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# Synthesis, spectroscopic characterization, redox properties and catalytic activity of some ruthenium(II) complexes containing aromatic aldehyde and triphenylphosphine or triphenylarsine

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# Abstract

A series of new mixed ligand penta-coordinated square pyramidal ruthenium(II) complexes containing benzaldehyde or its substituents and triphenylphosphine or triphenylarsine have been synthesized and characterized. In the electronic spectra, three well-defined peaks in the visible region were observed and assigned to d–d transitions in  $D_{4h}$  and low spin axially distortion from  $O_h$  symmetry. The spectrochemical parameters of the complexes were calculated and placed the ligands in the middle of the spectrochemical series. The redox properties and stability of the complexes toward oxidation were related to the electron-withdrawing or releasing ability of the substituent in the phenyl ring of the benzaldehyde. The electron-withdrawing substituents stabilized  $Ru^{2+}$  complexes, while electron-donating groups favored oxidation to  $Ru^{3+}$ . The mechanism and kinetics of the catalytic oxidation of benzyl alcohol by the complex  $[RuCl_2(Pph_3)(C_6H_5CHO)_2]$  in the presence of *N*-methylmorpholine-*N*-oxide have also been studied.

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# 1. Introduction

Transition metal complexes with some ligand systems containing N- and N,O-donors have been recognized as inorganic catalysts for olefin epoxidation, alcohols and aliphatic and aromatic hydroxylations [1–8]. The ruthenium(II or III) complexes containing weak donor ligands are lacking in comparison to other donor ligands [9–12]. Ruthenium(II) complexes have been characterized by their high stability mainly when ligands with donor atoms such as N, P, S, As or O are present in the coordination sphere [13,14].

Recent years have seen an upsurge of interest in finding versatile ruthenium(II) complexes that allow both catalytic and electrochemical behavior. In view of that and as a part of our continuing work on O,O-donor ligands we report herein the synthesis and characterization of some novel ruthenium(II) complexes containing triphenylphosphine (or triphenylarsine) and  $\pi$  acceptor aromatic aldehyde (Fig. 1). The nature of the electrode reactions of the prepared complexes and the oxidative behavior of one of the complexes were discussed.

#### 2. Experimental

#### 2.1. Reagents and materials

All the chemicals used are of analytical reagent grade. The reagent *N*-methylmorpholine-*N*-oxide (NMO), RuCl<sub>3</sub>·3H<sub>2</sub>O, benzaldehyde, 4-Br-benzaldehyde, anisaldehyde, *o*-phthaldehyde, triphenylphosphine (Pph<sub>3</sub>) and triphenylarsine (Asph<sub>3</sub>) were obtained from Aldrich. The complex [RuCl<sub>2</sub>(Pph<sub>3</sub>)<sub>2</sub>] was prepared as reported [15]. The supporting electrolyte tetrabutylammonium-hexafluorophosphate (TBA)<sup>+</sup>PF<sub>6</sub><sup>-</sup> was dried in vacuum before use. The solvents used were degassed and the ruthenium percentage in the complexes was determined by the reported methods [16,17]. The electrochemical measurements were carried out at 30 °C.

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Fig. 1. Atom numbering scheme of the aldehyde molecules. X=H, Y=CH<sub>3</sub>O; X=H, Y=Br and X=CHO, Y=H.

