ANODICALLY-INDUCED ISOMERIZATION OF
cis-[Mo (SC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(CNBu^t)$_4$] , A MECHANISTIC STUDY

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Abstract

The low temperature electrochemical study of the 16-electron thiolate isocyanide complex cis-[Mo(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(CNBu^t)$_4$] indicated the occurrence of a single-electron anodically-induced isomerization according to an EC-square type mechanism for which rate and equilibrium constants have been estimated by digital simulation of cyclic voltammetric data.

Results and Discussion

In view of the known dependence of the molecular geometry on the electronic configuration of coordination compound [1], mainly investigated [2] for cis and trans isomers of octahedral-type redox pairs with 18-/ 17-/ 16-electrons (the last ones in a much lesser number of cases), a subject of considerable debate which has been attracting our attention [3], we have studied in detail, by digital simulation, the electrochemical behaviour of the 16-electron complex cis-[Mo(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(CNBu^t)$_4$] and found that at low temperature it isomerizes upon a single-electron oxidation. This study provides the first detailed kinetic investigation of the rather limited range of studies [4] of electron-transfer-induced rearrangements in 16-/15-electron redox-pair systems.

The thiolate-isocyanide complex under study was prepared by reaction of the five coordinate Mo complex [MoH(SC$_6$H$_2$ Pr$^i_3$-2,4,6)$_3$(PMePh$_2$)] with an excess of CNBu^t, as reported earlier [5].

The cyclic voltammogram of the Mo complex at a Pt disc electrode in 0.2M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ solutions and at ambient temperature reveals a first apparently single-electron diffusion-controlled, reversible anodic wave which is followed, at a higher potential, by a second irreversible anodic wave (Fig. 1a). Under these experimental conditions, the complex is unstable and its anodic waves are progressively replaced by another one with a full conversion achieved after ca. 5h. As a result of the complex instability, its exhaustive controlled potential electrolysis (CPE) on the plateau of the first anodic wave consumes much less than 1

Faraday/mole due to the spontaneous conversion, during the electrolysis, of the starting complex into a derived product of decomposition (X, Fig. 1b, c). A subsequent electrolysis on the plateau of wave X leads to another product (Y, Fig 1d, e) with a total consumption of 0.8 Faraday/mole.
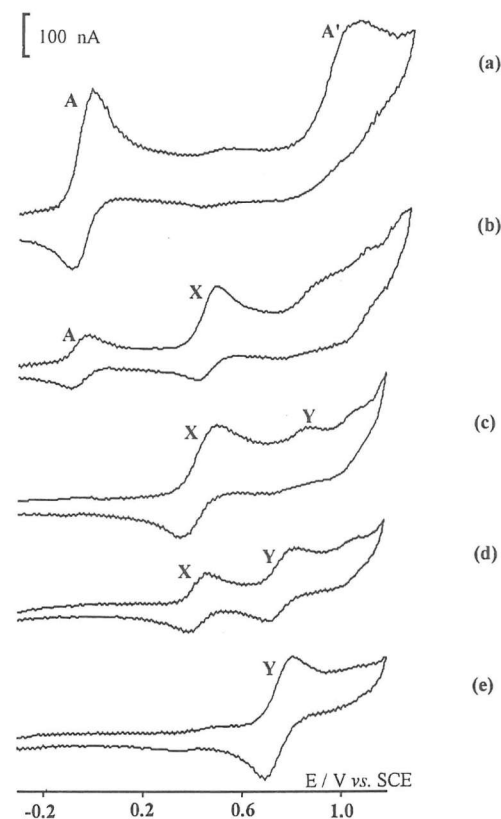

Fig. 1 - Cyclic voltammograms of *cis*-[Mo(tipt)$_2$(CNBu^t)$_4$] (0.4 mM in CH$_2$Cl$_2$ with 0.2 M [NBu$_4$][BF$_4$]) at ambient temperature and at a Pt disc working (d = 0.5 mm) electrode before electrolysis (a), after the consumption of *ca.* 0.25 (b) and a total of 0.33 (c) Faraday/mole at wave A, and after the consumption of *ca.* 0.34 (d) and a total of 0.47 (e) Faraday/mole at wave X. Scan rate of 0.2 V s^{-1}.

