

Ligand C–C Bond Cleavage on Ruthenium: Observation of a Reversible Ruthenium(V)–Imido/Ruthenium(II)–Amine Couple and X-Ray Crystal Structure of $[\text{Ru}(\text{bpy})_2(\text{NH}=\text{CMe}_2)_2](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine)

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A reversible three-proton three-electron couple has been observed for the electrochemical oxidation of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ (L = 2,3-dimethyl-2,3-diaminobutane) in aqueous acidic solution; controlled-potential electrochemical oxidation of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ led to C–C bond cleavage in L and formation of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{NH}=\text{CMe}_2)_2]^{2+}$ whose structure has been determined by X-ray crystallography.

The study of transition metal complexes containing organo-imido ligands is of current interest. Although osmium imido complexes are known,¹ there are few reports on ruthenium imido complexes.^{2–4} Presumably, these species are very reactive and it is more difficult for them to be isolated or observed. Sargeson and coworkers⁵ first noted that oxidative deprotonation of $[\text{Ru}(\text{sar})]^{2+}$ (sar = 3,6,10,13,16,19-hexazabicyclo[6.6.6]icosane) to a Ru^{II}–imine species proceeds through a short-lived Ru^{IV}–imido species which has been characterized by UV–VIS spectroscopy and electrochemical means. We expected that the stability of Ru–imido complexes in solution may be enhanced if the coordinated amine does not contain an $\alpha\text{-C-H}$ group. In this context, the ligand L (L = 2,3-dimethyl-2,3-diaminobutane)⁶ is attractive for the investigation of high-valent ruthenium–amido and –imido chemistry. We describe here the electrochemical properties of $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ (bpy = 2,2'-bipyridine) which facilitates C–C bond cleavage in L via an Ru^V–imido intermediate.

Reaction of $\text{cis-}[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ with L in refluxing ethanol gave $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ **1** which was isolated as an air-stable red perchlorate or hexafluorophosphate salt. The complex $[\mathbf{1}](\text{ClO}_4)_2$ or $[\mathbf{1}](\text{PF}_6)_2$ is diamagnetic and shows an intense metal-to-ligand charge-transfer (MLCT) transition at 494 nm (ϵ_{max} ca. 8190 mol⁻¹ dm³ cm⁻¹ in MeCN). It was characterized by IR [$\nu(\text{N-H})$ at 3200 and 3300 cm⁻¹] and ¹H NMR spectroscopy [δ in CD₃CN, 0.83 (s, Me), 1.16 (s, Me),

3.19–3.33 (d, NH₂), 3.77–3.91 (d, NH₂), 7.16–7.30 (m, 2H), 7.72–7.96 (m, 6H), 8.08–8.56 (m, 6H) and 9.36 (d, 2H)] and elemental analysis. In 0.1 mol dm⁻³ CF₃CO₂H with edge-plane pyrolytic graphite as working electrode, the cyclic voltammogram of **1** shows a reversible–quasi-reversible couple I (ΔE_p ca 60 mV, $i_{\text{pa}}/i_{\text{pc}}$ ca. 0.9 at a scan rate of 50 mV s⁻¹) at 0.75 V and an irreversible wave at 1.00 V vs. standard calomel electrode (SCE) [Fig. 1(a)]. Couple I remains reversible in the pH range 1–3. At pH > 3, couple I becomes ill defined. Comparison of rotating disk voltammograms of **1** and $[\text{Ru}(\text{bpy})_3]^{2+}$ of the same concentration (1 mmol dm⁻³) in 0.1 mol dm⁻³ CF₃CO₂H established that the plateau current of couple I is three times as large as that for $[\text{Ru}(\text{bpy})_3]^{2+}$ and that for the oxidative wave II. This suggests couple I and the oxidative wave II are due to three-electron and one-electron oxidation respectively. Controlled potential coulometry of **1** at 0.85 V in 0.1 mol dm⁻³ CF₃CO₂H established that the overall electrochemical process of couple I is three-electron ($n = 3.0$). Both the E° and E_{pa} of I and II were found to shift cathodically by 60 mV/pH as the pH of the medium was raised from 1 to 3 [Fig. 1(b)]. As the ligand L cannot be oxidised in this potential range, the electrode reactions involved are those in Scheme 1. To our knowledge, this is the first observation of a reversible metal–imido/metal–amine couple in aqueous solution.

