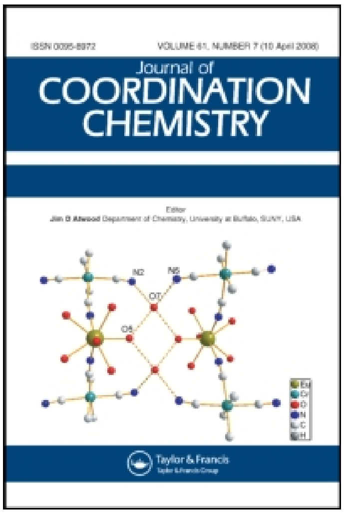

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization, and catalytic properties of some new ruthenium(II)/(III) complexes containing *N*,*N*-donor ligands

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To cite this Article Shoair, Abdel Ghany F. and Mohamed, Ramadan H.(2007) 'Synthesis, characterization, and catalytic properties of some new ruthenium(II)/(III) complexes containing *N*,*N*-donor ligands', Journal of Coordination Chemistry, 60: 12, 1279 — 1289

To link to this Article: DOI: 10.1080/00958970601053743

URL: http://dx.doi.org/10.1080/00958970601053743

Journal of Coordination Chemistry
Vol. 60, No. 12, 15 June 2007, 1279–1289

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Synthesis, characterization, and catalytic properties of some new ruthenium(II)/(III) complexes containing *N*,*N*-donor ligands

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(*Received 26 April 2006; in final form 26 June 2006*)

This article describes the preparation and characterization of *cis*-$[Ru(bipy)_2L](ClO_4)_2$ and *trans*-$[RuCl_2L_2]\cdot Cl$ (bipy = 2,2′-bipyridyl and L = ortho-phenylenediamine (o-phd), 2-aminopyridine (2-apy) and 2-aminobenzonitrile (2-abn), and examines the catalytic oxidations of benzyl alcohol, benzohydrol and pipronyl alcohol by *cis*-$[Ru(bipy)_2(o\text{-}phd)](ClO_4)_2$ and *trans*-$[RuCl_2(o\text{-}phd)_2]\cdot Cl$ complexes at room temperature and in the presence of N-methyl morpholine-N-oxide (NMO) as co-oxidant.

Keywords: Ruthenium; Catalytic oxidation; N-methylmorpholine-N-oxide (NMO); *N*,*N*-donor ligands

1. Introduction

The synthesis of ruthenium complexes and their applications as oxidation catalysts is an area of special interest [1–5]. A group of complexes $[RuCl_2(PPh_3)_2(OCHC_6H_5\text{-}R)_2]$ (R = H, CH_3, CH_3O, Cl and Br) has been prepared and characterized, of which the complex $[RuCl_2(pph_3)_2(OCHC_6H_5)_2]$ catalytically oxidizes benzyl alcohol to benzaldehyde at room temperature [3]. In earlier work the ruthenate-persulfate reagent *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ was prepared and the catalytic dehydrogenation of benzylamine to benzonitrile was studied. To explain the mechanism and the role of ruthenium for this catalytic oxidation reaction, the benzylamine complex *cis*-$[Ru(bipy)_2(NH_2CH_2C_6H_5)_2](PF_6)_2$ was prepared and oxidized by aqueous persulfate to the corresponding benzonitrile complex, *cis*-$[Ru(bipy)_2(NCC_6H_5)_2](PF_6)_2$. The single X-ray crystal structures for the two complexes were reported [4]. Still more recently, the oxidative cleavage of some linear and cyclic alkenes to their corresponding dicarboxylic acids by the catalyst system *cis*-$[RuCl_2(bipy)_2]\cdot nH_2O/IO(OH)_5$ [5], was also reported. Attempts to oxidize primary aromatic alcohols to aldehydes by

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970601053743

cis-$[RuCl_2(bipy)_2] \cdot nH_2O$ with N-methylmorpholine-N-oxide (NMO) were all unsuccessful, because the complex causes aromatic ring degradation [6].

