Electron-transfer Chain Catalysed Chelation of $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2\{\sigma\text{-}SC(S)NMe_2\}]$: a Reaction which can be Initiated either by Oxidation or by Reduction

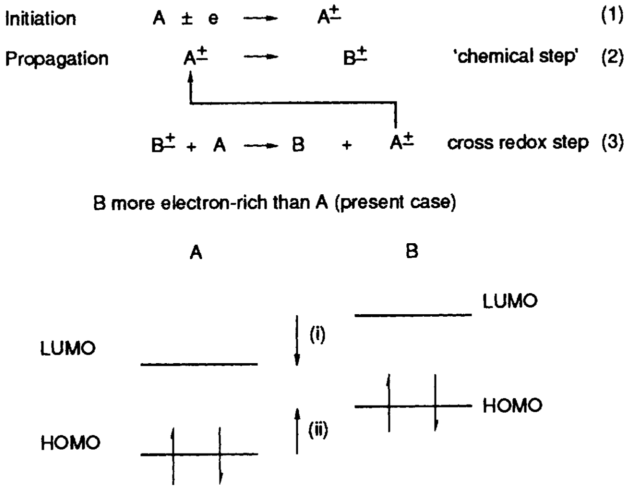
Marie-Hélène Desbois and Didier Astruc*

Laboratoire de Chimie Organique et Organométallique, U.R.A. CNRS No. 35, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cédex, France

The electron-transfer chain catalysed chelation of the dithiocarbamate ligand in Fp*(σ-dtc) (**1**) [Fp* = $Fe(\eta^5\text{-}C_5Me_5)(CO)_2$; dtc = $SC(S)NMe_2$] can be initiated by cathodic reduction or by naphthyl-sodium (as well as by ferricinium salts) to give $[Fe(C_5Me_5)(CO)(\eta^2\text{-dtc})]$ (**2**) and CO; the choice of the reducing agent is crucial because of counter-ion effects in the propagation cycle, and the oxidative and reductive modes of initiation are compared.

Electrocatalysis or electron-transfer chain (ETC) catalysis,[1] first disclosed in organic chemistry,[2] was applied to ligand exchange reactions on a transition metal centre by Feldberg[3] almost twenty years ago. This latter type of reaction has been widely used in the 1980's and we have noticed that it works when it is driven by an exergonic cross redox step [equations (1)—(3), Scheme 1].[4] This is achieved by oxidative initiation in mononuclear complexes when the incoming ligand is less electron-donating than the displaced ligand[3] (*e.g.* exchange of MeCN by a P donor)[5] or by reductive initiation in cluster complexes when the incoming ligand is more electron-releasing than the displaced ligand[3] (*e.g.* exchange of CO by a P donor).[6]

From a thermodynamic standpoint, the means of initiation (oxidation or reduction) should not matter because the overall free energy change (ΔG°) for the reaction A → B does not depend on the mechanism. In practice, however, the only reactions which do take place are those which have an exergonic cross ET step. For kinetic reasons, the side reactions of the radical intermediates are faster than the endergonic cross ET step (Marcus theory: an endergonic ET is slow).[7] Few cases are known with such an endergonic cross ET step,[8] and in those cases the catalytic efficiency is low. This is the case for the electrocatalytic chelation of the dithiocarbamate ligand in iron complexes which is driven by a very fast chemical step (chelation) between paramagnetic (17/19e) complexes, the irreversibility compensating the endergonicity of the cross ET step. We take this example to show that, in these cases, the initiation can be either an oxidation or a reduction. We already know that the reaction of complex (**1**) leading to (**2**) and CO (Scheme 2) can be catalysed by $[Fe(C_5H_5)_2]^+X^-$ to give modest yields[9] owing to (i) the endergonicity of the cross redox step and (ii) the insolubility of the reactants in tetrahydrofuran (THF) or side reactions of $(\mathbf{1})^+X^-$ in polar solvents.[10]



Scheme 1. Ergonicity of the cross redox step of electrocatalytic propagation cycles. (i) Exergonicity of the cross redox step [equation (3)] involved in reductively induced electrocatalysis when B is more electron-rich than A; (ii) endergonicity of the cross redox step involved in oxidatively induced electrocatalysis under analogous conditions. Note that the relative energy levels of the LUMOs of A and B always follow those of the HOMOs. If B is less electron-rich than A, *i.e.* the relative order of the HOMOs (and thus of the LUMOs) is opposite, a similar reasoning would also apply.

In this case,[9] (**1**) is not completely converted and 1 equiv. of the catalyst quantitatively gives the insoluble $(\mathbf{1})^+X^-$, which disrupts the chain. Thus, we investigated the reaction of Scheme 2 under the conditions of reductive initiation. At 20 °C, complex (**1**) reacts completely after addition of 0.33 equiv. of naphthyl-sodium by canula to a stirred THF solution of complex (**1**) (this was not the case when oxidizing initiation conditions were used). ^1H NMR titration followed by separation of the pentane-insoluble Fp^*_2 [Fp* = $Fe(\eta^5\text{-}C_5Me_5)(CO)_2$] from the pentane-soluble complex (**2**) showed the formation of a 67% yield of (**2**)[11] and a 33% yield of Fp^*_2[12] in a millimolar scale reaction. The yield of (**2**) is thus higher than those obtained with ferricinium salts but the coulombic efficiency remains low owing to the side reaction.

