Chelation of Iron(II) Dithiocarbamates: an Electrocatalytic Process with an Endergonic Cross Electron-transfer Propagation Step

Christian Amatore,*[a] Jean-Noël Verpeaux,[a] Alex Madonik,[b] Marie-Hélène Desbois,[c] and Didier Astruc*[c]

[a] *Ecole Normale Supérieure, UA CNRS N° 1110 'Activation Moléculaire,' Laboratoire de Chimie, 24, rue Lhomond, 75231 Paris Cédex 05, France*

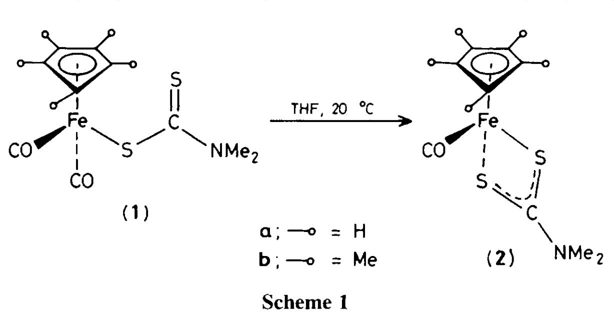
[b] *Laboratoire de Chimie des Organométalliques, UA CNRS No. 415, Université de Rennes I, 35042 Rennes Cédex, France*

[c] *Laboratoire de Chimie Organique et Organométallique, UA CNRS N° 35, Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence Cédex, France*

The electrocatalysed chelation of the dimethyldithiocarbamate ligand (dtc) in [Fe(η^5-C_5R_5)(CO)$_2$(σ-dtc)] (R = H or Me) is shown to involve a dual role of the oxidant in an efficient process involving an endergonic ($\Delta G^\circ \geqslant 12$ kcal mol^{-1}) cross electron-transfer propagation step; the preparative yields are subject to a 'specific anion effect' which controls the importance of the deactivation of the overall chain conversion.

Metal dithiocarbamates (dtc) are an important class of inorganic and organometallic complexes for which several modes of co-ordination are well known.[1] Although the mode is bidentate in most cases, the monodentate complexes [Fe(η^5-C_5R_5)(CO)$_2$(σ-dtc)] (**1**) are stable and easy to make[2] and their thermal conversion to chelates is difficult and proceeds with low yields.[2b] Thus, we have examined the possibility of effecting the chelation reaction of Scheme 1 using electrocatalysis,† a method which has already proved efficient for a number of organic,[3] inorganic,[4] and organometallic[5] reactions. The chelation of potentially bidentate ligands is also important because, if suitably designed, it can bring about asymmetric induction. Moreover its feasibility using electrocatalysis has not yet been examined.

The ligand exchange of CO has been shown to proceed most efficiently by electrocatalysis in cluster chemistry[5] (using



Scheme 1

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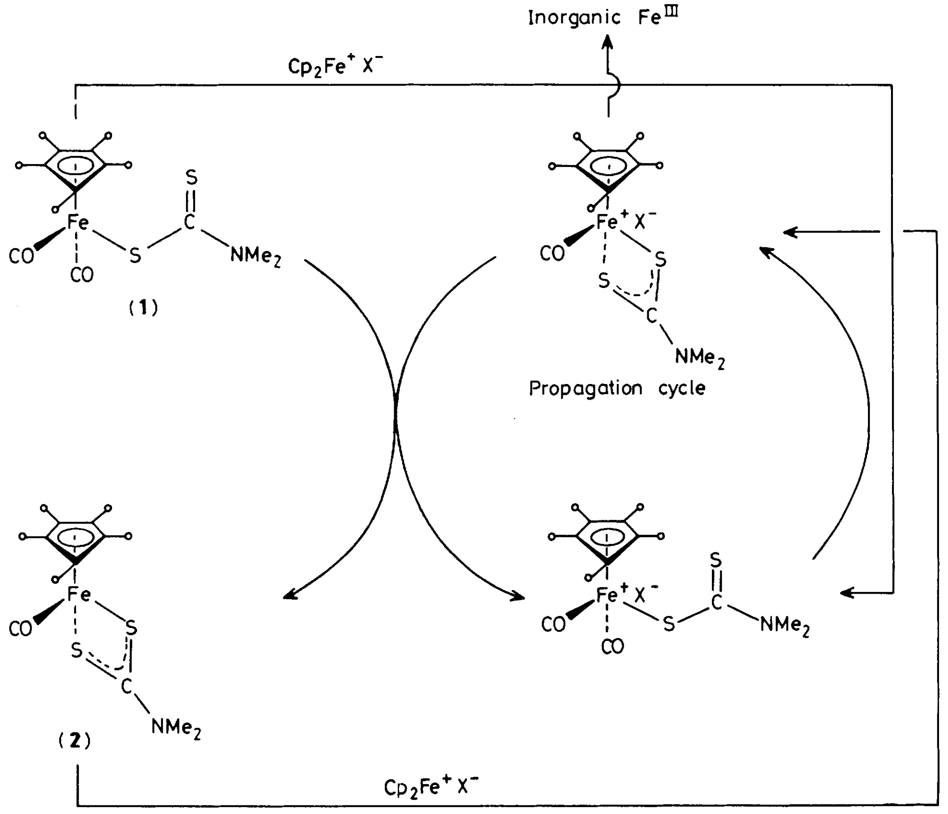
† Careful visible photolysis of (**1**) also gives (**2**). Electrocatalytic studies were carried out in the dark.



