Electron Transfer Catalysis of Arene Deco-ordination in the Cationic (η^5-Cyclopentadienyl)(η^6-arene)iron(II) Complexes

Andre Darchen

Laboratoire d'Electrochimie, E.R.A. C.N.R.S. 896, Université de Rennes I, Campus de Beaulieu, 35042 - Rennes Cédex, France

Replacement of the arene group in $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_{6-n}Me_n)]^+$ ($n \leqslant 4$) by three $P(OMe)_3$ ligands is carried out under mild conditions by reductive electron transfer catalysis in acetonitrile and gives the free arene and $[(\eta^5\text{-}C_5H_5)Fe\{P(OMe)_3\}_3]^+$ in good yields.

Recovery of the arene under mild conditions remains a key step in the development of arene metal complexes in organic synthesis.[1] A good method of decomplexation[2] has not been proposed so far or $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]^+$ $[Fe(cp)Ar]^+$ and therefore I report here a fast arene deco-ordination process under mild conditions by electron transfer catalysis (E.T.C.).

When $[Fe(cp)C_6H_6]^+$ is studied in dimethylformamide (DMF) containing $P(OMe)_3$, the voltammetric curve is characteristic of an $\overrightarrow{E}\overleftarrow{C}E$ mechanism[3] (Figure 1). Under these conditions, the reversibility[4] of the well known one-electron reduction [equation (1)] is lost; the ratio of peak currents $i^p{}_a/i^p{}_c$ is less than unity and, as soon as the first cathodic peak decreases, a new irreversible reduction appears at $E^p = -1.78$ V *vs.* standard calomel electrode (S.C.E.) with increasing intensity. This latter peak is due to the reduction of $[Fe(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}_3]^+$ formed [equation (2)] in the vicinity of the electrode during the cathodic scan. This overall non-redox chemical reaction (2) is induced by the labile nature of the neutral 19-electron complex $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ allowing the exchange of the arene ligand for three $P(OMe)_3$ groups [equation (3)] followed by chain propagation of the electron [equation (4)].

$$[Fe^{II}(cp)(\eta^6\text{-}C_6H_6)]^+ + 1e^- \rightleftharpoons [Fe^I(cp)(\eta^6\text{-}C_6H_6)] \qquad (1)$$

$$[Fe(cp)(\eta^6\text{-}C_6H_6)]^+ + 3\,P(OMe)_3 \rightarrow [Fe(cp)\{P(OMe)_3\}_3]^+ + C_6H_6 \qquad (2)$$

$$[Fe^I(cp)(C_6H_6)] + 3\,P(OMe)_3 \rightarrow [Fe^I(cp)\{P(OMe)_3\}_3] + C_6H_6 \qquad (3)$$

$$[Fe^{II}(cp)(C_6H_6)]^+ + [Fe^I(cp)\{P(OMe)_3\}_3] \rightarrow [Fe^I(cp)(C_6H_6)] + [Fe^{II}(cp)\{P(OMe)_3\}_3]^+ \qquad (4)$$

The electrochemically induced chemical reaction (2) is an unprecedented example of polyhapto ligand replacement. In the field of organometallic electrochemistry all the reactions[5] reported up to now occur by an $\overrightarrow{E}\overleftarrow{C}E$ mechanism involving monohapto ligand replacement. Owing to the high molecularity of reaction (3) it is likely that the deco-ordination of the arene occurs in three steps but the voltammogram does not show intermediate peaks corresponding to products containing an arene partially bound to iron.

In view of the behaviour of diamagnetic complexes during exchange reactions,[6] the influence of the solvent was investigated. The rate of deco-ordination of the arene, estimated by the decrease of the cathodic peak of $[Fe(cp)(C_6H_6)]^+$ after addition of $P(OMe)_3$, was found to be solvent dependent. The rate decreases in the order: acetonitrile (ACN) > DMF > CH_2Cl_2 or MeCOMe. It is noteworthy that the reduction of $[Fe(cp)(C_6H_6)]^+$ appears irreversible in ACN at low scan rate. In this solvent the reduction follows an EC mechanism, not previously reported, in agreement with the fast decomposition of $[Fe^I(cp)(C_6H_6)]$ noted by Nesmeyanov *et al.*[7] Moreover, the rate of arene deco-ordination in ACN or DMF is independent of the concentration of $P(OMe)_3$, in contrast to the reaction in CH_2Cl_2. These observations suggest that reaction (3) primarily involves the co-ordination of solvent molecules S in a rate