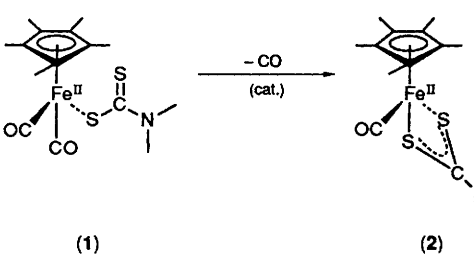
The reductive initiation provides a 19e anionic intermediate $[Fp^*(\sigma\text{-dtc})]^-$ which can either loose a CO ligand to propagate the catalytic chain [reaction (4)], or the dtc⁻ anion[13] to give the side reaction in equations (5) and (6). The ratio of the rate constants of these two reactions, $k_{\mathrm{CO\ dis.}}/k_{\mathrm{dtc\ dis.}}$, is *ca.* 2.

$$\underset{19e}{[Fp^*(\sigma\text{-dtc})]^-} \rightarrow \underset{17e}{[Fe(\eta^5\text{-}C_5Me_5)(CO)(\sigma\text{-dtc})]^-} + CO \qquad \text{(chain reaction)} \quad (4)$$

$$\underset{19e}{[Fp^*(\sigma\text{-dtc})]^-} \rightarrow \underset{17e}{Fp^{*\cdot}} + dtc^- \qquad \text{side reaction} \quad (5)$$

$$2\,Fp^{*\cdot} \rightarrow Fp^*_2 \qquad \text{side product} \quad (6)$$

The chelation of the dtc ligand in the 17e anionic intermediate $[Fe(\eta^5\text{-}C_5Me_5)(CO)(\sigma\text{-dtc})]^-$, giving the 19e inter-



(**1**) (**2**)

Scheme 2

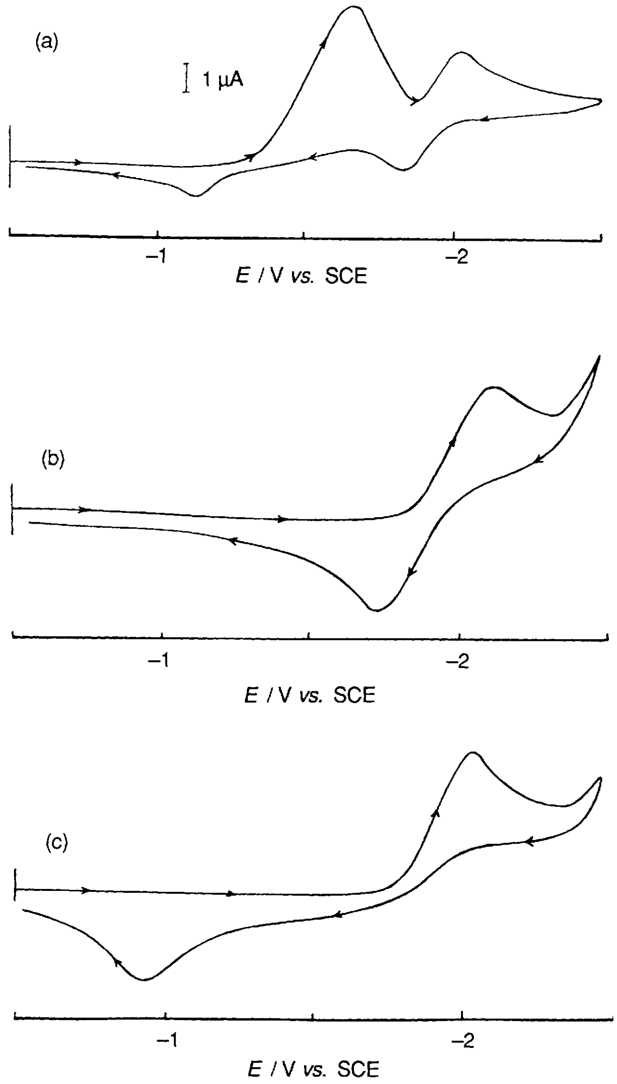
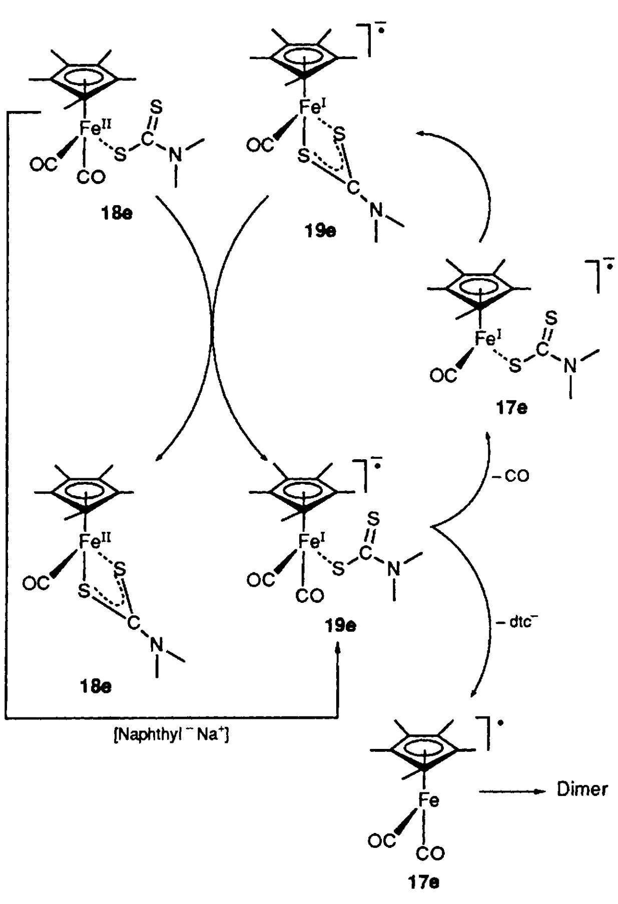