## 2.2. Physical measurements

Infrared (IR) spectra (200-4000 cm<sup>-1</sup>) as KBr discs were measured on a Matson 500 FT-IR spectrometer at room temperature. <sup>1</sup>H NMR in DMSO-d<sub>6</sub> and electronic spectra in CH<sub>2</sub>Cl<sub>2</sub> ( $\sim 5 \times 10^{-4}$  M) were recorded on a Varian Gemini VM-200 and a Unicam UV<sub>2-100</sub> UV-visible spectrometers, respectively. Cyclic voltammograms (CVs) were recorded on a potentiostate/wave generator (Oxford Electrodes) equipped with a 7000 AM X-Y recorder. A conventional three-electrode electrochemical cell was used comprising a platinum micro-cylinder working electrode, a spiral platinum wire (0.5 mm diam) as a counter electrode and Ag/AgCl reference electrode to which all potentials are referred. The electrochemical experiments were performed using a concentration of  $1 \times 10^{-3}$  mol dm<sup>-3</sup> of the complexe and  $1 \times 10^{-2}$  mol dm<sup>-3</sup> of the supporting electrolyte in CH<sub>2</sub>Cl<sub>2</sub>. The solutions of the complexes were bubbled with dry N<sub>2</sub> for 20 min before CV measurements. All microanalyses (C, H, Cl) analyses were performed on a Perkin-Elmer, 240 C elemental analyzer at Plymouth University, UK.

## 2.3. Recommended procedures

## 2.3.1. Synthesis of ruthenium(II) complexes

2.3.1.1. [RuCl<sub>2</sub>(Pph<sub>3</sub>)L<sub>2</sub>], L=HC<sub>6</sub>H<sub>4</sub>CHO, 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-CHO or 4Br-C<sub>6</sub>H<sub>5</sub>CHO. A suspension of L (2 mmol) and RuCl<sub>2</sub>(Pph<sub>3</sub>)<sub>3</sub> (0.95 g, 1 mmol) in degassed ethanol (40 cm<sup>3</sup>) was refluxed for 3 h during which the complex RuCl<sub>2</sub>(Pph<sub>3</sub>)<sub>3</sub> was dissolved and the reaction mixture was turned to brownich (or green) color. A brown or green precipitate appeared after slow evaporation of the solvent, filtered off, washed with ethanol, diethylether and finally dried in vacuum.

2.3.1.2. [RuCl<sub>2</sub>(Asph<sub>3</sub>)L<sub>2</sub>], L=HC<sub>6</sub>H<sub>4</sub>CHO or 4-CH<sub>3</sub>-OC<sub>6</sub>H<sub>4</sub>CHO. An accurate weight (0.104 g; 0.5 mmol) of hydrated RuCl<sub>3</sub> in ethanol (10 cm<sup>3</sup>) was mixed with benzaldehyde or anisaldehyde (1 mmol) and triphenylarsine (0.15 g, 0.5 mmol) in 10 cm<sup>3</sup> ethanol under constant stirring. The reaction mixture was refluxed for 2 h. Green precipitate was separated out, filtered off, washed with ethanol and finally dried in vacuum.

2.3.1.3. [RuCl<sub>2</sub>(MPh<sub>3</sub>)L'<sub>2</sub>], M=P or As, L'=2-CHO  $C_6H_4$ CHO. To a solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.21 g, 1 mmol) in degassed methanol (20 cm<sup>3</sup>), the reagent *o*-phthaldehyde (0.27 g, 2 mmol) in 10 cm<sup>3</sup> methanol was added and the reaction mixture was refluxed for 1 h. A solution of triphenylphosphine (0.25 g, 1 mmol) or triphenylarsine (0.29 g, 1 mmol) in methanol (10 cm<sup>3</sup>) was then added slowly to the hot solution with constant stirring. The resulting reaction mixture was refluxed for 2 h. On concentrating and cooling the solution, a brown or purple precipitate was separated out, filtered off, washed with diethylether and finally dried in vacuum.