In order to modulate the catalytic activity of *cis*-$[RuCl_2(bipy)_2] \cdot nH_2O$ towards catalytic oxidation of primary and secondary aromatic alcohols to the corresponding carbonyl compounds, it was decided to synthesize and characterize some new ruthenium(II) and ruthenium(III) complexes derived from *cis*-$[RuCl_2(bipy)_2] \cdot nH_2O$ and/or $RuCl_3 \cdot nH_2O$ with some *N*,*N*-donor ligands and study the catalytic activities of *cis*-$[Ru(bipy)_2(o\text{-}phd)](ClO_4)_2$ and *trans*-$[RuCl_2(o\text{-}phd)_2] \cdot Cl$ as representative examples towards oxidation of benzyl alcohol, piperonyl alcohol and benzohydrol to the corresponding carbonyl compounds.

2. Experimental

2.1. *Chemicals*

Ruthenium trichloride, NMO and tetrabutyl-ammoniumchloride (TBAC) were obtained from Aldrich and used without further purification. Benzyl alcohol, benzohydrol and piperonyl alcohol were obtained from Fluka. Other chemicals and solvents were reagent grade and used as received. The complex *cis*-$[RuCl_2(bipy)_2] \cdot nH_2O$ was prepared using the method suggested by Sullivan [7].

2.2. *Instrumentation*

Infrared spectra were recorded on Mattson 5000 FT-IR and electronic spectra were recorded on UV-visible Vision software V 3.2.

Microanalysis was carried out at Cairo University Microanalytical Unit. ^1H NMR spectra were obtained using a 300 MHz Varian FT-NMR spectrometer and EPR spectra were recorded on Bruker ECS 106 EPR spectrometer (Department of Chemistry, College of Science, Tamkang University, Taiwan). Cyclic voltammetric studies were recorded on a potentiostat wave generator (Oxford electrodes) using a platinum-wire working electrode, platinum-wire auxiliary electrode and an $Ag^+/AgCl$ reference electrode in conjunction with a Phillip PM 8043 X-Y recorder. Tetrabutylammonium chloride (TBAC) was used as supporting electrolyte; solution concentration was $\sim 1.0 \times 10^{-3}$ M. The half-wave potential $E_{1/2}$ was set equal to $0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials, respectively. The electrochemical experiments were carried out in dinitrogen at room temperature.

2.3. *Preparation of* cis-*$[Ru(bipy)_2L](ClO_4)_2$ complexes*

The complex *cis*-$[RuCl_2(bipy)_2] \cdot 2H_2O$ (520 mg, 1 mmol) was dissolved in an aqueous methanol (20 cm^3) under reflux and the ligand (1.5 mmol) was added. The reaction mixture was refluxed under nitrogen for 3 h during which the initial dark brown color turned to dark red. The reaction was cooled to room temperature, methanol was evaporated under reduced pressure and the aqueous solution filtered through a sintered glass crucible. The complexes were precipitated by dropwise addition of a saturated aqueous solution of $NaClO_4$ (500 mg in 10 cm^3 H_2O), collected by filtration, washed by water (3 × 10 cm^3) and dried *in vacuo* over P_4O_{10}. The yield was 60–75%.

2.4. *Preparation of* trans-*[RuCl$_2$L$_2$] • Cl complexes*

$RuCl_3.nH_2O$ (240 mg, 1 mmol) was refluxed in ethanol (20 cm^3) until the initial black color turned green and an ethanolic solution of the ligand (2.5 mmol in 5 cm^3 ethanol) was added. Upon refluxing brown microcrystals formed. The complexes were collected by filtration, washed with ethanol (3 × 10 cm^3) and dried *in vacuo* over P_4O_{10}. The yield was 60–70%.

2.5. *General procedure for catalytic oxidation of alcohol by* trans-*[RuCl$_2$L$_2$] • Cl and* cis-*[Ru(bipy)$_2$L](ClO$_4$)$_2$ complexes*

The oxidation of benzyl alcohol is typical.

To a solution of benzyl alcohol (2 mmol) in DMF, NMO (3 mmol) was added followed by the ruthenium complex (0.01 mmol). The reaction mixture was stirred at room temperature for the periods listed in table 3. The mixture was reduced *in vacuo*, the residue was taken up in diethylether, and was filtered through a bed of silica gel. The carbonyl compounds formed were quantified as their 2,4-dinitrophenylhydrazone derivatives.

