

Electrocatalytic hydrogenation on poly[Rh^{III}(L)₂(Cl)₂]⁺ (L = pyrrole-substituted 2,2'-bipyridine or 1,10-phenanthroline) films electrodes

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Abstract

The electrocatalytic hydrogenation (ECH) in aqueous electrolytes of cyclohexanone, substituted cyclohexanones, cryptone, dihydrocarvone and carvone has been performed on carbon felt electrodes modified by electropolymerization of [Rh(L)₂(Cl)₂]⁺ complexes, in which L is a 2,2'-bipyridine (L=L₁ or L₃) or a 1,10-phenanthroline (L=L₄) substituted with pyrrole groups. The efficiency and the stability of these electrocatalytic materials, tested through the hydrogenation of millimolar amounts of substrates, depend on the nature of the linkage between the metal complex and the polymer skeleton. Turnovers around 5000 were reached with polymeric materials in which the complex is attached by an alkyl chain to the polypyrrolic matrix (L=L₁ or L₄), without appreciable loss of catalytic activity. In contrast, L₃-based materials appeared markedly less stable. This behaviour was attributed to the loss of complex molecules from the polymer film, due to hydrolysis of the carboxy-ester linkage. Regio- and stereoselectivity changes have been noted, according to the composition of the polymerized catalyst.

Keywords: Electrocatalysis; Film electrodes; Hydrogenation; Pyridine derivatives; Phenanthroline; Pyrrole-substituted derivatives

1. Introduction

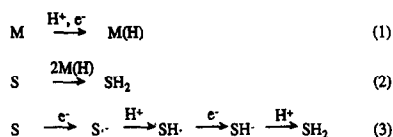
Modification of electrodes by molecular reagents such as transition metal complex catalysts affords a means to design electrodes exhibiting the desired electrocatalytic properties. From a general point of view, electrocatalysis with a catalyst immobilized in a polymer film at an electrode surface has a number of advantages over the homogeneous case, including easier products and catalyst recovery, and the use of much lower quan-

ties of catalyst highly concentrated in the reaction layer [1]. However, modified electrodes have the disadvantage of rather poor stability. Recent developments in the electrochemical preparation of functionalized polypyrrole film electrodes has allowed laboratory scale electrosynthesis to be carried out. Easy to be formed, leading to remarkably stable coating, allowing the anchorage of complex and/or bulky molecules such as transition metal complexes, functionalized polypyrroles are good candidates for the development of electrocatalysis on modified electrodes [2].

An attractive application of catalytic electrodes is electrocatalytic hydrogenation [3], which is the

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Scheme 1. Electrocatalytic hydrogenation and electrohydrogenation processes.

reaction (Scheme 1) of an unsaturated organic substrate S with hydrogen formed (Eq. (2)) at the surface of an hydrogen active electrode (a metal electrode denoted M, for example) by reduction of water or protons (Eq. (1)). Electrocatalytic hydrogenation (ECH) must be distinguished from electrohydrogenation which proceeds through an electronation–protonation mechanism (Eq. (3)), and requires an initial electron transfer to the substrate [4].

ECH on active cathodes such as massive transition metals electrodes, Raney nickel or noble metals deposited on carbon is now well documented [3]. These different cathodes can be considered as electrochemical analogues for regular heterogeneous hydrogenation catalysts. In contrast, the application of transition metal complexes-based polymeric electrode materials to the ECH of organic substrates in aqueous electrolytes

has only been reported recently by our group [5–7]. In particular, we have recently reported our preliminary results about the hydrogenation of carvone and substituted cyclohexanones, on carbon electrodes modified by electropolymerization of the $[\text{Rh}^{\text{III}}(\text{L}_3)_2(\text{Cl})_2][\text{BF}_4]$ complex, where L_3 is a pyrrole-substituted 2,2'-bipyridine [7]. To investigate the factors which influence the efficiency, the stability, and the selectivity of these electrocatalytic materials, we have undertaken a study of the effect of changing the structure of the pyrrole-substituted bipyridyl ligand. In this paper, we present a detailed study on the electrocatalytic behaviour of carbon felt electrodes modified by electropolymerization of $[\text{Rh}(\text{L})_2(\text{Cl})_2][\text{BF}_4]$ complexes ($\text{L} = \text{L}_1, \text{L}_3, \text{L}_4$) towards the hydrogenation of various organic substrates (Fig. 1).

