



ELSEVIER

Journal of Organometallic Chemistry 540 (1997) 105–111

Journal
of Organometallic
Chemistry

(Pentamethylcyclopentadienyl)(polypyridyl) rhodium and iridium complexes as electrocatalysts for the reduction of protons to dihydrogen and the hydrogenation of organics

Chrystelle Caix, Sylvie Chardon-Noblat, Alain Deronzier, Jean-Claude Moutet^{*},
Sophie Tingry

Laboratoire d'Electrochimie Organique et de Photochimie Rédox, UMR CNRS 5630, Université Joseph Fourier Grenoble 1, BP 53, 38041
Grenoble Cedex 9, France

Received 6 December 1996; revised 21 January 1997

Abstract

The ability of $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}^{\text{III}}(\text{L})\text{Cl}]^+$ complexes ($\text{M} = \text{Rh}$ and Ir , $\text{L} = 2,2'$ -bipyridine and 1,10-phenanthroline) to act as electrocatalysts for the hydrogenation of unsaturated organic substrates has been examined in homogeneous acetonitrile solution, using formic acid as a proton source, as well as in aqueous electrolytes with electrodes modified by oxidative electropolymerization of pyrrole-substituted $\text{Rh}(\text{III})$ and $\text{Ir}(\text{III})$ complexes. The hydrogenation process involves the formation of an electrogenerated hydrido complex, followed by the insertion of the substrate in the metal–hydride bond. It appears that rhodium complexes are better catalysts than the iridium ones, and that their immobilization onto an electrode surface decreases their catalytic activity. © 1997 Elsevier Science S.A.

Keywords: Rhodium and iridium complexes; Electrocatalysis; Hydrogenation; Modified electrodes; Functionalized polypyrrole

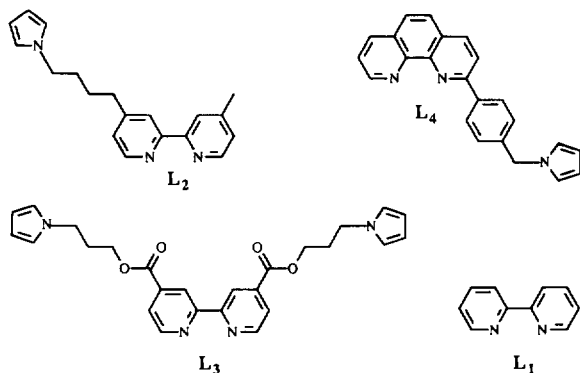
1. Introduction

During recent years we have been interested in the synthesis of molecular electrode materials via the functionalization of polypyrrole with transition metal complexes [1]. Many of these materials have shown attractive potential applications in electrocatalysis. For example, electrodes modified by polymer films containing polypyridyl rhodium complexes have been shown active for the electrocatalytic hydrogenation (ECH) of unsaturated organic substrates in aqueous electrolytes [2–5]. On the other hand, rhodium(III) complexes of the type $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{Cl}]^+$ ($\text{L} = 2,2'$ -bipyridine, 1,10-phenanthroline and their derivatives) are a class of attractive catalysts for proton reduction [6]. They have been shown active for processes such as the photochemical [7] and electrochemical [8,9] reduction of protons or

water to dihydrogen, the electrochemical regeneration of NADH from NAD^+ [10,11], and the electrocatalytic activation of carbon dioxide [12]. It should be noted that the indirect electrochemical reduction of cyclohexanone to cyclohexanol using $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{Cl}]^+$ as catalyst has been briefly reported in the literature [10]. Furthermore, our group has demonstrated the electrocatalytic activity of these rhodium(III) complexes immobilized in a polypyrrolic film coated on an electrode surface, in terms of proton reduction [13,14] and coenzyme conversion [15]. We were therefore interested as to whether these complexes and their iridium analogues could also be used as electrocatalysts for the ECH reaction. These experiments have been first conducted with $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}^{\text{III}}(\text{L})\text{Cl}]^+$ complexes ($\text{M} = \text{Ir}$ and Rh) in homogeneous acetonitrile solutions, using an organic acid as proton source. Hydrogenations in aqueous electrolytes were performed on carbon electrodes modified by electropolymerization of parent complexes containing pyrrole groups on their polypyridyl ligand. We present evidence that a rhodium-hydride is formed upon reduction of these complexes in the presence of

^{*} Corresponding author. Fax: (+33) 04 76 42 67; e-mail: Secretariat.Leopr@ujf-grenoble.fr.