#### 2.3.2. Catalytic oxidation

The catalytic activity of the prepared complexes for the oxidation of benzyl alcohol (phCH2OH) to benzaldehyde (phCHO) was tested in the presence of NMO as a co-oxidant. A typical reaction using the complex  $[RuCl_2(Pph_3)(C_6H_5CHO)_2]$  as a catalyst and BA as a substrate at 1:200 molar ratio is described as follows: A solution of  $[RuCl_2(Pph_3)(C_6H_5CHO)_2]$  (0.001 g, 0.01 mmol) in 10 cm<sup>3</sup> CH<sub>2</sub>Cl<sub>2</sub> was added to a solution of benzyl alcohol (2 mmol) and NMO (20 cm<sup>3</sup>, 3 mmol) with constant stirring. The solution mixture was refluxed for 2 h and the solvent was then evaporated from the mother liquor under reduced pressure. The solid residue was then extracted with diethylether  $(3 \times 10 \text{ cm}^3)$  and the ethereal extract was then filtered off and quantified as 2,4-dinitrophenylhydrazone derivative. The catalytic activity of the complex was determined from the percent yield (Y%) and the turnover (T.O) conversion of BA to benzaldehyde as follows:

$$Y (\%) = \frac{\text{Weight of BA oxidized to}}{\text{Total weight of BA}} \times 100$$
(1)

$$T.O = \frac{\text{mmoles of product}}{\text{mmoles of catalyst}}$$
(2)

#### 3. Results and discussion

The prepared complexes are listed in Table 1 together with their elemental analyses and colors. The complexes are green/brown, dark green and purple in color. Two types of complexes having the general formulae [RuCl<sub>2</sub>(MPh<sub>3</sub>)L<sub>2</sub>] and [Ru<sub>2</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(MPh<sub>3</sub>)<sub>2</sub>L'<sub>2</sub>] where M=P or As, L=H-C<sub>6</sub>H<sub>4</sub>CHO, *p*-Br-C<sub>6</sub>H<sub>4</sub>CHO or *p*-CH<sub>3</sub>O·C<sub>6</sub>CH<sub>4</sub>CHO and L'=*o*-CHO-C<sub>6</sub>H<sub>4</sub>CHO are formed. The proposed chemical structures of the complexes are in good agreement with the stoichiometries concluded from their analytical data (Table 1). During the course of these synthetic reactions, ruthenium(III) undergoes a

Table 1 Analytical data and color of the prepared ruthenium(II) complexes

Complex	Color	Calculated (found) %				
		C	Н	Ru	Cl	
$[RuCl_2(Pph_3)(C_6H_5CHO)_2]$	Brown	59.4 (60.2)	4.1 (4.2)	15.6 (15.34)	10.9 (11.2)	
$[RuCl_2(Pph_3)(p-CH_3OC_6H_4CHO)_2]$	Brown	57.7 (58.4)	4.3 (4.1)	14.3 (14.0)	10.0 (10.3)	
$[RuCl_2(Pph_3)(p-BrC_6H_4CHO)_2]$	Green	47.7 (48.8)	3.1 (3.4)	12.5 (12.1)	8.8 (8.6)	
$[RuCl_2(Asph_3)(p-CH_3OC_6H_4CHO)_2]$	Brown	54.4 (55.8)	4.1 (4.3)	13.4 (12.9)	9.4 (9.8)	
$[RuCl_2(Asph_3)(C_6H_5CHO)_2]$ Green		55.6 (55.1)	3.9 (3.6)	14.6 (14.1)	10.2 (9.7)	
$[Ru_2Cl_4(Pph_3)_2(H_2O)_2(o-CHOC_6H_4CHO)_2]$	Brown	54.9 (54.2)	3.6 (3.9)	17.1 (17.4)	12.5 (12.1)	
$[Ru_2Cl_4(Asph_3)_2(H_2O)_2(o-CHOC_6H_4CHO)_2]$	Brown	66.6 (66.1)	3.4 (3.2)	16.5 (15.8)	11.6 (11.2)	
[RuCl <sub>2</sub> (Pph <sub>3</sub> ) <sub>3</sub> ]	Green	49.7 (48.9)	3.4 (3.2)	23.2 (24.1)	16.3 (15.7)	

one-electron reduction and the solvent may serves as the reductant. The isolated solid complexes are stable in air at room temperature, non-hygroscopic in nature and almost insoluble in common organic solvents. The complexes are easily soluble in dichloromethane, DMF and DMSO. The conductivity measurements of the complexes fall in the range for non-electrolytes [18]. Magnetic susceptibility measurements showed that, all the complexes are diamagnetic at room temperature as expected for ruthenium(II) (low spin d<sup>6</sup>, S=0) complexes.

