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Luminescent property and catalytic activity of Ru(II) carbonyl complexes containing N, O donor of 2-hydroxy-1-naphthylideneimines

M. Sivagamasundari, R. Ramesh *

School of Chemistry, Bharathidasan University, Tiruchirappalli 620024, India

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Abstract

The reaction of the chelating ligands (obtained by the condensation of 2-hydroxy-1-naphthaldehyde with various primary amines) with $[RuHCl(CO)(EPh_3)_2(B)]$ (where E = P; B = PPh_3, py or pip: E = As; B = $AsPh_3$) in benzene afforded new stable ruthenium(II) carbonyl complexes of the general formula $[Ru(Cl)(CO)(EPh_3)(B)(L)]$ (L = anion of bidentate Schiff bases). The structure of the new complexes was investigated using elemental analyses, spectral (FT-IR, UV–vis and ^1H NMR) and electrochemical studies and is found to be octahedral. All the metal complexes exhibit characteristic MLCT absorption and luminescence bands in the visible region. The luminescence efficiency of the ruthenium(II) complexes was explained based on the ligand environment around the metal ion. These complexes catalyze oxidation of primary and secondary alcohols into their corresponding carbonyl compounds in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as the source of oxygen. The formation of high valent $Ru^{IV}{=}O$ species as a catalytic intermediate is proposed for the catalytic process.

Keywords: Ru(II) carbonyl complexes; Synthesis; Characterization; Luminescence; Oxidation

1. Introduction

Multidentate ligands are extensively used in coordination chemistry, since they can be applied in the construction of new frameworks with interesting properties [1]. Among these ligands the linear or cyclic Schiff bases obtained by the condensation of primary amines with carbonyl compounds and their metal complexes find a variety of applications including biological, clinical, analytical and industrial, in addition to their important role in catalysis and organic synthesis [2,3]. The central metal ion in these complexes act as active sites and thereby successfully catalyzes chemical reactions [4,5]. Metal-ligand luminescence probes with microsecond decay time have numerous potential applications in the biophysical and clinical sciences. Ruthenium(II) MLCT compounds display long luminescence life time and are extremely photo stable [6,7]. Recently light-emitting devices (LED) based on the small molecule like tris-2,2′-bipyridyl ruthenium(II) were demonstrated [8]. In contrast to the considerable growth of literature on the chemistry of ruthenium bi or polypyridyl complexes, the luminescent chemistry of ruthenium(II) complexes containing Schiff bases is not well developed.

The catalytic conversion of primary and secondary alcohols into their corresponding aldehydes and ketones is an essential reaction in organic synthesis. Traditional methods for performing such transformation generally involve the use of stoichiometric quantities of inorganic oxidants like Cr(IV) and generate large quantities of waste. The development of effective, greener catalytic systems that use clean and inexpensive oxidants is an important challenge [9]. The Schiff base transition metal complexes are attractive oxidation catalysts because of their cheap, easy synthesis and their chemical and thermal stability [10]. Ruthenium complexes have been extensively investigated as catalysts for alcohol oxidation in combination with various oxidants such as dioxygen [11], iodosobenzene [12], *t*-BuOOH [13], H_2O_2 [14] and NMO [15]. Further the catalytic activities of ruthenium complexes containing tertiary phosphine or arsine ligands are well established [16,17].

Therefore, in continuation of our interest in synthesis of new ruthenium compounds [18–20], we describe here the synthesis, characterization, luminescent and redox properties of ruthenium(II) complexes containing bidentate Schiff bases along with their catalytic activity towards oxidation of organic substrates

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* Corresponding author. Tel.: +91 431 2407035;
fax: +91 431 2407045/2407020.
E-mail address: ramesh_bdu@yahoo.com (R. Ramesh).

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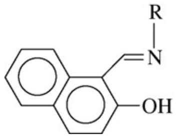


Where R= $-CH_3$; Naphmet (HL1)
$-C_6H_{11}$; Naphchx (HL2)
$-C_5H_4N$; Naphampy (HL3)
$-C_6H_4Br$; NaphBranil (HL4)

Scheme 1. Structure of the bidentate Schiff bases.

in the presence of NMO. The bidentate Schiff bases were derived from the condensation of 2-hydroxy-1-naphthaldehyde with methylamine, cyclohexylamine, 2-aminopyridine and 4-bromoaniline. The Schiff bases used to prepare the new ruthenium(II) complexes were shown in Scheme 1.