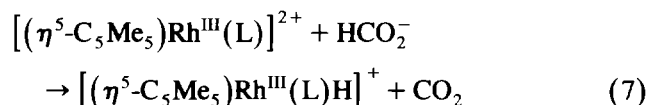
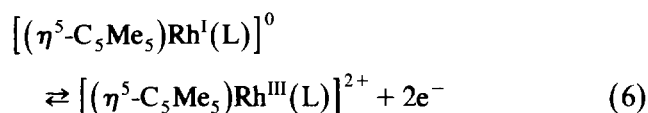
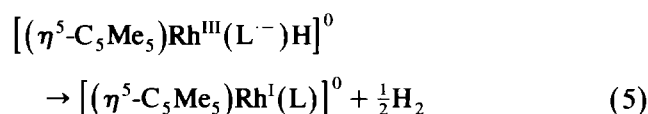
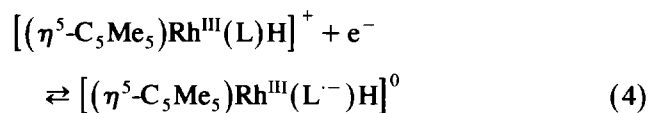
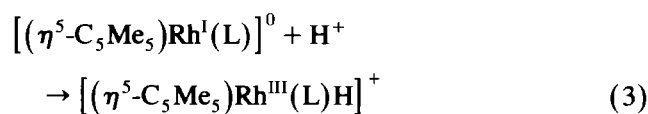
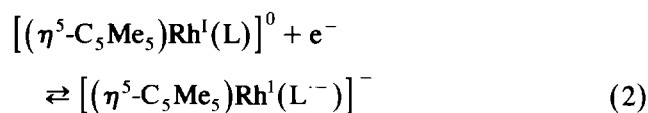
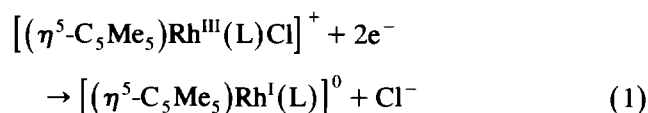
formic acid or water. Such a species was postulated as the key intermediate in the ECH mechanism [3–5].



2. Results and discussion

2.1. Electrogeneration of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{H}]^+$ hydrido complexes

The electrochemical behaviour of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{Cl}]^+$ complexes in homogeneous organic and aqueous electrolytes [7,8], or immobilized in a polypyrrole film coated on an electrode surface [13–15] is now well-established. Their reduction involves an irreversible two-electron metal-centred process ($\text{Rh}^{\text{III}} \rightarrow \text{Rh}^{\text{I}}$) coupled with the release of the chloro ligand (Eq. (1)), followed by the reversible one-electron reduction (L/L^- ; Eq. (2)) of the nitrogen ligand (see for example Fig. 1, curve (a)):



It has been shown [8] that the addition of one molar equivalent of sulphuric acid to an acetonitrile solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{Cl}]^+$ led to the appearance a weak quasi-reversible peak system ($E_{p_c} = -1.35$ V vs. a saturated calomel electrode (SCE)), which was attributed to the formation of the hydrido complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{H}]^+$ (Eq. (3)). The size of this wave increased by increasing the concentration of sulphuric acid. However, in these experimental conditions the growth of a large wave at $E_{p_c} = -0.37$ V corresponding to the reduction of protons was responsible of complicated voltammograms. The appearance of ill-defined waves attributed to the formation of a hydride complex ¹ was also observed in neutral or acidic aqueous solutions of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{Cl}]^+$ [8,11].

In contrast, clean voltammograms characterized by a large wave reduction ($E_{p_c}^2 = -1.70$ V) corresponding to the poorly reversible reduction of the hydrido complex (Eq. (4)) are obtained by adding one molar equivalent of formic acid to an acetonitrile solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{Cl}]^+$ (Fig. 1, curve (b)). This behaviour is markedly different to that already observed with the corresponding iridium complex, which presented in the same experimental conditions a well-reversible reduction wave corresponding to the ligand-centred one-electron reduction of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{L}_1)\text{Cl}]^+$ complex [16,17]. It can be anticipated that the rhodium-hydride complex decomposes upon reduction, to give $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{\text{I}}(\text{L})]^0$ and dihydrogen (Eq. (5)). This assumption is corroborated by the presence on the reverse scan of an anodic peak p_a^1 (Fig. 1, curve (b)) corresponding to the oxidation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{\text{I}}(\text{L})]^0$ (Eq. (6)).