### 3.1. Spectroscopic studies

The IR spectra of the complexes (Table 1) displayed the characteristic bands due to triphenylphosphine at 440-455  $cm^{-1}$  or triphenylarsine at 272–295  $cm^{-1}$  [19]. The free aldehydes showed their characteristic strong carbonyl frequency  $\nu$ (C–O) in the region 1675–1710 cm<sup>-1</sup> [13,19]. In the IR spectra of the complexes, the  $\nu$ CO vibrational mode was shifted ( $\sim$ 30–40 cm<sup>-1</sup>) towards the lower frequency region from that observed for the free ligands confirming participation of the oxygen atom of the aldehyde (-CHO) group in the complex formation [13,19]. The medium IR bands between 450 and 520  $\text{cm}^{-1}$  in the spectra of the complexes are assigned to v(Ru-O) vibration [13,1,9]. The observed bands in the regions 430–470 and 320–330  $\text{cm}^{-1}$  in the mononuclear complexes (1-5) are tentatively assigned to the  $v_{Ru-Cl}$  vibrations [19]. The two bands located in the region 320–330 cm<sup>-1</sup> are consistent with  $v_{Ru-Cl}$  vibrations of the di-chloro ligands in cis- geometry as previously reported for cis-[RuCl<sub>2</sub>(Pph<sub>3</sub>)<sub>2</sub>(RCN)<sub>2</sub>] [20]. In the O-phthaldehyde complexes the presence of coordinated water molecules in the complexes (6 and 7) was confirmed by the appearance of a sharp band around 3440-3445 cm<sup>-1</sup> and two weaker bands around 700 and 850  $cm^{-1}$ . The latter two bands are safely assigned to wagging and/or rock vibrations of aqua ligands [21,22]. Therefore, in the o-phthaldehyde complexes we postulated that, the two O-phthaldehyde molecules (or the two chlorine atoms) bridge the two ruthenium(II) atoms as shown Fig. 2. This structure was also confirmed on the basis of the spectroscopic data and by the analogy with related complexes [12–14].

The <sup>1</sup>H NMR spectra of the free aldehydes and their ruthenium(II) complexes (Table 2) showed a similar pattern and are in accordance with the reported data [12,13]. The -CHO proton signal in the free aldehydes was appeared as a sharp singlet in the region  $\delta$  9.8–10.2 ppm. In the ruthenium(II) complexes, the aldehyde proton signal was shifted down field as a singlet at  $\delta$  10.0–10.25 and 10.10–10.3 ppm for mono- and o-dialdehyde, respectively. These data confirm participation of the -CHO group upon complex formation [17,18] and the structure (Fig. 2) proposed for the o-phthaldehyde complexes. Similar features have been observed for the 2-hydroxy-1-naphthaldehyde ruthenium complexes [12,23]. The de-shielding caused by the donation of the lone pair of electrons of the aldehyde oxygen atom to the central metal ion could account for the observed chemical shift in the<sup>1</sup>H NMR spectra [22,24]. The observed signal



Fig. 2. Proposed chemical structure of the binuclear O-phthaldehyde ruthenium(II) complex [RuCl<sub>2</sub>(MPph<sub>3</sub>)(o-CHO-C<sub>6</sub>H<sub>4</sub>CHO)]<sub>2</sub>, M=P or As.