2. Experimental

2.1. Materials

All the reagents used were chemically pure and AR grade. Solvents were purified and dried according to standard procedure. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie Pvt. Ltd., Bombay, India and was used without further purification. 2-Hydroxy-1-naphthaldehyde and *N*-methylmorpholine-*N*-oxide were purchased from Aldrich. $[RuHCl(CO)(PPh_3)_3]$ [21], $[RuHCl(CO)(PPh_3)_2(B)]$ [22] (where B = py, pip) and $[RuHCl(CO)(AsPh_3)_3]$ [23] were prepared by reported literature methods.

2.2. Physical measurements

The analysis of carbon, hydrogen and nitrogen were performed on elementar systeme model vario EL111 at Sophisticated Test and Instrumentation Center, Cochin, India. IR spectra were recorded in KBr pellets in the range 4000–400 cm^{-1} region in Jasco 400 plus spectrophotometer. Electronic spectra were recorded in CH_2Cl_2 solution with a Cary 300 Bio UV–vis Varian spectrophotometer in the range of 800–200 nm. ^1H NMR spectra were recorded on a Bruker 400 MHZ instrument using TMS as an internal reference. Using Jasco FP-6500 spectrofluorimeter with 5 nm exit slit the emission intensity measurements were carried out. Electrochemical measurements were made using a Princeton EG and G-PARC model potentiostat using a glassy carbon working electrode and all the potentials were referenced to Ag/AgCl electrode. Melting Points were recorded with a Boetius micro-heating table and are uncorrected.

2.3. Preparation of Schiff base ligands

The monobasic bidentate Schiff base ligands were prepared by the condensation of 2-hydroxy-1-naphthaldehyde (0.43 g; 0.0025 mmol) with primary amines such as methylamine, 2-aminopyridine, cyclohexylamine and *p*-bromoaniline (0.08–0.43 g; 0.0025 mmol) in 1:1 molar ratio in methanol (20 cm^3) [24]. The solution was heated under reflux for 2 h and then concentrated to 5 cm^3. On cooling the product was separated out which was then recrystallised from hot methanol and the purity was checked by TLC.

2.4. Synthesis of Ru(II) carbonyl complexes

All operations were carried out under strictly anhydrous conditions. All the new complexes were prepared by the following general procedure. To a preheated benzene (20 cm^3) solution of $[RuHCl(CO)(EPh_3)_3]$ (where E = P or As) or $[RuHCl(CO)(PPh_3)_2(B)]$ (where B = PPh_3, py or pip) (76.9–108.4 mg; 0.1 mmol) the Schiff base (16.9–32.6 mg; 0.1 mmol) (HL1–HL4) was added slowly. The solution was refluxed for 5 h until the mixture gradually changed to deep color. The solution mixture was concentrated to ca. 3 cm^3 under reduced pressure and cooled. The complex separated out upon the addition of petroleum ether (60–80 °C). The solid was filtered off washed with petroleum ether and recrystallised from CH_2Cl_2/petroleum ether and dried under vacuum. The purity of the compounds was checked by TLC.

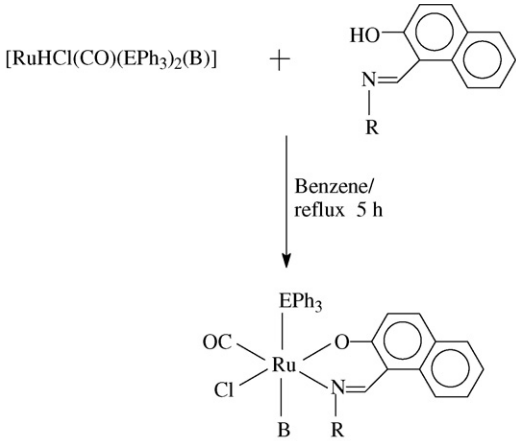
2.5. Catalytic oxidation of alcohol

Catalytic oxidation of primary and secondary alcohols to corresponding aldehydes and ketones respectively, by ruthenium(II) carbonyl complexes was studied in the presence of NMO as co-oxidant. A typical reaction using the ruthenium complexes as catalyst and benzyl alcohol, cinnamyl alcohol, cyclohexanol and benzoin as substrates at 1:100 molar ratio is described as follows. A solution of ruthenium complex (0.01 mmol) in 20 cm^3 CH_2Cl_2 was added to the solution of substrate (1 mmol) and NMO (3 mmol). The solution mixture was refluxed for 3 h and the solvent was then evaporated from the mother liquor under reduced pressure. The solid residue was then extracted with petroleum ether (60–80 °C) (20 cm^3) and the ether extracts were evaporated to give corresponding aldehydes/ketones which were then isolated and quantified as their 2,4-dinitrophenylhydrazone derivative [25].

