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Synthesis and electrochemical, spectral and catalytic properties of diphosphine–polypyridyl ruthenium complexes

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Abstract

Two new ruthenium aqua complexes containing phosphines and polypyridine as ligands were synthesized: $[Ru(L)(totpy)(H_2O)](PF_6)_2$ (L = 1,2-bis(dimethylphosphino) ethane and 1,2-bis(dichlorophosphino)ethane; totpy = 4′-(4-tolyl)-2,2′:6′,2″-terpyridine). The synthetic routes for both complexes are similar. The complexes were characterized by elemental analysis, cyclic voltammetry and differential pulse voltammetries, UV–Vis and EPR spectra. E_{pa} versus pH studies are consistent with a one-electron, one-proton transfer; at high pH, potentials become pH independent. Catalytic tests with benzyl alcohol, cyclohexanol, cyclohexene, ethylbenzene, 1,2-butanediol and 1,4-butanediol were carried out using the oxo complexes, which are electrochemically generated from the corresponding aqua complexes, in solution and immobilized in carbon paste and ITO/Nafion® electrodes. In the presence of excess substrates, the cyclic voltammograms of the complexes and of the modified electrodes show an enhancement of the oxidation peaks and a decrease of the reduction peaks upon potential reversal, indicating catalytic activities. Plots of the anodic peak currents (I_{pa}) against organic substrate concentrations showed straight lines, indicating pseudo-first-order kinetics behavior. For the modified electrodes the plots of I_{pa} versus $v^{1/2}$ showed that the anodic peak currents change linearly with the square root of the scan rate; this is characteristic of surface electrocatalysis with the catalyst confined to the electrode surface with diffusion control of the substrates.

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Keywords: Ruthenium complexes; Oxo complexes; Phosphine ligands; Polypyridyl ligand; Modified electrodes; Electrocatalysis

1. Introduction

Ruthenium-aqua/oxo complexes containing polypyridyl and bidentate phosphine ligands have been recently investigated [1–3]; several complexes containing tertiary phosphine ligands were previously studied [4,5]. Phosphine ligands can modify the oxidation chemistry of ruthenium-aqua/oxo complexes because they provide a broad variety of well-characterized steric and electronic ligand properties [4].

The reactivity of high oxidation state ruthenium(IV) polypyridyl complexes has played an increasingly important role in studies involving electrocatalytic processes of several organic substrates [3,6–13]. The orbital and energetic properties of $Ru^{IV}{=}O^{2+}$ promote complex mechanisms; these complexes are remarkably versatile oxidants mechanistically in providing pathways for atom transfer, C–H insertion, and proton-coupled electron transfer [3,11,14–16]. Some attempts to combine the oxidative properties of these complexes in solution with the advantage offered by modified electrodes, with respect to their potential application in electrocatalysis, have been described [17–19]. In this context, ruthenium(II) complexes have been immobilized within Nafion® films on electrodes and in carbon paste electrodes, and catalytic activities in the presence of alcohols have been studied [7,20–23].

In this work, we have synthesized the complexes $[Ru(L)(totpy)(H_2O)](PF_6)_2$ (L = 1,2-bis(dimethylphosphino)ethane and 1,2-bis(dichlorophosphino)ethane;

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totpy = 4′-(4-tolyl)-2,2′:6′,2″-terpyridine); their spectral, electrochemical and catalytic properties were studied. The ability of the complexes to act as catalysts for electrooxidations of benzyl alcohol, cyclohexanol, cyclohexene, ethylbenzene, 1,2-butanediol and 1,4-butanediol were studied in homogeneous solution and with the complexes immobilized in carbon paste electrodes and within Nafion® films on electrodes.

2. Experimental

2.1. Materials

Water was doubly distilled from alkaline potassium permanganate. $RuCl_3 \cdot xH_2O$, 1,2-bis(dichlorophosphine)-ethane and 1,2-bis(dimethylphosphine) ethane were purchased from Aldrich Chemical Co. Methylene chloride and acetonitrile were kept in an alumina column before use. All other reagents and solvents were of reagent quality and were used without further purification.

