A Novel and Stable Catalyst for the Electrochemical Oxidation of Methanol and Tetrahydrofuran: Electrochemical Oxidation of Organic Substrates Catalysed by *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ (6,6′-Cl_2bpy = 6,6′-dichloro-2,2′-bipyridine)

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The electrochemical oxidations of alcohols to aldehydes/ketones and tetrahydrofuran to γ-butyrolactone at 1.2 V [*vs.* standard calomel electrode (s.c.e.)] are catalysed by *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ (6,6′-Cl_2bpy = 6,6′-dichloro-2,2′-bipyridine), with current efficiency > 80%; a Nafion-coated basal-plane pyrolytic graphite electrode incorporating *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ is active in catalysing the electrochemical oxidation of propan-2-ol to acetone.

The search for new inorganic materials capable of catalysing the electrochemical oxidation of hydrocarbons is currently of intense interest.[1–4] There are several reports of the use of ruthenium oxo complexes of aromatic amines, such as $[Ru^{IV}(trpy)(bpy)O]^{2+}$, (trpy = 2,2′,2″-terpyridine; bpy = 2,2′-bipyridine)[2,4] and *trans*-$[Ru^{VI}(phen)_2O_2]^{2+}$ (phen = 1,10-phenanthroline)[3] as electrochemical catalysts; however, the reported examples are either unstable when subjected to extended electrolyses, or exhibit complex electrochemistry, with the Ru=O/Ru–OH_2 couples strongly affected by the nature of the electrode surface.[2] Our recent work has shown that the *cis*-dioxoruthenium(VI) system can be stabilized by the 6,6′-Cl_2bpy (6,6′-dichloro-2,2′-bipyridine) ligand; the *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2]^{2+}$ complex is a powerful oxidant which easily oxidizes the unactivated C–H bonds of cyclohexane and tetrahydrofuran.[5] The reversible electrochemical behaviour and stability of this Ru^{VI} complex in fluid solution suggest that its precursor *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ is an important electro-oxidative catalyst. We describe here the electrochemical oxidation of alcohols and tetrahydrofuran catalysed by this Ru^{II} complex.

At pH 1.1, the cyclic voltammogram of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ displays two reversible/quasireversible couples, I at 0.93 and II at 1.17 V *vs.* standard calomel electrode (s.c.e.).[5] In the presence of organic substrates (0.4 M), such as methanol, ethanol, propan-2-ol, benzyl alcohol, tetrahydrofuran, glucose, or acetaldehyde, the couple I remains unchanged whereas the couple II is replaced by a large catalytic oxidative wave at *ca.* 1.2 V; the cyclic voltammograms with propan-2-ol and tetrahydrofuran are shown in Figure 1. Since the couple II is due to the oxidation of Ru^{III} to Ru^{VI}, the catalytic oxidative wave can be explained by fact that at 1.2 V the electro-generated ruthenium - oxo complex, possibly *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2]^{2+}$, rapidly oxidizes the organic substrates and is itself reduced back to *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$. With propan-2-ol, the magnitude of the oxidative current is little affected upon repetitive cycling between 0.4 and 1.2 V (50 times; scan rate 50 mV s^{-1}), indicating that no deterioriation of the ruthenium complex has occured. The current is also insensitive to scan rate (10 to 100 mV s^{-1}), and when measured for different alcohols under the same conditions decreases in the order propan-2-ol > ethanol > methanol. This suggests that the rate-limiting step of the electrochemical reaction is the oxidation of the organic substrate by the ruthenium oxo complex. Controlled potential electrolyses of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ in the presence of methanol, ethanol, propan-2-ol, and tetrahydrofuran at 1.2 V yielded formaldehyde, acetaldehyde, acetone, and γ-butyrolactone, respec-

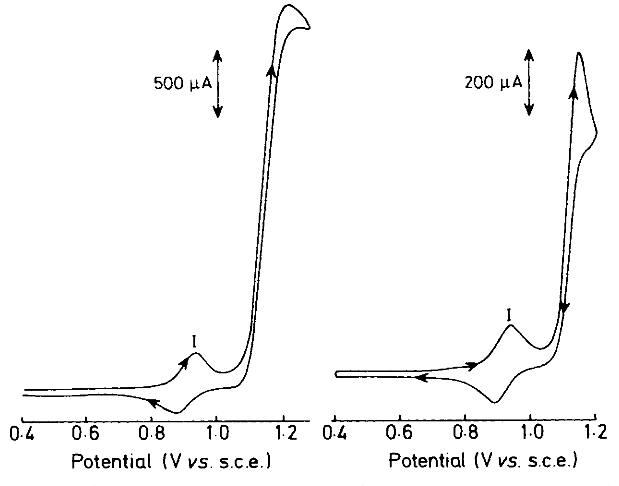

Figure 1. Cyclic voltammograms of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ in the presence of (a) 0.4 M-propan-2-ol and (b) 0.4 M-tetrahydrofuran at pH 1.1, scan rate 50 mV s^{-1}; basal-plane pyrolytic graphite working electrode.