3. Results and discussion

Diamagnetic, stable hexa-coordinated low spin ruthenium(II) complexes of general formula $[RuCl(CO)(PPh_3)(B)(L)]$ and $[RuCl(CO)(AsPh_3)_2(L)]$ (where B = PPh_3, py or pip; L = bidentate Schiff bases) are prepared by reacting $[RuHCl(CO)(PPh_3)_3]$, $[RuHCl(CO)(py)(PPh_3)_2]$, $[RuHCl(CO)(pip)(PPh_3)_2]$ and $[RuHCl(CO)(AsPh_3)_3]$ with the respective Schiff bases in a 1:1 mole ratio in benzene as shown in Scheme 2.

All the new Schiff base ruthenium(II) complexes are highly colored, stable in air, non-hygroscopic in nature and highly soluble in common solvents such as dichloromethane, acetonitrile, chloroform and DMSO. The analytical data are listed in Table 1 and are in good agreement with the general molecular formula proposed for all the complexes. In all reactions, the Schiff base replaced one PPh_3/$AsPh_3$ group and a hydride from the starting complexes. The Schiff bases behave as monobasic bidentate ligand in all cases. The heterocyclic nitrogen bases (pyridine, piperidine) remained intact because the Ru–P bond is more labile than the Ru–N bond, because of the better σ donating ability of the nitrogen bases compared to triphenylphosphine.



Scheme 2. Formation of Ru(II) carbonyl Schiff base complexes (where E = P; B = PPh_3, py or pip; E = As, B = $AsPh_3$; R = $-CH_3$, $-C_6H_{11}$, $-C_5H_4N$, $-C_6H_4Br$).

3.1. Spectroscopic characterization

The IR spectra of the complexes, in comparison with those of the free ligands, display certain changes, which give an idea about the type of coordination and their structure. Significant IR spectral bands of the complexes are listed in Table 2. Free Schiff bases show a very strong absorption around 1642–1618 cm^{-1} characteristic of azomethine (>C=N) group [19]. Coordination of the Schiff bases to the ruthenium ion through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and thus, lower the ν(C=N) absorption frequency. Hence this band undergoes a shift to lower frequency to 1620–1600 cm^{-1} after complexation, indicating coordination of the azomethine nitrogen to ruthenium [18,26]. The free ligands exhibit a broad band at 3435–3427 cm^{-1}, which may be assigned to the ν(OH) and this band is absent in the spectra of all the complexes, conferring the deprotonation of the Schiff base prior to coordination. The hydroxy protons are displaced by the metal leading to higher ν(C–O) (1350–1329 cm^{-1}) compared to that of the free ligands ν(C–O) (1324–1314 cm^{-1}) suggesting that the other coordinating atom is phenolic oxygen [25]. The binding of the metal to the ligand through nitrogen and oxygen atom is further supported by the appearance of new band in 460–400 cm^{-1} and 540–510 cm^{-1} ranges due to ν(M–N) and ν(M–O) [27], respectively, in the spectra of all the complexes. A strong band in the region 1957–1935 cm^{-1} due to terminally coordinated carbonyl group at higher frequency than in the ruthenium starting complexes. In the complexes **2**, **3**, **6**, **7**, **10**, **11**, **14**, **15** a medium intensity band is observed in the 1020 cm^{-1} region characteristic of the coordinated pyridine or piperidine [27]. In addition Schiff base complexes show strong vibrations near 520, 695, 740 and 1430 cm^{-1}, which are attributed to the triphenylphosphine or triphenylarsine fragment [28].