2.2. Instrumentation and measurements

Routine UV–Vis spectra were obtained in 1-cm quartz cells by using a Hewlett–Packard 8453 spectrophotometer. Electrochemical experiments were conducted by using a PAR Model 273A Potentiostat/Galvanostat. Cyclic voltammetric and differential pulse voltammetric experiments were performed in a one-compartment cell using a carbon working electrode, a platinum wire auxiliary electrode and a saturated calomel (SCE) or a Ag/AgCl reference electrode. The $E_{1/2}$ values for reversible couples were calculated from half the difference between E_p values for the cathodic and anodic waves. The catalytic tests were performed at 25 ± 1 °C. The pH values of aqueous solutions were buffered at an ionic strength of 0.25 mol L^{-1} by HNO_3 and $NaNO_3$ (pH 2.0), potassium hydrogen phthalate, HNO_3 and $NaNO_3$ (pH 3.0), potassium hydrogen phthalate, NaOH and $NaNO_3$ (pH 4.0–5.5), Na_2HPO_4 and NaH_2PO_4 (pH 6.0–8.0), $Na_2B_4O_7 \cdot 10H_2O$ and $NaNO_3$ (pH 9.0) and $Na_2B_4O_7 \cdot 10H_2O$ and NaOH (pH 10.0–10.8). Elemental analyses were performed using a CHNS-O CE Instruments Model EA 1110 elemental analyzer. Ruthenium analyses were performed with a Model V-85 B Braun ICP-AES-atomic emission spectrometer. EPR spectra of the solid complexes were recorded at room temperature on a Bruker EP 200D spectrometer. ^1H NMR spectra were obtained with a Bruker AC-80 spectrometer. Mass spectra were obtained with a Hewlett–Packard gas chromatograph/MS system 5988A.

2.3. Preparation of the ligand 4′-(4-tolyl)-2,2′:6′,2″-terpyridine (totpy)

The 4′-(4-tolyl)-2,2′:6′,2″-terpyridine ligand was prepared analogously to the literature procedure [24,25]; a 2:1 ratio of 2-acetylpyridine:*p*-tolualdehyde was used. The solid was recrystallized from ethanol to obtain 1.01 g (54%) of light green crystals, identified as 4′-(4-tolyl)-2,2′:6′,2″-terpyridine (totpy) (Fig. 1). ^1H NMR: m, 8.65–8.85 ($H_{3,3''}$; $H_{6,6''}$; $H_{3',5'}$); m, 7.80–8.00 ($2H_o$; $H_{4,4''}$); m, 7.35–7.45 ($2H_m$; $H_{5,5''}$); s, 2.47 ($-CH_3$). ESI MS: *m/z* 323.20. *Anal.* Calc. for $C_{22}H_{17}N_3$: C, 81.71; H, 5.30; N, 12.99. Found: C, 82.09; H, 5.28; N, 13.38%.

2.4. Preparation of the complexes

$[RuCl_3(totpy)]$ was prepared according to the literature procedure [1,2]. Yield: 85%. *Anal.* Calc. for $C_{22}H_{17}N_3Cl_3Ru$: C, 49.78; H, 3.23; N, 7.92. Found: C, 48.95; H, 3.28; N, 7.67%.

2.4.1. [Ru(L)(totpy)Cl](PF$_6$) (L = 1,2-bis(dimethylphosphino)ethane)

A mixture of $[RuCl_3(totpy)]$ (0.38 g, 0.71 mmol) and 1,2-bis(dimethylphosphino)ethane (0.15 g, 1.00 mmol) were heated to reflux, under a N_2 atmosphere, in 115 mL of 3:2 ethylene glycol:water in the presence of NEt_3 (0.5 mL) and LiCl (0.15 g, 3.55 mmol) for 2.5 h. The hot solution was filtered and 2.0 mL of a saturated aqueous solution of NH_4PF_6 was added to the filtrate. The resulting red-brown crystals were washed with cold water and dried under vacuum. The product was recrystallized by dissolution in acetone and precipitated by adding diethyl ether. Yield: 0.32 g (60%). The complex is pure enough to be used in the synthesis of the aqua complex described in Section 2.4.3.

2.4.2. [Ru(L′)(totpy)Cl](PF$_6$) (L′ = 1,2-bis(dichlorophosphino)ethane)

The complex was prepared analogously to that described in the above section, except that a 4:1 ratio of acetonitrile:water and *N*-ethylmorpholine (30 drops) were used. Yield: 0.40 g (68%). The complex is pure enough to be used in the synthesis of the aqua complex described in Section 2.4.4.

