Redox and spectral properties of [Ru(4,4′-Me$_2$bpy)$_2$(AsPh$_3$)(H$_2$O)](ClO$_4$)$_2$ Application to electrocatalytic oxidations of organic compounds

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Abstract

The complex [Ru(4,4′-Me$_2$bpy)$_2$(AsPh$_3$)(H$_2$O)](ClO$_4$)$_2$ (4,4′-Me$_2$bpy = 4,4′-dimethyl-2,2′-bipyridine) has been prepared and their spectral and redox properties has been investigated. The catalytic activity of the complex has been investigated at pH 7.0 in the homogeneous electrooxidation of benzyl alcohol, 1-phenylethanol and cyclohexene. The reactivity was found to decrease in the order 1-phenylethanol > benzyl alcohol > cyclohexene. The higher reactivity of this complex compared to the analogous complex [Ru(4,4′-Me$_2$bpy)$_2$(PPh$_3$)(H$_2$O)](ClO$_4$)$_2$ is attributed to the higher hydrophobic character of the arsine ligand.
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1. Introduction

High-valent ruthenium oxo complexes have proved to be useful catalysts for electrooxidation of organic compounds [1–4]. The extraordinary reactivity properties of the system aquo/oxo are based on their wide range of reversibility allowing the access to several oxidation states varying from M(II) to M(IV). An important element in these reactivities is the ability to control redox potential in a systematic way by varying the ancilliary ligands [5–7].

The chemistry and use as oxidants of oxo ruthenium complexes containing polypyridyl and tertiary phosphine ligands have been studied [8–10]. Phosphine and arsine ligands modify the oxidation chemistry of ruthenium oxo complexes due to their variety of steric and electronic properties [11–16]. The hydrophobic character of these ligands influences the selectivity. It has been reported the unusual hydrophobic selectivity of primary alcohol oxidation by phosphine ruthenium(IV) oxo complexes [16].

In this work, we report the synthesis and the electrochemical and spectrochemical properties of [Ru(4,4′-Me$_2$ bpy)$_2$(AsPh$_3$)(H$_2$O)](ClO$_4$)$_2$ (4,4′-Me$_2$bpy = 4,4′-dimethyl-2, 2′-bipyridine). Electrooxidations of benzyl alcohol, 1-phenylethanol and cyclohexene by using this complex have been studied. The arsine ligand complex has shown to be more reactive than the analogous [Ru(4,4′-Me$_2$bpy)$_2$(PPh$_3$) (H$_2$O)](ClO$_4$)$_2$ phosphine complex [14] and we have shown that the hydrophobic effects of the arsine ligand, compared to the phosphine ligand, induce a higher activity, thus, a lower selectivity in the benzyl alcohol oxidation.

2. Experimental

2.1. Materials

Water was distilled twice from alkaline potassium permanganate. RuCl$_3$·xH$_2$O, 4,4′-dimethyl-2,2′-bipyridine, AsPh$_3$, 1-phenylethanol, benzyl alcohol and cyclohexene were purchased from Aldrich Chemical Co. Before being used, dichloromethane was kept in an alumina column and acetone was distilled from potassium carbonate. All other reagents and solvents were of analytical reagent grade and were used without further purification.

2.2. Instrumentation and measurements

UV–vis spectra were obtained in 1 cm optical pathway quartz cells by using a 8453 Hewlett-Packard spectrophotometer.

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Electrochemical experiments were carried out with a PAR model 273A potentiostat/galvanostat. Cyclic voltammetric experiments were conducted in a 10 mL one-compartment cell using glassy carbon working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE). The $E_{1/2}$ values for reversible couples were calculated from half the difference between E_p values for the cathodic and anodic waves. Spectroelectrochemical experiments were performed in a two-compartment quartz cell with 1 cm optical pathway using transparent gold gauze working electrode, a platinum wire auxiliary electrode and Ag/AgCl as reference electrode; the bulk electrolyses were performed in 8:2 phosphate buffer:*tert*-butyl alcohol solutions, in a 50 mL two-compartment cylindrical cell, using a platinum gauze working electrode (164 cm^2), a platinum plate auxiliary electrode (1 cm^2) and a SCE; both the electrolyses and the spectroelectrochemical experiments were carried out at a fixed applied potential of +0.90 V, at $25 \pm 1\,^{\circ}$C; this potential is sufficient to generate the Ru^{IV}=O^{2+} oxidant from the correspondent Ru^{II}–OH$_2$$^{2+}$ complex. The electrolyses were continued until the current fell to about residual values or upon reaching the desired number of coulombs. The products of the electrolyses were extracted with diethyl ether and analyzed by gas chromatography (GC); the chromatograms were recorded with Intralab 3000 gas chromatograph; benzoic acid obtained in the oxidation of benzyl alcohol was transformed to the sodium salt, extracted with water, acidified, precipitated, recrystallized and characterized by melting point.