The nuclear magnetic resonance spectra of the diamagnetic compounds taken in $CDCl_3$ solution confirms the complex formation (Table 3). In the spectra of all complexes a sharp singlet appeared at around 8.10–9.10 ppm has been assigned to azomethine proton (>C=N). The positions of azomethine signal in the complexes are up field compared to that of the free ligands indicating coordination through the azomethine nitrogen atom [10]. Multiplets are observed around 6.65–8.06 ppm in all the complexes and have been assigned to the aromatic protons of triphenylphosphine, triphenylarsine, pyridine and naphthalene Schiff base ligands [29]. Methyl protons appear as singlet in the region 2.17–2.50 ppm in the complexes **1**, **2** and **4**. A broad singlet appeared in the region 1.57–1.61 ppm for the methylene protons of the cyclohexyl group for **13**, **14**, **15** and **16**. In the spectra of **7**, **11** and **15** the methylene protons appear as singlet around 1.59–2.05 ppm and another singlet in the region 10.10–10.31 ppm due to NH protons. The absence of a resonance at 13.25–15.21 ppm in the complexes indicate deprotonation of the phenolic group of the Schiff bases on complexation and coordination to ruthenium through the phenolic oxygen [18,19]. The spectra did not show any signal in the up field region for the hydride ligand, thus proving its substitution by the Schiff bases.

Table 1
Analytical data of Ru(II) carbonyl complexes containing N, O donors of 2-hydroxy-1-napthylideneimines

S. No.	Complexes	Formula	Color	m.p. (°C)	Found (calculated) (%)		
					C	H	N
1	$[Ru(Cl)(CO)(PPh_3)_2(L1)]$	$C_{49}H_{10}NO_2P_2ClRu$	Green	222	67.39 (67.61)	4.61 (4.72)	1.61 (1.88)
2	$[Ru(Cl)(CO)(PPh_3)(py)(L1)]$	$C_{36}H_{30}N_2O_2PClRu$	Green	154	62.65 (62.33)	4.38 (4.25)	4.05 (4.25)
3	$[Ru(Cl)(CO)(PPh_3)(pip)(L1)]$	$C_{36}H_{35}N_2O_2PClRu$	Green	160	62.20 (62.46)	5.07 (5.32)	4.02 (4.31)
4	$[Ru(Cl)(CO)(AsPh_3)_2(L1)]$	$C_{49}H_{40}NO_2As_2ClRu$	Green	176	61.20 (61.08)	4.19 (4.02)	1.45 (1.60)
5	$[Ru(Cl)(CO)(PPh_3)_2(L2)]$	$C_{54}H_{47}NO_2P_2ClRu$	Green	147	69.00 (69.37)	5.10 (5.33)	1.42 (1.43)
6	$[Ru(Cl)(CO)(PPh_3)(py)(L2)]$	$C_{41}H_{37}N_2O_2PClRu$	Green	137	65.00 (65.41)	4.91 (4.46)	3.60 (3.81)
7	$[Ru(Cl)(CO)(PPh_3)(pip)(L2)]$	$C_{41}H_{42}N_2O_2PClRu$	Green	148	64.60 (64.29)	5.50 (5.25)	3.61 (3.34)
8	$[Ru(Cl)(CO)(AsPh_3)_2(L2)]$	$C_{54}H_{48}NO_2As_2ClRu$	Brown	148	63.20 (63.48)	4.71 (4.89)	1.36 (1.51)
9	$[Ru(Cl)(CO)(PPh_3)_2(L3)]$	$C_{53}H_{41}N_2O_2P_2ClRu$	Brown	217	69.80 (69.57)	4.40 (4.19)	2.99 (2.73)
10	$[Ru(Cl)(CO)(PPh_3)(py)(L3)]$	$C_{40}H_{32}N_3O_2PClRu$	Brown	180	63.70 (63.49)	4.20 (4.29)	5.56 (5.36)
11	$[Ru(Cl)(CO)(PPh_3)(pip)(L3)]$	$C_{40}H_{36}N_3O_2PClRu$	Brown	131	63.36 (63.60)	4.78 (4.54)	5.50 (5.39)
12	$[Ru(Cl)(CO)(AsPh_3)_2(L3)]$	$C_{53}H_{41}N_2O_2As_2ClRu$	Brown	135	62.14 (62.41)	4.03 (4.31)	2.71 (2.85)
13	$[Ru(Cl)(CO)(PPh_3)_2(L4)]$	$C_{54}H_{41}NO_2P_2ClBrRu$	Green	167	63.95 (63.63)	4.07 (4.19)	1.30 (1.46)
14	$[Ru(Cl)(CO)(PPh_3)(py)(L4)]$	$C_{41}H_{31}N_2O_2PClBrRu$	Green	150	56.80 (56.51)	3.60 (3.87)	3.22 (3.09)
15	$[Ru(Cl)(CO)(PPh_3)(pip)(L4)]$	$C_{41}H_{36}N_2O_2PClBrRu$	Brown	148	58.91 (58.67)	4.30 (4.16)	3.30 (3.12)
16	$[Ru(Cl)(CO)(AsPh_3)_2(L4)]$	$C_{54}H_{41}NO_2As_2ClBrRu$	Brown	132	58.84 (58.51)	3.75 (3.82)	1.72 (1.49)

