Electrochemically Induced Dehydrogenation of the Hydride Complexes [ReClH(NCR)($Ph_2PCH_2CH_2PPh_2$)$_2$][BF_4]. A Mechanistic Study

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The electrochemical behaviour of the hydride complexes [ReClH(NCR)(dppe)$_2$][BF_4] (R = Ph, 4-ClC_6H_4 or 4-FC_6H_4; dppe = $Ph_2PCH_2CH_2PPh_2$), prepared by protonation of the corresponding nitrile compounds [ReCl(NCR)(dppe)$_2$], has been studied by cyclic voltammetry (CV) and controlled-potential electrolysis in aprotic media, at a Pt electrode; they undergo anodically induced deprotonation and cathodically induced dehydrogenation, the former involving an overall bimolecular process as indicated by CV simulation techniques.

The relevance of transition metal–hydrogen bonds in coordination chemistry has been well recognized for a long time,[1] particularly in catalysis and in biological systems, and electrochemical methods should, in principle, provide convenient probes for the study of their activation by electron transfer. However, in contrast to the well developed chemistry of transition-metal hydride complexes, electrochemical investigation on them has not yet been adequately explored, although a few promising studies have been quoted, particularly in terms of electroactivation of such bonds with application, *inter alia*, in the production of hydrogen (*e.g.* from water, by proton reduction at a metal centre[2,3]) and in the induction of a further versatile chemical reactivity.[4–7]

Therefore, and also in pursuit of our interest in the study of the activation of small *C*- or *N*-unsaturated molecules by electron-rich transition metal centres,[8] we have initiated the electrochemical investigation of hydride complexes with such types of ligands, in particular *trans*-[FeH(CNR)(dppe)$_2$][BF_4] (R = alkyl or aryl),[7] and now we report the results obtained with [ReClH(NCR)(dppe)$_2$][BF_4] **1**$^+$ (R = Ph, 4-ClC_6H_4 or 4-FC_6H_4). These seven-coordinate complexes have been obtained by reaction of [Et_2OH][BF_4] with the appropriate parent neutral compounds, *cis*-[ReCl(NCR)(dppe)$_2$], in CH_2Cl_2, which, alternatively (depending, *e.g.*, on the experimental conditions and on the electronic properties of R), can undergo β-protonation at the nitrile ligand[9] to give methyleneamido complexes (R = 4-OMePh).

The electrochemical behaviour of complexes **1**$^+$ has been studied by CV in the 300 V s^{-1}–50 mV s^{-1} scan rate range, at Pt disc electrodes (with 500 or 125 μm diameter), in 0.3 mol dm^{-3} [Bu_4N][BF_4]–tetrahydrofuran (thf) (or CH_2Cl_2).

They undergo anodic and cathodic processes which, at sufficiently high scan rates, are both chemically reversible and involve a single-electron transfer, at $E°(\mathbf{1}^{2+}/\mathbf{1}^{+})$ = 0.7–0.9 V and $E°(\mathbf{1}^{+}/\mathbf{1})$ = −1.0 to −1.2 *vs.* saturated calomel electrode (SCE) respectively. However, upon lowering the scan rate, a pronounced decrease of the reversible character is observed for both waves and, moreover, the anodic one then tends to a two-electron irreversible process with proton loss as indicated by acid–base titration of the electrolysed solution obtained upon controlled potential electrolysis at the anodic wave.

Moreover, it is noteworthy to mention (see below) that an increase of the concentation of **1**$^+$ results in an increase of the scan rate required to achieve chemical reversibility in oxidation.

Typical cyclic voltammograms are depicted in Fig. 1 (for **1**$^+$, R = 4-ClC_6H_4).

As a result of the anodic oxidation of the hydride complexes **1**$^+$, the novel species **2**$^{2+}$ is formed as detected by the appearance of the new reversible waves at $E°(\mathbf{2}^{2+}/\mathbf{2}^{+})$ = 0.71 and $E°(\mathbf{2}^{+}/\mathbf{2})$ = −0.31 V (for **1**$^+$, R = 4-ClC_6H_4). Moreover, the same set of waves at $E°(\mathbf{2}^{+}/\mathbf{2})$ and $E°(\mathbf{2}^{2+}/\mathbf{2}^{+})$, is also observed upon cathodic reduction of **1**$^+$.