3. Results and discussion

3.1. *Synthesis of complexes*

Three different *N*,*N*-donor ligands, ortho-phenylenediamine (o-phd), 2-aminobenzonitrile (2-abn) and 2-aminopyridine (2-apy) react with *cis*-$[RuCl_2(bipy)_2] \cdot 2H_2O$ under nitrogen in aqueous methanol to afford complexes of the type *cis*-$[Ru(bipy)_2L](ClO_4)_2$ in good yields and with $RuCl_3 \cdot nH_2O$ in refluxing ethanol to give complexes of the type *trans*-$[RuCl_2L_2] \cdot Cl$ according to equations (1) and (2).

$$cis\text{-}[RuCl_2(bipy)_2] \cdot 2H_2O + L \rightarrow cis\text{-}[Ru(bipy)_2L](ClO_4)_2 \tag{1}$$

$$RuCl_3 \cdot nH_2O + L \rightarrow trans\text{-}[RuCl_2L_2] \cdot Cl \tag{2}$$

Since the ligands are symmetrical bidentate and coordinate through nitrogen atoms the complexes *cis*-$[Ru(bipy)_2L](ClO_4)_2$ (A) have C_2-symmetry while the complexes *trans*-$[RuCl_2L_2] \cdot Cl$ (B) have D_{2h}-symmetry. The composition of these complexes has been confirmed by elemental analysis (table 1). The magnetic susceptibility measurements show that the complexes *cis*-$[Ru(bipy)_2L](ClO_4)_2$ are diamagnetic (low spin d^6 $S = 0$) while *trans*-$[RuCl_2L_2] \cdot Cl$ are paramagnetic (μ_{eff} 1.75–1.85 BM,

Table 1. Analytical, spectroscopic (IR and UV-Vis) and cyclic voltammetric data for ruthenium(II)/(III) complexes.

	Analytical Found (Calcd)%			IR data (cm^{-1})				Cyclic voltammetric data	
								Reduction	Oxidation
Complex	C	H	N	$\upsilon(NH_2)$	υ(Ru-Cl	υ(Ru-N)	UV-Vis data λ_{max} (nm)	$E_{1/2}$ (V), ΔE (mV)	$E_{1/2}$ (V), ΔE (mV)
cis-$[Ru(bipy)_2(2\text{-}apy)](ClO_4)_2$	42.50 (42.62)	3.11 (3.32)	11.90 (11.95)	3309 3220	–	433	420, 610	–	0.465 (70)
cis-$[Ru(bipy)_2(o\text{-}phd)](ClO_4)_2$	43.33 (43.52)	3.31 (3.37)	11.70 (11.75)	3300 3228	–	430	462, 542	–	0.405 (70)
cis-$[Ru(bipy)_2(2\text{-}abz)](ClO_4)_2$	44.40 (44.22)	3.00 (3.11)	11.50 (11.73)	3314 3224	–	432	461, 650	–	0.570 (60)
trans-$[RuCl_2(2\text{-}apy)_2]Cl$	30.30 (30.22)	3.00 (3.11)	14.20 (14.73)	3320 3320	316	450	395, 621	−0.480 (80)	0.499 (11)
trans-$[RuCl_2(o\text{-}phd)_2]Cl$	34.00 (34.41)	3.80 (3.51)	13.20 (13.42)	3340 3255	328	433	462, 655	−0.351 (78)	0.435 (130)
trans-$[RuCl_2(2\text{-}abz)]Cl$	37.90 (37.22)	2.70 (2.90)	12.60 (12.32)	3325 3234	324	435	450, 545	−0.780 (90)	0.500 (120)

Conditions: supporting electrolyte: tetrabutyammonium chloride (0.1TBAC), the concentration of the complex; $\sim 10^{-3}$ M $\Delta E = E_{pa} - E_{pc}$ and $E_{1/2} = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials.

Table 2. Magnetic and ESR g-values for *trans*-$[RuCl_2L_2]Cl$ complexes.