2. Experimental

2.1. Materials and equipment

The electrochemical equipment has been described previously [8]. Acetonitrile (Rathburn

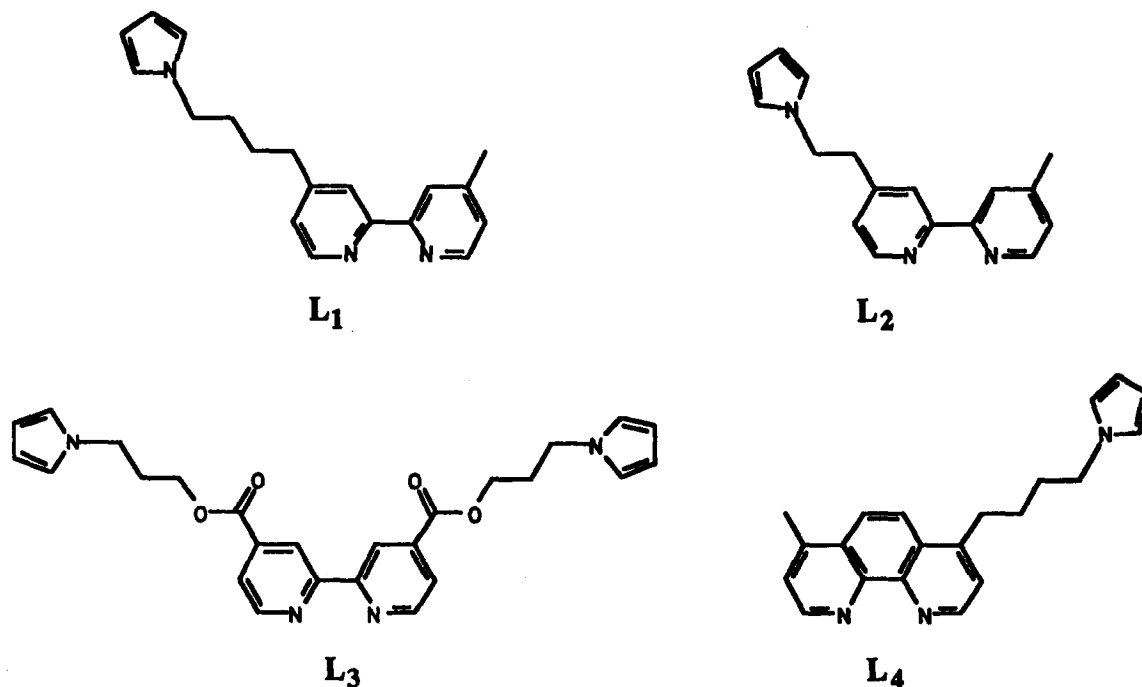


Fig. 1.

HPLC grade S) was used as received. Water was doubly distilled in a quartz apparatus. The purification of tetrabutylammonium perchlorate (TBAP) from Fluka has been described previously [5]. Lithium perchlorate (GF Smith) was used without further purification. Unless otherwise noted, potentials are reported relative to the saturated calomel electrode (SCE). All electrochemical experiments were run under an argon atmosphere.

^1H nuclear magnetic resonance (NMR) spectra were recorded on a 200 MHz Bruker AC 200 spectrometer. Fast atom bombardment mass spectra (FAB MS) were obtained using an AIE Kratos MS 50 spectrometer fitted with an ion gun (Ion Tech Ltd).

GC analysis were performed on a Shimadzu GC-14 A chromatograph with flame ionisation detection equipped with a 20% Carbowax 20 M column (2.5×2 mm); yields were determined by GC; the measurements were made using a Merck D2000 integrator. All the products were purified by preparative GC using a Varian Aerograph chromatograph with a 10% Carbowax 20 M column (2.5×6 mm).