Scheme 2

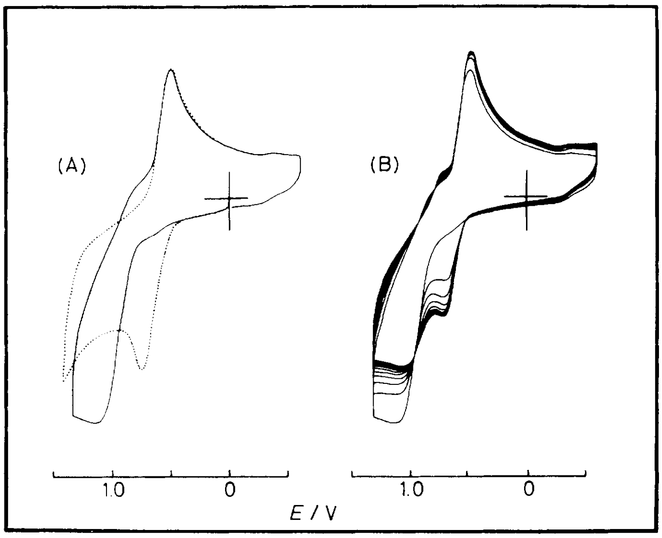


Figure 1. C.V. of a 2 mM solution of (**1**) in THF with 0.3 M NBu_4BF_4 at a scan rate, v, of 20 V s^{-1}. (A) Single scan C.V. (B) Repetitive scan C.V. The C.V. of an authentic sample of (**2**) under identical conditions is shown as a broken line in (A). Potentials refer to the standard calomel reference electrode [$E°$ (**2b**)/(**2b**)$^+$ 0.605 V, Ep(**1b**)/(**1b**)$^+$ 1.25 V].

reductive initiation) but, interestingly, attempts to do so in mononuclear chemistry have generally met with failure.[5,6] In the present reaction, the electrocatalytic chelation with CO loss is induced by an oxidant [equations (1)—(3); Scheme 2].

The reaction product (**2**) is more electron-rich that the starting compound (**1**) because CO is replaced by the electron-releasing sulphur-containing ligand. This means that the cross electron-transfer propagation step [equation (3)] is endergonic, and the cyclic voltammograms (C.V.) of (**1**) and (**2**) show that it is so by at least 12 kcal mol^{-1} ($\Delta E° \geqslant 0.6$ V; cal = 4.184 J).

$$\underset{(\mathbf{1})}{[FeCp(CO)_2\{\sigma\text{-}SC(S)NMe_2\}]} \xrightarrow{-e^-} FeCp(CO)_2 \rightarrow \{\sigma\text{-}SC(S)NMe_2\}^+ \quad (1)$$

$$(\mathbf{1})^+ \longrightarrow \underset{(\mathbf{2})^+}{[FeCp(CO)(\eta^2\text{-}S_2CNMe_2)]^+} \quad (2)$$

$$(\mathbf{2})^+ + (\mathbf{1}) \rightleftharpoons \underset{(\mathbf{2})}{[FeCp(CO)(\eta^2\text{-}S_2CNMe_2)]} + (\mathbf{1})^+ \quad (3)$$

$$(\mathbf{2})^+ \longrightarrow \text{inorganic Fe}^{III}\text{ salt} \quad (4)$$

$$Cp = \eta^5\text{-}C_5H_5 \text{ or } \eta^5\text{-}C_5Me_5$$

Thus the cycle is driven by the other propagation step [equation (2)], leading to the chelation. The C.V.s of (**1**) show a totally irreversible anodic wave even at scan rates as high as 5000 V s^{-1}, which indicates the extremely short lifetime of the 17-electron cation (**1**)$^+$. They also show the formation of the relatively stable cation (**2**)$^+$, identified by comparison with the C.V. of an authentic sample of (**2**). The conversion of (**1**) to (**2**) is increased upon repeating the C.V. cycles, provided the anodic potential is high enough to reach the anodic wave of the starting compound (**1**). However the electrocatalytic conversion of (**1**) to (**2**) (Scheme 2), at the level of the rising branch of