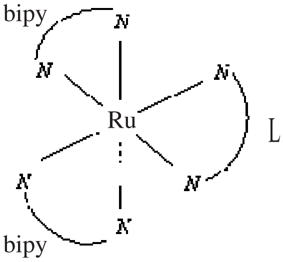
Complex	μ_{eff} (BM)	*g*-values		
		g_x	g_y	g_z
trans-$[RuCl_2(2\text{-apy})_2]Cl$	1.85	2.23	2.31	1.81
trans-$[RuCl_2(o\text{-phd})_2]Cl \cdot H_2O$	1.84	2.36	2.38	1.82
trans-$[RuCl_2(2\text{-abz})]Cl$	1.75	2.41	2.35	1.84

Table 3. Catalytic oxidiation of alcohols by *cis*-$[Ru(bipy)_2(o\text{-phd})_2](ClO_4)_2$ and *trans*-$[RuCl_2(o\text{-phd})_2] \cdot Cl$ complexes.

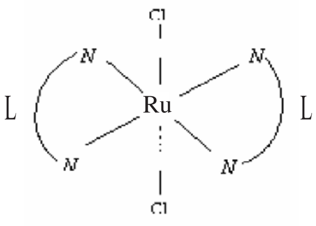
Substrate	Product	*cis*-$[Ru(bipy)_2(o\text{-phd})_2](ClO_4)_2$		*trans*-$[RuCl_2(o\text{-phd})_2] \cdot Cl$		Time (h)
		Yield %	Turnover	Yield %	Turnover	
Benzylalcohol	Benzaldehyde	70	(140)	90	(180)	3
Pipronylalcohol	Pipronaldehyde	65	(130)	80	(160)	3
Benzohydrol	Diphenyl ketone	74	(148)	94	(188)	3

Reaction conditions: 0.01×10^{-3} M of the complex, 3.0×10^{-3} M of NMO and the substrate 2.0×10^{-3} M were all added to 20 cm^3 of DMF solvent. Turnover = moles of product/moles of catalyst.

low spin d^5 $S = ½$), as is normal for ruthenium(II) and ruthenium(III) complexes, respectively [8], (table 2).



cis-$(Ru(bipy)_2L)(ClO_4)_2$ (A)



trans-$(RuCl_2L_2).Cl$ (B)

3.2. *Infrared spectra*

The infrared spectra of the ruthenium(II) and ruthenium(III) complexes were compared to those of the free ligands. The stretching vibrations of the NH_2 group and CN groups were observed near 3335 and 2225 cm^{-1}, respectively, lower than those of the corresponding free ligands. This indicates that the ligands coordintate to the ruthenium metal via nitrogen atoms of both amino and cyano groups. A single and strong band was observed for all ruthenium(III) complexes near 330 cm^{-1} assigned to the *trans*-Ru-Cl_2 group [9]. Such a band is absent in the spectra of ruthenium(II) complexes. Another weak band was observed for all complexes near 450 cm^{-1}, probably due to the ν(Ru-N) stretching vibration [10]. For all ruthenium(II) complexes, two bands were observed near 1100 cm^{-1} and 630 cm^{-1} respectively, due to perchlorate [11].

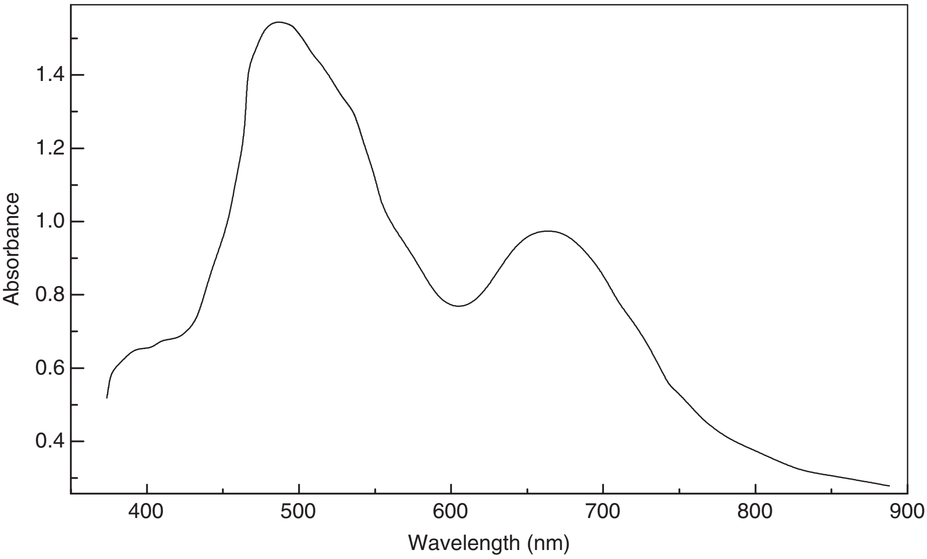


Figure 1. Electronic absorption spectrum of *trans*-$[RuCl_2(2\text{-aph})_2]Cl$ in DMF ($C \sim 3.0 \times 10^{-4}$ M).