Although the Ru^V–imido complex **2** is stable on the

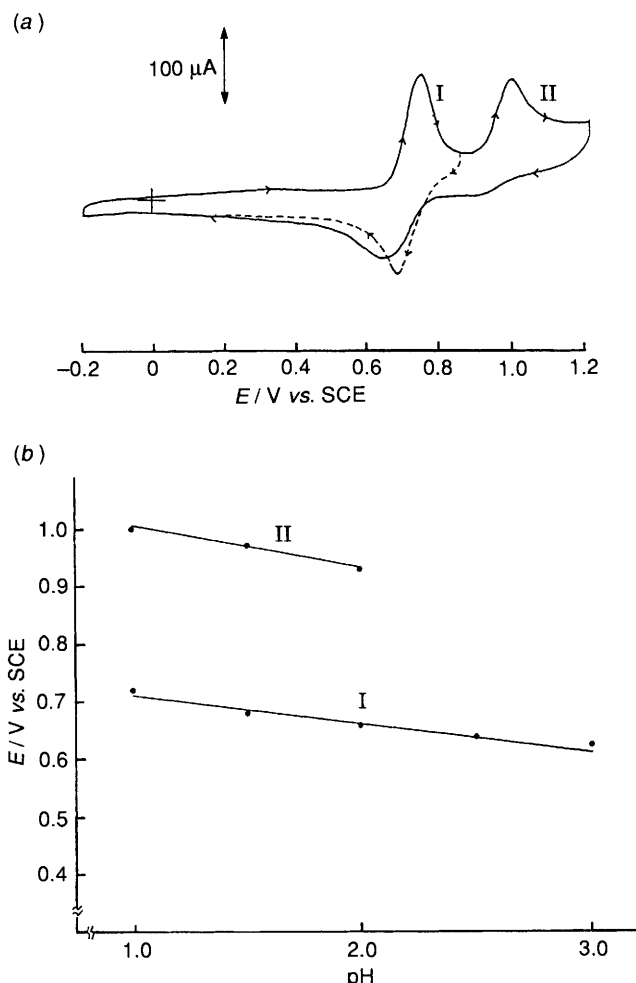
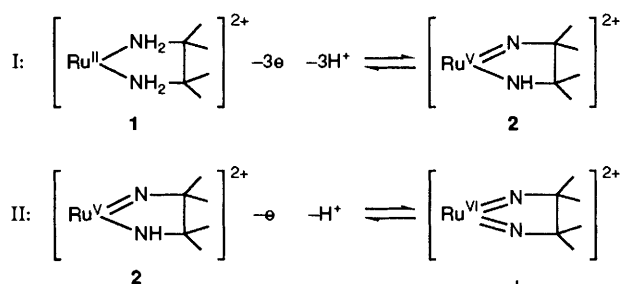


Fig. 1 (a) Cyclic voltammogram of **1** in 0.1 mol dm⁻³ CF₃CO₂H. Working electrode: edge-plane pyrolytic graphite; scan rate 50 mV s⁻¹. (b) pH dependence of formal potential for wave I and peak potential for wave II exhibited by **1** in aqueous acidic media (pH 1–3).



Scheme 1

time-scale of the cyclic voltammetric scans, it is a reactive species rendering its isolation in pure form difficult.[†] Constant-potential electrolysis of **1** at 0.85 V in 0.1 mol dm⁻³ CF₃CO₂H gave a new species **3** whose cyclic voltammogram is different from that of **1**. This new species exhibits a reversible one-electron couple whose E° at 0.66 V vs. SCE is indepen-

[†] Attempts have been made to isolate complex **2**. Addition of excess of (NH₄)₂[Ce(NO₃)₆] to an aqueous solution of [**1**] (PF₆)₂ followed by immediate precipitation with (NH₄)PF₆ at room temperature gave a yellow-brown solid analysed as [**2**] (PF₆)₂. This complex is paramagnetic ($\mu_{\text{eff}} = 1.5 \mu_{\text{B}}$ at 298 K, solid sample) and displays a similar cyclic voltammogram to that of **1** in 0.1 mol dm⁻³ CF₃CO₂H. However, it is unstable and slowly decomposes in solution and in the solid state.