Table 2
Important IR, electronic and fluorescence[a] spectral data of the Ru(II) carbonyl Schiff base complexes

Complexes	$\gamma_{C=N}$ (cm^{-1})	$\gamma_{C–O}$ (cm^{-1})	$\gamma_{C\equiv O}$ (cm^{-1})	λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1})	Fluorescence data λ_{max} (nm)
1	1617	1318	1946	694 (380)[b], 456 (3404)[c], 321 (9520)[d], 266 (15296)[e]	512
2	1617	1319	1944	679 (270)[b], 436 (3324)[c], 319 (9900)[d], 260 (13460)[e]	510
3	1616	1338	1942	653 (386)[b], 440 (4580)[c], 319 (10032)[d], 258 (15052)[e]	516
4	1617	1316	1935	670 (224)[b], 427 (4744)[c], 323 (12048)[d], 259 (16432)[e]	503
5	1616	1339	1942	661 (536)[b], 419 (4192)[c], 314 (11024)[d], 262 (15448)[e]	501
6	1613	1338	1935	657 (448)[b], 426 (5388)[c], 330 (13644)[d], 272 (17340)[e]	502
7	1616	1338	1941	631 (504)[b], 417 (4491)[c], 310 (12024)[d], 261 (17168)[e]	508
8	1620	1336	1954	680 (364)[b], 416 (3712)[c], 314 (10836)[d], 264 (15980)[e]	496
9	1615	1336	1950	464 (3240)[c], 321 (12812)[d], 259 (17024)[e]	538
10	1615	1341	1949	694 (228)[b], 456 (6000)[c], 326 (13952)[d], 259 (16064)[e]	540
11	1617	1364	1950	464 (3044)[c], 327 (11512)[d], 257 (17624)[e]	543
12	1616	1335	1950	719 (358)[b], 460 (5060)[c], 321 (11940)[d], 271 (17752)[e]	518
13	1599	1338	1946	697 (472)[b], 420 (4678)[c], 320 (10928)[d], 254 (15128)[e]	502
14	1600	1337	1945	690 (380)[b], 431 (4056)[c], 323 (11003)[d], 258 (166632)[e]	497
15	1601	1362	1948	431 (3582)[c], 324 (9888)[d], 267 (15948)[e]	506
16	1600	1335	1957	688 (140)[b], 435 (3054)[c], 319 (9892)[d], 271 (15852)[e]	–

[a] Excitation at MLCT.
[b] $^1A_{1g} \rightarrow {}^1T_{1g}$.
[c] Charge transfer.
[d] n–π^*.
[e] π–π^*.

Electronic spectra of all the complexes in chloroform showed three to four bands in the region 719–254 nm. All the complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$, arising from the $t_{2g}{}^6$ configuration. The excited state terms are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence four bands corresponding to the transition $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in order of increasing energy. The electronic spectral bands at around 719–653 nm are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ (Table 2). The other high intensity band in the visible region around 464–419 nm has been assigned to charge transfer transitions arising from the metal t_{2g} level to the unfilled π^* molecular orbital of the ligand [18,30–32]. The high intensity bands around 330–310 nm and 272–254 nm has been designated as n–π^* and π–π^* transitions respectively, for the electrons localized on the azomethine group of the Schiff bases. The pattern of the electronic spectra for all the complexes indicate the presence of an octahedral environment around the ruthenium(II) ion similar to that of other ruthenium octahedral complexes [18,19,31,32].