2.3. Synthesis of the complexes

[Ru(4,4'-Me$_2$bpy)$_2$(AsPh$_3$)(H$_2$O)](ClO$_4$)$_2$ (**1**) as well its precursors *cis*-[Ru(4,4'-Me$_2$bpy)$_2$Cl$_2$]·2H$_2$O (**2**) [17] and [Ru(4,4'-Me$_2$bpy)$_2$(AsPh$_3$)Cl](PF$_6$)$_2$ (**3**) [16,18] were prepared by procedures described for related complexes. The preparation of (**1**) was performed in a mixture of 3:2 ethanol:water; the reaction for (**2**) was conducted in ethylene glycol, and for (**3**), in 4:1 ethanol:water. Yield of (**1**) in the last step: 73%. Found: C, 49.4; H, 3.9; N, 6.0%. Calc. for C$_{42}$H$_{41}$N$_4$Cl$_2$O$_9$AsRu: C, 50.8; H, 4.2; N, 5.6%.

3. Results and discussion

3.1. cis-[Ru(4,4'-Me2bpy)2(AsPh3)(H2O)](ClO4)2: spectroscopic and redox properties

Table 1 shows spectroscopic and redox data for the synthesized complexes. The bands in the UV region are assignable to ligands π–π^* excitations; the bands in the visible region can be attributed to metal to ligands transitions typical of bpy–Ru complexes [19–22]. The position of the lowest energy absorption of the complex (**1**) in dichloromethane depends on the electronic nature of the group 5 ligand (for the complex *cis*-[Ru(4,4'-Me$_2$bpy)$_2$(SbPh$_3$)(H$_2$O)]$^{2+}$, this band appears at 486 nm). This poor coordination solvent (dichloromethane) was selected in order to prevent substitution of the aqua ligand; such substitution is known to occur, for instance, when acetonitrile is used as solvent [23]. The bands are shifted to higher energies for the dicationic aquo complexes compared to the corresponding chloro species, probably because of an increased formal charge on the ruthenium ion, thus, stabilizing the dπ(Ru) orbitals.

Spectroelectrochemical experiments showed that when an aqueous solution of (**1**) is submitted to a potential of +0.90 V, one can observe the disappearance of the band at 446 nm and the appearance of a band at 486 nm (Fig. 1), the same observation occurs when (**1**) is oxidized stoichiometrically by Ce^{4+}. When the oxidized solution is reduced electrochemically at +0.1 V, the band at 446 nm is regenerated but a low broad band at 650 nm appears. The same process is observed when an excess of hydroxylamine (three times the stoichiometric reaction) is added to the oxidized solution. The band at 446 nm can be due to the formation of Ru^{III}–O–Ru^{III} dimer [11] (Eq. (1)) which is formed as consequence of rapid comproportionation reaction (Eq. (2)); this kind of reaction has been reported to occur for oxo/aquo polypyridyl ruthenium complexes [24] and for similar complexes containing tertiary phosphine ligands [16].
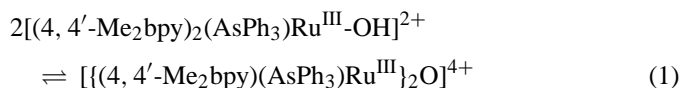
$$2[(4, 4'\text{-Me}_2\text{bpy})_2(\text{AsPh}_3)\text{Ru}^{III}\text{-OH}]^{2+}$$
$$\rightleftharpoons [\{(4, 4'\text{-Me}_2\text{bpy})(\text{AsPh}_3)\text{Ru}^{III}\}_2\text{O}]^{4+} \qquad (1)$$