Furthermore, exhaustive electrolysis at $E_{app} = -1.34$ V of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{Cl}]^+$ in the presence of one or two molar equivalents of formic acid gave a mixture of hydrido (70%) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)]^0$ (30%) complexes, as evidenced by the electrochemical features of the resulting solution. Owing to its poor chemical stability, the hydrido complex could not be isolated from the electrolyte, or characterized from spectroscopic experiments. This contrasts with the corresponding iridium-hydride complex, which could be

¹ It should be noted that the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{dmbpy})\text{H}]^+$ complex (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) chemically formed from the parent aquo complex in $\text{D}_2\text{O}-\text{HCO}_2\text{Na}$ has been detected by ¹H NMR spectroscopy [11].

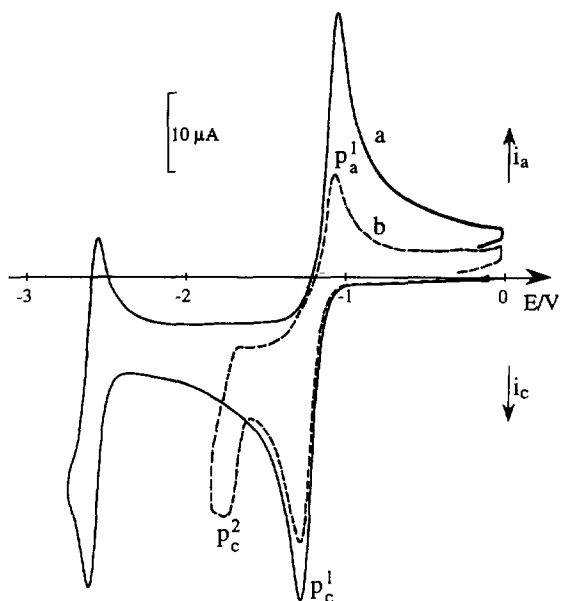


Fig. 1. Cyclic voltammograms at a carbon disc electrode (diameter 3 mm) for 1 mM $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_4)\text{Cl}]^+$ in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$ before (curve (a)) and after (curve (b)) the addition of 1 mM HCO_2H ; $\nu = 0.1 \text{ V s}^{-1}$.

synthesized quantitatively in the same experimental conditions and characterized by ^1H NMR spectroscopy [16,17].

The formation of rhodium-hydride species was also observed in polymer films synthesized by oxidative electropolymerization of complexes containing a pyrrole-substituted nitrogen ligand ($\text{L} = \text{L}_2, \text{L}_3, \text{L}_4$ [13,14]). For example, the electrochemical response of a $\text{C}/\text{poly}[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_4)\text{Cl}]^+$ -modified electrode which has been potentiostated at -1.2 V in an acidic ($0.5 \text{ mM HCO}_2\text{H}$) electrolyte, then thoroughly rinsed and transferred to clean $\text{CH}_3\text{CN} + \text{TBAP}$ electrolyte is characterized by the presence from the first scan of a large wave ($E_{p_c^2} = -1.60 \text{ V}$) corresponding to the irreversible reduction of the electrogenerated rhodium-hydride complex (Fig. 2, curve (a)). However, upon repeated cycles its reductive degradation to form $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{\text{I}}(\text{L})]^0$ is evidenced by the progressive build-up of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})]^{0/2+}$ redox peak system (p^1 ; Eq. (6)) at the expense of the reduction wave (p_c^2) of the hydrido complex.

Electrogeneration of rhodium-hydride species was also observed in aqueous electrolytes. This is demonstrated in Fig. 3, for a $\text{C}/\text{poly}[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_3)\text{Cl}]^+$ -modified electrode cycled in a water-ethanol equimolar mixture containing 0.1 M LiClO_4 . The redox peak system corresponding to the metal-centred process ($\text{Rh}^{\text{III}}/\text{Rh}^{\text{I}}$; $E_{p_c^1} = -0.57 \text{ V}$, $E_{p_a^1} = -0.43 \text{ V}$ vs. SCE) which is seen at $\text{pH} \geq 4$ (Fig. 3, curve (a)) is fully transformed on lowering of the pH. At $\text{pH} 3$ (curve (b)), the electrochemical response of the modified electrode is characterized by a small $\text{Rh}^{\text{III}} \rightarrow$

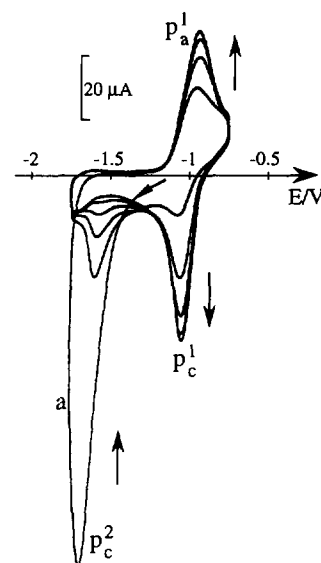


Fig. 2. Cyclic voltammograms in clean $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$ for a modified carbon disc electrode (diameter 3 mm; $\Gamma_{\text{Ru}} = 2 \times 10^{-8} \text{ mol cm}^{-2}$) prepared by the oxidative electropolymerization of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_4)\text{Cl}]^+$, then reduced at -1.2 V (charge passed, 0.3 mC) in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP} + 0.5 \text{ mM HCO}_2\text{H}$: first (curve (a)) to fifth scan; $\nu = 0.1 \text{ V s}^{-1}$.