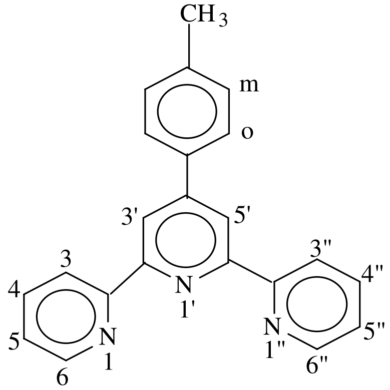


Fig. 1. 4′-(4-Tolyl)-2,2′:6′,2″-terpyridine (totpy).

2.4.3. $[Ru(L)(totpy)(OH_2)](PF_6)_2$ (L = 1,2-bis(dimethylphosphino)ethane) (**1**)

One hundred and seventy milligrams (0.23 mmol) of $[Ru(L)(totpy)Cl](PF_6)$ and 0.07 g (0.27 mmol) of silver *p*-toluenesulfonate were heated to reflux in 46 mL of 1:1 acetone:water under a N_2 atmosphere for 1 h; the hot solution was filtered and 3.0 mL of a saturated aqueous solution of NH_4PF_6 was added to the filtrate. The volume was reduced to 20 mL in a rotatory evaporator. The brown crystals were collected by filtration, washed twice with cold water and dried under vacuum. The complex was reprecipitated twice from acetone–diethyl ether. Yield: 0.14 g (69%). *Anal.* Calc. for $C_{28}H_{35}N_3OP_4F_{12}Ru$: C, 39.11; H, 4.00; Ru, 11.47. Found: C, 39.44; H, 4.29; Ru, 11.46%.

2.4.4. $[Ru(L')(totpy)(OH_2)](PF_6)_2$ (L′ = 1,2-bis(dichlorophosphino)ethane) (**2**)

The complex was prepared analogously to **1**, except that a 1:2 ratio of acetone:water was used. Yield: 0.10 g (43%). *Anal.* Calc. for $C_{24}H_{23}ON_3Cl_4P_4F_{12}Ru$: C, 29.90; H, 2.40; Cl, 14.7; Ru, 10.48. Found: C, 31.40; H, 2.39; Cl, 14.2; Ru, 10.27%.

2.5. Modified electrodes

2.5.1. Carbon paste electrodes

Carbon paste electrodes [7,20] containing 3:2 by weight of carbon powder: mineral oil were used for cyclic voltammetric studies. The modified electrodes contained 3:22 by weight of complex:paste. The carbon paste holder was constructed of a thick-walled Teflon tube with 0.3 cm i.d. A copper sleeve equipped with a copper wire plunger was mounted at the top of the Teflon tube. By rotating the sleeve, the plunger could be made to extrude a used paste layer which was sliced off to form a fresh paste surface.

2.5.2. Nafion® transparent ITO modified electrode [21–23]

Sixty microliters of Nafion® ethanolic solution (2.5%) was cast on the ITO electrode surface (effective area = 1.0 cm^2); the solvent was air evaporated at room temperature; the coated electrode was dipped in pure water for 1 h and then soaked in an aqueous solution of the complex (2.0 mmol L^{-1}) for 30 min.

3. Results and discussion

3.1. Spectroscopic and redox properties of the aqua complexes in solution

Fig. 2 shows the absorption spectrum of **1** in methylene chloride. Cyclic and differential pulse voltammograms of **2** in methylene chloride are shown in Fig. 3. Table 1 shows spectroscopic and redox data for the complexes. The aqua complexes have similar spectra. Both aqua complexes exhibit several very intense bands in the UV region, assignable to polypyridyl ligand $\pi \rightarrow \pi^*$ excitations; in the visible region the bands at $\lambda_{max} = 490$ nm ($\varepsilon =$

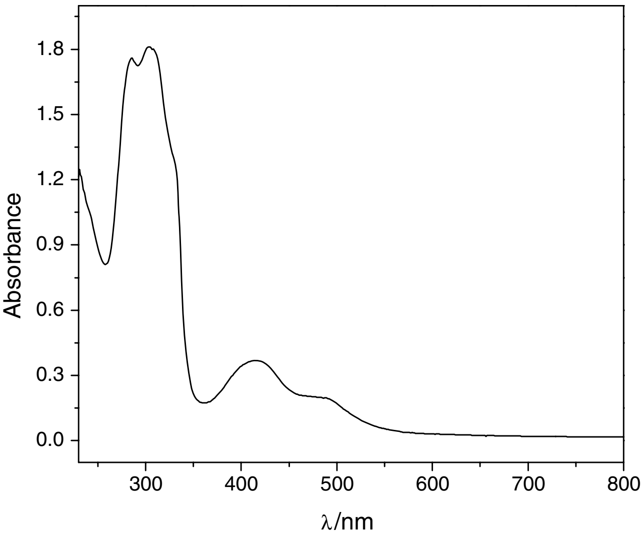


Fig. 2. UV–Vis spectrum of 1.0×10^{-4} mol L^{-1} $[Ru(L)(totpy)(H_2O)](PF_6)_2$ (**1**) (L = 1,2-bis(dimethylphosphino)ethane) in CH_2Cl_2.

