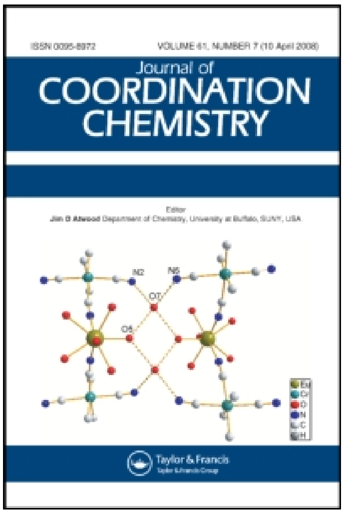


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and catalytic properties of ruthenium(III) complexes containing 4-hydroxy-3-(<i>p</i>-X-phenylazo)-benzopyrane-2-one

Abdel-Ghany F. Shoair[a]
[a] Faculty of Science, Department of Chemistry, Mansoura University, Egypt

To cite this Article Shoair, Abdel-Ghany F.(2007) 'Synthesis, characterization and catalytic properties of ruthenium(III) complexes containing 4-hydroxy-3-(**<i>p</i>**-X-phenylazo)-benzopyrane-2-one', Journal of Coordination Chemistry, 60: 10, 1101 — 1109

To link to this Article: DOI: 10.1080/00958970601003797

URL: http://dx.doi.org/10.1080/00958970601003797

Journal of Coordination Chemistry
Vol. 60, No. 10, July 2007, 1101–1109

Taylor & Francis
Taylor & Francis Group

Synthesis, characterization and catalytic properties of ruthenium(III) complexes containing 4-hydroxy-3-(*p*-X-phenyl-azo)-benzopyrane-2-one

ABDEL-GHANY F. SHOAIR*

Faculty of Science, Department of Chemistry, Mansoura University, 34517 Domiat El-Gadida, Egypt

(*Received 16 August 2006; in final form 12 September 2006*)

Ruthenium(III) complexes of the type *trans*-$[Ru(L)_2(AsPh_3)_2]Cl$ (L = mono anions of 4-hydroxy-3-(*p*-X-phenylazo)-benzopyrane-2-one derivatives (For L_1, X = H; L_2, X = CH_3; L_3, X = Cl; and L_4, X = NO_2; $AsPh_3$ = triphenylarsine) have been synthesized and characterized by elemental analysis, spectroscopic (IR, UV-VIS and ESR), magnetic and cyclic voltammetric techniques. The mechanism and the catalytic oxidation of benzyl alcohol, cyclohexanol and cinnamyl alcohol by *trans*-$[Ru(L_1)_2(AsPh_3)_2]Cl$ with hydrogen peroxide as co-oxidant were described.

Keywords: Ruthenium complexes; Catalytic oxidation; Hydrogen peroxide

1. Introduction

As a part of our continuing work on the synthesis, characterization and applications of ruthenium complexes for specific oxidation of organic compounds [1–6], it was observed that changes in ligands, co-oxidants and reaction conditions had profound effects on selectivity and activity of the ruthenium catalysts as well as the yield of the organic products obtained. The synthesis and characterization of the complexes $[RuCl_2(PPh_3)_2(OCHC_6H_5\text{-}R)_2]$ (R = H, CH_3, CH_3O, Cl and Br) have already been reported; $[RuCl_2(PPh_3)_2(OCHC_6H_5)_2]$ catalytically oxidizes benzyl alcohol to benzaldehyde at room temperature in the presence of *N*-methymorpholine-*N*-oxide (NMO) as co-oxidant [4]. In earlier work the ruthenate-persulfate reagent, *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ was prepared and the catalytic oxidation benzylamine to benzonitrile by this reagent was carried out [5]. Recently, we reported the catalytic oxidation of piperonyl alcohol to piperonaldehyde by *trans*-$[RuCl_2(o\text{-phd})_2]Cl$ (*o*-phd = ortho-phenylenediamine) in the presence of *N*-methymorpholine-*N*-oxide (NMO) as co-oxidant at room temperature [1].

