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Preliminary communication

Electrochemical studies on organometallic compounds

XXXI *. The electrooxidation of $[(\eta^5\text{-t-BuC}_5H_4)_2\text{-}Zr^{IV}(\eta^1\text{-}1,\eta^1\text{-}1')(\eta^5\text{-}(C_5H_4)_2Fe^{II}]$: another example of an electrocatalytic process with an endergonic cross electron-transfer propagation step

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Abstract

The electrooxidation of [bis(η^5-t-butylcyclopentadienyl)(η^1-1,η^1-1′-ferrocenediyl)-zirconium(IV)] in the presence of traces of water gives [bis(η^5-t-butylcyclopentadienyl(η^1-ferrocenyl)(η^1-hydroxy)zirconium(IV)] via an electrocatalytic process with an endergonic cross electron-transfer propagation step.

Ligand exchange reactions play a major role in organometallic chemistry. They can often be described by the square scheme [1–6] first described by Jacq [7]. Amatore et al. [8] have recently given the first example of an electrocatalytic process with an endergonic cross electron-transfer propagation step in the framework of this formulation. We report in this note another example of this type of reaction.

The cyclic voltammogram of the title zirconium(IV) complex **1** (Scheme 1) is shown in Fig. 1 (tetrahydrofuran, containing residual water, from a distillation over sodium benzophenone ketyl; platinum electrode; supporting electrolyte, 0.2 *M* tetrabutylammonium hexafluorophosphate).

During the first cycle, three peaks appear: an oxidation peak A'_1 corresponding to the formation of the 17-electron cation $\mathbf{1}^+$, and two reduction peaks A_1 and A_2. Peak A_1 corresponds to the partial reduction of $\mathbf{1}^+$ to **1**; peak A_2 is due to the reduction of $\mathbf{2}^+$ to **2**, since compound **2** which we prepared chemically, shows the reversible voltammetric system A'_2/A_2 (Scheme 1).

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* For part XXX see ref. 11.

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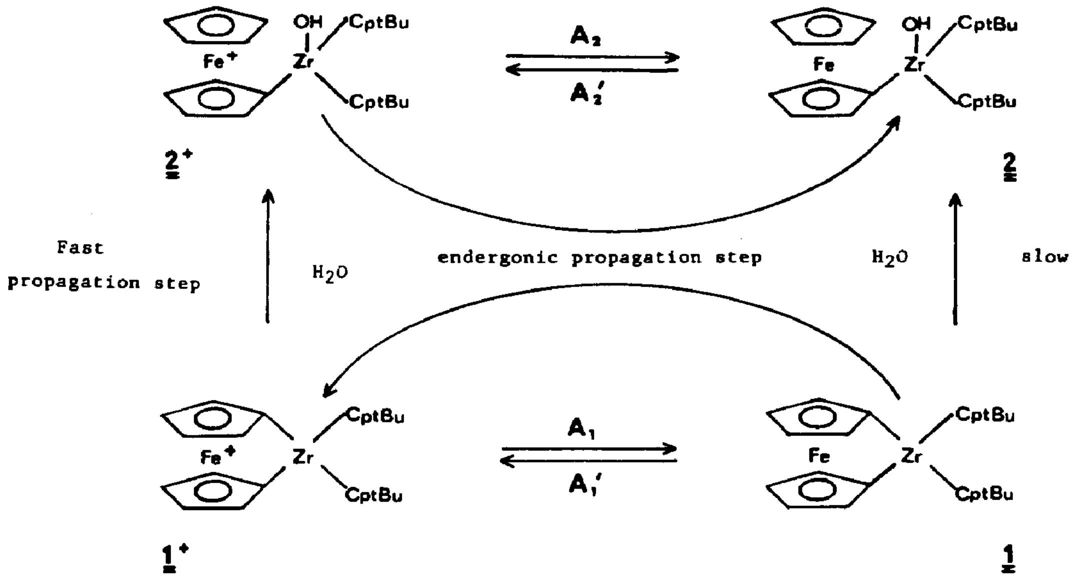

Scheme 1.

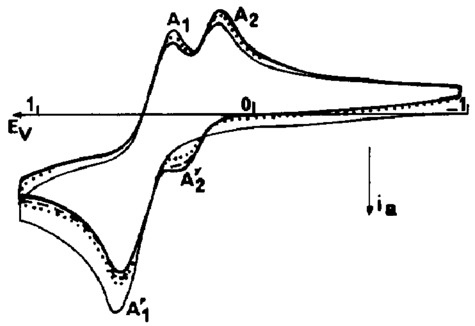

Fig. 1. Voltammogram of **1** in thf (starting potential -1 V; sweep rate 0.5 V s^{-1}); (———): first sweep; (· · · · · ·): second sweep; (— — —): third sweep); (━━━): fourth sweep.

Upon repetition of the cycles, peak A'_1 decreases, and peak A'_2 increases. At slower scan rates, in thin layer electrochemistry [9*], peak A_1 practically disappears, whereas peak A'_2 increases significantly even during the second sweep (Fig. 2).

