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Investigation of the Electrochemical Reduction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ by Scanning Electrochemical Microscopy

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Summary: The reduction of the rhenium aryldiazenido complex $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ results in the formation of the corresponding metal-bound dinitrogen complex $Cp^*Re(CO)_2(N_2)$. The mechanism of this transformation has been investigated by cyclic voltammetry (CV), controlled-potential electrolysis (CPE), and scanning electrochemical microscopy (SECM). The SECM analysis supported an electrochemical E_rC_i mechanism for the reduction of the cationic aryldiazenido complex to the neutral dinitrogen complex.

Interest in transition-metal complexes containing dinitrogen itself, or diazenide (N_2H) and other reduced forms of the dinitrogen ligand, stems from their potential as models for steps in biological nitrogen fixation and the possibility of designing synthetic nitrogen fixation catalysts.[1] The interrelationship of metal-bound N_2 and N_2H is particularly important to understand if indeed the first stage of reduction is the formal addition of a single hydrogen atom to a coordinated N_2 molecule. Thus far, reactions in which the N_2H ligand is believed to have been formed are quite rare, and its characterization is far from complete.[2–5] In contrast, the aryl-substituted diazenide ligand (N_2Ar) is very well established in numerous complexes for a wide variety of transition metals[1e–g] and can be considered a reasonable model for evaluating the chemistry of metal-bound N_2H.

Several years ago Sutton and co-workers[6] observed that the aryldiazenide ligand in cationic manganese and rhenium complexes of the type $[Cp'M(CO)_2(N_2Ar)]^+$ (Cp' = C_5H_5, C_5H_4Me) was transformed into the dinitrogen ligand by Cl^-, Br^-, I^-, CN^-, and SCN^- to yield the neutral complexes $Cp'M(CO)_2(N_2)$. For the iodide reaction, a nucleophilic displacement mechanism was consistent with the limited available experimental evidence. The manganese aryldiazenido complex also yielded the dinitrogen complex when reacted with PPh_3, and this appeared to be a radical process.[6b] Subsequently, a wide variety of C_5H_5 and C_5Me_5 rhenium aryldiazenido complexes have been converted to corresponding dinitrogen complexes by the use of $NaBH_4$,[7] Bu^tLi,[7] or Cp_2Co.[8] While the mechanisms of these transformations may not be identical in the case of each of these reagents,[9] we were interested in determining whether electron transfer could be responsible. Here we report the results of cyclic voltammetry (CV) and controlled-potential electrolysis (CPE) and the application of scanning electrochemical microscopy (SECM)[10] to the aryldiazenido complex $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$, ($\mathbf{1}(BF_4)$; $Cp^* = \eta^5\text{-}C_5Me_5$).

Assuming that **1** is reduced to the neutral 19-electron complex **2**, which then decomposes to give products (eq 1), allows treatment as an electrochemical E_rC_i mechanism[11] following eqs 2 and 3, wherein O and R correspond to the cationic and neutral forms of the Re complex, respectively, and P designates products.

$$\underset{\mathbf{1}}{[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+} \xrightarrow{e^-} \underset{\mathbf{2}}{Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)} \rightarrow Cp^*Re(CO)_2(N_2) \quad (1)$$

$$O + e^- \rightarrow R \quad (2)$$

$$R \xrightarrow{k_c} P \quad (3)$$

SECM has recently emerged as a useful technique for studying the kinetics of chemical reactions coupled to

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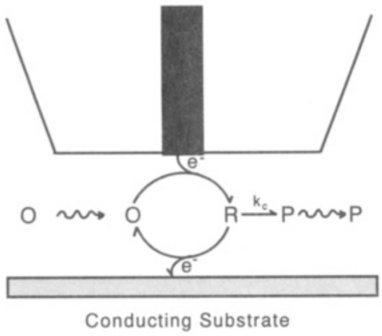

Figure 1. SECM scheme for an EC mechanism with competing feedback from the substrate electrode. Decreased tip–substrate separations result in enhanced currents as increasing amounts of R are reoxidized by the substrate before decomposing to P.

electron transfer.[12,13] Detailed theory for the SECM feedback response for this mechanism is presented in a recent publication[13] and allows determination of the rate constant (k_c) for the decomposition of the neutral 19-electron complex **2** (R) to products (P). The SECM scheme for this mechanism is shown in Figure 1, wherein the tip and substrate potentials are biased so the rates of the redox reactions, reduction of **1** to **2** at the tip and oxidation of **2** to **1** at the substrate, are diffusion-controlled. For an SECM microelectrode tip in solution (far from any substrate), the diffusion-limited current (i) for an electroactive species is given by eq 4,[14] where n is the number of electrons