Rh^{I} reduction peak, followed at a more negative potential by a large reduction wave ($E_{p_c^2} = -0.96 \text{ V}$ vs. SCE) which can be attributed to the irreversible reduction of the hydrido complex. This behaviour is similar to that observed in acidic acetonitrile. At lower pH ($\text{pH} 1$; Fig. 3, curve (c)), the cyclic voltammetry curve

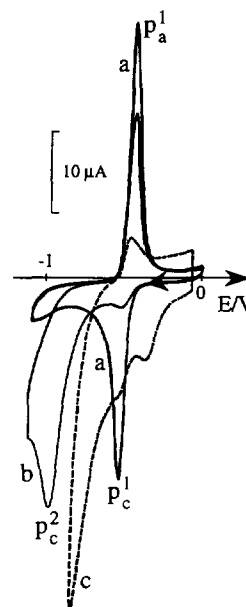


Fig. 3. Cyclic voltammograms for a $\text{C}/\text{poly}[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_3)\text{Cl}]^+$ -modified electrode (diameter 5 mm; $\Gamma_{\text{Ru}} = 5.3 \times 10^{-9} \text{ mol cm}^{-2}$) in equimolar $\text{H}_2\text{O} + \text{EtOH}$ mixture containing 0.1 M LiClO_4 : curve (a) $\text{pH} 4$, curve (b) $\text{pH} 3.1$, curve (c) $\text{pH} 1.1$; $\nu = 0.02 \text{ V s}^{-1}$.

shows a large current from -0.7 V, which corresponds to the electrocatalytic reduction of the protons to dihydrogen [13,14].

In summary, all these observations are in agreement with the formation of a reactive rhodium-hydride complex upon electrochemical reduction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{Cl}]^+$ complexes in acidic organic and aqueous electrolytes. The electrogeneration of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{H}]^+$ can be performed as well in homogeneous solution, as in polymer films synthesized by oxidative electropolymerization of pyrrole-containing rhodium complexes. These rhodium-hydride complexes appeared too unstable in our experimental conditions to be characterized from spectroscopic experiments. It has been assumed that these reactive intermediates and their iridium analogues [16,17] are involved in photochemically [7] and electrochemically [13,14,16] induced proton reduction and hydrogen evolution, and in carbon dioxide activation [12]. We will see below that they are effective catalysts for the electrochemical hydrogenation of unsaturated substrates in both organic and aqueous electrolytes.

2.2. ECH of 2-cyclohexen-1-one in homogeneous media

The hydrogenation of 2-cyclohexen-1-one with $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{L}_1)\text{Cl}]^+$ complexes ($\text{M} = \text{Rh}$ and Ir) as electrocatalysts has been studied in acetonitrile electrolyte containing formic acid as proton source. Some significant results are summarized in Table 1. Usually, electrolyses were carried out at a potential close to that of the metal-localized ($\text{M}^{\text{III}} \rightarrow \text{M}^{\text{I}}$) reduction, i.e. -1.30 V (rhodium complex) and -1.40 V (iridium complex). They were arbitrarily stopped after the consumption of 70–75 C. Owing to the low reduction currents obtained (less than 1 mA), experiments took between 30 and 40 h. In a separate experiment, we have verified that 2-cyclohexen-1-one was not reduced in the same experi-

mental conditions but in the absence of complex catalyst. Moreover, 2-cyclohexen-1-one was not hydrogenated with molecular hydrogen in the presence of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{Cl}]^+$.

Cyclohexanone was produced with reasonable yields and turnovers, especially when the rhodium complex was used as catalyst. No cyclohexanol was detected by GC in the reaction mixtures. It should be noted that hydrogenation experiments were carried out using substoichiometric amounts of formic acid to limit the competitive hydrogen evolution reaction. A comparison between entries 2, 3 and 4 clearly shows that an increase of the formic acid on substrate ratio goes with a marked decrease of the product yield. The best result was obtained with a 1:2 (formic acid/2-cyclohexen-1-one) ratio. In these experimental conditions, the product yield (25%; entry 2) was close to the maximum yield expected (25.5%, taking into account that the hydrogenation reaction consumes two protons per molecule of substrate). However, current efficiencies higher than 100% were measured with the rhodium complex, taking into account that the reduction of a carbon-carbon double bond requires two electrons. This result seems to indicate that the activation of the catalyst is partially accomplished via a chemical process. This point will be discussed below.

