ANODIC DEPROTONATION OF METHYLENEAMIDO TO NITRILE LIGANDS AT A RHENIUM CENTRE

M. Fátima C.G. Silva and Armando J.L. Pombeiro*

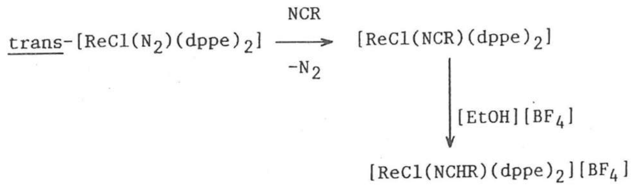
Centro de Química Estrutural, Complexo I
Instituto Superior Técnico, Av. Rovisco Pais
1096 Lisboa Codex, Portugal

ABSTRACT

The activation of a nitrile ligand by an electron rich Re(I) metal centre towards electrophilic attack at carbon to give a ligating methyleneamido species has previously been demonstrated [1]. We now report the electrochemical behaviour of the latter type of complexes, $[ReCl(NCHR)(dppe)_2][BF_4]$ ($\underline{1}$; $R=C_6H_4$-OMe-$\underline{4}$, C_6H_4Me-$\underline{4}$, C_6H_5, C_6H_4F-$\underline{4}$; dppe=$Ph_2PCH_2CH_2PPh_2$), which are shown to undergo an anodically induced deprotonation to afford novel nitrile compounds ($\underline{2}$) the redox properties of which are also indicated.

RESULTS AND DISCUSSION

The methyleneamido complexes ($\underline{1}$) were isolated as light yellow solids upon the sequence of reactions outlined in the scheme:



$$\begin{tikzcd} \underline{trans}\text{-}[ReCl(N_2)(dppe)_2] \arrow[r, "NCR", "-N_2"'] & {[ReCl(NCR)(dppe)_2]} \arrow[d, "{[EtOH][BF_4]}"] \\ & {[ReCl(NCHR)(dppe)_2][BF_4]} \end{tikzcd}$$

Cyclic voltammetry of these complexes, in CH_2Cl_2/ 0.2M $[Bu_4N][BF_4]$, at a platinum electrode and at sufficiently high scan rates, reveals a reversible one-electron oxidation (wave I) followed, at a higher potential, by an irreversible anodic process (wave II), (Fig. 1).

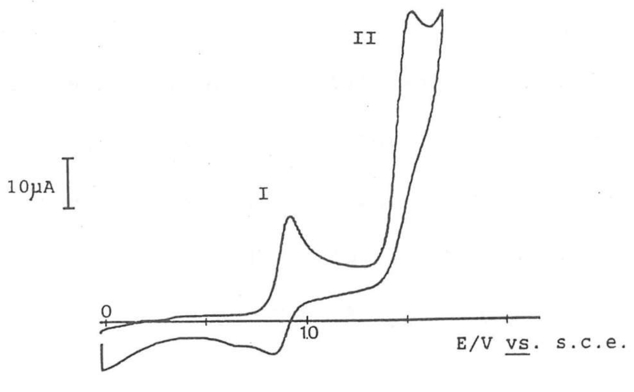


Fig. 1: Cyclic voltammogram for (1, R=C_6H_4OMe-4)

The reversible anodic process at wave I occurs at a considerably higher potential ($E_{\frac{1}{2}}^{ox}$= 0.915 - 0.938V vs. s.c.e.) than that observed for the neutral parent nitrile compounds (-0.13 to -0.11V vs. s.c.e.).

From the knowledge of $E_{\frac{1}{2}}^{ox}$ for complexes (1), as well as of the electron-richness (E_S) and polarisability (ß) of the metal centre {$ReCl(dppe)_2$}, we have been able to estimate, for the methyleneamido ligands, the P_L ligand parameter [2], a measure of their net electron π acceptor/σ donor character. By comparing the estimated P_L values (0.069-0.076V) with those known [3] for other related species, one observes that the methyleneamido ligands are better net electron acceptors than CO, approaching the aminocarbyne species CNH_2.

By controlled potential electrolysis at the first anodic wave of the methyleneamido complexes (1), ligand deprotonation occurs as measured by acid-base titration. The process involves a two-electron transfer and generates a nitrile complex of rhenium(III) (2) [equation (1)]. In fact, as shown by cyclic voltammetry, compounds (2) undergo two successive one-electron reversible reduction processes (Fig. 2) and the final neutral Re(I)-nitrile complexes are easier to oxidise ($E_{\frac{1}{2}}^{ox}$ in the -0.40 to -0.31V range) than the starting nitrile complexes of Re(I).

$$\underset{(\underline{1})}{[ReCl(NCHR)(dppe)_2]^+} \xrightarrow[-H^+]{-2e^-} \underset{(\underline{2})}{[ReCl(NCR)(dppe)_2]^{2+}} \qquad (1)$$

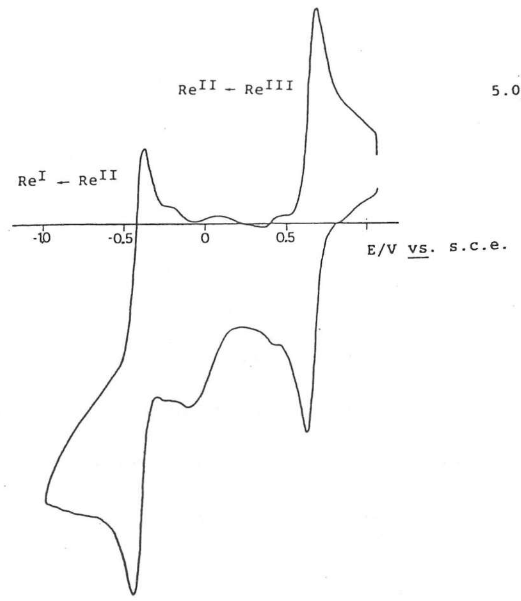


Fig. 2: Cyclic voltammogram for the rhenium(III)-nitrile complex obtained upon anodic C.P.E. of the methyleneamido complex (1, R = C_6H_4Me-4)

Based on some spectroscopic data for the two types of rhenium(I)-nitrile complexes and taking into account that different geometries can affect the redox potential, as already reported for isoelectronic group VI transition metal complexes [4], we are tempted to consider that the final neutral nitrile compounds correspond to the trans isomers whereas the starting rhenium(I)-nitrile complexes present the cis geometry.

As indicated above, methyleneamido complexes are formed by ß-protonation of the corresponding nitrile compounds. However, the latter cannot be regenerated either upon addition of a base, or electrochemically were an isomer of the parent compound appears to be produced.

In contrast, with the related aminocarbyne complexes, $[ReCl(CNHR)(dppe)_2]^+$, obtained from ß-protonation at ligating isocyanides, the starting compounds are fully regenerated either chemically (reversible protonation-deprotonation reaction) or electrochemically [3].

ACKNOWLEDGEMENTS

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