---

*Email: shoairaksm@hotmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970601003797

Although a wide variety of ruthenium-catalyzed systems have been developed for catalytic oxidation of alcohols [7], there are few reports on ruthenium-catalyzed oxidation of alcohols with hydrogen peroxide as co-oxidant [8]. We seek a new methodology for catalytic oxidation of alcohols with benign co-oxidants such as hydrogen peroxide, since it is cheap and gives water as the sole by-product at the end of the catalytic oxidation reactions [9–10]. In this article, we report the synthesis and characterization of ruthenium(III) complexes *trans*-$[Ru(L)_2(AsPh_3)_2]Cl$. This article gives an account of the investigation of the catalytic oxidations of benzyl alcohol, cyclohexanol and cinnamyl alcohol by *trans*-$[Ru(L_1)_2(AsPh_3)_2]Cl$ with hydrogen peroxide as co-oxidant at room temperature.

2. Materials and methods

2.1. *Chemicals*

Ruthenium trichloride, hydrogen peroxide, triphenylarsine and tetrabutylammonium chloride (TBAC) were directly obtained from Aldrich and used without further purification. Benzyl alcohol, cyclohexanol and cinnamyl alcohol were obtained from Fluka. Other chemicals and solvents were also of reagent grade and used as received.

2.2. *Instrumentation*

Infrared spectra were recorded on a Matteson 5000 FT-IR and electronic spectra were recorded on a UV-Visible Lamba 2S spectrometer (Perkin Elmer). Microanalysis was carried out at the Cairo University Microanalytical Unit. Magnetic measurements were carried out at room temperature on a Johnson Matthey magnetic susceptibility balance using Gouy's method. The EPR spectra were recorded on a 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 was used as supporting electrolyte (concentration $\sim 1.0 \times 10^{-3}$ M). The half-wave potential $E_{1/2}$ was set equal to $0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} were the anodic and cathodic cyclic voltammetric peak potentials. The electrochemical experiments were carried out in a dinitrogen atmosphere at room temperature.

2.3. *Preparation of novel azo-dye ligands*

Novel azo-dye ligands were prepared according to the following procedure:

Aniline or its para-substituted derivatives (10 mmol) were dissolved in hydrochloric acid (25 mmol/25 cm^3 distilled water). The aniline salts produced were diazotized below $-5°C$ with a solution of sodium nitrite (80 mg, 10 mmol, 30 cm^3 distilled water). The obtained diazonium salts were coupled with a pyridine solution of 4-hydroxycoumarin (1660 mg, 10 mmol/5 cm^3 pyridine). The crude dyes were collected by filtration, crystallized from dimethylformamide and dried in a vacuum dessicator over P_2O_5. The azo-dye ligands were checked by melting points, IR and ^1H NMR.

2.4. *Preparation of trans-[Ru(L)$_2$(AsPh$_3$)$_2$]Cl complexes*

$RuCl_3 \cdot nH_2O$ (240 mg, 1 mmol) was refluxed in ethanol (20 cm^3) until the initial black color turned green and a dimethylformamide solution of the ligand (2.5 mmol in 5 cm^3 DMF) was added with refluxing, followed by further addition of an ethanolic solution of triphenylarsine (610 mg, 2 mmol). Brown microcrystals were formed which 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. *Catalytic oxidation of alcohols by trans-[Ru(L$_1$)$_2$(AsPh$_3$)$_2$]Cl/H$_2$O$_2$*

The oxidation of benzyl alcohol is typical.