3.3. *Electronic spectra of complexes*

The electronic spectra of all complexes are recorded in DMF solvent in the range 300–700 nm. The spectral data are listed in table 1 and representative spectra are shown in figure 1. The ground state of ruthenium(III) ion ($t_{2g}{}^5$configuration) is $^2T_{1g}$ and the first excited doublet levels in order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$ which arise from $t_{2g}{}^4\ e_g{}^1$ configuration.

Bands that were observed in the 600–670 nm region are LMCT to ruthenium(III), while bands in the 450–550 nm region have been assigned to MLCT. These results conform with assignments made for similar ruthenium(III) complexes [12].

The electronic spectra of ruthenium(II) complexes display two bands near 550 nm and 450 nm attributable to $d\pi(Ru^{II}) \rightarrow \pi^*$(bipy) (symmetric) and $d\pi(Ru^{II}) \rightarrow \pi^*$(bipy) (antisymmetric) metal ligand charge transfer transitions (MLCT) [13–16]. The band near 400 nm is due to $d\pi(RuII) \rightarrow L$ (MLCT) transitions. The higher energy bands in the UV-region are of intra-ligand $\pi \rightarrow \pi^*$ type or charge transfer transitions involving energy levels which are higher in energy than the ligands lowest unoccupied molecular orbital (LUMO).

3.4. *ESR spectra of* trans-*$[RuCl_2L_2] \cdot Cl$ complexes*

The complexes *trans*-$[RuCl_2L_2]$ are one electron paramagnetic species (low spin d^5, $S = ½$), confirming the +3 oxidation state of ruthenium. The ESR spectra for the solid complexes were recorded in DMF/toluene at 77 K, and the spectra of all complexes showed no hyperfine splitting. By ignoring the non-planarity of the carbon atoms, relative to the coordinated nitrogen atoms of the ligands, a D_{2h}-symmetry for the complexes is suggested in which the two chlorides are on the Z-axis while the

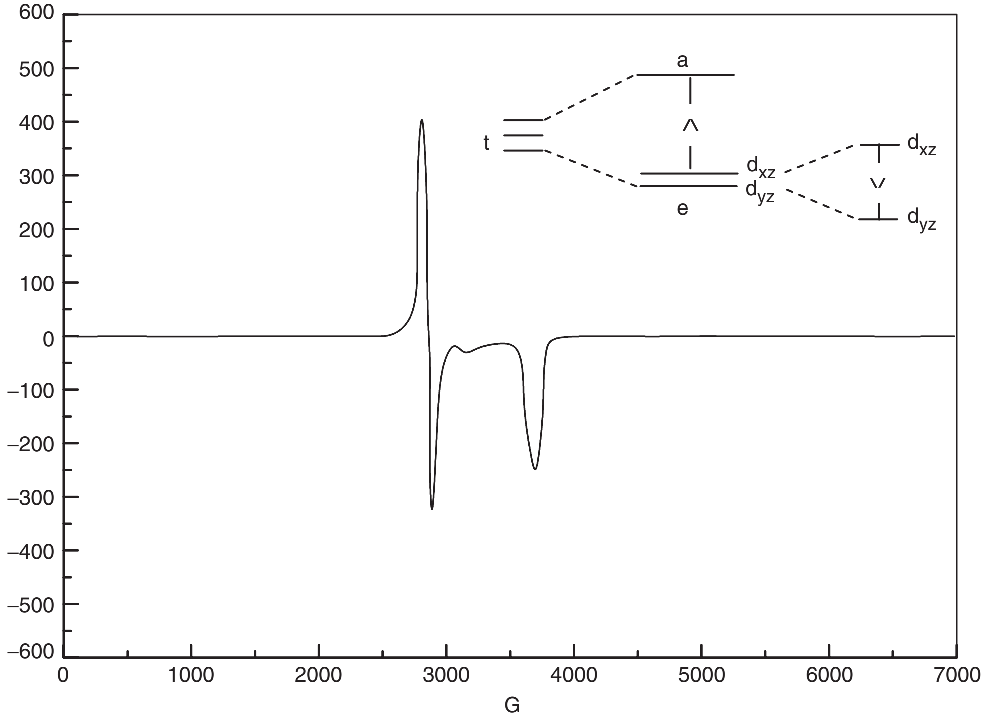


Figure 2. ESR spectrum of *trans*-[$RuCl_2$(8-hq)$_2$]Cl at 77 K in DMF/toluene.