$$i = 4nFD_Oc_Oa \qquad (4)$$

transferred, F is the Faraday constant, D_O and c_O are the diffusion coefficient and concentration of the electroactive species, respectively, and a is the electrode radius. When the tip is sufficiently far from the substrate that essentially all of the tip-generated product, R, decomposes before it can diffuse to the conductive substrate, the current decreases compared to that in the bulk solution (eq 4) as the tip is moved toward the substrate, because diffusion of the electroactive species (O) to the tip is restricted by the substrate and the glass insulator of the microelectrode. As the tip–substrate separation continues to decrease, there comes a point at which (depending upon the magnitude of k_c) the rate of diffusion of R to the oxidizing substrate becomes competitive with the decomposition of R to electroinactive P (Figure 1). At this point, the current begins to increase as the decomposition of R to P is offset by the influx of O and recycling of O and R between the tip and substrate. As the spacing becomes smaller, an increasing fraction of R diffuses to the substrate before decomposing to P, and the current at the tip (governed increasingly by mass transport of O and R between tip and substrate) increases exponentially with decreasing tip–substrate separations. Approach curves, i.e., plots of current vs tip–substrate separation, vary with k_c and can be used to determine such rate constants. Although mechanisms such as this can be quantified by cyclic voltammetry, the SECM analysis is simpler in that there is no need for subtraction of background charging current, nor are there possible complications from slow heterogeneous kinetics, adsorption, and uncompensated resistance. We thus proceed with a quantitative SECM analysis and support the results by CV and CPE. The SECM apparatus has been described previously.[15,16]

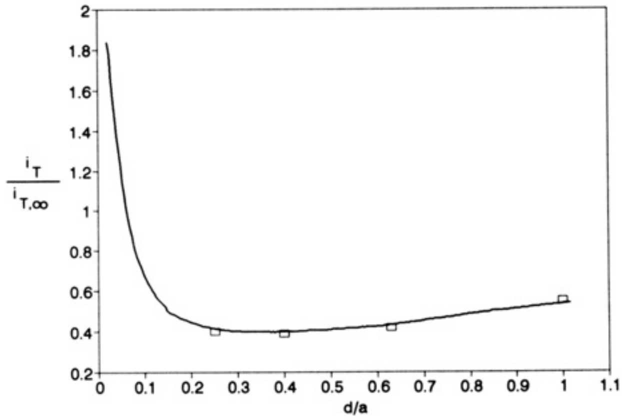

Figure 2. SECM approach curve (solid line) for 1.0 mM [Cp*Re(CO)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$] (**1**(BF$_4$)) in acetonitrile at a 25-μm-diameter Pt-tip electrode (biased at −0.8 V vs AgQRE) opposed by a 1-mm-diameter Pt substrate (biased at 0.0 V vs AgQRE) (supporting electrolyte, 0.1 M TBA(BF$_4$); scan rate, 0.05 μm/s). Squares represent theoretical values taken from ref 13.

With respect to the SECM study, the approach curve (normalized steady-state tip current vs tip–substrate separation) obtained for reduction of **1**(BF$_4$) is shown in Figure 2, where d is the tip–substrate separation in micrometers, a is the electrode radius (12.5 μm), i_T is the current corresponding to a given tip–substrate separation, and $i_{T,\infty}$ is the steady-state diffusion-limited current at the microelectrode disk in the bulk solution far from the substrate (eq 4). For this experiment, the tip was biased at −0.8 V and the substrate at 0.0 V vs Ag quasi reference electrode (AgQRE). Similar results were obtained for approach velocities of 0.02 and 0.1 μm/s. To support the assumption that the enhanced current at low d/a values in Figure 2 is due to recycling of **1** and **2** (O and R) between the tip and substrate electrodes, qualitative tip generation/substrate collection experiments were undertaken. For these experiments, the tip was positioned ~2.5 μm from the substrate (d/a = 0.2). The substrate was then biased at −0.35 V vs AgQRE and cyclic voltammograms were recorded for the tip and substrate electrodes as the tip potential was scanned from −0.35 to −0.80 V. As expected, reduction of **1** at the tip generated a cathodic current which was simultaneously mirror-imaged by an anodic current at the substrate due to oxidation of **2** that diffused to the substrate before decomposing. This experiment supports the assumption that the **1**/**2** couple is responsible for the observed SECM response shown in Figure 2. From these data, assuming an E$_r$C$_i$ mechanism, we determine from theory[13] a value of the dimensionless parameter $K = k_ca^2/D$ = 15.85 (from log K = 1.2). This analysis assumes the same diffusion coefficient for O and R, which was determined (from eq 4) to be $D = 1.4 \times 10^{-5}$ cm^2/s. Solving for k_c yields a value of k_c = 145 ± 10 s^{-1}. The validity of this rate constant is substantiated by cyclic voltammetry (Figure 3), wherein a return wave for the oxidation of the 19-electron neutral complex **2** is first resolved at 10 V/s and becomes well-defined at 50 V/s. Digital simulation[17]