Cyclic voltammetry of the complex at -50°C reveals an interesting behaviour (Fig. 2). When the potential scan is inverted after the first anodic wave, two reduction waves are detected; one of these is the cathodic counterpart of the anodic wave A and the other one, at a lower potential, corresponds to the reduction of another species, here denoted by B$^+$, which is generated at the anodic process of the starting complex, wave A. This new cathodic wave has an anodic component, thus forming a reversible redox pair B$^+$/B.
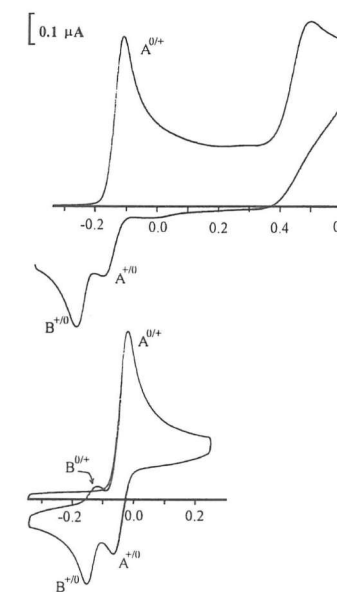

Fig. 2 - Cyclic voltammograms of *cis*-[Mo(tipt)$_2$(CNBu^t)$_4$] (1.13 mM, in CH$_2$Cl$_2$ with 0.2 M [NBu$_4$][BF$_4$]) at -50 °C and at a platinum disc (d = 0.5 mm) working electrode. Potentials are given in V *vs.* SCE. **A** and **B** denote the *cis* and the *trans* isomers, respectively (see text). Scan rate: 0.2 V s^{-1}.

This behaviour is rather dependent on the scan rate. Although the current-function of the anodic wave A is constant over the entire scan rate range from 20 mVs^{-1} up to 50 Vs^{-1}, for a sufficiently high (> ~ 50 V s^{-1}) or low (< ~20 mV s^{-1}) scan rate the cathodic component of the anodic wave of A is the only one observed upon scan reversal; the redox wave thus appears to correspond to a single-electron, reversible process (A/A$^+$).

As shown in the plot of Fig. 3, the new cathodic wave (B^+ reduction) is detected at intermediate scan rates and its relative intensity, given by the current peak ratio $\rho = i_p(B^{+/0}) / i_p(A^{0/+})$, passes through a maximum at *ca.* 1.0 V s^{-1}; its formation occurs at the expense of the cathodic counterpart of the anodic wave of A [$i_p(A^{+/0}) / i_p(A^{0/+})$ varies inversely].
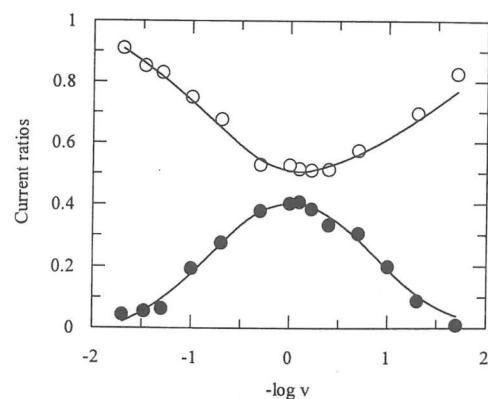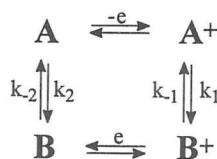

Fig. 3 Experimental (symbols) and theoretical (lines) variations of the reversibility of wave A, $i_p(A^{+/0}) / i_p(A^{0/+})$ (top), and of the parameter $\rho = i_p(B^{+/0})/i_p(A^{0/+})$ (bottom) as a function of log. scan rate (in V s^{-1}). The solid lines correspond to the working curves for the mechanism described in Scheme 1.