To a solution of the catalyst *trans*-[Ru(L$_1$)$_2$(AsPh$_3$)$_2$]Cl ($1.28 \times 10^{3-}$ mg, 0.01 mmol in 5 cm^3 dimethylformamide), benzyl alcohol (2 mmol) was added with stirring. Hydrogen peroxide (20 cm^3, 30%) was then added dropwise within half an hour and the reaction mixture was further stirred for 5 h at room temperature. The mixture was reduced *in vacuo* and the residues were collected in diethylether, filtered through a bed of silica gel and dried over anhydrous $MgSO_4$. The carbonyl compounds formed were isolated and quantified as their 2,4-dinitrophenylhydrazone derivatives.

3. Results and discussion

3.1. *Synthesis of complexes*

The azo-dye ligands obtained through coupling of the diazonium salts of aniline and its para derivatives (*p*-Cl, *p*-CH_3 and *p*-NO_2) with 4-hydroxy-3H-benzopyrane-2-one (4-hydroxycoumarin), react with $RuCl_3 \cdot nH_2O$ in a refluxing dimethylformamide (DMF)/ethanol mixture and, in the presence of two equivalents of triphenylarsine yield complexes of the type *trans*-[Ru(L)$_2$(AsPh$_3$)$_2$]Cl according to the following equation:

$$RuCl_3 \cdot nH_2O + 2LH + 2AsPh_3 \rightarrow \textit{trans}\text{-}[Ru(L)_2(AsPh_3)_2]Cl + 2HCl$$

The ligands are asymmetrical bidentate and coordinate through nitrogen of the azo and oxygen of the hydroxy. Hence, the complexes *trans*-[Ru(L)$_2$(AsPh$_3$)$_2$]Cl have D_{2h}-symmetry as shown in figure 1. The composition of these complexes has been confirmed by elemental analysis and magnetic susceptibility measurements show that the complexes *trans*-[Ru(L)$_2$(AsPh$_3$)$_2$]Cl are paramagnetic ($\mu_{\text{eff}} = 1.85-2.1$ BM, low spin d^5 $S = 1/2$), as normal for ruthenium(III) complexes in an octahedral environment [11] (table 1).

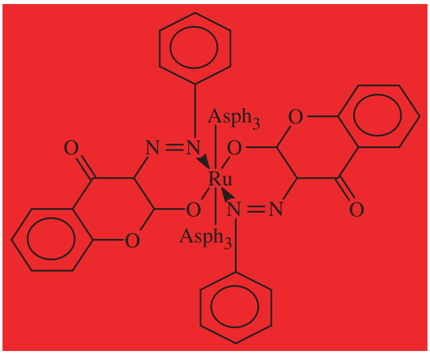


Figure 1. Structure of *trans*-$[Ru(L_1)_2(AsPh_3)_2]Cl$ complexes (–NO = monoanion of the ligand).

Table 1. Elemental and infrared data for the ruthenium(III) complexes *trans*-$[Ru(L)_2(AsPPh_3)_2]Cl$. ($L = L_1$, L_2, L_3 and L_4).

Analytical data found (Calcd)			Infrared data (cm^{-1})					
Complex	C%	H%	N%	ν(OH)	ν(N=N)	ν(C–O)	ν(CO)	ν(Ru–N)
HL_1	67.8 (67.7)	4.0 (3.8)	10.6 (10.5)	3440	1610	1260	1690	–
$[Ru(L_1)_2(AsPPh_3)_2]Cl$	61.5 (61.9)	4.1 (3.9)	4.5 (4.4)	–	1600	1290	1691	440
HL_2	68.8 (68.6)	4.5 (4.3)	10.2 (10.0)	3442	1605	1270	1685	–
$[Ru(L_2)_2(AsPPh_3)_2]Cl$	62.4 (62.4)	4.2 (4.1)	4.5 (4.3)	–	1595	1295	1685	440
HL_3	59.5 (59.9)	3.2 (3.0)	9.5 (9.3)	3452	1600	1265	1680	–
$[Ru(L_3)_2(AsPPh_3)_2]Cl$	58.5 (58.7)	3.8 (3.6)	4.5 (4.2)	–	1596	1293	1681	450
HL_4	57.6 (57.9)	3.1 (2.9)	13.5 (13.5)	3430	1608	1267	1680	–
$[Ru(L_4)_2(AsPPh_3)2]Cl$	57.6 (57.8)	3.5 (3.5)	6.3 (6.1)	–	1590	1310	1680	435