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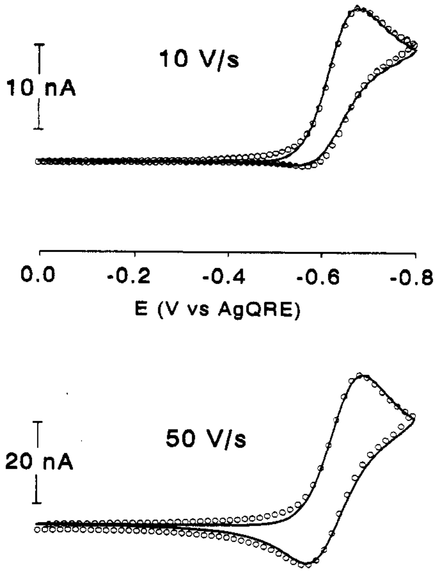

Figure 3. Experimental (circles) and simulated (solid lines) cyclic voltammograms for the reduction of 1.1 mM [Cp*Re(CO)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$] (1(BF$_4$)), in acetonitrile at a 25-μm-diameter Pt electrode (supporting electrolyte, 0.1 M TBA(BF$_4$)).

of an EC mechanism using $k_c = 145$ s^{-1} produces excellent agreement between theory and experiment.

The CPE study lends further support to the electrochemical E_rC_i mechanism. Exhaustive controlled-potential electrolysis of 1(BF$_4$) (60 min) at −0.56 V vs a AgCl/Ag reference electrode indicated the consumption of 1 equiv of electrons. This value was obtained by application of eq 5,[18] where q_∞ is the total charge consumed at the end

$$q_\infty = nFcV \qquad (5)$$

of the experiment, c is the concentration of 1(BF$_4$), V is the volume of solution in the working electrode compartment, and n is the number of electrons consumed. This result is obviously consistent with the production of the neutral 19-electron complex 2 (eq 1) and its subsequent decomposition.

Monitoring the progress of the electrolysis by IR spectroscopy showed the sole production of the dinitrogen complex Cp*Re(CO)$_2$(N$_2$), which was accompanied by the complete disappearance of 1(BF$_4$) (Figure 4). Upon completion of the electrolysis, the solvent and volatiles were removed by vacuum, and a gas chromatograph of the condensate confirmed the presence of anisole, as is expected to result from hydrogen abstraction from the solvent by the p-methoxyphenyl radical formed in the irreversible chemical step.

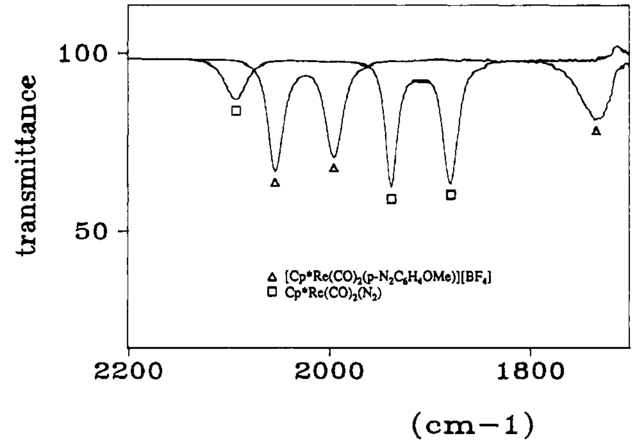

Figure 4. IR spectra obtained before and after the CPE of 4.9 mM [Cp*Re(CO)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$] (1(BF$_4$)) in acetonitrile at a reductive potential of −0.56 V vs AgCl/Ag, illustrating the formation of Cp*Re(CO)$_2$(N$_2$) (Pt-gauze working electrode; supporting electrolyte, 0.2 M [Et$_4$N][ClO$_4$]). [Cp*Re(CO)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$]: ν(CO) 2054, 1995 cm^{-1}; ν(NN) 1732 cm^{-1}. Cp*Re(CO)$_2$(N$_2$): ν(CO) 1939, 1879 cm^{-1}; ν(NN) 2121 cm^{-1}.

The SECM analysis supports an electrochemical E_rC_i mechanism for the reduction of the cationic aryldiazenido complex [Cp*Re(CO)$_2$(p-N$_2$C$_6$H$_4$OMe)]$^+$ (1) to the neutral dinitrogen complex Cp*Re(CO)$_2$(N$_2$), with the first-order decomposition rate constant $k_c = 145 \pm 10$ s^{-1} for the intermediate 19-electron complex 2. The validity of this result is corroborated by cyclic voltammetry and controlled-potential electrolysis.

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Supplementary Material Available: Text giving details of the experimental procedure for SECM, CPE, and CV measurements and a figure depicting the electrochemical cell used for CPE (5 pages). Ordering information is given on any current masthead page.

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