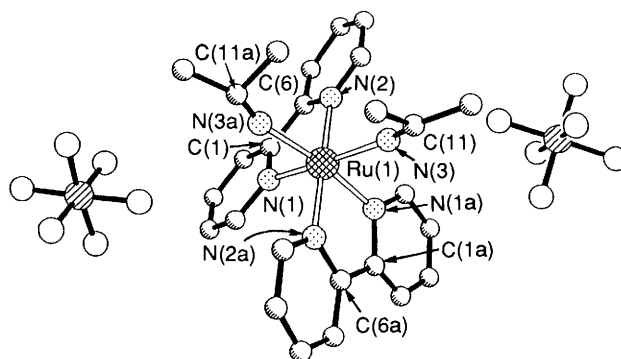
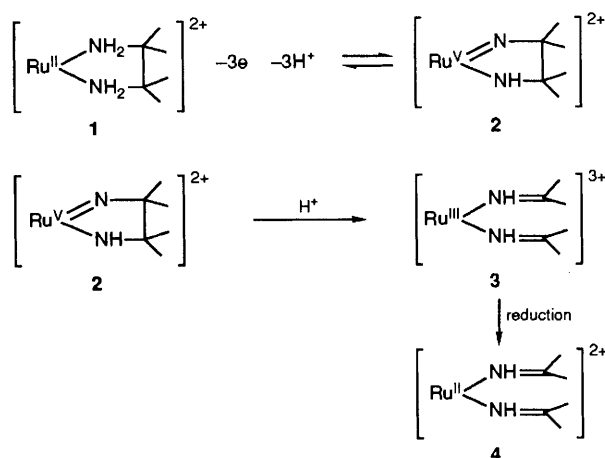


Fig. 2 Perspective view of **4**, which exhibits C₂ molecular symmetry, with atom numbering. Selected bond distances (Å) and angles (°): Ru(1)–N(1) 2.035(9), Ru(1)–N(2) 2.081(9), Ru(1)–N(3) 2.06(1), N(3)–C(11) 1.16(2), N(1)–Ru(1)–N(1a) 87.3(5), N(2)–Ru(1)–N(2a) 172.8(4), N(1)–Ru(1)–N(3) 171.2(5), N(2)–Ru(1)–N(3) 93.4(4), N(3)–Ru(1)–N(3a) 97.7(7), Ru(1)–N(3)–C(11) 159(1).



Scheme 2

dent of pH. Complex **3** has not been isolated. However, constant-potential electrolysis of **3** at 0.50 V established $n = 1.0$. Its reduction product **4**, which could also be obtained by constant-potential oxidation of **1** in acetonitrile and allowing the oxidized solution to stand in air for two days, has been characterized by IR spectroscopy [$\nu(\text{N}=\text{H})$ 3230 cm⁻¹, $\nu(\text{C}=\text{N})$ 1610–1620 cm⁻¹] and X-ray crystallography[‡] to be *cis*-[Ru(bpy)₂(NH=CMe₂)₂]²⁺.

A perspective view of **4** is shown in Fig. 2. The Ru(1)–N(3)–C(11) angle of 159(1)° is consistent with an Ru^{II}–imine

[‡] Crystal data for [4](PF₆)₂: (C₁₀H₈N₂)₂(C₃H₇NH)₂Ru(PF₆)₂, $M = 819.57$, space group C₂/c (No. 15), $a = 17.314(5)$, $b = 10.591(3)$, $c = 16.921(5)$ Å, $\beta = 97.86(2)^\circ$, $V = 3073.9(1)$ Å³, $Z = 4$, $D_c = 1.77$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 7.02$ cm⁻¹, $F(000) = 1648$, no. of variables 215, no. of unique data measured 2477, no. of observed data with $|F_o| \geq 6\sigma(|F_o|)$ 1556, $R_F = 0.071$, $R_w = 0.087$. The residual extrema in the final difference map were 0.68 and -1.12 e Å⁻³. Raw intensities ($h, k, \pm l$; $2\theta_{\text{max}} = 50^\circ$) were collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). Structure solution was accomplished by Patterson and Fourier methods. The non-hydrogen atoms in the imine ligands have abnormally large thermal parameters, so that the ordered model used in refinement does not rule out the possibility of disorder. The PF₆-group also exhibits two-fold orientational disorder; accordingly it was treated as a superposition of two octahedra with P–F and F \cdots F distance constraints and centred at the P atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

complex formulation. It is interesting that the C–C bond in L has been cleaved to give two imine groups. The mechanism in Scheme 2 is proposed.

The present work clearly indicates that pH-dependent reversible Ru–imido/Ru–amine couples, like that of Ru=O/Ru–OH₂, can readily be observed using amine ligands containing no α -C–H groups. By appropriate choice of amine ligands, one would expect that stable ruthenium–imido complexes could be isolated.

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