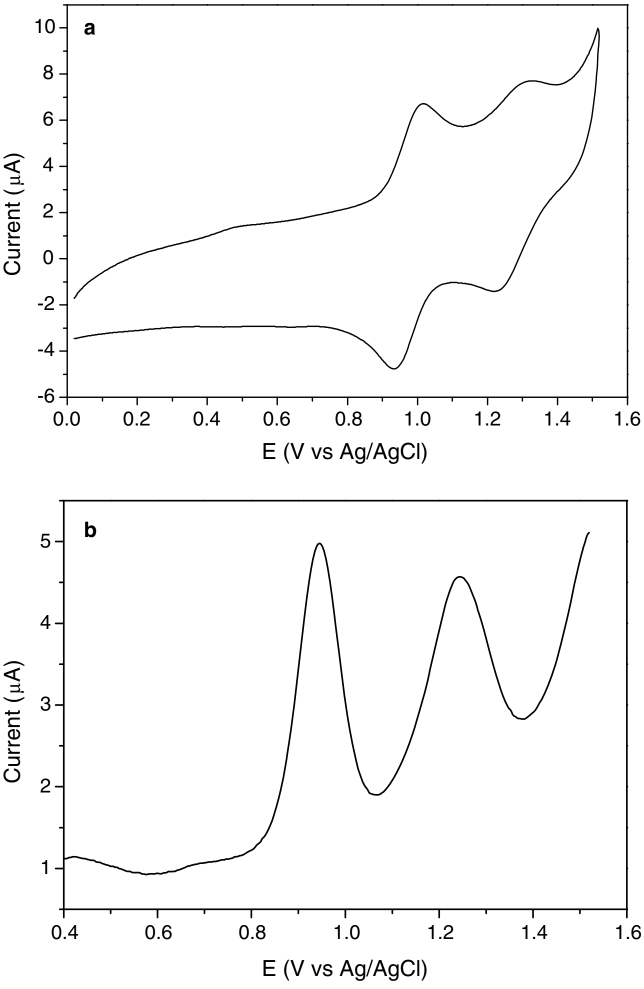


Fig. 3. (a) Cyclic voltammogram and (b) differential pulse voltammogram of 1.0×10^{-3}mol L^{-1} $[Ru(L')(totpy)(H_2O)](PF_6)_2$ (**2**) (L′ = 1,2-bis(dichlorophosphino) ethane) in CH_2Cl_2 + 0.1 mol L^{-1} TBAP, glassy carbon working electrode; (a) $v = 100$ mV s^{-1}; (b) 10 mV s^{-1}.

Table 1
Electrochemical and spectral data for the complexes

Complexes	$E_{1/2}$ (V)		λ_{max}/nm ($\varepsilon_{max} \times 10^3$/mol^{-1} L cm^{-1})
	$Ru^{III/II}$	$Ru^{IV/III}$	
$[RuCl_3(totpy)]$	+0.05[a]		226 (17), 285 (16), 310 (13), 406 (4.7)[b]
$[Ru(L)(totpy)(H_2O)](PF_6)_2$ (**1**)	+0.85	+1.02[c]	285 (17), 305 (18), 414 (3.7), 490 (1.9)[e]
	+0.46	+0.66[d]	
$[Ru(L')(totpy)(H_2O)](PF_6)_2$ (**2**)	+0.96	+1.26[c]	285 (39), 310 (41), 475 (7.9)[e]
	+0.57	+0.77[d]	

[a] MeCN + 0.1 mol L^{-1} TBAP; glassy carbon working electrode; $v = 100$ mV s^{-1}.

[b] CH_3CN.

[c] CH_2Cl_2 + 0.1 mol L^{-1}; glassy carbon working electrode; $v = 100$ mV s^{-1}.

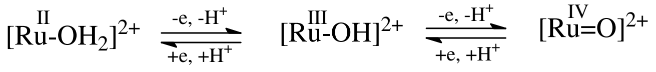
[d] In 7:3 phosphate buffer ($\mu = 0.20$ mol L^{-1}): *tert*-butyl alcohol solution, pH 6.8.