ECH of organics has been assumed to proceed via a hydride route with a number of polypyridinyl rhodium complexes [3,4]. This assumption has been confirmed by the study of the electrocatalytic activity of rhodium complexes containing both nitrogen and phosphine ligands, which have been proved to form catalytically active hydrido complexes upon electroreduction in the presence of water or formic acid [5]. It can be assumed that $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{L}_1)\text{H}]^+$ complexes ($\text{M} = \text{Rh}$ and Ir) are also key intermediates in the ECH reaction. In the catalytic cycle which is proposed (Scheme 1, in the case of the rhodium complex), the hydrido complex formed

Table 1

Homogeneous electrocatalytic hydrogenation ^a of 2-cyclohexen-1-one to cyclohexanone with $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{L}_1)\text{Cl}]^+$ complexes ($\text{M} = \text{Rh}$ or Ir) and formic acid

Entry	Complex ^b (amount/ μmol)	Amount of substrate (mmol)	Amount of HCO_2H (mmol)	Applied potential ^c (V)	Consumed current (C)	Yield ^d (%)	Current efficiency ^e (%)	Turnover ^f
1	A (14.1)	9.3	2.1	-1.30	71	13	338	89
2	A (7.7)	4.7	2.4	-1.30	75	25	296	149
3	A (7.7)	4.7	3.2	-1.30	76	14	171	87
4	A (7.6)	4.7	3.7	-1.30	76	11	134	69
5	B (7.7)	7.6	3.2	-1.40	69	6	73	34

^a Carried out in 5 ml of CH_3CN containing 0.1 M TBAP, on a vitreous carbon plate ($S = 4 \text{ cm}^2$).

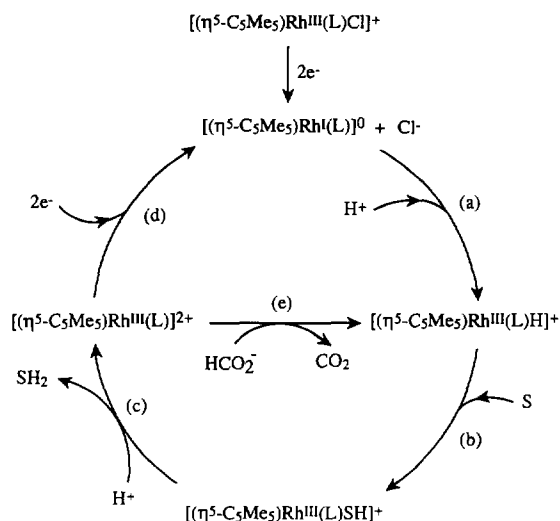
^b A: rhodium complex; B: iridium complex.

^c Potential vs. $\text{Ag}/10 \text{ mM Ag}^+$.

^d Yield determined by GC.

^e The ratio moles of product to moles of electrons passed, assuming that the hydrogenation of a carbon-carbon double bond consumes two electrons per substrate molecule.

^f The ratio moles of product to moles of complex catalyst.



Scheme 1. Chemical and electrochemical pathways for the hydrogenation of 2-cyclohexen-1-one (noted S) catalysed by $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{L})\text{Cl}]^+$ in the presence of formic acid.

from the electrochemically reduced Rh^{I} complex (step (a)) reacts with the substrate S (step (b)). Further protonation gives the hydrogenated product SH_2 (step (c)) and an Rh^{III} complex which is electrochemically reactivated (step (d)). This catalytic cycle is similar to that proposed for hydrogen transfer reactions promoted by rhodium polypyridinyl complexes [18].

The observation of current yields higher than 100% (Table 1, entries 1–4) can be explained by the chemical generation of the rhodium-hydride intermediate via hydride transfer from formate to the rhodium complex. The formation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{H}]^+$ from $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{H}_2\text{O}]^{2+}$ in the presence of formate anions has already been demonstrated in aqueous media [19,20]. In our experimental conditions, the competitive chemical activation of the catalyst has been established from the experiments described below. An ECH was carried out in similar experimental conditions as described in Table 1 (entries 2–4). The electrolysis was stopped after a quantity of electricity corresponding to the consumption of one-third of the initial amount of formic acid had been passed. Half of the resulting solution was immediately treated and analysed by GC (see Section 4). The second part of the reaction mixture was left aside for 21 h before any treatment. Analysis of the first sample showed that cyclohexanone was formed with a 4% chemical yield, while a 15% yield was found with the second sample. Obviously, chemical activation of the rhodium complex with formate ions formed by electrochemical reduction of formic acid, to produce the catalytically active rhodium-hydride intermediate (Eq. (7)) is competitive with the electrochemical activation (Eqs. (1) and (3)). The overall hydrogenation process is described in Scheme 1, where appear the two paths for the formation of the hydride species, i.e. by protonation