Table 1
$E_{1/2}$ potentials and UV–vis spectral data for the complexes

Complexes	$E_{1/2}$ (V)		λ, nm ($\varepsilon \times 10^3$ mol^{-1} L cm^{-1})
	Ru$^{III/II}$	Ru$^{IV/III}$	
[RuCl$_2$(4,4'-Me$_2$bpy)$_2$]·2H$_2$O (**2**)	+0.22[a]		296 (29.9), 376 (8.0), 558 (6.7)[b]
[Ru(4,4'-Me$_2$bpy)$_2$(AsPh$_3$)Cl]$^{2+}$ (**3**)	+0.81[c]		292 (29.5), 342 (7.1), 476 (6.5)[b]
[Ru(4,4'-Me$_2$bpy)$_2$(AsPh$_3$)(H$_2$O)]$^{2+}$ (**1**)	+0.89[d]	+1.21[d]	238 (26.2), 290 (33.9), 446 (5.3)[d]
	+0.48[e]	+0.74[e]	226 (26.5), 252 (20.0)
			292 (31.7), 446 (5.0)[e]

[a] MeCN + 0.1 mol L^{-1} TBAP, glassy carbon working electrode, $\nu = 100$ mV s^{-1}.
[b] CH$_2$Cl$_2$.
[c] MeCN + 0.1 mol L^{-1} TBAP, $\nu = 50$ mV s^{-1}.
[d] CH$_2$Cl$_2$ + 0.1 mol L^{-1} TBAP, glassy carbon working electrode, $\nu = 100$ mV s^{-1}.
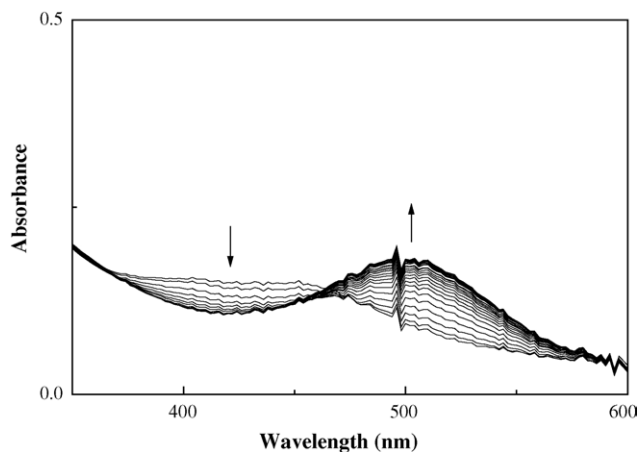[e] 8:2 aqueous phosphate buffer:*tert*-butyl alcohol, pH 7.0 ($\mu = 0.25$ mol L^{-1}).

Fig. 1. Spectroelectrochemistry of 1.1×10^{-4} mol L^{-1} [Ru(4,4'-Me$_2$bpy)$_2$(AsPh$_3$)(H$_2$O)]$^{2+}$ in 8:2 phosphate buffer solution:*tert*-butyl alcohol, pH 7.0 ($\mu = 0.25$ mol L^{-1}), $E = +0.90$ V vs. Ag/AgCl.