coordinated nitrogen atoms of the ligands pass through X and Y axes (B). These complexes show a tetragonal ESR spectrum with three distinct *g*-values. The first isolated signal was found near 1.81–1.84 ($g_{\|}$ in the axial case) and two relatively close signals near 2.33–2.40 and 2.31–2.38 (rhombic component of $g_{\perp}$). Accordingly, the axial distortion Δ that splits the t_2 into a and e components is expected to be larger than the rhombic distortion V. Thus, two possible transitions are expected within these levels, $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{xz}$. These transitions could not be observed due to the presence of an intense charge transfer transition of similar energy, or it may be that the solvent used is not transparent in this region. The results of ESR spectra for all complexes are summarized in table 2 and a representative spectrum is shown in figure 2.

3.5. ^{1}*H NMR spectra*

The spectra of the complexes were recorded in $(CD_3)_2SO$ using a 300 MHz instrument. Due to the similarity of the aromatic protons signals they all appear in a narrow range. The spectra of the ruthenium(II) complexes show the aromatic proton signals within the range 7.0–8.0 ppm as overlapped signals. However, intensity measurements correspond accurately to the total number of aromatic protons in these complexes. An isolated signal was observed within the range 4.8–5.2 ppm and this signal was assigned to the amino group protons of the ligands.

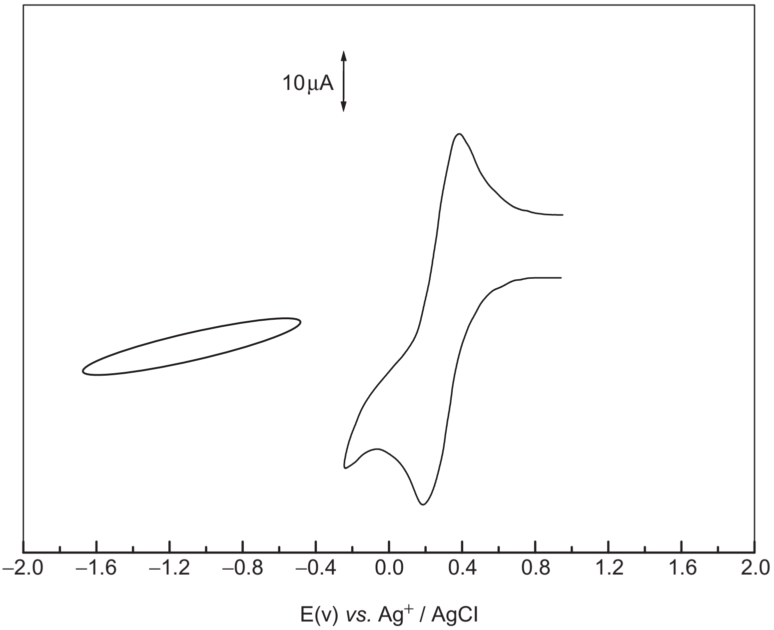


Figure 3. Cyclic voltammogram of *cis*-[Ru(bipy)$_2$(8-hq)](ClO$_4$)$_2$ (0.1 M TBAC) solute concentration $\sim 6 \times 10^{-3}$ M solute at scan rate 50 mVs^{-1} E (V) *vs.* Ag$^+$/AgCl.