However, the reduction wave of **1**$^+$ was almost chemically reversible, leading to the detection of relatively small waves for the oxidation of **2** and the derived **2**$^+$. Although the degree of chemical reversibility of the **1**$^+$ reduction wave was almost total for each run even at small scan rates (0.1 V s^{-1}), we

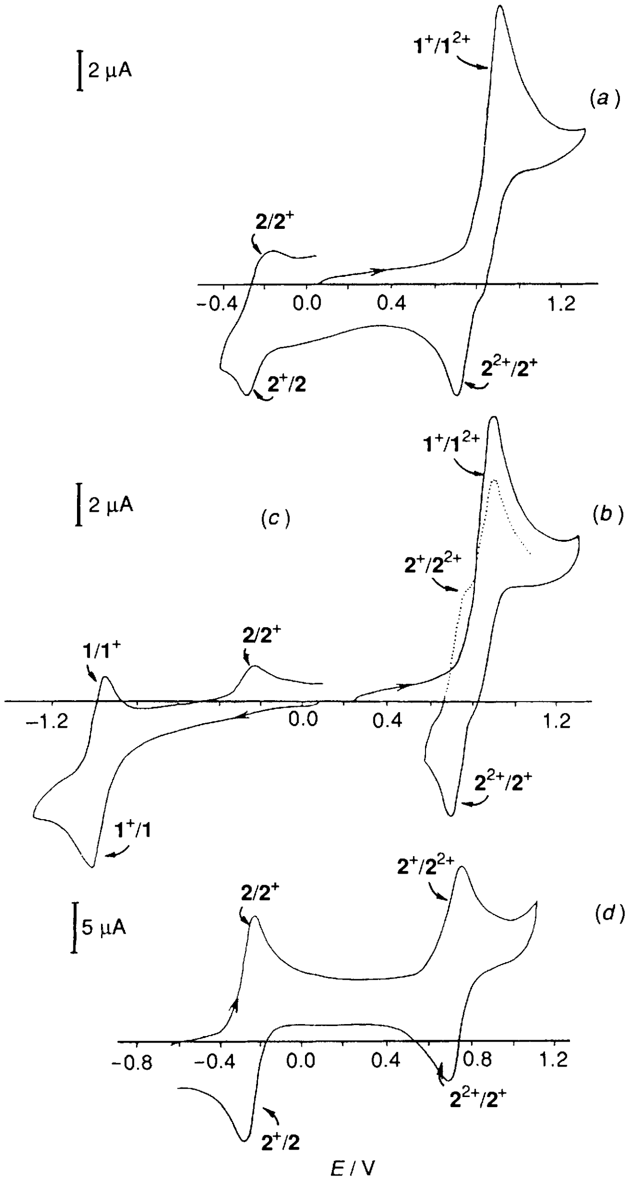

Fig. 1 Cyclic voltammograms for 0.6 mmol dm^{-3} [ReHCl(NCR)(dppe)$_2$][BF$_4$] **1**$^+$ (R = 4-ClC$_6$H$_4$) (*a*)–(*c*) and 0.8 mmol dm^{-3} *trans*-[ReCl(NCR)(dppe)$_2$] **2** (R = 4-ClC$_6$H$_4$) (*d*), in 0.3 mol dm^{-3} [Bu$_4$N][BF$_4$]–CH$_2$Cl$_2$, at a Pt electrode (scan rate = 100 mV s^{-1}; potential in V *vs.* SCE)

observed that the exact value of i_p^c/i_p^a (ratio of the cathodic to the anodic peak currents) was critically dependent on the particular set of conditions. Nevertheless, the same species **2** is obtained quantitatively as the reduction product of preparative electrolysis of **1**$^+$ with the consumption of one Faraday per mole. It is also generated upon treatment of a solution of **1**$^+$ with a base, such as [Bu$_4$N]OH; it was isolated and shown to undergo two successive single-electron reversible processes at the expected potentials, $E^\circ(2^+/2)$ and $E^\circ(2^{2+}/2^+)$ [Fig. 1(*d*)].