[e] CH_2Cl_2.

1.9×10^3 mol L^{-1} cm^{-1}) and 475 nm ($\varepsilon = 7.9 \times 10^3$ mol L^{-1} cm^{-1}) for **1** and **2**, respectively, can be attributed to metal-to-ligand dπ(Ru) → π* (diphosphine) transitions. One additional band is observed for **1** at 414 nm ($\varepsilon = 3.7 \times 10^3$ mol L^{-1} cm^{-1}) and can be attributed to metal-to-ligand dπ(Ru) → π* (polypyridyl) transitions [26]. For **1**, the MLCT band appears at higher wavelength; this reflects the electron-donation effect of the methyl substituents on the phosphine ligand, which destabilize the dπ(Ru) electrons, causing the dπ(Ru) → π* (diphosphine) transitions to occur at lower energy. On the other hand, for **2**, the MLCT band appears at higher energy, due to the electron-withdrawing effect of the chloro substituents on the phosphine ligand; similar effects were observed for a substituted bipyridine ligand [10]. It can be observed that the MLCT bands are shifted to higher energies upon substitution of the anionic chloride ligand for the neutral aqua ligand.

The cyclic voltammograms for both **1** and **2** in methylene chloride exhibit two reversible redox waves corresponding to the $Ru^{III/II}$ and $Ru^{IV/III}$ couples (0.85/1.02 and 0.96/1.26 V versus Ag/AgCl, respectively). The oxo-aqua ligands allow rapid proton transfer to be concomitant with electron transfer, permitting the accessibility of several oxidation states via gain or loss of protons (Scheme 1). The redox potentials of **1** are less positive, reflecting the electron-donation effect of the methyl substituents on the phosphine ligand. The observed potentials in methylene chloride are more positive than those obtained in aqueous solution (Table 1); for **2**, the separation between the two couples (mV) is larger than in water. This behavior can be due to a very slow deprotonation of the first oxidized species; the deprotonation of the aqua ligand to form Ru^{III}–OH is facilitated in aqueous solution but not in methylene chloride (low protic and polar solvent).

EPR spectra of ruthenium(III) complexes show *g* tensor values [27] that can be used to derive ground states. The **1** and **2** aqua complexes show no EPR signals, indicating the oxidation state Ru(II).



$$[\overset{II}{Ru}\text{-}OH_2]^{2+} \underset{+e,\,+H^+}{\overset{-e,\,-H^+}{\rightleftharpoons}} [\overset{III}{Ru}\text{-}OH]^{2+} \underset{+e,\,+H^+}{\overset{-e,\,-H^+}{\rightleftharpoons}} [\overset{IV}{Ru}{=}O]^{2+}$$

Scheme 1.

3.2. $E_{1/2}$ versus pH of the aqua complexes

The potentials of the $Ru^{IV/III}$ couple of **1** and the potentials of the $Ru^{III/II}$ couple of **2** vary with the pH of the solution, resulting in the $E_{1/2}$ versus pH variations shown in Fig. 4 for **2**. Within the 8.3 > pH > 2.0 region, the plot for **1** is a straight line, with slope −0.062; for **2**, within the 9.6 > pH > 2.0 region, the straight line has slope −0.059; the slopes are very close and coincident with the Nernstian prediction of −0.059 V/pH unit, indicative of one-electron oxidation accompanied by the dissociation of one proton [7,28] (Schemes 2 and 3).

For **1**, the potentials become pH independent at pH > 8.3, indicating that, in this region, $[Ru^{III}(L)(totpy)(O)]^+$ is the dominant species (Scheme 4).

The same behavior is shown for **2** at pH > 9.6; in this case $[Ru^{II}(L')(totpy)(OH)]^+$ is the dominant species (Scheme 5):