2.2. Ligands and complexes

L_1 [9] and L_3 [5] were prepared as previously reported. L_4 was synthesized by the same method as 4,7-dialkylated-1,10-phenanthrolines [10], by the reaction at -70°C in THF between equimolar quantities of 1-(3-iodopropyl)pyrrole and 4,7-dimethyl-1,10-phenanthroline anion. Purification by elution chromatography on a silica column with 1:9 hexane + CH_2Cl_2 afforded L_4 as a yellow gummy product; yield 66%. ^1H NMR (CDCl_3) δ/ppm : 1.77 (m, 4H), 2.68 (s, 3H), 3.00 (t, 2H, $J=7.6$ Hz), 3.85 (t, 2H, $J=6.5$ Hz), 6.09 (t, 2H, $J=2.0$ Hz), 6.58 (t, 2H, $J=2.0$ Hz), 7.30 (d, 1H, $J=4.4$ Hz), 7.35 (d, 1H, $J=4.4$ Hz), 7.85 (d, 1H, $J=9.4$ Hz), 7.90 (d, 1H, $J=9.4$ Hz), 8.95 (d, 1H, $J=4.4$ Hz), 8.98 (d, 1H, $J=4.4$ Hz).

The synthesis of $[\text{Rh}(\text{L}_3)_2(\text{Cl})_2][\text{BF}_4]$ has already been described [5,11]. The complexes based on the ligands L_1 and L_4 were prepared

following the same procedure, by the reaction in EtOH between 1 mol of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 2 moles of L_1 or L_4 .

$[\text{Rh}(\text{L}_1)_2(\text{Cl})_2][\text{BF}_4]$: yield, 97%. FAB MS: m/e , positive mode, $[\text{Rh}(\text{L}_1)_2(\text{Cl})_2]^+$ 756. ^1H NMR (CD_3CN) δ/ppm : 1.58 (m, 8H), 2.50 (s, 3H), 2.71 (s, 3H), 3.06 (m, 4H), 3.92 (m, 4H), 6.01 (m, 4H), 6.66 (m, 4H), 7.22 (m, 2H), 7.43 (m, 2H), 7.78 (m, 2H), 8.32 (m, 4H), 9.57 (m, 2H).

$[\text{Rh}(\text{L}_4)_2(\text{Cl})_2][\text{BF}_4]$: yield, 40%. FAB MS: m/e , positive mode, $[\text{Rh}(\text{L}_4)_2(\text{Cl})_2]^+$ 803. ^1H NMR (CD_3CN) δ/ppm : 1.80 (m, 8H), 2.86 (s, 3H), 3.13 (s, 3H), 3.30 (m, 4H), 3.97 (m, 4H), 6.08 (m, 4H), 6.66 (m, 4H), 7.44 (m, 2H), 7.60 (m, 2H), 8.20 (m, 6H), 10.02 (m, 2H).

2.3. Preparation of the polymer films

Catalytic cathodes were prepared by controlled-potential oxidation at 0.70–0.75 V vs. the Ag/10 mM AgNO_3 (in 0.1 M TBAP + CH_3CN) reference electrode, of $[\text{Rh}(\text{L})_2(\text{Cl})_2]^+$ complexes ($\text{L} = \text{L}_1, \text{L}_3, \text{L}_4$) 4×10^{-3} M in $\text{CH}_3\text{CN} + 0.1$ M TBAP [5,11], on carbon felt electrodes (RVC 2000, 65 mg cm^{-3} , from Le Carbone Lorraine) of dimensions $15 \times 15 \times 4$ mm. The electropolymerization was continued until a charge of 0.8 to 3.0 C was passed. The amount of rhodium complex in the polymer film was determined after transfer of the electrode to clean acetonitrile electrolyte, from the charge under the reduction peak of the $[\text{Rh}^{\text{I}}(\text{L})_2]^+ / [\text{Rh}^{\text{I}}(\text{L})(\text{L}^-)]^0$ redox couple [5,11].

2.4. Electrocatalytic hydrogenation procedure

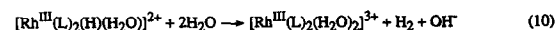
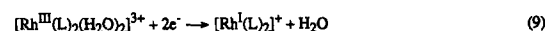
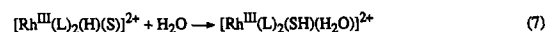
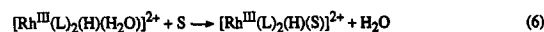
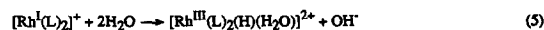
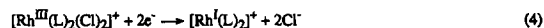
Electrocatalytic hydrogenations were conducted in a three-compartment electrochemical cell. The cathodic compartment was charged with the substrate dissolved in 25 ml of water/ethanol equimolar mixture containing 0.1 M LiClO_4 , pH 8–9. The cathode potential was held at -1.2 to -1.4 V. The reaction progress was followed by periodic withdrawals. Samples (0.5 ml) were extracted with 1 ml of diethyl ether. The identifi-

cation of products was based on GC comparisons with authentic samples. Isolated products were characterized by spectral data. The *cis:trans* ratio for substituted cyclohexanols [12] and dihydrocarvone [13], and the configuration of the isolated diastereoisomers of dihydrocarveol [14] were determined by ^1H NMR spectroscopy.

