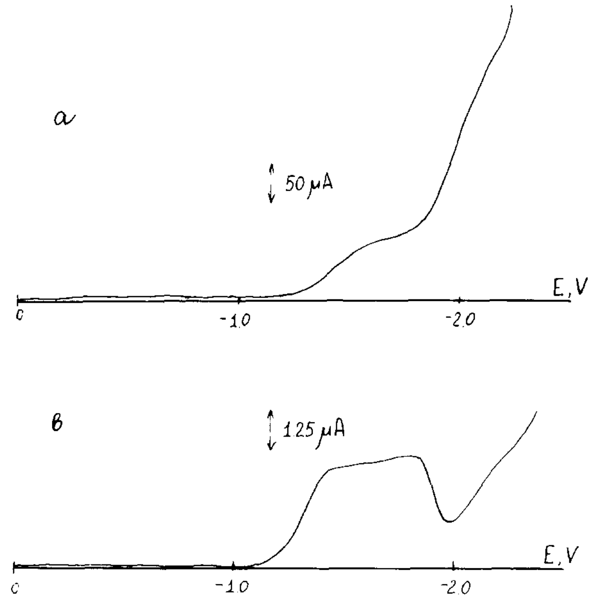

Fig. 1. Voltammograms of p-diiodobenzene (1×10^{-3} M) in the presence of $[CpFe(CO)_2]_2$ (5×10^{-4} M) which were taken (a) at the disk($i_d = f(E_d)$) and (b) at the ring ($i_r = f(E_d)$). The ring potential is -0.65 V. (DMSO, 0.05 M n-Bu_4NBF_4, vs. Ag/AgCl, 20°C, v = 20 mV/s, w = 2230 rpm).

fixed potential, the yields of both $CpFe(CO)_2C_6H_4I$ and $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$ were poor. The electrolysis, carried out under potential cycling at a sweep rate of 500 mV/s, appears to be more effective but the yield of the products depends on the cycling limits as well. The maximum yield of $CpFe(CO)_2C_6H_4I$ was obtained when the potential was scanned from −1.70 V (the potential of IC_6H_4I reduction) to −1.55 V (the potential of the generation of $CpFe(CO)_2^-$-anions) within 3 h. An increase in the duration of electrolysis results in an increase in the relative amount of $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$. Potential cycling is likely to decrease the probability of the radicals formed in reactions (3) and (6) being further reduced at the electrode, so they would be able to diffuse into the bulk of the solution. Therefore, the potential scanning favours reactions (4) and (5).

The yield of $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$ can be expected to increase when the cathodic potential limit is shifted towards more negative potentials, because reaction (5) in this case will be deferred at the electrode. However, no increase in the yield of $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$ was observed. The most probable explanation is that under these conditions, the reduction of $(C_6H_4I)^{\cdot}$ and $(C_6H_4Fe(CO)_2Cp)^{\cdot}$ radicals at the electrode dominates over their interaction with $CpFe(CO)_2^-$ (reactions (4) and (7)) and the main electrolysis product is iodobenzene.

The yield of $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$ can be considerably increased if we take $CpFe(CO)_2C_6H_4I$ instead of *p*-diiodobenzene as a starting compound. Preparative-scale electrolysis of the mixture of $CpFe(CO)_2C_6H_4I$ and $[CpFe(CO)_2]_2$ under potential cycling from −1.85 V (the potential of reduction of $CpFe(CO)_2C_6H_4I$) to −1.55 V (the potential of creation of $CpFe(CO)_2^-$-anions) gives $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$ with a yield of 57%.

It seems likely that the method of cycling electrolysis can be applied to obtaining σ-arylderivatives of other transition metal carbonylmetallates as well. However we failed to obtain $CpW(CO)_3C_6H_4I$ from *p*-diiodobenzene by electrochemical reductive activation of the C–I bond. Preparative-scale electrolysis of IC_6H_4I in the presence of $[CpW(CO)_3]^-$ yields $CpW(CO)_3I$ (66%) and only traces of $CpW(CO)_3C_6H_4I$. The nucleophilicities of $[CpFe(CO)_2]^-$ and $[CpW(CO)_3]^-$ are known to differ considerably: the former is approximately five orders of magnitude greater than the latter [4]. Hence, any reaction similar to (4) is retarded and $[CpW(CO)_3]^-$ is likely to act as a reducing agent.