Since no significant variation of the above behaviour was detected upon changing the concentration of the complex, this suggests the involvement of first-order chemical steps which can be interpreted by considering an EC square-type process of the type described in Scheme 1, and which was investigated in detail by digital simulation of the cyclic voltammograms [6] at the entire range of scan rates.
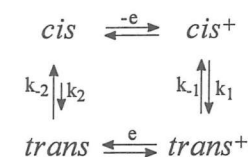
$$\begin{array}{ccc} A & \xrightleftharpoons{-e} & A^+ \\ k_{-2} \big\Vert k_2 & & k_{-1} \big\Vert k_1 \\ B & \xrightleftharpoons{e} & B^+ \end{array}$$

Scheme 1

An excellent fit was obtained for the following rate constant values: $k_1 = 5$ s^{-1}, $k_{-1} = 2.5$ s^{-1}, $k_{-2} = 1$ s^{-1} and $k_2 \ll k_{-2}$ (*i.e.* $k_2 \sim 0$ s^{-1}) as is also shown by the plot in Fig. 3.

The low value of the rate constant $k_2 = 1.7 \times 10^{-4}$ s^{-1} could be estimated by considering that $\Delta G^\circ = 0$ along the thermochemical cycle of Scheme 1. Hence, the equilibrium $A \rightleftharpoons B$ lies very much in favor of A in agreement with the fact that the anodic wave of A is the only one detected during the anodic scan. However, oxidation of A to A^+ promotes thermodynamically its conversion into the new species (B^+); moreover, the kinetics are also accelerated upon oxidation and the conversion into the more stable species is faster at the cationic 15-electron level than at the neutral 16-electron compounds since k_1 is higher than k_{-2}.

In view of the high similarity of the electrochemical behaviour stressed above between our complex and those which undergo anodically-induced *cis*-to-*trans* isomerization, we propose that a similar geometric isomerization is occurring in the present systems, *i.e.* the redox $B^{+/0}$ pair corresponds to the *trans*-isomer of the Mo compound. As a further circumstantial evidence, we can mention that the free energy variation associated to the K_2 chemical reaction of our system ($\Delta G_2^\circ = 3.9$ kcal mol^{-1}) is much higher than that estimated for the energy difference between the *syn* and the *anti* conformers in the model compound [Mo(SH)$_2$(CNH)$_4$] (0.007 kcal mol^{-1}) [7] and it is lower than the energy required to convert any of these conformers into the less stable "in-plane" ones. Therefore, the chemical transformation of the system of this study can be expected to be of a different nature, involving a more complex process (Scheme 2), the most plausible electron-transfer induced transformation being the *cis*-to-*trans* isomerization.

$$\begin{array}{ccc} cis & \xrightleftharpoons{-e} & cis^+ \\ k_{-2} \big\Vert k_2 & & k_{-1} \big\Vert k_1 \\ trans & \xrightleftharpoons{e} & trans^+ \end{array}$$

Scheme 2

References

[1] W.E. Geiger, in *Progr. Inorg. Chem.*, S.J. Lippard (ed.), Wiley, New York, 33, (1985) 275.

[2] A.M. Bond, R. Colton, J.B. Cooper, J.C. Traeger, J.N. Walter and D.M. Way, *Organometallics*, 13 (1994) 3434; A.M. Bond, B.S. Grabaric and J.J. Jacowski, *Inorg. Chem.*, 17 (1978) 2153; and refs. Therein; T.A. George, J.R.D. Debord, B.B. Kaul, C.J. Pickett and D.J. Rose, *Inorg. Chem.*, 31 (1992) 1295.

[3] M.F.C. Guedes da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, C. Amatore, J.-N. Verpeaux, *Organometallics*, 13 (1994) 3943.