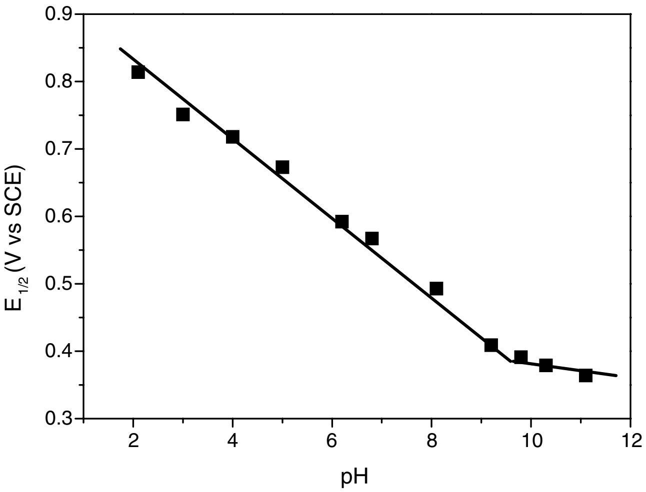


Fig. 4. Plot of $E_{1/2}$ vs. pH for the $Ru^{III/II}$ redox couple of $[Ru(L')(totpy)(H_2O)](PF_6)_2$ (**2**) (L′ = 1,2-bis(dichlorophosphino)ethane); glassy carbon working electrode.

$$[\mathrm{Ru^{III}(L)(totpy)(OH)}]^{2+} \underset{+e^-,\,+H^+}{\overset{-e^-,\,-H^+}{\rightleftharpoons}} [\mathrm{Ru^{IV}(L)(totpy)(O)}]^{2+}$$

Scheme 2.

$$[\mathrm{Ru^{II}(L')(totpy)(OH_2)}]^{2+} \underset{+e^-,\,+H^+}{\overset{-e^-,\,-H^+}{\rightleftharpoons}} [\mathrm{Ru^{III}(L')(totpy)(OH)}]^{2+}$$

Scheme 3.

$$[\mathrm{Ru^{III}(L)(totpy)(O)}]^{+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [\mathrm{Ru^{IV}(L)(totpy)(O)}]^{2+}$$

Scheme 4.

3.3. Electrocatalytic oxidations of organic substrates in homogeneous solution

The catalytic activities of **1** and **2** for the oxidation of organic substrates were investigated by cyclic voltammetric experiments in 7:3 phosphate buffer (pH 6.8):*tert*-butyl alcohol solutions. Mixed solvent systems have been used by other groups for similar experiments with no adverse effects [12]. In the presence of a 50-fold excess of substrate, the cyclic voltammograms of **1** and **2** show an enhancement of the oxidation peaks and a decrease of the reduction peaks upon reversal potential scan. This is indicative of catalytic activity [7].

Catalytic tests can give the reactivity order for the electrooxidations: for **1**, benzyl alcohol > 1,4-butanediol > cyclohexanol > cyclohexene > ethylbenzene > 1,2-butanediol; for **2**, 1,4-butanediol > benzyl alcohol > cyclohexanol > cyclohexene > 1,2-butanediol > ethylbenzene. The oxidation products were identified in bulk electrolyses experiments using polypyridyl and phosphine ruthenium complexes described previously [6–10]: benzyl alcohol was oxidized to benzaldehyde and benzoic acid, 1-4 butanediol to δ-butyrolactone, 1-2-butanediol to 1-hydroxy-2-butanone, cyclohexanol to cyclohexanone, cyclohexene → 2-cyclohexen-1-one, and ethylbenzene to acetophenone. The proposed mechanism for oxidations using ruthenium oxo complexes suggests the formation, in the transition state, of an electron-deficient carbon [29]. A substituent can decrease the activation energy, inducing delocalization of the positive charge by hyperconjugation, inductive or resonance effects. In this way, the benzyl alcohol has a higher reactivity than cyclohexene: the resonance effect in the benzyl alcohol aromatic ring is responsible by positive charge delocalization; in cyclohexene, the allylic carbocation formed at C-3 before the water molecule attack (S_N2 reaction) induces a stabilization by resonance with a conjugated unsaturation at the carbon ring. Nevertheless, as cyclohexene has fewer canonic structures than benzyl alcohol, the lower positive charge delocalization decreases the reactivity. The higher reactivity of a primary alcohol compared to a secondary one was also observed in homogeneous catalysis by using $[\mathrm{Ru(tpy)(bpy)(H_2O)}]^{2+}$ [8].

$$[\mathrm{Ru^{II}(L')(totpy)(OH)}]^{+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [\mathrm{Ru^{III}(L')(totpy)(OH)}]^{2+}$$

Scheme 5.

A generalization can be made: benzyl alcohol and 1,4-butanediol are more reactive than cyclohexanol; cyclohexene has an intermediate reactivity; ethylbenzene and 1,2-butanediol have the lowest reactivities.