Table 3
^{1}H NMR data of Ru(II) carbonyl Schiff base complexes

Complexes	^{1}H NMR data (ppm)
1	6.65–7.19 (Ar, m), 9.12 (CH=N, s), 2.25 (CH$_3$, s)
2	6.90–7.81 (Ar, m), 8.82 (CH=N, s), 2.17 (CH$_3$, s)
3	6.58–7.72 (Ar, m), 8.11 (CH=N, s), 2.50 (CH$_3$, s)
4	6.51–8.00 (Ar, m), 8.72 (CH=N, s), 1.30 (CH$_2$, s)
5	6.80–7.81 (Ar, m), 8.70 (CH=N, s), 1.41 (CH$_2$, s)
6	6.91–7.80 (Ar, m), 8.36 (CH=N, s), 1.30 (CH$_2$, s), 9.50 (NH, s)
7	6.90–7.70 (Ar, m), 8.30 (CH=N, s), 1.35 (CH$_2$, s)
8	6.54–7.72 (Ar, m), 8.41 (CH=N, s)
9	6.75–7.80 (Ar, m), 8.36 (CH=N, s), 2.05 (CH$_2$, s), 9.65 (NH, s)
10	6.80–7.91 (Ar, m), 8.36 (CH=N, s)
11	6.91–7.92 (Ar, m), 8.80 (CH=N, s)
12	6.81–7.74 (Ar, m), 8.63 (CH=N, s), 1.3 (CH$_2$, s), 9.72 (NH, s)
13	6.90–7.80 (Ar, m), 8.25 (CH=N, s)

3.2. Luminescence property

Emission properties of the ruthenium(II) Schiff base complexes were examined in chloroform at room temperature. The excitation of these complexes was made at their charge transfer band. The emission maxima fall in the range 496–543 nm and the emission maxima of the complexes are listed in Table 2. The emission maxima for all the complexes have experienced a positive shift of the order of 56–84 nm, when compared to those of excitation maxima. A representative spectrum is shown in Fig. 1. The observed CT luminescence in these complexes may be due to the presence of the imine functional group. It is likely that the emission originates from the lowest energy metal to ligand

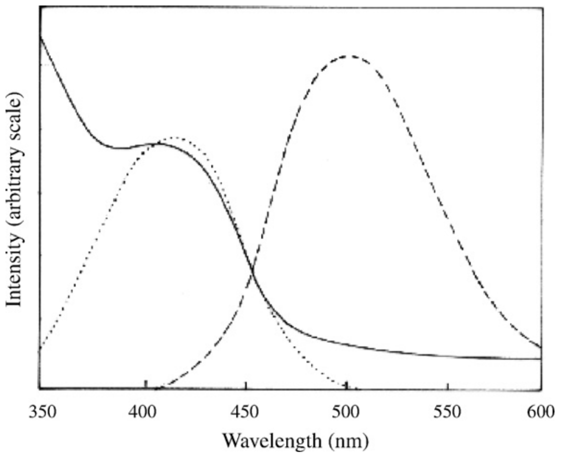


Fig. 1. Absorption (—), fluorescence (- - -) and excitation (· · ·) spectra of [Ru(Cl)(CO)(PPh3)(py)(L2)] in chloroform.

charge transfer (MLCT) state, probably derived from the excitation involving a dπ(Ru) → π* (imine) MLCT transition [33].

The present results show that the emission maxima are comparatively lower than those observed for the ruthenium(II) bipyridyl complexes due to smaller ligand field splitting in the Schiff base complexes and thus reduces the activation energy for the radiation less process to such an extent that the emission is quenched [34]. However, the emission maxima are influenced by the substituents on the coordinating imines and it decreases slightly with increasing number of substituents at the coordinated nitrogen [35]. Hence complexes **5–8** have lower emission maxima [34] than **1–4**, where methyl is the substituent. Further the presence of this electron rich methyl group in **1–4** makes them have higher emission maxima compared to the complexes **13–16** where the substituent is electron-withdrawing bromine. Complexes **9–12** having the amino pyridine substituent has the greater emission maxima compared to other complexes and this may be attributed to the presence of an additional chromophoric group >C=N of the pyridine [36]. Among triphenylphosphine and triphenylarsine complexes, the emission maxima are slightly reduced in the arsine complexes where the heavier atom As induces the spin forbidden transition.