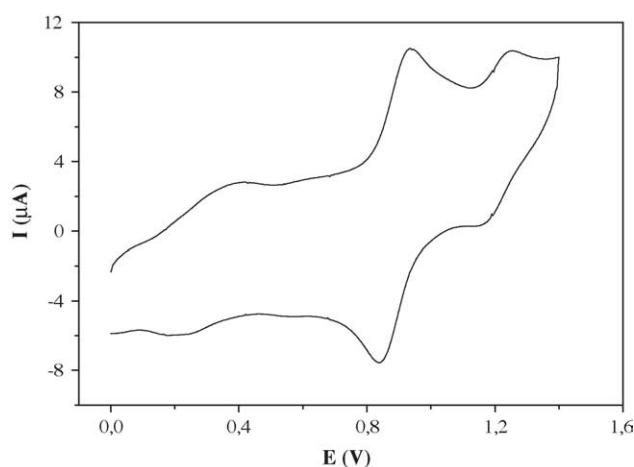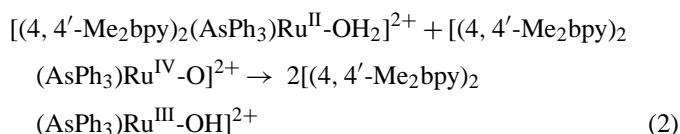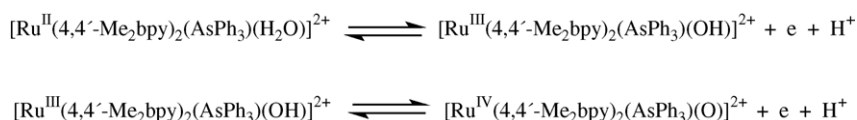Fig. 2. Cyclic voltammogram of 1.0×10^{-3} mol L^{-1} [Ru(4,4'-Me$_2$bpy)$_2$(AsPh$_3$)(H$_2$O)]$^{2+}$ in TBAP/dichloromethane, glassy carbon working electrode (diameter 3 mm), $\nu = 100$ mV s^{-1} vs. SCE.

$$[(4, 4'\text{-Me}_2\text{bpy})_2(\text{AsPh}_3)\text{Ru}^{II}\text{-OH}_2]^{2+} + [(4, 4'\text{-Me}_2\text{bpy})_2$$

$$(\text{AsPh}_3)\text{Ru}^{IV}\text{-O}]^{2+} \rightarrow 2[(4, 4'\text{-Me}_2\text{bpy})_2$$

$$(\text{AsPh}_3)\text{Ru}^{III}\text{-OH}]^{2+} \qquad (2)$$

The band at 486 nm is due to the oxidation of Ru^{III}-O-Ru^{III} dimer to [(4,4'-Me$_2$bpy)$_2$(AsPh$_3$)Ru^{III}-O-Ru^{IV}(AsPh$_3$)(4,4'-Me$_2$bpy)$_2$]$^{5+}$ [11].

Cyclic voltammetry of (**1**) in 0.1 mol L^{-1} tetra-*n*-butylammonium perchlorate solution (Fig. 2) shows chemically reversible oxidation and reduction waves for two redox couples, according to Scheme 1.

The $E_{1/2}$ and $\Delta E_{1/2}$ values are higher in dichloromethane than in aqueous solution, this can be attributed to the easier electron and proton loss in water (Scheme 1). In these redox couples, electrons are gained and lost from dπ levels orbitals of the coordinated metal [25]. Changes in electron contents do not occur in the σ-bonding framework. This is the reason for stability of the ligands in coordination sphere during the formation of the three adjacent oxidation states. The cyclic voltammogram of (**1**) shows a third redox couple at +0.31 V (+0.24 V in water) which can be attributed to the formation of the trans isomer; the appearance of redox couples at lower values were also observed for the complexes *cis*-[Ru(bpy)$_2$(PR$_3$)(H$_2$O)](ClO$_4$)$_2$ [16], *cis*-[Ru(tpy)(PR$_3$)Cl$_2$] [12], *cis*-[Ru(dppm)$_2$Cl$_2$] (dppm = bis (diphenylphosphino)methane) [13], *cis*-[Ru(bpy)$_2$Cl$_2$] and *cis*-[Ru(Me$_2$bpy)$_2$Cl$_2$] [26]; the authors have referenced to this as fast *cis*–*trans*-photochemical isomerizations.

3.2. Electrocatalytic oxidations of organic compounds in homogeneous solutions

Table 2 shows the results obtained in electrooxidations of benzyl alcohol, 1-phenylethanol and cyclohexene. The efficiency of current by time unit relationship can give a reactivity order for the electrooxidations: 1-phenylethanol > benzyl alcohol > cyclohexene. This reactivity order is in according to that observed in electrooxidations using the [Ru(4,4'-Me$_2$bpy)$_2$(PPh$_3$)(H$_2$O)]$^{2+}$ analogous complex [14]. The proposed mechanism for oxidations using ruthenium oxo complexes suggests the formation, in the transition state, of an electron-deficient carbon [15]. A substituent group can decrease the activation energy, inducing a delocalization of the positive charge by hyperconjugation, inductive or resonance effects. In this way, the secondary 1-phenylethanol is more reactive because of the methyl group bound to the benzylic carbon. 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$_N$2 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.