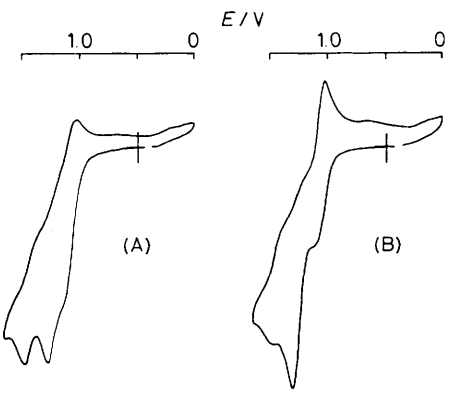


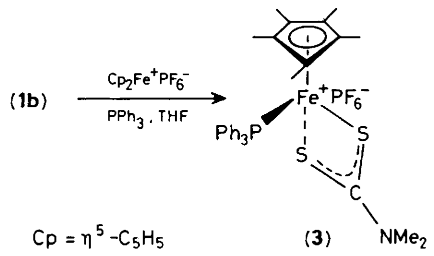
Figure 2. C.V. of (**1**) under the same conditions as in Figure 1, but at v = 0.1 (A) and 0.5 (B) V s^{-1}.

the C.V. of (**1**), occurs only when the sweep rate is decreased to < 1 V s^{-1} (Figures 1 and 2). Thus the half time of the cycle is estimated to be of the order of a second (kinetic studies will be reported in the full paper). Recording several such C.V.s was enough to convert 25% of (**1b**) to (**2b**) in 2 h at 20 °C.

The preparative electrocatalytic syntheses of (**2**) from (**1**) is accessible using a ferricinium salt in tetrahydrofuran (THF). The amount of (**1**) which is converted to (**2**) depends on the nature of the counter anion of the ferricinium cation (all these salts are insoluble in THF). For instance, 10% of ferricinium tetrafluoraborate converts only 24% of (**1b**) to (**2b**) but the yields reach 37% with PF_6^- and 52% with $SbCl_6^-$ [63% for (**1a**) → (**1b**)]. With more ferricinium, the yields are slightly increased but do not approach 100%, especially with small anions, although unconverted (**1**) remains in solution. The stoicheiometric oxidation of (**1**) with ferricinium salts gives an insoluble inorganic Fe^{III} product $(\mathbf{2})^+$ [equation (4)]. If this stoicheiometric oxidation of (**1b**) is effected in the presence of stoicheiometric amounts of PPh_3, the stable 17-electron burgundy complex $[Fe(\eta^5\text{-}C_5Me_5)(\eta^2\text{-dtc})(PPh_3)]PF_6$ (**3**)‡ is isolated (Scheme 3). Thus the oxidant ferricinium plays two roles in the process: one is to initiate the electrocatalytic chain and the other is to oxidize the final product (**2**) (the easier to oxidize in the medium). The latter role is only possible because of the endergonicity of the cross electron-transfer step and it stops the electrocatalytic chain. This explains why the coulombic efficiency is poor with ferricinium salts. The counter anion effect found on the reaction yield shows that the precipitation of $(\mathbf{2})^+$ is faster when the 17-electron cation $(\mathbf{2})^+$ is not stabilized by a large anion. With a large counter anion, this precipitation still occurs but it is slow enough not to compete with the electrocatalytic cycle.

In conclusion, this study emphasizes the feasibility of an electrocatalytic process for which the electron-transfer propagation step is slightly endergonic:[7,8] the condition is that the other propagation step should be exergonic. Since a relatively unstable radical cation $(\mathbf{2})^+$ is involved in the disruption of the chain, it also requires that this propagation step should be fast.

Added in proof: an ECE mechanism for the chelation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\sigma\text{-}SC(S)OEt)$ has been reported by Morán *et al.*[9]



Scheme 3

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‡ Complex (**3**) (60% yield); i.r. (KBr): ν_{CN} 1550 cm^{-1}; satisfactory elemental analyses were obtained.