3. Results and discussion

3.1. Electrocatalytic behaviour of rhodium(III) complexes films in aqueous electrolytes

As already reported for C/poly $[\text{Rh}(\text{L}_2)_2(\text{Cl})_2]^+$ and C/poly $[\text{Rh}(\text{L}_3)_2(\text{Cl})_2]^+$ modified electrodes [5], the reduction of the rhodium complex trapped in the polymer films turns irreversible in neutral or basic aqueous electrolytes. Fairly stable catalytic currents were observed from -1.1 V ($\text{L}=\text{L}_3$) and -1.3 V ($\text{L}=\text{L}_2$). These potentials corresponds to the metal-localized ($\text{Rh}^{\text{III}} \rightarrow \text{Rh}^{\text{I}}$) reduction [5,11,15]. It should be noted that the substitution of the bpy ligand with carboxy-ester groups ($\text{L}=\text{L}_3$) results in a positive shift in these reduction potentials. These observations indicate the electrocatalytic behaviour of immobilized Rh complexes towards H_2O reduction and H_2 evolution. The insensitivity to pH, between pH 5 to 9, of the catalytic currents recorded on the modified electrodes confirms that H_2O reduction is mostly catalyzed by electrogenerated Rh^{I} species [5]. The new catalytic materials based on ligands L_1 and L_4 have shown a catalytic behaviour similar to that of L_2 -based materials, giving stable catalytic currents from -1.3 V. Thus, electrocatalytic experiments were conducted in weakly basic media (pH 8–9). The potential applied to the catalytic cathodes was not more negative than -1.4 V to avoid any direct reduction of water at the carbon felt/film interface. We have also checked that under the same electrolysis conditions the unsaturated substrates studied here were not reduced or hydrogenated at a bare carbon electrode.



Scheme 2. Hydrogenation of a substrate S electrocatalyzed by a rhodium complex.


















The addition to the cathodic compartment of an unsaturated substrate such as a substituted cyclohexanone or cyclohexen-1-one produced an increase of the catalytic current from 20 to 100% according to the catalytic material studied and the substrate added. This observation clearly shows that unsaturated organic substrates strongly interact with a catalytically active rhodium species, which is likely to be a rhodium–hydride intermediate [7] formed in aqueous solution from the reduced Rh^{I} complex (see Scheme 2).

3.2. Electrocatalytic hydrogenation on poly $[\text{Rh}(\text{L}_3)_2(\text{Cl})_2]^+$ films

Preliminary results have shown that millimolar amounts of cyclohexanone [5], substituted cyclohexanones and carvone [7] could be efficiently hydrogenated on C/poly $[\text{Rh}(\text{L}_3)_2(\text{Cl})_2]^+$ modified electrodes, with current yields as high as 60–70%. In the catalytic cycle (Scheme 2) which has been proposed [7], the key intermediate is a rhodium–hydride complex formed (Eq. (5)) from $[\text{Rh}^{\text{I}}(\text{L})_2]^+$, this reduced Rh^{I} complex being produced electrochemically (Eq. (4)) [11,15]. Coordination of the substrate S (Eq. (6)) is followed by rapid reactions (Eqs. (7) and (8)) to give the hydrogenated product SH_2 and a Rh^{III} complex which can be electrochemically re-activated (Eq. (9)).

The influence of the amount of immobilized catalyst and substrate concentration on the efficiency of the electrocatalytic system, and the sta-

Table 1: Electrocatalytic hydrogenation of cyclohexanone, substituted cyclohexanones, and cryptone on C/poly[Rh(L₃)₂(Cl)₂]⁺ modified electrodes^a

Entry	Starting material	Amount (mmol)	Amount of complex (μmol)	Consumed current (electrons per molecule)	Product	Yield (%) ^b	Total current efficiency (%) ^c	Cis:trans ratio ^d
1		0.8	2.0	2		73	73	
2		2	2.0	2		91	91	
3		2	6.0	2		53	53	
4		2	9.0	4		80	40	
				2		79	79	80:20
				3		95	64	
5		0.8	6.6	3.8		38	85	
						62		
6		0.8	6.6	2		49	78	
						14		
7				6.3		2	63	26:74
						98		

^aCarried out at -1.2 to -1.3 V vs SCE in 25 ml of water-ethanol equimolar mixtures containing 0.1 M LiClO₄, pH 8–9. ^bYield determined by GC.