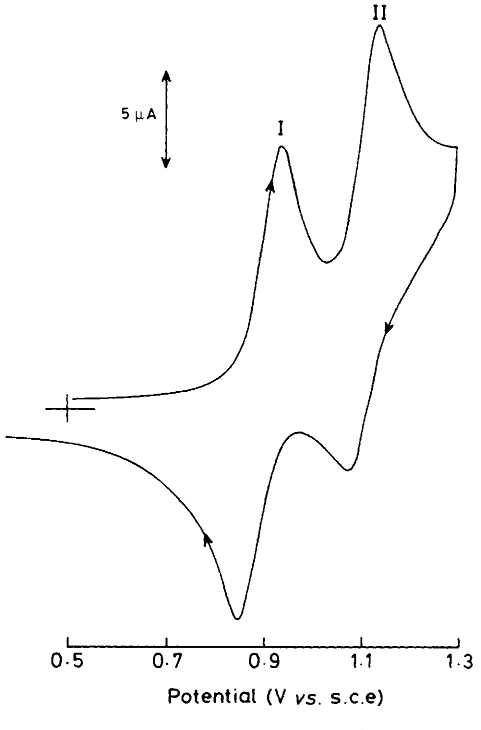

Figure 2. Cyclic voltammogram of a *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$-modified pyrolytic graphite electrode in 0.1 M-CF_3CO_3H; scan rate 50 mV s^{-1}.

Table 1. Electrochemical oxidation of alcohols (0.4 M) and tetrahydrofuran (0.4 M) in 0.1 M-CF_3CO_2M/0.1 M-CF_3CO_2Na (30 ml) catalysed by *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ (1 mM).

Substrate	Product	Current efficiency (%)	Turnover	Time of electrolysis (h)
Methanol	Formaldehyde	80	26	8
Ethanol	Acetaldehyde	96	27	4
Propan-2-ol	Acetone	97	43	4
Tetrahydrofuran	γ-Butyrolactone	85	17	8

tively, with current efficiency over 80% in each case; the results are summarized in Table 1.† After electrolysis, *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ remains virtually unchanged (over 80% recovery, determined by spectrophotometric methods), in contrast to the *trans*-$[Ru^{III}(phen)_2(OH)(OH_2)]^{2+}$ (ref. 3) and $[Ru^{IV}(trpy)(bpy)O]^{2+}$ (ref. 4) systems, which are transformed into a green substance upon extended electrolysis. Table 1 shows that the turnover numbers fall in the order propan-2-ol > ethanol > methanol > tetrahydrofuran, in accord with their relative susceptibility to oxidation.

The complex *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ can be incorporated into a modified electrode, which may be useful in electrochemical sensors. A nafion-coated electrode was fabricated by applying a solution of nafion (0.5% w/w) in propan-2-ol (450 μl) to the surface of a basal-plane pyrolytic graphite electrode (surface area 15 cm^2), and evaporating the propan-2-ol. The resulting nafion-coated electrode was dipped into aqueous 1 mM-*cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2][ClO_4]_2$ for 10 min then rinsed with deionized water. Cyclic voltammetric measurements (scan rate 5 mV s^{-1}) showed that the amount of Ru^{II} complex incorporated was 4.7×10^{-7} mol. In aqueous solution , this Ru-modified nafion-coated electrode is stable for 8 h and has the same cyclic voltammogram (redox couples at 0.92 and 1.12 V *vs.* s.c.e., with ΔE_p 60 and 30—40 mV, respectively) as *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ in homogeneous solution (Figure 2). It catalyses the electrochemical oxidation of propan-2-ol to acetone in water (pH 1.1) at 1.2 V, with current efficiency 87% and 198 turnovers in a 5 h electrolysis.

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† Conditions for controlled potential electrolyses: glassy carbon cup (diam. 5 cm; height 5 cm) as working electrode; 1 mM-*cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2][ClO_4]_2$, in 0.1 M-$CF_3CO_2H$/0.1 M-$CF_3CONa$ (30 ml) and 0.4 M-organic substrate at 25 °C. Acetaldehyde, acetone, and γ-butyrolactone were measured by g.l.c.–mass spectrometry. Formaldehyde was estimated by conversion into the 2,4-dinitrophenylhydrazone, followed by g.l.c.–mass spectrometry.