Table 2
Significant IR-vibrational frequencies (cm <sup>-1</sup> ) and <sup>1</sup> H NMR ( $\delta$ ppm) of the ruthenium(II) complexes with relevant bands of the free aldehyde in parentheses

Complex	νсο	$\nu_{Ru-O}$	$\nu_{Ru-Cl}$	$\nu_{Ru-P}$	$\nu_{Ru-As}$	Complexed H <sub>2</sub> O	δ (ppm)
1	1685(s), (1715)	480(m)	460(s)	445			10.12, 7.2, 7.58, 7.5
2	1675(s),(1710)	450(m)	430(s)	451			10.20, 6.90, 7.36, 7.3, 3.9, (10.1), (7.12), (7.4),
							(3.92)
3	1700(s), (1730)	505(m)	450(s)	455			10.20, 6.98, 7.5, 7.46
4	1795, (1735)	520(m)	445(s)	440			10.25, 7.38, 7.4, 7.3, 3.8
5	1690, (1730)	490(m)	465(s)		272		10.2, 7.25, 7.52, 7.5
6	1710(s), (1745)	510(m)	470		285	3440(s), 850(w), 700(w)	10.16, 7.28, 7.6, 7.6, (9.85), (7.10), 7.56, 7.50
7	1710(s), (1745)	510(m)	470(s)		295	3445(m, br), 860(w), 705(w)	10.3, 7.01, 7.6, 7.5
8			475	455	295		

\* s, strong; m, medium; br, broad and w, weak.

at  $\delta$  3.8–3.94 ppm in the anisaldehyde and its complexes is attributed to the methoxy proton [22,25]. This proton undergoes deshielding to a magnitude of 0.45 ppm in the complexes supporting the involvement of the -CHO group in the complex formation. The resonance arising from H<sub>3</sub> and H<sub>5</sub> (see Fig. 1 for atom numbering scheme) in the mono aldehydes were shifted as double-doublet (7.1-7.6 ppm) to high field to a greater extent than  $H_2$  and  $H_6$  (7.4–7.9 ppm). A sharp multiplet signal in the range  $\delta$  6.90–7.29 ppm was observed and was attributed to the pph<sub>3</sub> or Asph<sub>3</sub> protons. In the free benzaldehyde and O-phthaldehyde ligands, the H<sub>3</sub>, H<sub>4</sub> and H<sub>5</sub> protons appeared as doublets at 7.3, 8.1 and 7.9 ppm. In the complexes, the signals arising from  $H_3$ ,  $H_5$ and H<sub>6</sub> protons were observed at high field similar to that reported for  $Sb^{3+}$  and  $Zn^{2+}$  complexes with similar ligands [23]. This behavior is most likely due to the decreasing in the electronic density of the aromatic ring of the coordination. The multiple peaks of the substituted aromatic protons resonate in the region  $\delta$  7.15–7.20 ppm due to one bound triphenylphosphine (or triphenylarsine) and two inequivalent aldehyde ligands. These data confirmed that the Pph<sub>3</sub> or AsPh<sub>3</sub> and chloride ligands are mutually cis- as reported for similar geometry of ruthenium(II) complexes [26,27].

The UV–visible spectra of the complexes are similar to those observed for other analogous of low spin penta-coordinated square pyramidal ruthenium(II) complexes [26,27]. The spectral of the complexes with their ligand field parameters ( $10D_q$ , B) in CH<sub>2</sub>Cl<sub>2</sub> are summarized in Table 3. The spectra of these complexes are similar and displayed three well bands in the range (16.9-17.8)× $10^3$ ,

 $(19.4-23.6) \times 10^3$  and  $(24.9-27.6) \times 10^3$  cm<sup>-1</sup>. The molar extinction coefficients of these bands are low relative to those of metal to ligand charge transfer (MLCT) transition [27]. Assuming that, the complexes belong to D<sub>4</sub> or low spin axially distortion from octahedral symmetry, the first two bands (Table 3) are safely assigned to the  $v_1$  $({}^{1}A_{1g} \rightarrow {}^{1}E_{2g})$  and  $v_2$   $({}^{1}A_{1g} \rightarrow {}^{1}A_{2g})$  d–d transitions in the range corresponding to the spin allowed transitions from the lower frequency side [26,28]. The third peak is possibly assigned to a contribution form the spin forbidden d–d  $v_3$  ${}^{1}T_2({}^{1}A_{1g} \rightarrow {}^{1}E)$  besides the CT transition (Ru<sup>2+</sup>  $\rightarrow$  ligand), respectively [28].