3.6. *Electrochemical studies*

Electrochemical properties of all complexes have been investigated by cyclic voltammetry in DMF (0.1 M TBAC). Voltammetric data are presented in table 1 and selective voltammograms are shown in figure 3 and 4. All ruthenium(II) complexes show one reversible oxidation wave ($\Delta E = 60$–70 mV) on the positive side assigned to Ru(II)/Ru(III) oxidation with anodic peak current (i_{pa}) and cathodic peak current (i_{pc}) almost equal. Under the same conditions ruthenium(III) complexes show one reversible reduction wave ($\Delta E = 78$–90 mV) on the negative side against Ag$^+$/AgCl, and a quasi-reversible oxidation wave (ΔE 110–130 mV) on the positive side. The former is assigned to Ru(III)/Ru(II) reduction and the latter is assigned to Ru(III)/Ru(IV) oxidation. The one electron nature of these waves can be established by comparing the peak heights for each wave with that of the ferrocene–ferrocenium couple under the same conditions. Similar results were reported for octahedral ruthenium(III) complexes [9].

3.7. *Catalytic oxidation of alcohols*

Attempts to oxidize benzyl alcohol by *cis*-[RuCl$_2$(bipy)$_2$] · 2H$_2$O/NMO catalyst system were all unsuccessful since an unidentified product was found at the end, probably due to degradation of the aromatic ring by the complex [6]. Benzyl alcohol, piperonyl alcohol and benzohydrol were oxidized to benzaldehyde, pipronaldehyde and diphenylketone respectively by *cis*-[Ru(bipy)$_2$L](ClO$_4$)$_2$ · 2H$_2$O or *trans*-[RuCl$_2$(o-phd)$_2$] · Cl with NMO as co-oxidant. The catalytic oxidation reaction occurs according

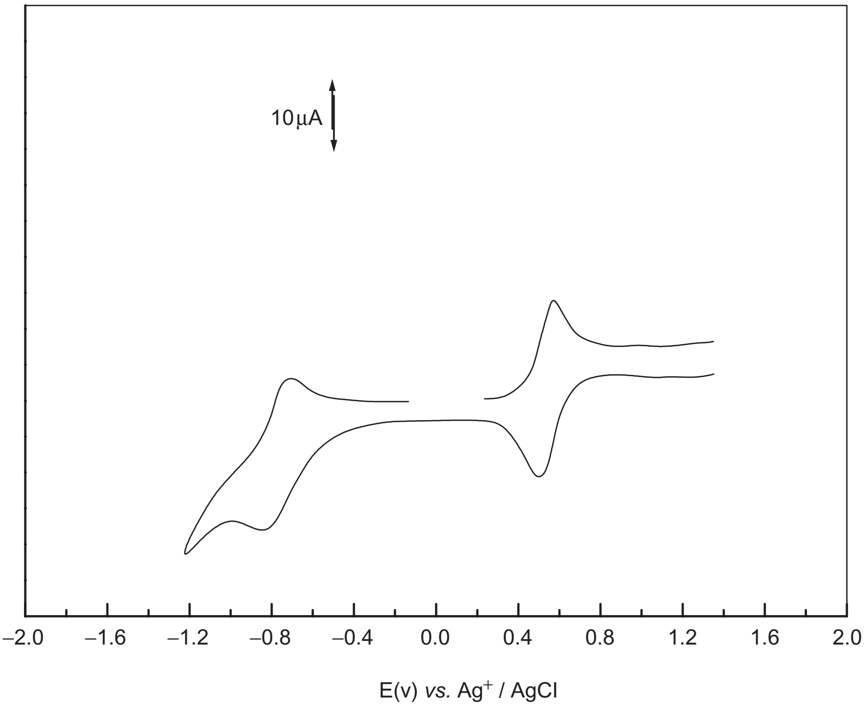


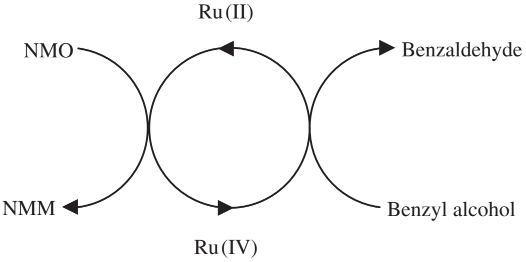
Figure 4. Cyclic voltammogram of *trans*-[$RuCl_2(2\text{-apy})_2$)]Cl (0.1 M TBAC) solute concentration ~6×10^{-3} M solute at scan rate $50\,mVs^{-1}$.

to the following equations:

$$PhCH_2OH \xrightarrow[\text{NMO}]{\text{Ru-catalyst}} PhCHO + H_2O + NMM \qquad (3)$$

In a typical experiment, a DMF solution of an excess of NMO was added to a stirred solution of an alcohol and a catalytic amount of *cis*-[$Ru(bipy)_2L](ClO_4)_2 \cdot 2H_2O$ or *trans*-[$RuCl_2$(o-phd)$_2$] · Cl in DMF. After stirring for 15 min the red color of the reaction mixture turned brown, probably due to the coordination of alcohol to ruthenium centre.