3.4. Electrocatalytic oxidation of organic substrates at a carbon paste electrode (CPE) containing *1* and *2*

The cyclic voltammetric behavior of the CPE containing **1** and **2** in 7:3 phosphate buffer (pH 6.8):*tert*-butyl alcohol solutions, in the presence of benzyl alcohol, cyclohexanol, 1,4-butanediol, 1,2-butanediol and ethylbenzene shows pronounced enhancement of the anodic currents. The observed reactivity order for **1** is benzyl alcohol > cyclohexanol > 1,4-butanediol > 1,2-butanediol > cyclohexene > ethylbenzene and for **2** is benzyl alcohol > ethylbenzene > cyclohexanol > 1,4-butanediol cyclohexene > 1,2-butanediol. The reactivities of CPE containing **1** and **2** were somewhat different from those of homogeneous catalysis; surprisingly, high reactivity in the oxidation of ethylbenzene by **2** was observed. Higher reactivity of the primary alcohol was also observed in homogeneous catalysis by using **1** and **2**. The high reactivity of benzyl alcohol can be due to its higher permeability into the active surface of the carbon paste electrode.

For quantitative evaluation of the electrocatalysis surface, the dependence of the peak height on the benzyl alcohol concentration and on the potential scan rate was studied [30]. The peak height was linearly dependent (Fig. 5) (correlation coefficient 0.998, with plot intercept near zero) on the concentration of benzyl alcohol, indicating that the electrocatalysis is *pseudo-first-oder* in this

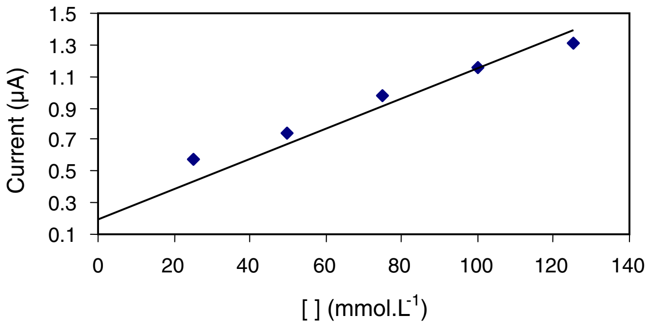


Fig. 5. Plot of the oxidation peak currents of the CPE containing $[\mathrm{Ru(L)(totpy)(H_2O)}](\mathrm{PF_6})_2$ (**1**) (L = 1,2-bis(dimethylphosphino)ethane) against benzyl alcohol concentrations; in 7:3 phosphate buffer (pH 6.8):*tert*-butyl alcohol solution, $v = 100\ \mathrm{mV\ s^{-1}}$.

benzyl alcohol concentration range. The anodic peak currents change linearly with the square root of the scan rate; this is characteristic of surface electrocatalysis with the catalyst confined to the electrode surface under diffusion control of the substrates.

3.5. Electrocatalytic oxidation of organic substrates at a ITO/Nafion® /complex electrode

The cyclic voltammogram of **1** in the ITO/Nafion® transparent electrode shows the $Ru^{IV/III}$ redox couple only ($E_{1/2} = +0.74$ V versus SCE). This is probably due to the sluggishness of the $Ru^{III/II}$ couple observed in modified electrodes [18b].

The reactivity of $Ru^{IV}{=}O^{2+}$ complexes has been explored with ITO electrodes [31]. The cyclic voltammogram in the presence of 50 mmol L^{-1} of benzyl alcohol shows a decrease of the anodic current, as a consequence of the dissolution of the aqua complex adsorbed in the Nafion® polymer film. The dissolution of the aqua complex is clearly noticed when the solution changes from colorless to yellow. Therefore, benzyl alcohol being a polar substrate can dissolve the Nafion® film. When the substrate is cyclohexene, that which has a low polarity, the catalytic activity is noticed by the significant increase of the anodic current and the decrease of the cathodic current (Fig. 6).

The dependence of the anodic peak current with scan rate was studied from 50 to 500 mV s^{-1}, in the presence cyclohexene (Fig. 7(a)). The plot of I_{pa} versus $v^{1/2}$ (Fig. 7(b)) shows that the anodic peak current varies linearly with the square root of the scan rate (correlation coefficient 0.998), indicating that the reaction is also controlled by diffusion of the substrate [7].