The bands (or shoulder) observed in the range  $(34.01-40.5)\times 10^3$  and  $(32.1-32.8)\times 10^3$  cm<sup>-1</sup> in the UV-region are safely assigned to intraligand (IL)  $\pi \rightarrow \pi^*$  type of CT transitions of the carbonyl group of the ligands or an allowed Ru<sup>2+</sup> $\rightarrow$ Cl transitions [29,30]. The in-equivalence of the ligands decreased the ligand field strength of the complexes as compared with [RuCl<sub>2</sub>(MPh<sub>3</sub>)<sub>3</sub>]. This effect reduces the energy gap between Ru ( $d\pi$ ) and ligand ( $\pi^*$ ) orbitals [27,30]. Thus, substitution of one or two  $\pi$  acidic MPh<sub>3</sub> ligand in the complex [RuCl<sub>2</sub>(MPh<sub>3</sub>)] by one di or two mono-aldehyde ligand decreased the MLCT energy.

The spectrochemical parameters  $10D_q$  and B (Table 3) were found in the range 1461–1614 and 616.2–465.6 cm<sup>-1</sup>, respectively. The  $D_q$  values are far closer to the range observed for RuCl<sub>2</sub>P<sub>3</sub> (or As<sub>3</sub>) and slightly closer to the RuO<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub> or RuO<sub>2</sub>Cl<sub>2</sub>As<sub>2</sub> [27]. These data confirm the coordination of chlorine, oxygen and P (or As) atoms. The  $10D_q$  values also placed the ligands in the middle range of

Table 3

Electronic spectral data (cm<sup>-1</sup>) and molar absorptivity in parentheses of the prepared complexes with ligand field parameters in CH<sub>2</sub>Cl<sub>2</sub> solution<sup>a</sup>

Complex	$\pi \rightarrow \pi^*, n \rightarrow \pi^* \times 10^3$	$^{1}A_{1} \rightarrow ^{1}E_{2}, \nu_{1} \times 10^{3} (\log \varepsilon)$	$^{1}A_{1} \rightarrow ^{1}A_{2}, \nu_{2} \times 10^{3} (\log \varepsilon)$	$^{1}A_{1} \rightarrow ^{1}E, \nu_{3} \times 10^{3} (\log \varepsilon)$	В	$10D_{q} (cm^{-1})$
1	40.48, 35.84	17.85 (2.6)	19.80 (3.32)	24.69 (3.51)	427.5	1614
2	40.84, 35.84	17.24 (2.57)	19.42 (3.47)	24.69 (3.6)	465.6	1538
3	40.48, 35.84	17.70 (2.72)	19.80 (3.21)	24.69 (4.1)	436.8	1595
4	34.01, 32.15	16.92 (2.74)	23.20 (4.3)	27.10 (4.8)	636.2	1445
5	35.33, 32.78	17.24 (2.6)	23.58 (4.12)	27.77	658.1	1461
6	40.0, 35.71	17.54 (2.91)	22.22 (sh) (3.96)	24.69 (4.92)	446.8	1575
7	34.48, 32.36	17.24 (2.98)	21.27 (4.21)	27.10 (4.96)	616.2	1475

<sup>a</sup> Logarith molar absorptivity of each absorption band is given in parentheses.