[4] T. Adachi, M.D. Durrant, D.L. Hughes, C.J. Pickett, R.L. Richards, J. Talarmin and T. Yoshida, *J. Chem. Soc., Chem. Commun.*, (1992) 1464; G. Barrado, G.A. Carriedo, C. Diaz-Valenzuela and V. Riera, *Inorg. Chem.*, 30 (1991) 4416; F.C.

Anson, T.J. Collins, S.L. Gipson, J.T. Keech, T.E. Knafft and G.T. Peake, *J. Am. Chem. Soc.*, 108 (1986) 6593.

[5] M.F.C. Guedes da Silva, P.Y Hitchcock, D.L. Hughes, K. Marjani, A.J.L. Pombeiro and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, in press.

[6] D.K. Gosser Jr. and F. Zhang, *J. Electroanal. Chem.*, 38 (1991) 715.

[7] M. Kamata, K. Hirotsu, T. Higuchi, K. Tastsumi, R. Hoffman, T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, 103 (1981) 5772.

ELECTROCHEMICAL INVESTIGATION OF THE COMPLEXES
trans-[MCl(NCOCH2I)(Ph2PCH2CH2PPh2)2][BPh4]

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Summary

The electrochemical behaviour of the complexes *trans*-[MCl(NCOCH2I)(dppe)2][BPh4] (M = Mo or W, dppe = Ph2PCH2CH2PPh2)2) was investigated by cyclic voltammetry and controlled potential electrolysis. The complexes undergoe two successive monoelectronic reductions. The first reduction process follows a well-defined EC mechanism, leading to iodide loss. The second reduction is reversible and is associated with the novel complex *trans*-[MCl(NCOCH3)(dppe)2]$^+$ produced after the first reduction process.

Key words: Dinitrogen complex, molybdenum, tungsten, nitride ligand, alkylimide complex, electrosynthesis.

Introduction

Development of a chemical dinitrogen-fixing system converting a quite inert dinitrogen molecule into nitrogenous compounds under mild conditions is a challenging topic in chemistry. In certain systems, molecular nitrogen is incorporated into organometallic compounds with concurrent nitrogen-nitrogen bond scission, although in most cases the resultant nitride species are poorly defined [1, 2].

Nitrides complexes of the type *trans*-[MX(N)(dppe)2] (X = halide) can be synthesised from the dinitrogen complexes *trans*-[M(N2)2(dppe)2] by reaction with trimethylsilyl azide or cleavage of the N-N bond after conversion of coordinated dinitrogen to a M^{II} dialkylhydrazide [3, 4, 5].

The nitride ligand is a strong nucleophile and reacts with protons or other electrophiles to form the cationic imide complexes *trans*-[MX(NR)(dppe)2] (R = H or alkyl) [6]. The M-N bond can be electrochemically cleaved in the presence of a weak acid to give the free amine. The cleavage reaction occurs with conservation of the *trans*-{M(dppe)2} assembly and, under molecular nitrogen, the parent dinitrogen complex is regenerated in reasonable yields [7, 8].

In this work the results obtained on the reductive electrochemistry of *trans*-[MCl(NCOCH2I)(dppe)2]$^+$ are reported and compared with other imide complexes. On the basis of the evidence found, a mechanism is proposed.

Results and Discussion

Cyclic voltammetry in thf - 0.2 mol dm^{-3} [NBu4][BF4] at a vitreous carbon-disc electrode shows that the molybdenum and tungsten organoimide cations, *trans*-[MCl(NR)(dppe)2]$^+$, undergo an irreversible, diffusion-controlled reduction which is nominally an one-electron process on the basis of current function measurements. The irreversibility remains even at low temperatures.

Table 1 summarises reduction potential data together with the yields for the products of the electrochemical clevage in acid media for some imide complexes.

It can be seen that both the metal and the axial ligands influence the reduction potentials.