3.2. *Infrared spectra*

Coordination of the ligands to ruthenium were assigned through comparison of the infrared spectra of the ruthenium(III) complexes with the spectra of the free ligands and 4-hydroxy-3H-benzopyrane-2-one(4-hydroxycoumarin). The ligands are likely to be present in two isomeric forms (I and II) and their spectra display bands near 3330–3450, 1690 and 1600 cm^{-1}, assigned to the stretching vibrations of ν(OH), ν(CO) and ν(N=N) respectively. The absorption due to carbonyl of the pyrane ring remains unaltered in the spectra of the complexes indicating non-involvement of the carbonyl group in coordination. The spectra of the ligands showed strong bands in the range 1250–1270 cm^{-1}, assigned to the phenolic stretching vibration of ν(C–O). The existence of ν(OH) as a broad band in the spectra of the ligands indicates the presence of hydrogen bonding as shown in figure 2.

The presence of intramolecular hydrogen bonding is also supported by the existence of broad weak bands in the range 2600–1990 cm^{-1} attributable to $O–H \cdot N$ stretching and bending vibrations [12].

Bands due to $O–H \cdot N$ disappeared and the stretching frequencies of ν(C–O) were shifted to higher frequencies 1279–1310 cm^{-1} in the spectra of all complexes, indicating deprotonation of hydroxy and coordination of the phenolic oxygen to the

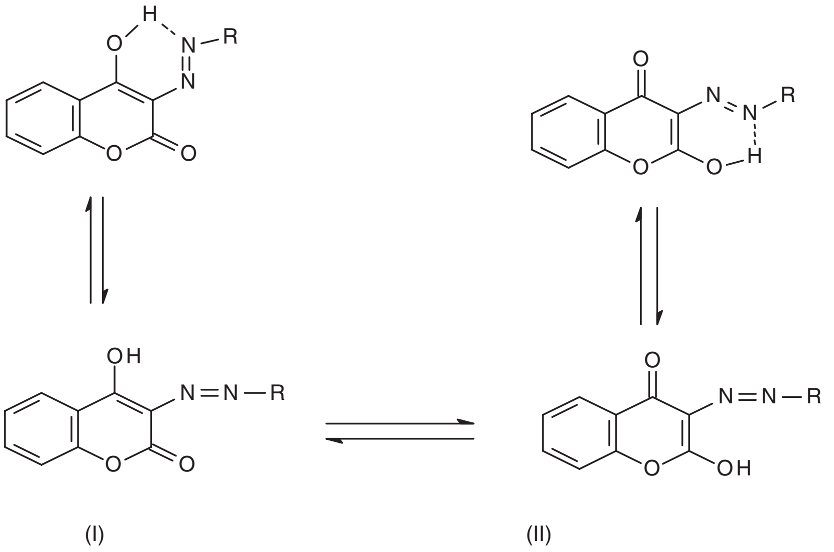


Figure 2. General formula of the ligands (LH) and their hydrogen bonding. (R = C_6H_5, *p*-CH_3-C_6H_4, *p*–Cl–C_6H_4 and *p*-NO_2-C_6H_4).

ruthenium centre. The stretching frequencies of *ν*(N=N) were observed at lower frequencies than those found in the spectra of the ligands, indicative of the coordination of the azo-nitrogen to ruthenium centre. These results are supported by the appearance of a new weak band at about 454 cm^{-1} attributable to *ν*(Ru–N). In addition to the above, three strong bands were also observed in the spectra of all complexes near 529, 697 and 740 cm^{-1} which are attributable to the coordinated triphenylarsine.