^cThe ratio mol of products to mol of electron passed. ^dMeasured by ¹H NMR [12].

bility of the catalytic cathodes have been studied in more details with L₃-based polymeric materials. Some significant results are summarized in Table 1. First, ECH of cyclohexanone showed that the current yield increased with the concentration of substrate, from 73% ([cyclohexanone] = 32 mM; entry 1) to 91% ([cyclohexanone] = 80 mM; entry 2). Competition between H₂ evolution (eq. (10)) and substrate complexation–hydrogenation (Eqs. (6–8)) can explain this variation. It should also be noted that the intensity of the catalytic current increased when the applied potential was moved from -1.2 V to -1.3 V, without appreciable change in the current efficiency. For example, the initial electrolysis current for cyclohexanone hydrogenation (entry 2) was 15 mA at -1.2, and 25 mA at -1.3 V. An amount of 1.8 mmol of cyclohexanol has been produced on this cathode modified with 2 mmol of rhodium complex. This corresponds to a turnover (the ratio number of molecules of product to number of molecules of catalyst) of 900.

The amount of Rh^{III} complex deposited on the electrode has a significant effect on the catalytic efficiency of these cathodes. In the case of 2-methylcyclohexanone hydrogenation (Table 1, entries 3 and 4), the current yield measured after the consumption of 2 electrons per substrate molecule increased from 53% (entry 3) to 79% (entry 4) when the amount of complex catalyst immobilized was increased from 6 to 9 μmol. In the last case, the conversion yield after the consumption of 3 electrons per substrate molecule was almost quantitative. Obviously, the polymer film is permeable enough to substrate molecules to allow their reaction with catalytic sites located in the polymer film, and not only at the film–solution interface.

Results from experiments carried out with cryptone, namely the 4-isopropyl-2-cyclohexen-1-one (Table 1, entries 5–7) have shown that the polymerized rhodium complex is a good hydrogenation catalyst for carbon–carbon double bonds in α,β-unsaturated ketones. The corresponding saturated ketone was obtained in 49% yield after

the consumption of 2 electrons per cryptone molecule (entry 6). However, the selectivity is low since an appreciable amount of 4-isopropylcyclohexanol was present. This saturated alcohol could be quantitatively produced with a good current efficiency (63%) if the electrolysis was carried on up to the consumption of 6.3 electrons per molecule of substrate (entry 7). Thus, the regioselectivity for cryptone ECH is similar to that already reported for the catalytic hydrogenation of α,β -unsaturated ketones with $[\text{Rh}(\text{bpy})_2(\text{Cl})_2]^+$ (bpy = 2,2'-bipyridine) and hydrogen gas in MeOH/MeONa [16]. This result is also in agreement with our results relative to the ECH of carvone with the same electrocatalytic material [7].













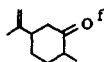

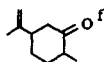

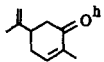


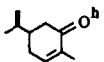

The experiments described in entries 5 to 7 of Table 1 have been carried out using the same modified electrode. A total amount of 1.8 mmol of hydrogenated products has been formed. This corresponds to a turnover of 270. However, the cathode had gradually lost some of its catalytic activity, since the initial electrolysis current dropped from 15 mA for the first experiments, to 8 mA for the second one. In the same way, current yields decreased from the first to the second experiment. Cyclic voltammetry experiments carried out with modified electrodes before and after controlled potential electrolysis have shown that the polypyrrolic film was not peeled from the carbon electrode, since the quasi-reversible redox wave depicting the electroactivity of the polypyrrole itself [5,11] remained intact. Thus, the loss of catalytic activity of the cathodes could be due either to an irreversible chemical degradation of the rhodium species, or to a loss of catalyst molecules in the electrolyte following hydrolysis of the carboxy-ester groups linking the metal complex to the polypyrrolic frame. However, we could not obtain clear information about this degradation from cyclic voltammetry experiments carried out after electrolysis in the hydrogenation solution, or on the modified cathodes.

