

Carbon/Poly{pyrrole-[(C₅Me₅)Rh^{III}(bpy)Cl]⁺} Modified Electrodes; a Molecularly-based Material for Hydrogen Evolution (bpy = 2,2'-bipyridine)

Serge Cosnier, Alain Deronzier,* and Nicolas Vlachopoulos

Laboratoire d'Electrochimie Organique et de Photochimie Rédox, URA CNRS D1210, Université Joseph Fourier, Grenoble 1, BP 53X, 38041 Grenoble Cédex, France

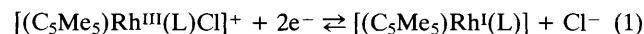
A rhodium(III) complex containing a 2,2'-bipyridine ligand substituted with pyrrole groups has been anodically electropolymerized on either a Pt or a C electrode; the polymer attached to C acts as an efficient molecularly-based cathode material for hydrogen evolution in aqueous solution (pH 1).

There has been considerable interest recently in the development of chemically modified electrodes with electroactive transition metal complexes attached to a conductive polymer such as polypyrrole, especially with the monomer units covalently linked to 2,2'-bipyridine.¹ Owing to the ability of some rhodium complexes with 2,2'-bipyridine to act as catalysts for the photo-induced reduction of protons and the hydrogenation of organic compounds,² we have synthesized [(C₅Me₅)Rh^{III}(L)Cl]⁺BF₄⁻ (**1**),[†] in which L is bis-4,4'-[bis(pyrrol-1-ylmethyl)methoxycarbonyl]-2,2'-bipyridyl.^{1e}

[†] The structure of (**1**) was established by f.a.b. m.s.: *m/z* positive mode C⁺ 861, negative mode C⁺, 2BF₄⁻ 1035; and ¹H n.m.r. (CDCl₃) δ 1.77 (s, 15H), 4.20 (m, 4H), 4.42 (m, 4H), 5.64 (m, 2H), 6.12 (m, 8H), 6.75 (m, 8H), 8.25 (m, 8H), 9.01 (d, 2H, *J* 5 Hz), 9.20 (d, 2H, *J* 5 Hz).

Compound (**1**) was obtained in quantitative yield by the reaction of [(C₅Me₅)Rh^{III}Cl(μ-Cl)]₂ with a slight excess of L in ethanol.

On a platinum or glassy carbon electrode, the cyclic voltammogram of (**1**) (10⁻³ M) in 0.1 M Et₄NClO₄-MeCN, Ar-purged, (Figure 1) indicates an electrochemically irreversible two-electron reduction process [*E*_{pc} -1.04 V, *E*_{pa} -0.66 V at 100 mV s⁻¹ (vs. Ag/10⁻² M Ag⁺)], metal-localized, as previously observed for some other Rh^{III}-bipyridine complexes,^{2b,3} corresponding to the reaction in equation (1).



The exhaustive reduction of the solution at -1.3 V consumes 2 e⁻/molecule and leads to a violet-coloured solution of [(C₅Me₅)Rh^I(L)]. The u.v. visible absorption

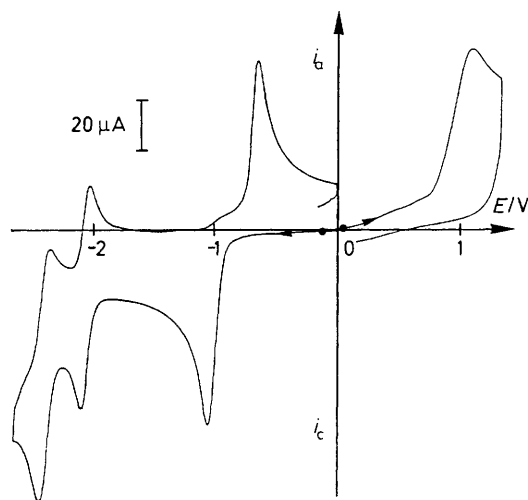


Figure 1. Cyclic voltammogram at a glassy carbon electrode (diam. 5 mm) of $[(C_5Me_5)Rh^{III}(L)Cl]^+$ ($10^{-3} M$) in 0.1 M Et_4NClO_4 -MeCN under Ar, sweep rate ν 100 $mV s^{-1}$.

spectrum (λ_{max} 590 nm) is in good agreement with a similar complex, $[(C_5Me_5)Rh^I(L)]$ ($L = 2,2'$ bipyridine-4,4'-dicarboxylic acid), obtained by chemical reduction.^{2b} On extension of the scan to -2.6 V, this process is followed by two successive reversible one-electron transfers, due to the bipyridine ligand and leading to $[(C_5Me_5)Rh^I(L^{\cdot-})]^-$ ($E_{1/2} -2.06$ V) and $[(C_5Me_5)Rh^I(L^{2-})]^{2-}$ ($E_{1/2} = -2.41$ V) species. On a positive scan between 0 and $+1.3$ V, only the peak of the irreversible oxidation of pyrrole units is observed (E_{pa} 1.1 V).