Table 4 Cyclic voltammetric data of the prepared ruthenium(II) complexes in dichloromethane–(TBA) $PF_6$  solutions

Complex	Mph <sub>3</sub> rec	luction	Ru <sup>II</sup> /Ru <sup>II</sup>	I	Ru <sup>III</sup> /Ru <sup>IV</sup>	
	$E^{\circ}$	$\Delta E_{\rm p}$	$E^{\circ}$	$\Delta E_{\rm p}$	$\overline{E^{\circ}}$	$\Delta E_{\rm p}$
1	-0.460	0.68	0.15	0.50	0.60	0.62
2	-0.630	0.130	-0.54	0.40	0.73	0.47
3	-0.80	0.80	-0.45	0.38	0.550	0.80
4	-0.70	0.9	0.25	0.86	0.98	0.216
5	-0.92	0.84	-0.170	0.06	0.66	0.960
6	-0.28	0.140	0.075	0.170	0.360	0.20
7	-0.570	0.180	-0.30	0.180	0.660	0.30
8	-0.65	0.210	0.26	0.210	0.52	0.26

the spectrochemical series and provided reassurance that the aldehyde oxygen of the ligands was coordinated to ruthenium(II) ions. The B values of the complexes (Table 3) were found in the range 56–74% of that of the free ion [27] indicating considerable overlap with strongly covalent metal–ligand bond [27,28]. The decrease in B values is most likely associated with the reduction in the nuclear charge on the cation.

#### 3.2. Redox properties

The CVs of the complexes were studied versus Ag/AgCl in CH<sub>2</sub>Cl<sub>2</sub>-(TBA)PF<sub>6</sub> solutions. The electrochemical response of the complexes RuCl<sub>2</sub>(Mph<sub>3</sub>)L<sub>2</sub> were found similar and displayed three well defined electrode couples in the range  $E^{\circ} = -0.92$  to -0.46 V.  $E^{\circ} = -0.54$  to +0.26 V and  $E^{\circ}=0.52$  to 0.98 V versus Ag/AgCl electrode (Table 4), respectively. Representative voltammograms are also shown in Fig. 3. The ratio of  $i_c/i_a$  due to cathodic and anodic sweeps was found not close to unity at the scan rates (50-200 mV s<sup>-1</sup>). The potential difference ( $\Delta E_p = E_a - E_c$ ) of the first electrode couple increased with increasing the scan rate. This behavior was reported for related complexes confirming the occurrence of a slow chemical reaction following the electrode process [26]. Thus, the electron transfer process is irreversible, the mass transfer is limited and the species that initially formed in the electrode process may also react further to give products that are not reoxidized at the same potential as the first formed species [31]. A possible mechanism account for one electron reduction of the coordinated Mph<sub>3</sub> could be proceeded as follows:

$$\operatorname{Ru}^{II}\operatorname{Cl}_{2}(\operatorname{Mph}_{3})L_{2} + e^{-} \rightarrow [\operatorname{Ru}^{II}\operatorname{Cl}_{2}(\operatorname{Mph}_{3})L_{2}]^{-}$$
(3)

The reduction wave, which is expected to occur at much more negative potential for the aldehyde ligand (L) is not observed owing to solvent cut-off.

The one electron nature of the second irreversible electrode couple (0.54–0.26 V) has been established by comparing its current height with those of the electrode couple  $Ru^{II}/Ru^{III}$  displayed by other analogous ruthenium(II) [30]



Fig. 3. CVs of  $[RuCl_2(Pph_3)(p-BrC_6H_4CHO)_2]$ , (a) and  $RuCl_2(Asph_3)(p-CH_3OC_6H_4CHO)_2$ , (b) in dichloromethane–(TBA)PF<sub>6</sub> solution vs. Ag/AgCl electrode.

complexes. Thus, this electrode couple is safely assigned to  $Ru^{II}/Ru^{III}$  oxidation as follows:

$$Ru^{II}Cl_2(Mph_3)L_2 \rightarrow [Ru^{III}Cl_2(Mph_3)L_2]^+ + e^-$$
(4)

The potential of this couple was found not sensitive to the nature of the substituent in the *para*-position of the aldehyde ligand. The electrode potential ( $E^{\circ}$ ) slightly increased with increasing electron-withdrawing character. The plot of  $E^{\circ}$  versus Hammett constant (2 $\partial$ ) [32] of the para-substituent in the aldehyde was found linear.