On the basis of IR data, NMR spectroscopy and elemental analysis, species **2**, obtained either upon cathodic reduction of **1**$^+$ or upon deprotonation of the latter by base, was shown to be the neutral nitrile complex *trans*-[ReCl(NCR)(dppe)$_2$].[10]

Moreover, the corresponding dioxidized form of *trans*-[ReCl(NCR)(dppe)$_2$]$^{2+}$ **2**$^{2+}$, is the product, formed quantitatively, of the preparative scale oxidation of **1**$^+$ which was found to obey the balance eqn. (1).

$$\underset{\mathbf{1}^+}{\mathrm{ReH}^+} - 2e \rightarrow \underset{\mathbf{2}^{2+}}{\mathrm{Re}^{2+}} + \mathrm{H}^+ \qquad (1)$$

The mechanism of this reaction was investigated by simulation (programme CVSIM[11]) of the voltammograms at different scan rates and various concentrations of **1**$^+$.

A classical reversible ECE[12] (electron transfer/chemical/electron transfer) mechanism [eqns. (2)–(4)] was shown to lead to a poor agreement with the experimental data, mainly because it involves a first-order behaviour in the rhenium complex, in contradiction with the observation of an increased irreversibility of the oxidation wave upon increasing the ReH$^+$ concentration.

$$\mathrm{ReH}^+ - e \rightleftharpoons \mathrm{ReH}^{2+} \qquad (2)$$

$$\mathrm{ReH}^{2+} \rightleftharpoons \mathrm{Re}^+ + \mathrm{H}^+ \qquad (3)$$

$$\mathrm{Re}^+ - e \rightleftharpoons \mathrm{Re}^{2+} \qquad (4)$$

An almost perfect agreement between the experimental and the simulated voltammograms was obtained upon assuming a DISP2-type mechanism[12] [eqns. (5)–(7)], where the oxidation of Re$^+$ is performed homogeneously, by electron transfer to ReH^{2+}, rather than by the electrode. Such a behaviour, *via* a DISP2 type-mechanism instead of an ECE one, is consistent with previous theoretical considerations.[12] The simulations could not afford the independent values of K and k in the above mechanism owing to the steady state chemical behaviour of Re$^+$. Yet the apparent overall rate constant, $k_{\mathrm{ap}} = kK[\mathrm{B}]/[\mathrm{HB}^+]$ could be determined. In agreement with the formulation of the above mechanism, k_{ap} was shown to increase with the basicity of the medium; thus, k_{ap} = 100, 250 and 400 dm^3 mol^{-1} s^{-1} were determined respectively in CH$_2$Cl$_2$, thf and thf with 4 equiv. pyridine added.

$$\underset{\mathbf{1}^+}{\mathrm{ReH}^+} - e \rightleftharpoons \underset{\mathbf{1}^{2+}}{\mathrm{ReH}^{2+}} \qquad (5)$$

$$\mathrm{ReH}^{2+} + \mathrm{B} \overset{K}{\rightleftharpoons} \underset{\mathbf{2}^+}{\mathrm{Re}^+} + \mathrm{HB}^+ \qquad (6)$$

$$\mathrm{Re} + \mathrm{ReH}^{2+} \xrightarrow{k} \underset{\mathbf{2}^{2+}}{\mathrm{Re}^{2+}} + \mathrm{ReH}^+ \qquad (7)$$

It is worth noting that the same series of experiments showed that the basicity of the medium had no effect on the reduction wave of **1**$^+$. However, in view of the above-mentioned difficulties associated with the exact determination of the chemical reversibility of this cathodic wave, no reliable mechanism could be established. Nevertheless, the quantitative formation of **2** upon preparative scale cathodic electrolysis of **1**$^+$ indicates that its reduction involves a dehydrogenation reaction.

The rupture of a metal–hydride bond by electrochemical oxidation has been reported for a number of transition metal complexes,[6,13] and shown to involve either H$^+$ extrusion from the oxidized metal centre or the formal transfer of H to an acceptor; often, further reactivity occurs, involving, *e.g.*, a reductive elimination, a metal–metal bond formation (dimerization),[4] a disproportionation[5] or a further oxidation followed by a nucleophilic attack.[7] However, in these systems, the mechanisms of the proton loss have usually not been studied in detail. Our studies indicate that this reaction can involve a bimolecular process and be considerably more complex than a simple intramolecular M–H bond cleavage; moreover, we have also shown that dehydrogenation occurs upon reduction, although the mechanism could not be established in this case.

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