3.3. Electrocatalytic hydrogenation on $\text{poly}[\text{Rh}(\text{L}_1 \text{ or } \text{L}_4)_2(\text{Cl})_2]^+$ films

This rather low stability of the C/poly $[\text{Rh}(\text{L}_3)_2(\text{Cl})_2]^+$ cathodes led us to test the operational stability of the catalytic cathodes prepared by electropolymerization of monomer complexes containing the L_1 and L_4 ligands, in which the pyrrole groups are linked to the polypyridyl moieties through alkyl chains. Typical results from various ECH experiments are summarized in Table 2.

Hydrogenations carried out with substituted cyclohexanones (entries 1 to 6), dihydrocarvone (entries 7, 8), and carvone (entries 9, 10) have shown that the corresponding hydrogenated products were formed in high yields, and with current efficiencies as high as 87%. The more important point is that the poly $[\text{Rh}(\text{L}_1 \text{ or } \text{L}_4)_2(\text{Cl})_2]^+$ materials appeared markedly more active than the polymeric films containing the ligand L_3 . First, electrolysis currents ranging from 30 mA to 50 mA were usually observed, according to the substrate to be hydrogenated. The current decreased slowly as the substrate was consumed, to reach the value recorded in the absence of substrate. These catalytic currents compare favourably with those obtained (15 to 25 mA) on C/poly $[\text{Rh}(\text{L}_3)_2(\text{Cl})_2]^+$ cathodes of similar size. The amount of immobilized catalyst (from 1 to 6 μmol) had only a slight effect on the intensity of the catalytic current. Although we have not explored this last point in any detail, it seems that full utilization of the catalyst is not obtained, due to some limitations such as electron transport or substrate permeation through the polymer film. The operational stability of these catalytic materials was studied by performing several hydrogenations on each cathode. For example, we found that a C/poly $[\text{Rh}(\text{L}_4)_2(\text{Cl})_2]^+$ electrode containing 1.4 μmol of immobilized complex (Table 2, entry 2) could be re-used three times to hydrogenate additional amounts of substituted cyclohexanones. A total amount of 7.4 mmol of substituted cyclohexanols were produced with a high turnover (5300), without appreciable loss of cat-

Table 2 : Electrocatalytic hydrogenation of substituted cyclohexanones, dihydrocarvone, and carvone on C/poly[Rh(L)₂(Cl)₂]⁺ (L = L₁, L₄) modified electrodes^a

Entry	Ligand	Amount of complex (μmol)	Substrate ^b	Product	Yield (%) ^c	Total current efficiency (%) ^d	<i>cis:trans</i> ratio ^e
1	L ₁	3.6			78	78	23:77
2	L ₄	1.4			100	87	23:77
3	L ₁	1.1			100	66	73:27
4	L ₄	1.8			100	48	71:29
5	L ₁	6.0			100	56	74:26
6	L ₄	1.4			83	39	66:34
7	L ₁	5.3				34	
8	L ₄	1.8				60	
9	L ₁	6.0			61	76	21:79
					16		
10	L ₁	5.3			99	52	

^aSame experimental conditions as in Table 1, except that E_{app} = -1.4 V vs SCE. ^b2 mmol. ^cYield determined by GC. ^dThe ratio mol of product to mol of electrons consumed. ^eMeasured by ¹H NMR (see the experimental section). ^fCommercial dihydrocarvone (*cis:trans* ratio 23:77). ^gMixtures of three diastereoisomers (see the text). ^hR(-)-carvone.

alytic activity. As a matter of fact, the intensity of the initial electrolysis current remained high from the first (35 mA) to the fourth (43 mA) experiment, and the current efficiency for each hydrogenation was close to that obtained in the same conditions on a fresh modified electrode. The same results were observed with L₁-based materials. For example, a C/poly[Rh(L₁)₂(Cl)₂]⁺ cathode (1.1 μmol of immobilized complex; Table 2, entry 3) was re-used two times to hydrogenate quantitatively carvone to dihydrocarveol. On the whole, 5.4 mmol of hydrogenated products were formed on this electrode (turnover: 4900), without apparent loss of catalytic activity. Obviously, the use of polypyridyl ligands linked to the polypyrrolic matrix by alkyl chains, instead of carboxy-ester groups, lead to a strong stabilization of these catalytic cathodes. It should be emphasized that the polymers containing the ligands L₁ and L₄ present similar features, i.e., good catalytic activity and high operational sta-

bility. This is not surprising, since it has been found that [Rh(L)₂(Cl)₂][Cl] complexes in which L is 4,4'-dimethyl-2,2'-bipyridine or the 4,7-dimethyl-1,10-phenanthroline present similar catalytic activities in substituted cyclohexanones hydrogenation via hydrogen transfer from isopropanol [17].