3.3. *Electronic spectra*

The electronic spectra of all complexes were recorded in dimethylformamide in the range of 300–700 nm. The spectral data are listed in table 2. Bands observed in the 600–670 nm region have been assigned to d–d transitions, while bands in the 450–500 nm region have been assigned to charge transfer transitions. These results are in conformity with assignments for similar ruthenium(III) complexes [13].

3.4. *ESR spectrum of trans-[Ru(L_1)$_2$(AsPh_3)$_2$]Cl*

The complex *trans*-[Ru(L_1)$_2$(AsPh_3)$_2$]Cl can be characterized as one electron paramagnetic species (low spin d^5, $S = ½$). The ESR spectra for the solid complexes were measured in dimethylformamide/toluene at 77, where it was observed that the spectrum of *trans*-[Ru(L_2)$_2$(AsPh_3)$_2$]Cl (figure 3) showed no hyperfine splitting, while other complexes gave bad spectra. By ignoring the non-planarity of the carbon atoms, relative to the coordinated nitrogen and oxygen atoms of the ligands, a D_{2h}-symmetry for the complex is suggested in which the two triphenylarsine ligands pass through the Z axis while the coordinated nitrogen and oxygen atoms of the ligands pass through only X and Y axes as shown in figure 1. In light of the suggested stereochemistry, we visualize a rhombic ESR spectrum with three distinct *g*-values. The first isolated signal was found at 1.93 ($g_{\|}$ in the axial case) and two relatively close signals at 2.31 and 2.38 (rhombic component of $g_{\perp}$) confirming the axial symmetry and indicating a tetragonal distortion for the octahedral complex [14].

3.5. *Redox properties*

Electrochemical properties of all complexes were investigated by cyclic voltammetry in a dimethylformamide solvent (0.1 M TBAC). Voltammetric data are presented in table 2 and a selective voltammogram is shown in figure 4. All ruthenium(III) complexes show one irreversible reduction wave ($\Delta E = 240$–$280\,\text{mV}$) on the negative side against $Ag^+/AgCl$, and an irreversible oxidation wave ($\Delta E = 160$–$300\,\text{mV}$) 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 ($\Delta E = 230\,\text{mV}$, $E_{1/2} = 440\,\text{mV}$ and $I_{pa}/I_{pc} = 0.98$) under

Table 2. Magnetic, UV-VIS and cyclic voltammetric data for the ruthenium(III) complexes.

			Ru(III)/Ru(II) (mV)				Ru(III)/Ru(IV) (mV)			
Complex	μ_{eff} (BM)	λ_{max} (cm^{-1})	E_{pa}	E_{pc}	ΔE	$E_{1/2}$	E_{pa}	E_{pc}	ΔE	$E_{1/2}$
$[Ru(L_1)_2(AsPh_3)_2]Cl$	1.92	640, 450	680	400	280	540	620	360	260	490
$[Ru(L_2)_2(AsPh_3)_2]Cl$	2.1	612, 490	660	440	220	550	600	300	300	450
$[Ru(L_3)_2(AsPh_3)_2]Cl$	1.85	650, 444	620	380	240	500	600	400	200	500
$[Ru(L_4)_2(AsPh_3)_2]Cl$	1.89	670, 433	580	320	260	450	640	480	160	560

Conditions: supporting electrolyte, tetrabutyammonium chloride (0.1TBAC), the concentration of the complex $\sim 6 \times 10^{-3}$ 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.