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. *p-IC_6H_4I and $[CpFe(CO)_2]^-$*

0.0626 g (1.77×10^{-4} mol) of $[CpFe(CO)_2]_2$ was dissolved in 17 ml of CH_3CN in an electrochemical cell and potentiostatically controlled electrolysis was performed at a potential of −1.8 V until the current decreased to 0.038 A.

0.0577 g (1.75×10^{-4} mol) of IC_6H_4I was added to the solution of $[CpFe(CO)_2]^-$ thus obtained and cycling electrolysis was carried out, the potential being swept from −1.55 to −1.75 V at a scan rate of 500 mV/s. After separation of the reaction mixture the following compounds were obtained: $CpFe(CO)_2C_6H_4I$, 0.0182 g (40.86%) (MS: *m/z* 380^-($[M]^+$, 1%), 352 ($[M - CO]^+$, 10.7%), 324 ($[M - 2CO]^+$, 100%)); $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$, 0.0036 g (7.15%) (MS: *m/z* 430 ($[M]^+$, 1%), 402 ($[M - CO]^+$, 2%), 374 ($[M - 2CO]^+$, 2%), 346 ($[M - 3CO]^+$, 4%), 318 ($[M - 4CO]^+$, 26%), 262 ($[M - 4CO - 56]^+$, 100%)); $CpFe(CO)_2I$, 0.0126 g (35.4%) (MS: *m/z* 304 ($[M]^+$, 73%), 276 ($[M - CO]^+$, 19.5%), 248 ($[M - 2CO]^+$, 63%), 183 ($[M - 2CO - Cp]^+$, 100%, 121 ($[M - 2CO - I])^+$, 59%)) and starting IC_6H_4I, 0.0192 g.

3.2. *p-$IC_6H_4Fe(CO)_2Cp$ and $[CpFe(CO)_2]^-$*

After preparative electrolysis of 0.016 g (4.5×10^{-5} mol) of $[CpFe(CO)_2]_2$ and 0.0082 g (2.16×10^{-5} mol)

Table 2
Preparative electrolysis of *p*-diiodobenzene in the presence of $[CpFe(CO)_2]^-$ in the ratio of (1:2) (Hg, CH_3CN, 0.25 M Bu_4NBF_4, Ag/AgCl, 20°C).

Electrolysis time, h	Electrolysis potential, V	Yield of $IC_6H_4Fe(CO)_2Cp$, %	Yield of $Cp_2Fe_2(CO)_4C_6H_4$, %
3	cycling from −1.7 to −1.55 V	41	7.5
6	cycling from −1.7 to −1.55 V	18	17
3	cycling from −1.85 to −1.55 V	3.5	5
6	−1.7 V	3	6
6	−1.85 V	traces	traces
3 [a]	cycling from −1.85 to −1.55 V	18	57

[a] When $CpFe(CO)_2C_6H_4I$ is taken as a starting compound.

of p-$IC_6H_4Fe(CO)_2Cp$ at a potential cycling from −1.85 to −1.55 V the following compounds were isolated: $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$, 0.0043 g (56.8%), $CpFe(CO)_2I$, 0.0017 g (31.8%) and p-$CpFe(CO)_2C_6H_4I$, 0.0015 g (18%).

3.3. p-IC_6H_4I and $[CpW(CO)_3]^-$

After preparative electrolysis of 0.0429 g (6.44×10^{-5} mol) of $[CpW(CO)_3]_2$ and 0.015 g (4.5×10^{-5} mol) of p-IC_6H_4I at a potential cycling from −1.75 to −1.45 V $CpW(CO)_3I$, 0.0066 g (66%) was isolated (MS: 460 ($[M]^+$, 29.9%), 432 ($[M\text{-}CO]^+$, 37.1%), 404 ($[M-2CO]^+$, 44.3%), 376 ($[M-3CO]^+$, 100%).

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