Figure 1. Cyclic voltammograms of solutions (1.3 mmol l^{-1}) of (a) complex (**1**), (b) complex (**2**), and (c) Fp^*_2 in THF ($Bu^n_4NBF_4$, 0.1 M; 400 mV s^{-1}; 25 °C; Pt electrode) (SCE = standard calomel electrode).

mediate $[Fe(\eta^5\text{-}C_5Me_5)(CO)(\eta^2\text{-dtc})]^-$, must be extremely fast as is that of $[Fp^*(\sigma\text{-dtc})]^+$ in the oxidatively catalysed process.[9] In contrast with the latter, the cross redox step is now exergonic and thus fast[7] (Scheme 1).

Comparison between the cyclic voltammograms (CVs) of (**1**) and (**2**) [Figure 1(a) and (b)] indicates that ETC catalysis also proceeds upon reduction. The CV of (**1**) shows an irreversible reduction wave followed by the reduction of (**2**) which is chemically almost reversible but electrochemically irreversible.

In this CV, it is also possible to see the presence of the wave due to Fp^*_2 which we have checked by recording the CV of pure Fp^*_2 under identical conditions [Figure 1(c)]. This latter complex is the product of a side reaction of the ETC catalysis and limits the coulombic efficiency. We then checked the electrocatalytic process by using chemical reducing reagents as initiators. The mechanism for the reaction in Scheme 1 in the case of a reductive initiation can now be summarized as in Scheme 3.



Scheme 3

The choice of the reducing initiator is important for the electrocatalytic process. For example, when the organometallic electron reservoir complex $Fe^I(C_5H_5)(C_6Me_6)$[14] is used, reduction of (**1**) occurs, although with a large overpotential. In this case, only traces of (**2**) are obtained and Fp^*_2 is formed almost stoicheiometrically. The organometallic initiator is found in its 18e cationic form with dtc^- as counter-anion. The latter results from a selective cleavage, most probably in the 19e anion $[Fe(C_5Me_5)(CO)_2(dtc)]^-$ (Scheme 3).

Thus, the selectivity of ligand loss (CO *versus* dtc^- at the 19e level) very much depends on the nature of the counter-cation of this 19e radical anion. A possible driving force orientating this selectivity could be the precipitation of $[Fe(C_5H_5)(C_6Me_6)^+dtc^-]$ in THF. It is thus confirmed that medium effects (counter-anion, solubility, solvent) have a dramatic influence on the propagation chain. Note that, in the oxidatively induced ETC conversion of (**1**) to (**2**), both the nature of the counter-anion and the solvent also had a great influence on the yield of (**2**).[9]

In summary, when the chelation of (**1**) is catalysed by an oxidant, the reaction is driven by the chemical propagation step [chelation $(\mathbf{1})^+ \rightarrow (\mathbf{2})^+$] and limited by the endergonicity of the cross redox step $[(\mathbf{2})^+ + (\mathbf{1}) \overset{\rightarrow}{\longleftarrow} (\mathbf{2}) + (\mathbf{1})^+]$. When the chelation of (**1**) is catalysed by a reducing agent, the propagation is driven by an exergonic cross redox step but limited by the lack of specificity of the chemical step [ligand loss from $(\mathbf{1})^-$]. In both cases, the counter-ion of the radica ions involved in the propagation chain plays an important role and careful choice of counter-ion can lead to a grea improvement in the catalytic efficiency. Electrocatalysis of ligand exchange reactions in mononuclear complexes by reductive initiation remains a difficult exercise. However, it is possible that the use of electron-reservoir ligands such as hard chelating ligands can overcome this problem. Research is underway along these lines.

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