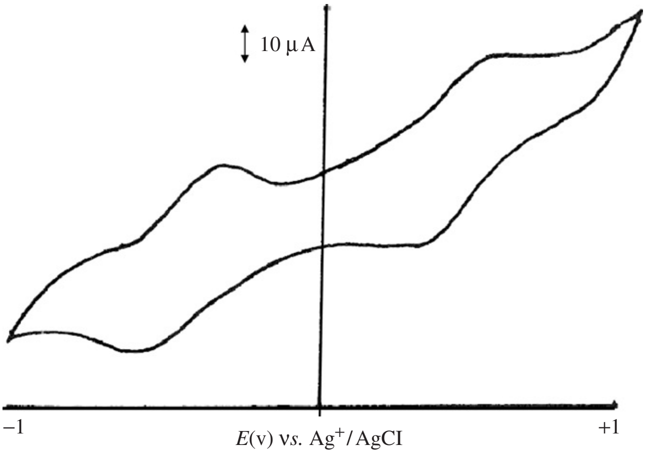


Figure 3. Cyclic voltammogram of $\sim 6 \times 10^{-3}$ M *trans*-$[Ru(L_2)_2(AsPPh_3)_2]Cl$ in 0.1 M TBAC in dimethylformamide at 298 K scan rate $50\,\text{mV}\,\text{s}^{-1}$.

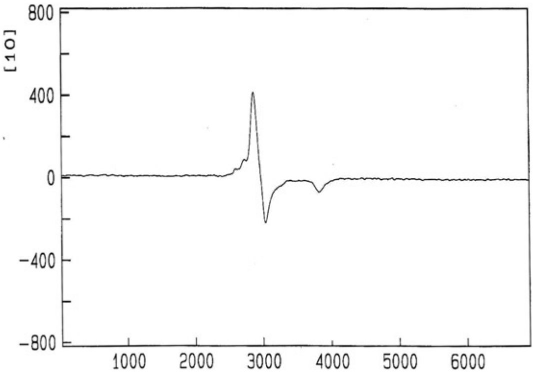


Figure 4. ESR spectrum of the complex *trans*-[Ru$(L_2)_2(AsPPh_3)_2$]Cl at 77 K in dimethylformamide/toluene.

the same conditions. Similar results were reported for other octahedral ruthenium(III) complexes [11]. The effect of the para-substituents (X) present in (LH) is much more pronounced in the case of ruthenium(III)–ruthenium(IV) irreversible oxidation. The potential $E_{1/2}$ increases with increase of the electron-withdrawing character of (X). The plot of $E_{1/2}$ *versus* $2\sigma[\sigma =$ Hammett constant of (R) [15], Me $= -0.17$, H $= 0.0$, Cl $= 0.23$ and $NO_2 = 0.78$] is linear, indicating that the single para-substituent on the ligand(HL) six bonds away from the electroactive ruthenium centre can influence the metal oxidation potential in a predictable manner.

3.6. *Catalytic oxidation of alcohols*

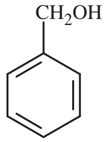
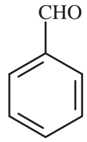
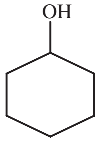
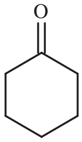
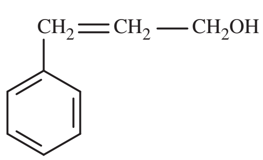
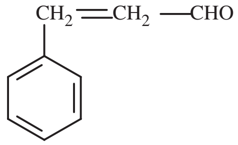
The catalytic oxidation of alcohols was carried out at room temperature, in the presence of catalytic amounts of the catalyst *trans*-[Ru$(L_1)_2(AsPh_3)_2$]Cl (L1 = 4-hydroxy-3-phenylazo-benzopyrane-2-one) as a model complex (figure 1) and H_2O_2 as a co-oxidant, according to the following equation:

$$PhCH_2OH \xrightarrow[H_2O_2]{\text{Ru-catalyst}} PhCHO + 2H_2O$$

Benzyl alcohol was selected as a model substrate for the optimization process. The experimental procedure was quite simple. The substrate (2 mmol) was added to the solution of the complex ($1.28 \times 10^{3-}$ mg, 0.01 mmol in 5 cm^3 dimethylformamide) and then H_2O_2 (20 cm^3, 30%) was added dropwise within 30 min. The reaction mixture was stirred at room temperature for 5 h, followed by extraction of the resultant carbonyl compound.