Electropolymerization of (1) was accomplished by controlled-potential oxidation at 0.85 V. The resulting modified electrode upon transfer into 0.1 M Et_4NClO_4 -MeCN solution not containing the monomer, exhibited the regular electroactivity of *N*-substituted polypyrroles with a quasi-reversible redox peak system (E_{pa} 0.2 V, E_{pc} 0.1 V), as seen in Figure 2A, curve a. By sweeping the potential, in the negative direction, irreversible peaks of the $[(C_5Me_5)Rh^{III}(L)Cl]^+ / [(C_5Me_5)Rh^I(L)]$ system ($E_{pc} -0.92$ V, $E_{pa} -0.68$ V) are still present along with the reversible ones of the $[(C_5Me_5)Rh^I(L)] / [(C_5Me_5)Rh^I(L^{\cdot-})Cl]^-$ couple ($E_{1/2} -2.10$ V) (Figure 2A, curves b and c). It should be noted that the peak intensity of the $[(C_5Me_5)Rh^{III}(L)Cl]^+ / [(C_5Me_5)Rh^I(L)]$ system is markedly lower than that of the $[(C_5Me_5)Rh^I(L)] / [(C_5Me_5)Rh^I(L^{\cdot-})]^-$ system, in accordance with the slowness of the process involving the former. Moreover, an intense pre-peak is obtained at the foot of the cathodic peak of the $[(C_5Me_5)Rh^I(L)] / [(C_5Me_5)Rh^I(L^{\cdot-})]^-$ system, as a consequence of the indirect reduction of $[(C_5Me_5)Rh^{III}(L)Cl]^+$ by $[(C_5Me_5)Rh^I(L^{\cdot-})]^-$ occurring at this potential. This pre-peak disappears on the second scan. A repeated scan of the potential over the range -0.4 to -1.6 V induces a transformation of the electrochemical response of the film (Figure 2B). As a consequence of the reduction, a new cathodic peak, whose height continuously increases, emerges at -0.76 V; the former anodic peak also increases, while remaining at the same potential. This phenomenon is enhanced by potentiostating the electrode at -1.6 V.

At the end of electrolysis, the new modified electrode exhibits the same electrochemical response, as in the case of continuous cycling. The new quasi-reversible system (ΔE_p 80 mV, ν 100 $mV s^{-1}$) depicts the bi-electronic conversion of the $[(C_5Me_5)Rh^{III}(L)]^{2+}$ to $[(C_5Me_5)Rh^I(L)]$ and *vice versa*. It appears that the Cl^- ions released upon the initial reduction of

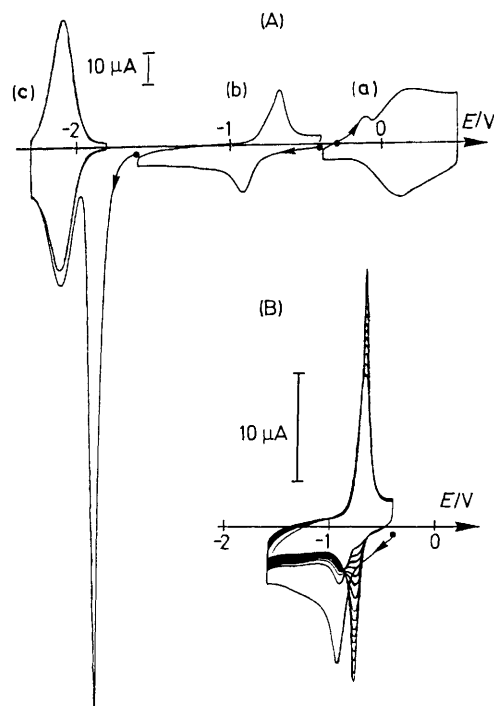


Figure 2. Cyclic voltammogram of a Pt (diam. 5 mm)/poly{pyrrole- $[(C_5Me_5)Rh^{III}(L)Cl]^+$ } electrode in 0.1 M Et_4NClO_4 -MeCN prepared by electrolysis at 0.85 V, $Q = 10^{-3} C$ ($\Gamma_{Rh^{III}} = 9.8 \times 10^{-10} mol cm^{-2}$); sweep rate $\nu = 100 mV s^{-1}$. (A) Curve a between -0.4 and $+0.5$ V; curve b between -0.4 and -1.6 V; curve c two successive scans between -1.8 and -2.3 V, the first scan starting from -1.6 V. (B) Evolution of the electrochemical response by repeated potential scanning between -0.4 and -1.6 V (17 scans).