The results obtained for oxidation of these alcohols by the present catalyst system are summarized in table 3. The yields and turnovers are good; benzyl alcohol was oxidized to benzaldehyde in 70% yield and piperonyl alcohol and benzhydrol were oxidized to piperonaldehyde and diphenylketone in 65 and 74% yields, respectively. Comparisons between ruthenium(III) and ruthenium(II) complexes suggested that the same substrates were oxidized using the complex *trans*-[$RuCl_2$(o-phd)$_2$] · Cl. Yields obtained with ruthenium(III) are higher than those obtained by the ruthenium(II) complex, probably due to the higher charge of ruthenium(III). Blank experiments were carried out under the same conditions and we observed that the yield of aldehyde obtained without addition of the catalyst was less than 5%, confirming the role of ruthenium catalyst in the catalytic oxidation reaction.



Scheme 1. Catalytic cycle for oxidation of benzyl alcohol to benzaldehyde by *cis*-[Ru(bipy)$_2$(o-Pdh)](ClO$_4$)$_2$ · 2H$_2$O/NMO.

3.8. *The mechanism of catalytic oxidation of benzyl alcohol to benzaldehyde by* cis-*[Ru(bipy)$_2$L]$^{2+}$*

The hydride abstraction mechanism suggested here is a process for catalytic oxidation of benzyl alcohol to benzaldehyde by ruthenium(II) complexes. An accurate mechanistic study for reactions containing low-valent ruthenium complexes as catalysts suggests the formation of metal-oxo intermediates [17–18]. The ruthenium(II) complex reacts with NMO to produce *cis*-[Ru^{IV}O(bipy)$_2$L]$^{2+}$ and N-methylmorpholine (NMM), and the ruthenium(IV) complex *cis*-[Ru^{IV}O(bipy)$_2$L]$^{2+}$ reacts with benzyl alcohol to form *cis*-[Ru^{IV}(OH)(PhCH$_2$O)(bipy)$_2$L]$^{2+}$. In the latter complex, the hydride ion H$^-$ is abstracted from benzylate anion, PhCH$_2$O$^-$ and then coordinates with ruthenium(IV) to form *cis*-[Ru^{IV}(H)(OH)(PhCHO)(bipy)$_2$L]$^{2+}$, which is unstable, losing water and giving benzaldehyde according the following equations:

$$\textit{cis}\text{-}[\mathrm{Ru^{II}(bipy)_2L}]^{2+}4 + \mathrm{NMO} \rightarrow \textit{cis}\text{-}[\mathrm{Ru^{IV}O(bipy)_2L}]^{2+} + \mathrm{NMM} \tag{4}$$

$$\textit{cis}\text{-}[\mathrm{Ru^{IV}O(bipy)_2L}]^{2+} + \mathrm{PhCH_2OH} \rightarrow \textit{cis}\text{-}[\mathrm{Ru^{IV}(OH)(PhCH_2O)(bipy)_2L}]^{2+} \tag{5}$$

$$\textit{cis}\text{-}[\mathrm{Ru^{IV}(OH)(PhCH_2O)(bipy)_2L}]^{2+} \rightarrow \textit{cis}\text{-}[\mathrm{Ru^{IV}(H)(OH)(PhCHO)(bipy)_2L}]^{2+} \tag{6}$$

$$\textit{cis}\text{-}[\mathrm{Ru^{IV}(H)(OH)(PhCHO)(bipy)_2L}]^{2+} \rightarrow \textit{cis}\text{-}[\mathrm{Ru^{II}(bipy)_2L}]^{2+} + \mathrm{PhCHO} + \mathrm{H_2O} \tag{7}$$

This catalytic cycle continues until all the substrate is completely consumed (scheme 1).

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