The results for the catalytic 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 95% yield; cinnamyl alcohol and cyclohexanol were oxidized to cinnamaldehyde and cyclohexanone in 87 and 75% yields, respectively. Comparable yields were obtained for oxidation of benzyl alcohol through the use of other ruthenium complexes too. The use of oxygen as co-oxidant instead of H_2O_2 under the same reaction conditions showed no reaction. This means that oxygen released due to decomposition of H_2O_2 plays no role in catalytic oxidation of benzyl alcohol.

Table 3. Catalytic oxidation of primary alcohols by $[Ru(L_1)_2(AsPh_3)_2]Cl/H_2O_2$.

Substrate	Product	Yield (%)	Turnover
		95	192
		87	174
		75	150

Reaction conditions: complex (0.01 mmol dissolved in 5 cm^3 of dimethylformamide), substrate (2 mmol) and H_2O_2 (20 cm^3, 30%). Turnover = moles of product/moles of complex.

A blank experiment was also carried out which revealed that in the absence of the complex, less than 5% yield of benzaldehyde was detected. Attempted oxidation using $RuCl_3 \cdot nH_2O$ in place of the complex resulted in a lower yield of benzaldehyde (20%). In conclusion, the catalyst system *trans*-$[Ru(L_1)_2(AsPh_3)_2]Cl/H_2O_2$ is selective, since all alcohols were converted to the corresponding aldehyde or ketone and it provides a safe and simple procedure for the catalytic oxidation of these substrates.

Acknowledgment

I would like to thank Professor Bill Griffith (Department of Chemistry, Imperial college, London University) for his helpful discussion and Mr. Hsien-Chang Kao (Department of Chemistry, Tamkang University, 151 Ying-chuan Road, Tamsui, Taipei 25137) for doing the ESR spectra for the complexes.

References

[1] A.G.F. Shoair, R.H. Mohamed. *J. Coord. Chem.* in press, 2006.
[2] A.G.F. Shoair, R.H. Mohamed. *Synth. Commun.*, **36**, 59 (2006).
[3] A.G.F. Shoair. *Bull. Korean Chem. Soc.*, **26**, 1525 (2005).
[4] M.S. El-Shahawi, A.G.F. Shoair. *Spectrochim. Acta Part A*, **60**, 121 (2004).

[5] W.P. Griffith, B. Reddy, A.G.F. Shoair, M. Suriaatmaja, A.J.P. White, D.J. Williams. *J. Chem. Soc., Dalton Trans.*, 2819 (1998).

[6] A.F. Shoair, A.A. El-bindary, A.Z. El-Sonbati. *Spectrochim. Acta Part A*, **58**, 3003 (2002).

[7] R.A. Sheldon, J.K. Kochi. *Metal Catalyzed Oxidation of Organic Compounds*, Chapter 6, Academic Press, New York (1981).

[8] S.E. Martin, A. Garrone. *Tetrahedron Lett.*, **44**, 549 (2003).

[9] S.-I. Murahashi. *Pure Appl. Chem.*, **403**(3), 64 (1992).

[10] D.H.R. Barton, S.D. Bévière, B.M. Chabot, W. Charasiri, S.K. Taylor. *Tetrahedron Lett.*, **35**, 4681 (1994).

[11] A.M. El-Hendawy, A.H. Al-Kubisi, A.G.F. Shoair. *Monat. Fûr Chemie*, **126**, 1291 (1995).

[12] K. Nakamoto. *Infrared and Raman spectra of Inorganic and Coordination Compounds*, 4th Edn, p. 244, Wiley-Science, New York (1986).

[13] B.N. Figgis. *Introduction to Ligand Field Theory*, 1st Edn, p. 287, Inter-Science Publisher Inc., New York (1966).

[14] G. Harris. *Theoret. Chim. Acta (Berlin)*, **26**, 47 (1996).

[15] L.P. Hammett. *Physical Organic Chemistry*, 2nd Edn, McGraw Hill, New York (1970).