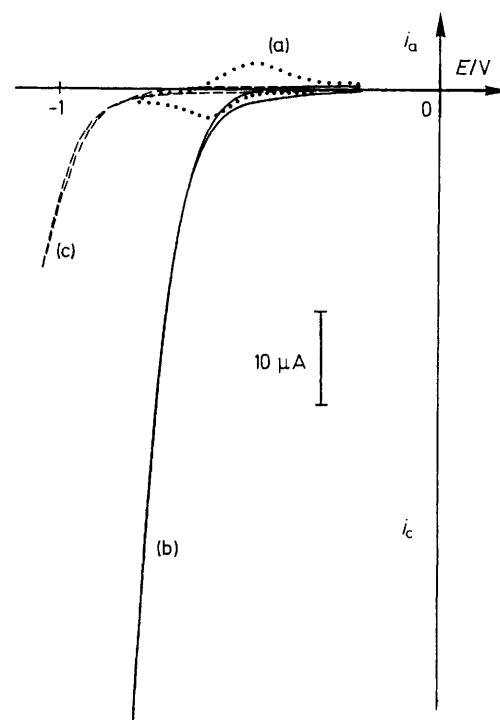


Figure 3. Cyclic voltammogram of a glassy carbon/poly{pyrrole- $[(C_5Me_5)Rh^{III}(L)Cl]^+$ } ($\Gamma_{Rh^{III}} = 2 \times 10^{-9} mol cm^{-2}$) in 0.1 M $LiClO_4$ aqueous solution, sweep rate ν 10 $mV s^{-1}$: (a) pH 5; (b) pH 1; (c) naked electrode, pH 1.

$[(C_5Me_5)Rh^{III}(L)Cl]^+$ to $[(C_5Me_5)Rh^I(L)]$ very slowly coordinate the product of the oxidation of the latter, $[(C_5Me_5)Rh^{III}(L)]^{2+}$. Therefore anchoring the complex to the electrode allows the build-up of the reactive species $[(C_5Me_5)Rh(L)]^{2+}$. The following further experimental evidence supports such a statement. (i) The initial electrochemical signal of $[(C_5Me_5)Rh^{III}(L)Cl]^+ / [(C_5Me_5)Rh^I(L)]$ is restored by potentiostating this newly modified electrode at -0.4 V for a few minutes. (ii) The response of the newly modified electrode is stable when the electrode is cycled in a fresh electrolyte solution, in the absence of any chloride anion. (iii) If this electrode is then transferred back into the initial electrolyte used to make it, the initial irreversible $[(C_5Me_5)Rh^{III}(L)Cl]^+ / [(C_5Me_5)Rh^I(L)]$ system reappears as a consequence of the capture of the remaining Cl^- ions. The same type of evolution of the modified electrode is also observed upon transfer into aqueous solution, Ar-purged, 0.1 M $LiClO_4$, pH 5. Upon cycling between -0.4 and -1.0 V vs. standard calomel electrode (S.C.E.), the peak system of the couple $[(C_5Me_5)Rh^{III}(L)]^{2+} / [(C_5Me_5)Rh^I(L)]$ appears at $E_{1/2} -0.55$ V (ΔE_p 130 mV, v 10 mV s^{-1}) (Figure 3, curve a).

In acidic solutions, pH 1, the anodic peak disappears and the cathodic current markedly increases, indicating catalytic behaviour of the Rh complex towards H_2 evolution (Figure 3, curve b). This effect is already detected at pH 4 but it appears less pronounced than under more acidic conditions. In order to corroborate the above effect, we performed a controlled-potential electrolysis experiment at -0.55 V, pH 1, on a carbon-felt electrode⁴ ($10 \times 10 \times 4$ mm) coated with polymer containing 4.8×10^{-7} mol of Rh complex. After 14 h of electrolysis, 3.8 cm³ of H_2 was obtained with a quantitative current efficiency corresponding to 353 turnovers (number of moles of H_2 /number of moles of Rh species). We have

checked that under the same electrolysis conditions a naked carbon-felt electrode does not produce any hydrogen. Further experiments using other Rh complexes anchored to modified electrodes with the aim to improve the rate of H_2 electrocatalysis are under way. Applications of these materials as halide sensors are also under investigation.

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