of the Rh(I) complex (step (a)) and by reaction of an Rh(III) complex with free formate ions (step (e)). Finally, we have confirmed the chemical activation of the rhodium complex from the following experiment. A mixture of 4.4 mmol of 2-cyclohexen-1-one, 1.7 mmol of formic acid, 0.8 mmol of tetraethylammonium formate and 8.1 μmol of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_1)\text{Cl}][\text{BF}_4]$ in 5 ml of CH_3CN containing 0.1 M TBAP, was stirred for 70 h under an argon atmosphere. GC analysis shown that cyclohexanone was formed with a 4% yield under these experimental conditions.

2.3. ECH on polymer-modified electrodes

The hydrogenation of various organic substrates has also been studied on carbon electrodes of dimension $15 \times 15 \times 4 \text{ mm}^3$, coated with poly $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L})\text{Cl}]^+$ films ($\text{L} = \text{L}_2, \text{L}_3, \text{L}_4$). Immobilization of these complexes in a film form at an electrode surface allows one to study their electrocatalytic activity in aqueous electrolytes, without any problems of solubility of the catalysts. Thus, hydrogenation experiments has been performed in 25 ml of water–ethanol equimolar mixture containing 0.1 M LiClO_4 .

First, experiments were attempted in pH 2–5 electrolyte with modified electrodes (1–2 μmol of immobilized complexes) synthesized by oxidative electropolymerization of rhodium and iridium complexes containing ligands L_2 and L_4 . Electrolyses were carried out at a potential corresponding to the formation of the M(I) complexes, i.e. -1.0 V and -1.15 V respectively for the rhodium- and iridium-based cathodes. Poor results were obtained for the hydrogenation of various organics. For example, the hydrogenation of 2-cyclohexen-1-one (1 mmol) on a C/poly $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_4)\text{Cl}]^+$ electrode (1.6 μmol of immobilized complex) gave a low yield of cyclohexanone (2.5%) with a poor current efficiency (17%). Poly $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_2)\text{Cl}]^+$ and poly $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{L}_4)\text{Cl}]^+$ films appeared still less efficient, giving less than 1% of 2-cyclohexen-1-one transformation. Furthermore, a more activated olefin such as cinnamaldehyde could not be hydrogenated on these different cathodes. These results indicate that the catalytic activity of these complexes for the hydrogenation of organics is lower in films than in homogeneous solution. This could be due to a more difficult insertion of the substrate in the metal–hydride bond, which favours the competitive dihydrogen evolution.

We then tested the electrocatalytic activity of poly $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_3)\text{Cl}]^+$ films containing 1–4 μmol of complex towards the hydrogenation of various unsaturated organic substrates as a function of pH of the electrolyte ($2 < \text{pH} < 4$), and at different applied potentials ($-1.1 \leq E_{\text{app}} \leq -0.5 \text{ V}$ vs. SCE). In the absence of substrate, low (less than 1 mA), fairly stable catalytic currents were obtained by potentiostating the