Results from our preliminary experiments carried out with C/poly[Rh(L₃)₂(Cl)₂]⁺ modified electrodes have demonstrated [7] that the stereoselectivity for the electrocatalytic hydrogenation of substituted cyclohexanones was quite different to that already reported for their catalytic hydrogenation with [Rh(bpy)₂(Cl)₂]⁺ and H₂ in MeOH/MeONa [16]. In these last conditions, the thermodynamically less stable isomers of the corresponding alcohols, namely the *cis*-2-methyl, the *trans*-3-methyl and the *trans*-4-*tert*-butylcyclohexanol were always the main isomers formed. The same result was obtained for 2- and 3-methylcyclohexanone hydrogenation on poly[Rh

$(L_3)_2(Cl)_2]^+$ films. In contrast, a reversed selectivity was observed for the ECH of the more bulky 4-*tert*-butylcyclohexanone, since the *trans* alcohol was formed in higher yield. This different stereoselectivity of the polymerized catalyst was attributed to control of the environment of the catalytic centre by the polymeric matrix [7]. This hypothesis was corroborated by the result of an ECH carried out with a rhodium complex as homogeneous electrocatalyst, which gave the *cis*-4-*tert*-butylcyclohexanol as the main isomer. C/poly[Rh(L₁ or L₄)₂(Cl)₂]⁺ cathodes have shown the same selectivity than L₃-containing polymer films for the hydrogenation of substituted cyclohexanones, dihydrocarvone and carvone (see Table 2), with the exception of 3-methylcyclohexanone hydrogenation. As a matter of fact, its reduction on C/poly[Rh(L₁ or L₄)₂(Cl)₂]⁺ modified electrodes gave mainly the thermodynamically more stable *cis* alcohol (Table 2, entries 5 and 6). At the present time, we have no clear explanation to this exception.

The ECH of *R*-(–)-carvone on poly[Rh(L₁)₂(Cl)₂]⁺ films (Table 2, entries 9 and 10) gave results close to that already reported for its hydrogenation on L₃-based materials [6]. Dihydrocarvone was the main product obtained (61%) when a limited amount of charge was passed (2.5 electron per molecule of carvone; entry 9). Its *trans* isomer, i.e. the (2*R*,5*R*)-5-isopropenyl-2-methylcyclohexanone, was the main isomer formed, as on a C/poly[Rh(L₃)₂(Cl)₂]⁺ electrode [7]. However, the selectivity is low since an appreciable amount of dihydrocarveol (16%) was present, following the hydrogenation of dihydrocarvone. This last point was corroborated by the results of the hydrogenation of dihydrocarvone, which could be quantitatively and selectively hydrogenated to dihydrocarveol on both cathodes (Table 2, entries 7 and 8). The best yield and current efficiency were obtained on a C/poly[Rh(L₄)₂(Cl)₂]⁺ electrode. The quantitative formation of dihydrocarveol with a fair current efficiency was also obtained when the ECH of carvone was carried out up to the consumption of 7.6 electrons per substrate molecule

(Table 2, entry 10). This result is another demonstration of the better efficiency and stability of L₁ and L₄-based catalytic materials, as compared with the polymer films elaborated from the complex containing the ligand L₃. With this last cathode, it was impossible to produce quantitatively the dihydrocarveol, since the ECH of carvone always led to a mixture of dihydrocarvone and dihydrocarveol [7]. It must also be emphasized that the isopropenyl group in carvone was not reduced. Only traces of carvomenthone (the 5-isopropyl-2-methylcyclohexanone) were formed, while carvotanacetone (the 5-isopropyl-2-methyl-2-cyclohexene-1-one) was not detected in the reaction media. This regioselectivity indicates that the catalytically active species in the film is a [Rh^I(L)₂]⁺ intermediate. The transient loss of a polypyridinyl ligand would give a catalytic species such as a [Rh^I(L)(S)₂]⁺ (S=solvent) intermediate able to catalyze the hydrogenation of the vinylic function, and unable to reduce the carbonyl function, as demonstrated by the results of carvone hydrogenation with [Rh^I(bpy)(S)₂]⁺ as homogeneous catalyst and hydrogen gas [16].