The irreversible one electron metal-centered oxidation in the potential range 0.52–0.98 V is safely assigned to the  $Ru^{III}/Ru^{IV}$  oxidation [30] as follows:

$$[Ru^{III}Cl_2(Mph_3)L_2]^+ \to [Ru^{IV}Cl_2(Mph_3)L_2]^{2+} + e^{-} (5)$$

The oxidation potential of this couple correlates linearly with the Hammett constant ( $\partial$ ) of *p*-substituent and the  $E^{\circ}$  of this couple is sensitive to the nature of *p*-substituent compared with Ru<sup>II</sup>/Ru<sup>III</sup>. The data also confirm that the electron-withdrawing groups attached to the aldehyde moiety stabilize the Ru<sup>II</sup> complexes while electron-donating groups favor oxidation of Ru<sup>III</sup>.

## 3.3. Catalytic oxidation

The applications of ruthenium(II) complexes as an inexpensive and easy to handle co-oxidant for selective oxidation of alcohols are well known in the literature [12,33]. No oxidation of benzyl alcohol to benzaldehyde was achieved employing NMO only. Thus, the catalytic oxidation of benzyl alcohol to phCHO by the precursor catalyst  $[RuCl_2(Pph_3)(C_6H_5CHO)_2]$  in the presence of NMO (1:200 molar ratio of catalyst to substrate) at room temperature in dry CH<sub>2</sub>Cl<sub>2</sub> was carried out. Excellent experimental yield  $(70\pm5\%)$  with good turnover (140±2) of BA to BCHO was successfully achieved. These results are better as compared with the data reported for  $[Ru^{II}(bpy)_2acac]PF_6$ ,  $[Ru^{II}(bpy)_2Cl_2]IO_4$ , [Ru<sup>II</sup>Cl<sub>2</sub>(Pph<sub>3</sub>)<sub>3</sub>] and Ru<sup>II</sup> complexes of 1,1'-bis isoquinoline (BIQN) [32,33]. The formation of benzaldehyde was confirmed by the formation of 2,4-dinitrophenylhydrazone.

The mechanism of oxidation of benzyl alcohol to benzaldehyde by the catalyst [RuCl<sub>2</sub>(Pph<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>CHO)<sub>2</sub>] in the presence of the co-oxidant could be proceeded via the formation of  $\mu$ -peroxoruthenium(IV) intermediate species which are capable to abstract hydrogen atom from the OH group in benzyl alcohol (Scheme 1). This mechanism is similar to that reported for [RuBr<sub>2</sub>(Pph<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>CHO)<sub>2</sub>], [Ru<sup>II</sup>Cl<sub>2</sub>(Pph<sub>3</sub>)<sub>3</sub>], [Ru<sup>II</sup>(terpy)(BIQN)Cl]ClO<sub>4</sub> and [R(trPy)(R<sub>2</sub>dppi)O]<sup>2+</sup> complexes [34,35], where terpy=2,2,6,2-terpyridine; H<sub>2</sub>dppi=3,6-bis(pyrid-2-yl) pyridazine and trpy=2,22terpyridine The reaction velocity of this type of reactions always shows first-order kinetics in terms of the amount of unconsumed benzyl alcohol [36].



Scheme 1.

#### 4. Conclusions

The weak O-donor aromatic aldehydes coordinate to ruthenium(II) ions. The mono- and di-aldehydes tend to impose penta-coordinated square-based pyramidal and octahedral coordination sphere, respectively, at the metal centers as a consequence of the reduced conformational flexibility caused by the presence of Pph<sub>3</sub> (or AsPh<sub>3</sub>). Substitution of the hard O- or Br-donor atom in the *para*-position of the benezaldehyde facilitates the redox properties. The catalytic reactivity of the complex [RuCl<sub>2</sub>(Pph<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>CHO)<sub>2</sub>] towards oxidation of benzyl alcohol was found higher than that reported for N,N- and some N,O-neutral ligands under similar conditions [33]. Further experiments are currently in progress to explore the mechanism and kinetics of the catalytic activity of some other complexes of this series.

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