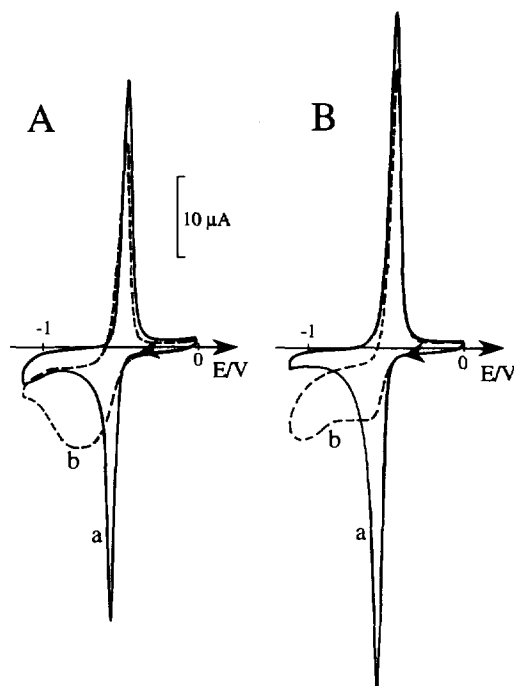


Fig. 4. Cyclic voltammograms in $\text{H}_2\text{O} + \text{EtOH} + 0.1 \text{ M LiClO}_4$ (pH 4) for $\text{C}/\text{poly}[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_3)\text{Cl}]^+$ -modified electrodes (diameter 5 mm). (A) $\Gamma_{\text{Ru}} = 5.6 \times 10^{-9} \text{ mol cm}^{-2}$, before (curve (a)) and after (curve (b)) the addition of 0.5 mM cryptone. (B) $\Gamma_{\text{Ru}} = 6.2 \times 10^{-9} \text{ mol cm}^{-2}$, before (curve (a)) and after (curve (b)) the addition of 0.5 mM cinnamaldehyde. $\nu = 0.02 \text{ V s}^{-1}$.

modified cathodes at -0.5 V . No evolution of the current was observed upon the addition of carvone, namely the (*R*)-*S*-isopropenyl-2-methyl-2-cyclohexenone, or 4-*tert*-butylcyclohexanone. Furthermore, no hydrogenation product could be detected in the reaction mixtures after several hours of electrolysis. In contrast, the addition to the electrolyte of a compound such as cryptone, namely the 4-isopropyl-2-cyclohexen-1-one, or cinnamaldehyde produced a marked increase in the catalytic current. This observation shows that these compounds interact strongly with the catalyst. The existence of a reversible interaction between the rhodium complex and these substrates was evidenced by the study of the cyclic voltammograms for $\text{C}/\text{poly}[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_3)\text{Cl}]^+$ -modified electrodes. The addition of cryptone (Fig. 4(A)) and cinnamaldehyde (Fig. 4(B)) is responsible for a strong distortion of the $\text{Rh}^{\text{III}} \rightarrow \text{Rh}^{\text{I}}$ reduction peak, while its corresponding re-oxidation peak was nearly unchanged.

On a carbon-felt electrode modified with $1.4 \mu\text{mol}$ of complex catalyst, the electrolysis current ($E_{\text{app}} = 0.5 \text{ V}$) increased from 0.2 mA to 1.2 mA after the addition of cryptone (1 mmol), then decreased quickly. However, 12.7 C could be passed before the complete loss of catalytic activity of the cathode. In these experimental conditions, the 4-isopropyl cyclohexanone was obtained in 6.5% yield with a good current efficiency (74%) and

a turnover of 46. No hydrogenation occurred in a less acidic electrolyte (pH 4), or when the applied potential was made more negative (-0.9 V). These observations support that the ECH involves a rhodium hydride complex. As a matter of fact, the analytical studies have shown that the hydrido complex is not formed at pH 4. Furthermore, its irreversible reduction at $E_{\text{app}} = -0.9 \text{ V}$ (Eqs. (4) and (5)) prevails over its chemical reaction with the substrate. Similar results were obtained in the presence of cinnamaldehyde (1 mmol) with a modified electrode containing $4 \mu\text{mol}$ of complex. At pH 3.2, this compound was hydrogenated to 3-phenylpropanal (yield 5%; turnover 12) with a high current efficiency (80%; $E_{\text{app}} = -0.7 \text{ V}$). This reaction was fully inefficient when the cathode potential was made more negative ($E_{\text{app}} = -0.92 \text{ V}$), at pH 3.2 or 2.3. The higher efficiency of $\text{poly}[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{L}_3)\text{Cl}]^+$ complex compared to L_2 - and L_4 -based films could be explained by the stronger reactivity of its corresponding hydride complex, due to the substitution of the bpy ligand by electron-withdrawing carboxy-ester groups.

3. Conclusion

The present study demonstrates that $\{(\eta^5\text{-C}_5\text{Me}_5)\text{M}^{\text{III}}(\text{L})\text{Cl}\}^+$ complexes ($\text{M} = \text{Rh}$ and Ir) are electrocatalysts for the hydrogenation of unsaturated organic substrates in both organic and aqueous electrolytes. The key step of the hydrogenation reaction is the electrochemically induced formation of a hydrido complex, followed by the insertion of the substrate in the metal-hydride bond. It must be emphasized that the rather low electrocatalytic activity of these complexes is quite similar to that of $\text{Rh}(\text{III})$ complexes containing both nitrogen and phosphine ligands [5], which also form stable hydrido complexes upon their electroreduction in the presence of a proton source. They are much less active than $[\text{Rh}(\text{L})_2\text{Cl}_2]^+$ complexes [3,4] of which hydrido derivatives appeared too unstable to be characterized in similar experimental conditions. Thus, the electrocatalytic activity of such metal complexes for the hydrogenation of organics appears strongly dependent on the stability of their hydrido derivatives, especially in their reduced forms.