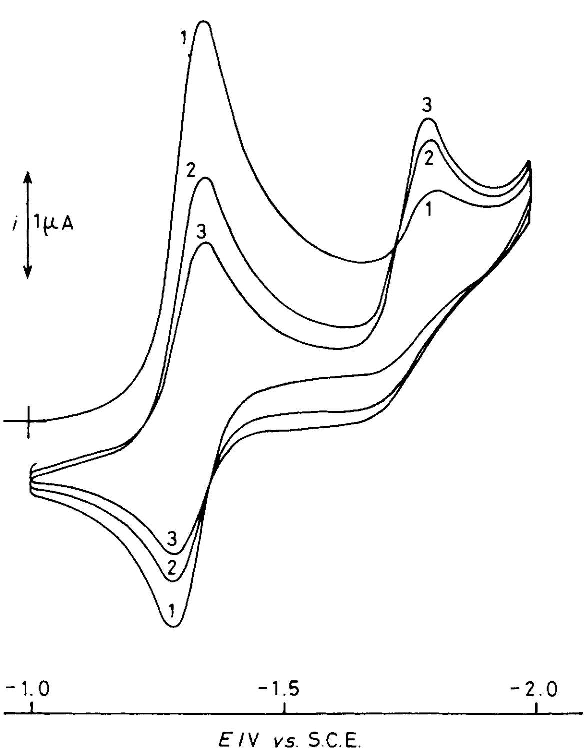

Figure 1. Cyclic voltammetry of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+[PF_6]^-$ (2×10^{-3} M) in the presence of $P(OMe)_3$ (8.4×10^{-3} M) at a platinum electrode. Solution: 0.1 M $Bu^n_4N^+$ BF_4^- in DMF. Scan rate: 0.1 V s^{-1}. The curves 1—3 represent three successive scans.

Table 1. Controlled potential electrolysis of $[Fe(cp)Ar]^+$.

Ar	Solvent	Ligand	Electricity used[a]	Yields of products isolated, (%)	
				$[Fe(cp)L_3]^+[PF_6]^-$	Ar
C_6H_6	DMF	$P(OMe)_3$	0.07	82	—
	ACN	$P(OMe)_3$	0.04	85	—
		Bu^tNC	0.10	81	—
p-Xylene	ACN	$P(OMe)_3$	0.03	85	—
1,2,4,5-Tetramethylbenzene	ACN	$P(OMe)_3$	0.52	53	74
Fluorene[b]	ACN	$P(OMe)_3$	0.09	85	90
9,10-Dihydroanthracene[b]	ACN	$P(OMe)_3$	0.15	85	90

[a] Units of electricity used are mol electron per mol $[Fe(cp)Ar]^+$. [b] 10^{-2} mol $[Fe(cp)Ar]^+$.

determining step (5) and then the replacement of S by $P(OMe)_3$, equation (6).

$$[Fe^I(cp)(C_6H_6)] + 3\,S \rightarrow [Fe^I(cp)\,S_3] + C_6H_6 \qquad (5)$$

$$[Fe^I(cp)S_3] + 3\,P(OMe)_3 \rightarrow [Fe^I(cp)\{P(OMe)_3\}_3] + 3\,S \qquad (6)$$

The catalytic scheme [reactions (1), (5), (6), and (4)] was confirmed by controlled potential electrolysis (−1.5 V *vs.* S.C.E.), carried out at a mercury cathode in a two compartment cell, under N_2 in the dark. The cathode electrolyte was 0.2 M $LiClO_4$ solution containing 5×10^{-3} mol $[Fe(cp)(C_6H_6)]^+[PF_6]^-$ and 3×10^{-2} mol $P(OMe)_3$. The consumption of electricity was very low (Table 1) and the reaction was complete within a few minutes. At the end of electrolysis, addition of water (DMF) or solvent removal (ACN) gave the salt $[Fe(cp)\{P(OMe)_3\}_3]^+[PF_6]^-$ in high yield. Analogous behaviour is observed when t-butyl isocyanide is used, in place of $P(OMe)_3$, leading to $[Fe(cp)(CNC_4H_9)_3]^+[PF_6]^-$. Microanalysis and ^1H n.m.r. spectra are in agreement with the structures given and literature data.[8]

Considering the interest in the temporary complexation of arenes by $[Fe(cp)]^+$, as an aid to synthetic modifications of the free aromatic compounds[9,10], the scope and limitations of the E.T.C. deco-ordination have been studied under more appropriate conditions: ACN solution containing $P(OMe)_3$. It appears that the rate of arene deco-ordination depends on the number of substituents on the arene owing to the enhanced stability of $[Fe^I(cp)(C_6H_{6-n}Me_n)]$ as n increases.[4a] It is shown by cyclic voltammetry that deco-ordination does not occur when $n = 6$, even at 50 °C. For Ar = 1,2,4,5-tetramethylbenzene a slow deco-ordination is observed with a low catalytic efficiency, as revealed by the consumption of electricity during electrolysis (Table 1). The same sequence of stability has been established for the paramagnetic complexes $[Fe^I(cp)Ar]$ in dimerization reactions[4a] and for arene exchange reactions in diamagnetic η^6-arene metal complexes.[6]

Typical examples of fast arene recovery are given by Ar = fluorene or 9,10-dihydroanthracene (Table 1). The overall decomplexation process follows a homogeneous pathway in solution. When the ligand exchange is fast, the reactions, carried out with 10^{-2} mol substrate, are achieved within ten minutes. The free organic ligands are easily separated from the ionic products (electrolyte and $[Fe(cp)\{P(OMe)_3\}_3]^+[PF_6]^-$). This deco-ordination by E.T.C. can be compared to the photochemical method[8] which is (more) useful in the removal of persubstituted arenes and their replacement by ligands including $P(OMe)_3$, CO, or other arenes. But with quantum yields less than unity, photolysis is much slower than E.T.C. for bulk quantities when the two methods are available.

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