For the oxidation of 1-phenylethanol, the acetophenone yield and the efficiency of current are higher compared to the oxidation using [Ru(4,4'-Me$_2$bpy)$_2$(PPh$_3$)(H$_2$O)]$^{2+}$ [14]. Hydrophobic alcohols are easily oxidized by complexes containing phosphine ligands substituted by hydrophobic groups [8]; in the arsine ligands, the phenyl groups are more exposed due to steric effects. Then, the higher reactivity observed with the arsine complex can be explained by the increase of the alcohol concentration around the oxo site because of the hydrophobic interactions.

$$[\text{Ru}^{II}(4,4'\text{-Me}_2\text{bpy})_2(\text{AsPh}_3)(\text{H}_2\text{O})]^{2+} \rightleftharpoons [\text{Ru}^{III}(4,4'\text{-Me}_2\text{bpy})_2(\text{AsPh}_3)(\text{OH})]^{2+} + e + \text{H}^+$$

$$[\text{Ru}^{III}(4,4'\text{-Me}_2\text{bpy})_2(\text{AsPh}_3)(\text{OH})]^{2+} \rightleftharpoons [\text{Ru}^{IV}(4,4'\text{-Me}_2\text{bpy})_2(\text{AsPh}_3)(\text{O})]^{2+} + e + \text{H}^+$$

Scheme 1.

Table 2
Electrocatalytic oxidation of organic compounds by *cis*-[Ru(4,4′-Me$_2$bpy)$_2$(AsPh$_3$)(OH$_2$)]$^{2+}$ [a]

Substrate[b]	Product	% Yield[c]	% Oxidative coulombs passed	% Efficiency of current	Reaction time (h)
1-Phenylethanol	Acetophenone	100	125[(1)]	80	14.0
Benzyl alcohol	Benzaldehyde	34	101[(1)]	74	15.3
	Benzoic acid	41			
Benzyl alcohol	Benzaldehyde	2	97[(2)]	98	23.0
	Benzoic acid	93			
Cyclohexene	2-Cyclohexen-1-one	48	74[(2)]	65	16.3

[a] In 25 mL 8:2 phosphate buffer ($\mu = 0.25$ mol L^{-1}):*tert*-butyl alcohol, pH 7.0. Catalyst concentration: 2.0 mmol L^{-1}.

[b] Substrate concentration: 50.0 mmol L^{-1}.

[c] Based on total coulombs passed, superscript (1) denotes 2 e/mol and (2) denotes 4 e/mol.

Benzaldehyde and benzoic acid are the products in the oxidation of benzyl alcohol, but using the phosphine complex, benzaldehyde is the only oxidation product. The hydrophobicity of the arsine ligand can also be responsible for the lower selectivity. Benzaldehyde, the initial oxidation product, is kept closer to the oxo site because of the greater hydrophobic influence of the triphenylarsine ligand, increasing the formation of benzoic acid. A very high yield in benzoic acid is obtained in the four-electron process.

In previous work [27], the exhaustive oxidation of cyclohexene using [Ru(tpy)(bpy)(H$_2$O)$_2$]$^{2+}$ yielded *p*-benzoquinone; the formation of 2-cyclohexen-1-one as the only oxidation product in the cyclohexene oxidation is a very interesting result; in this case, the oxidation process was interrupted when 74% of coulombs needed for a four-electron reaction had been passed.

4. Conclusions

The electrocatalytic capability of *cis*-[Ru(4,4′-Me$_2$bpy)$_2$(AsPh$_3$)(H$_2$O)]$^{2+}$ complex in electrooxidations of alcohols and specially of olefin shows that this complex can be useful in oxidations of other functional groups. The results show that when the oxo-arsine ruthenium complex is the oxidant, the higher hydrophobic character of the arsine ligand, compared to the phosphine ligand, induces kinetic and mechanistic changes.

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