Reaction **1** → **2** (Scheme 1) is slow (several hours in thf in the presence of added water [10*]) whereas reaction $\mathbf{1}^+ \rightarrow \mathbf{2}^+$ is relatively rapid, although the thf contained only traces of water (see the decrease of peak A_1 in Fig. 1 and 2). As in the example reported by Amatore et al. [8], the reaction involves formation of **2** from **1** via the sequence:

$\mathbf{1} \rightarrow \mathbf{1}^+$ (1)

$\mathbf{1}^+ \rightarrow \mathbf{2}^+$ moderately fast exergonic step (2)

$\mathbf{2}^+ + \mathbf{1} \rightarrow \mathbf{2} + \mathbf{1}^+$ endergonic propagation step (3)

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* Reference number with asterisk indicates a note in the list of references.

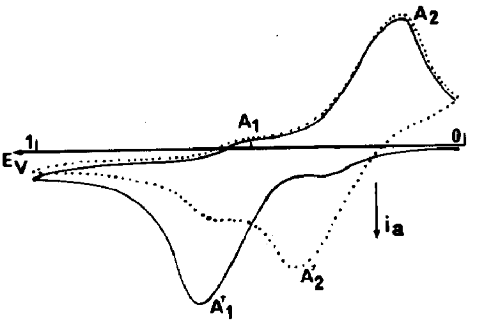

Fig. 2. Thin layer voltammogram of **1** in thf (starting potential 0 V; sweep rate 0.02 V s^{-1}); (———): first sweep; (· · · · · ·): second sweep.

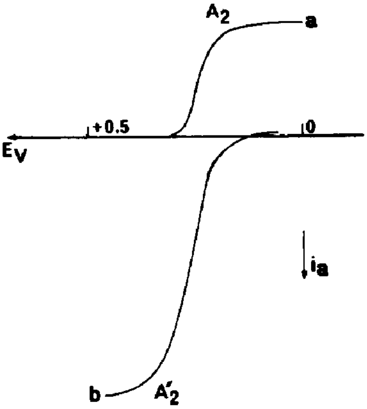

Fig. 3. Rotating disk electrode voltammograms in thf (a) of $\mathbf{2}^+$ (b) after addition of **1**.

The cross transfer reaction (3) takes place, even though it is endergonic, because it is driven by reaction (2). The propagation step (2) is moderately fast, in contrast to the case examined by Amatore et al. [8], but it should be noted that reaction (3) is only slightly endergonic (6 kcal mol^{-1}; $\Delta E^0 = 0.3$ V, much less than in the system studied by Amatore et al. [8] where $\Delta E^0 \simeq 0.6$ V). In an experiment that showed directly that the process is catalytic, we electrogenerated cation $\mathbf{2}^+$ by oxidation of **2** at +0.3 V. Upon addition of **1**, wave A_2 (reduction of $\mathbf{2}^+$) immediately disappeared and wave A'_2 (oxidation of **2**) appeared (Fig. 3).

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9 For the thin layer experiments, the disc electrode was lowered until it came into contact with the flat floor of the electrolytic cell, so that there was a thin layer of solution between them.

10 Bis(η^5-t-butylcyclopentadienyl)(η^1-ferrocenyl)(η^1-hydroxy)zirconium(IV) (**2**) was prepared by treating with water a solution of bis(η^5-t-butylcyclopentadienyl)(η^1-1,η^1-1′ ferrocenediyl)zirconium(IV) (**1**) in thf. The reaction requires 10 h for completion. Details of the synthesis of **1** and **2** will be presented elsewhere.

Complexes **1** and **2** were characterized by ^{1}H NMR and mass spectra. ^{1}H NMR spectrum (30 °C, C_6D_6): /TMS (s = singulet, t = triplet, pq = pseudoquadruplet): complex **1**: 1.31 (s, 18H, t-Bu), 3.96, 4.33 (t, each 4H, $(C_5H_4)Fe(C_5H_4)$), 5.53, 6.00 (t, each 4H, (C_5H_4)-t-Bu). Complex **2**: 1.19 (s, 18H, t-Bu), 4.20 (s, 5H, $(C_5H_5)Fe$), 4.02, 4.39 (t, each 2H, $(C_5H_4)Fe$), 4.48 (s, 1H, OH, D_2O exchangeable), 5.30, 5.74, 6.01, 6.49 (pq, each 2H, (C_5H_4)tBu).

Mass spectrum: m/e: complex **1**: 516 $(M)^+$, 379 $(M-\text{t-BuCp}-CH_4)^+$, 274 $(M-2\text{t-BuCp})^+$, 186 $(C_{10}H_{10}Fe)^+$, 121 $(\text{t-BuCp})^+$ or $(C_5H_4Fe)^+$, 107 $(C_8H_{11})^+$, 91 $(C_7H_7)^+$. Complex **2**: 534 $(M)^+$, 413 $(M-\text{t-BuCp})^+$, 370 $(C_{20}H_{18}Fe_2)^+$, 186 $(C_{10}H_{10}Fe)^+$, 121 $(\text{t-BuCp})^+$ or $(C_5H_5Fe)^+$, 107 $(C_8H_{11})^+$.

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