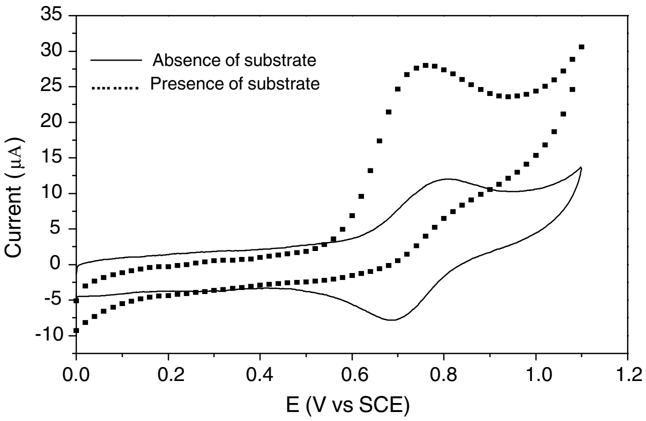


Fig. 6. Cyclic voltammograms of ITO electrode, modified by Nafion® containing $[Ru(L)(totpy)(H_2O)](PF_6)_2$ (**1**) (L = 1,2-bis(dimethylphosphino)ethane) in 4:1 $HNO_3/NaNO_3$ buffer (pH 2.3):*tert*-butyl alcohol solution (——), and in the presence of 50 mmol L^{-1} of cyclohexene (■■■), $v = 100$ mV s^{-1}.

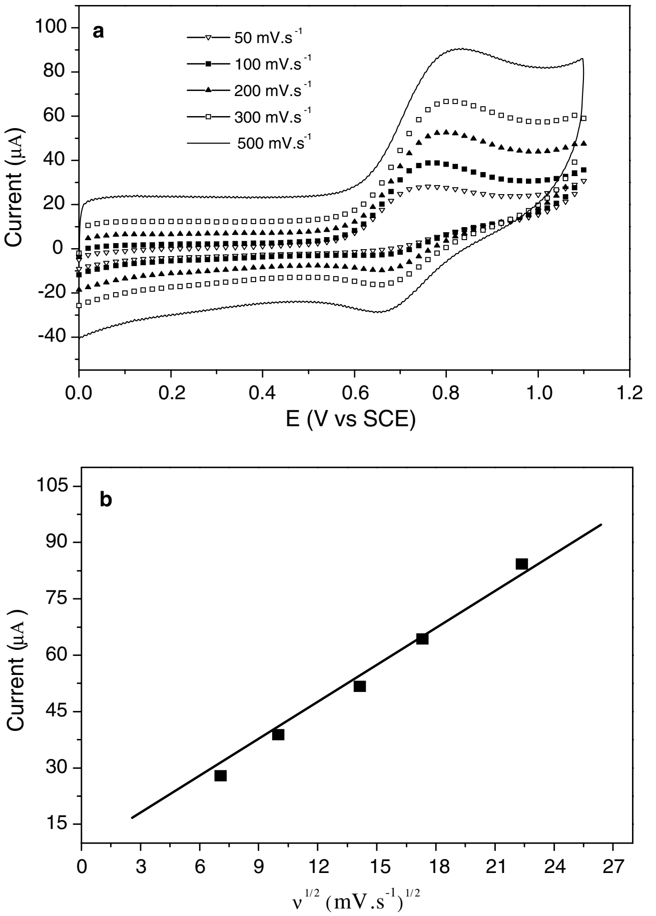


Fig. 7. (a) Cyclic voltammograms of ITO electrode, modified by Nafion® containing $[Ru(L)(totpy)(OH_2)](PF_6)_2$ (**1**) (L = 1,2-bis(dimethylphosphino)ethane), in 4:1 $HNO_3/NaNO_3$ buffer (pH 2.3):*tert*-butyl alcohol solution, in the presence of 50 mmol L^{-1} of cyclohexene, several scan rates. (b) Plot I_{pa} vs. $v^{1/2}$.

4. Conclusions

The results obtained in this work show that the complexes $[Ru(L)(totpy)(OH_2)](PF_6)_2$ (L = 1,2-bis(dimethylphosphino)ethane) (**1**) and $[Ru(L')(totpy)(OH_2)](PF_6)_2$ (L′ = 1,2-bis(dichlorophosphino)ethane) (**2**) can be used in electrooxidations of organic substrates containing different functional groups. The phosphine–ruthenium(IV)-oxo complexes have the advantage of being mild oxidants, since more powerful oxidants usually cause undesirable side reactions.

The preparations of carbon paste and ITO/Nafion® electrodes are simple and straightforward and the characteristics of the mediators are preserved upon transfer from solution to the immobilized state.

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