Three diastereoisomers of the dihydrocarveol were formed upon the quantitative hydrogenation of carvone (Table 2, entry 10). The (1*S*,2*R*,5*R*)-, (1*R*,2*R*,5*R*)- and (1*S*,2*S*,5*R*)-5-isopropenyl-2-methylcyclohexanol were produced in 77%, 11% and 12%, respectively. A similar distribution (73%, 16% and 11%) was obtained starting with dihydrocarvone (Table 2, entry 7). This is not surprising, since the *cis:trans* ratio (23:77) for the commercial dihydrocarvone used in this experiment was similar to that of the dihydrocarvone first formed upon carvone hydrogenation (Table 2, entry 9). A slightly different distribution (70%, 19% and 11%, respectively) was found when dihydrocarvone was hydrogenated on a poly[Rh(L₄)₂(Cl)₂]⁺ film (Table 2, entry 8). The same three diastereoisomers were formed by the ECH of carvone, as well on a C/poly[Rh(L₃)₂(Cl)₂]⁺ electrode, as with a similar complex used in solution [7]. However, their distribution was quite different according to the electrocatalytic system (homogeneous or hetero-

geneous) used. Although the (1*S*,2*R*,5*R*) isomer was always the main isomer formed, the (1*R*,2*R*,5*R*) and (1*S*,2*R*,5*R*) isomers were produced in higher yields on the modified electrode (homogeneous system: 83%, 11% and 6%; heterogeneous system: 44%, 30% and 26%, respectively). Thus, it appears that the distribution of the diastereoisomers of dihydrocarveol formed by using poly[Rh(L₁ or L₄)₂(Cl)₂]⁺ films is close to that obtained in an homogeneous electrocatalytic hydrogenation. These observations could be explained by taking into account the permeability of the different polymers. The L₃-based films which are obtained by electropolymerization of a monomer containing four pyrrole units, are likely to be more cross-linked and hence less permeable than L₁ and L₄-based polymers which have only two polymerizable groups per monomeric unit. Consequently, the more rigid environment of the catalytic sites in poly[Rh(L₃)₂(Cl)₂]⁺ films seems to have a large influence on their selectivity towards the reduction of the carbonyl function in dihydrocarvone.

Finally, the ECH of the *S*-(+)-carvone on C/poly[Rh(L₁)₂(Cl)₂]⁺ modified electrodes, in the same experimental conditions as its *R*-(-)-isomer, gave similar results. Dihydrocarvone was formed first. Its *trans* isomer, i.e., the (2*S*,5*S*)-isomer, was also the main isomer produced with a 77% yield. The exhaustive hydrogenation of the substrate could be achieved with a 69% current efficiency. GC and ¹H NMR data have shown the presence of the three (1*R*,2*S*,5*S*), (1*S*,2*S*,5*S*) and (1*R*,2*R*,5*S*) diastereoisomers in 83%, 12% and 5% yields, respectively.

4. Conclusion

The present study confirms that polypyrrole film electrodes functionalized with rhodium(III) complexes having 2,2'-bipyridine or 1,10-phenanthroline ligands can be efficiently used for the electrocatalytic hydrogenation of various unsaturated organic substrates in an aqueous electrolyte.

We have shown that the use of an alkyl chain, instead of a carboxy-ester group, to link the complexes to the polypyrrolic frame markedly improves the operational stability of these cathodes. High turnovers (as high as 5000) have been obtained, without appreciable loss catalytic activity, with L₁ and L₄-based modified electrodes which could be re-used several times. Owing to the fair stability of the polymerized catalyst in these experimental conditions, the poor stability of L₃-based films is probably due to the loss of catalyst molecules from the polymeric material, due to hydrolysis of the ester linkage. On the other hand, results of several hydrogenations provide evidence that the selectivity of the catalyst depends on the structure (cross-linking) of the polymeric matrix in which it is embedded.

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