4. Experimental

4.1. Materials and equipment

All electroanalytical experiments were run under an argon atmosphere in a glove-box, using a standard three-electrode electrochemical cell. Potentials are referred to an $\text{Ag}/10 \text{ mM Ag}^+$ reference electrode in MeCN electrolyte, and to an SCE reference in aqueous

electrolyte. The working electrode was a vitreous carbon disc (0.07 or 0.2 cm²) polished with 2 μm diamond paste. The electrolyte was a 0.1 M solution of supporting electrolyte in MeCN (Rathburn, HPLC grade S). Tetra-*n*-butylammonium perchlorate (TBAP; Fluka puriss, recrystallized from ethyl acetate–cyclohexane) was dried under vacuum at 80 °C for 3 days before use, and stored under argon. Electrochemical measurements were carried out using an EG&G PAR model 173 potentiostat equipped with a model 179 digital coulometer and a model 175 programmer with output recorded on a Sefram TGM 164 X–Y recorder.

Hydrogenation reactions in homogeneous acetonitrile solutions were performed on a naked vitreous carbon electrode of dimensions 20 × 20 mm². The procedures for hydrogenation on carbon-felt modified electrodes in aqueous electrolytes have already been described [3,4]. Reaction progress was followed by periodic withdrawals. In aqueous electrolytes, samples were extracted with diethyl ether. In acetonitrile electrolyte, samples were diluted with diethyl ether, then filtered. The identification of products was based on GC comparisons with authentic samples. GC analyses were performed on a Shimadzu GC-14A equipped with a 20% Carbowax 20 M column.

4.2. Complexes and polymer films

Rhodium [12–14] and iridium [16] complexes were synthesized as previously reported. For hydrogenation of organics, catalytic cathodes were obtained by coating films on carbon-felt electrodes (RVC 2000, 65 mg cm⁻², from Le Carbone Lorraine) of dimensions 15 × 15 × 4 mm³. The amount of immobilized metal complex was

determined from the charge under the polypyrrole oxidation wave [13,16].

References

- [1] J.-C. Moutet, A. Deronzier, *Coord. Chem. Rev.* 147 (1996) 339.
- [2] I.M.F. De Oliveira, J.-C. Moutet, N. Vlachopoulos, *J. Electroanal. Chem.* 291 (1990) 243.
- [3] I.M.F. De Oliveira, J.-C. Moutet, *J. Mol. Catal.* 85 (1993) L19.
- [4] S. Chardon-Noblat, I.M.F. De Oliveira, J.-C. Moutet, S. Tingry, *J. Mol. Catal. A* 99 (1995) 13.
- [5] H. Cano-Yelo Bettega, J.-C. Moutet, S. Tingry, *J. Electroanal. Chem.* 391 (1995) 51.
- [6] U. Koelle, *New J. Chem.* 16 (1992) 157.
- [7] U. Kölle, M. Grätzel, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 567.
- [8] U. Kölle, B.-S. Kang, P. Infelta, P. Comte, M. Grätzel, *Chem. Ber.* 122 (1989) 1869.
- [9] M. Ladwig, W. Kaim, *J. Organomet. Chem.* 419 (1991) 233.
- [10] R. Ruppert, S. Herrmann, E. Steckhan, *Tetrahedron Lett.* 28 (1987) 6583.
- [11] E. Steckhan, S. Herrmann, R. Ruppert, E. Dietz, M. Frede, E. Spika, *Organometallics* 10 (1991) 1568.
- [12] C. Caix, S. Chardon-Noblat, A. Deronzier, in preparation.
- [13] S. Cosnier, A. Deronzier and N. Vlachopoulos, *J. Chem. Soc. Chem. Commun.* (1989) 1259.
- [14] S. Chardon-Noblat, S. Cosnier, A. Deronzier, N. Vlachopoulos, *J. Electroanal. Chem.* 352 (1993) 213.
- [15] S. Cosnier, H. Gunther, *J. Electroanal. Chem.* 315 (1991) 307.
- [16] C. Caix, S. Chardon-Noblat, A. Deronzier, R. Ziessel, *J. Electroanal. Chem.* 262 (1993) 301.
- [17] C. Caix, S. Chardon-Noblat, A. Deronzier, R. Ziessel, *J. Electroanal. Chem.* 403 (1996) 189.
- [18] G. Zassinovich, G. Mestroni, S. Gladioli, *Chem. Rev.* 92 (1992) 1051.
- [19] R. Ruppert, S. Herrmann, E. Steckhan, *J. Chem. Soc. Chem. Commun.* (1988) 1150.
- [20] D. Westerhausen, S. Herrmann, W. Hummel, E. Steckhan, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1529.