3.3. Electrochemical study

The redox properties of all the complexes were investigated in acetonitrile solution by cyclic voltammetry and the redox potentials are expressed with reference to Ag/AgCl. The voltammetric data are presented in Table 4 and a representative cyclic voltammogram of **13** is shown in Fig. 2. Cyclic voltammogram of the complexes (1×10^{-3}) exhibit a quasi-reversible oxidation with $E_{1/2}$ value +0.61 to +0.82 V (Ru^{III}/Ru^{II}) and an irreversible reduction in the range −0.72 to −0.95 with respect to the Ag/AgCl at scan rate 100 mV s^{-1}. The oxidation observed is quasi-reversible in nature characterized by a large peak-to-peak separation (ΔE) of 110–220 mV and the cathodic peak current (i_{pc}) is less than the anodic peak current (i_{pa}). The one electron nature of this oxidation has been verified by comparing its current height (i_{pa}) with that of the ferrocene–ferrocenium couple under identical experimental conditions [37]

$$[Ru^{II}Cl(CO)(EPh_3)(B)(L)] \rightleftharpoons [Ru^{III}Cl(CO)(EPh_3)(B)(L)]^{+} + e^{-}$$

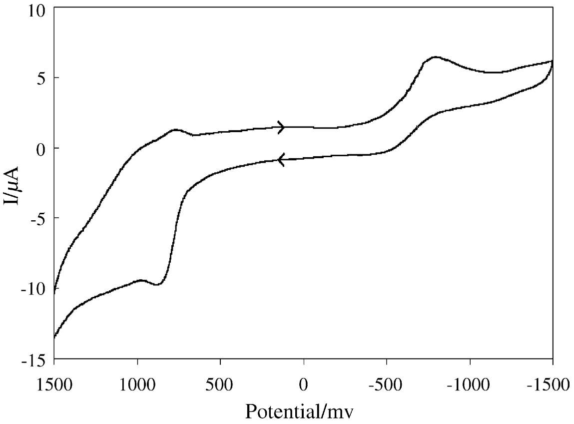


Fig. 2. Cyclic voltammogram of [Ru(Cl)(CO)(PPh3)(py)(L4)].

Table 4
Cyclic voltammetry data of Ru(II) carbonyl Schiff base complexes

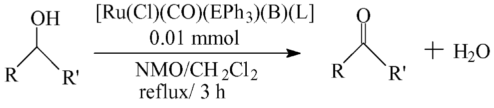
Complexes	Metal-based oxidation Ru^{III}/Ru^{II}				Metal-based reduction
	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)	Ru^{II}/Ru^{I} E_{pc} (V)
1	0.89	0.69	0.79	200	−0.95
2	0.71	0.51	0.61	200	−0.94
3	0.93	0.72	0.84	210	−0.89
4	0.86	0.72	0.79	140	−0.91
5	0.92	0.71	0.81	210	−0.72
6	0.90	0.70	0.80	192	−0.85
7	0.78	0.67	0.72	110	−0.78
8	0.81	0.68	0.74	130	−0.89
9	0.85	0.68	0.76	170	−0.77
10	0.86	0.69	0.77	180	−0.88
11	0.88	0.72	0.80	160	−0.99
12	0.93	0.71	0.82	220	−0.82
13	0.88	0.72	0.80	160	−0.84
14	0.89	0.70	0.79	190	−0.93
15	0.93	0.71	0.82	220	−0.87

Supporting electrolyte: NBu_4ClO_4 (0.005 M); complex: 0.001 M; solvent: CH_3CN; $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; $E_{1/2} = 0.5(E_{pa} + E_{pc})$; scan rate: 100 mV s^{-1}.

The reason for irreversibility observed in the reduction of all the complexes may be due to short lived reduced state of the metal ion [38] or due to oxidative degradation [39] of the ligands. It has been observed from the electrochemical data that there is little variation in the redox potentials due to replacement of triphenylphosphine by pyridine or piperidine or by triphenylarsine [19]. Hence it is inferred from the electrochemical data that the present ligand system is ideally suitable for stabilizing the higher oxidation state of ruthenium ion.

3.4. Catalytic activity

The primary and secondary alcohols (1 mmol) were efficiently oxidized by using 0.01 mmol of the catalyst in the coexistence of 3 mmol of NMO in dichloromethane (Table 5). All the complexes oxidize primary alcohols to corresponding aldehydes and secondary alcohols to corresponding ketones with high yield. This reaction provides an environmentally friendly route to the conversion of alcoholic functions to carbonyl groups and water is the only by product during the course of the reaction which was removed by using molecular sieves. The aldehydes and ketones formed after 3 h of reflux were isolated and quantified as their 2,4-dinitrophenylhydrazone derivatives. In the case of benzoin, the oxidation product was isolated and characterized by melting point, IR, ^1H NMR. Control experiments were carried out without the ruthenium catalyst under the same reaction conditions and in no case was there any detectable oxidation of alcohols



R,R'=alkyl (or) aryl (or) H

Table 5
Catalytic oxidation of alcohols by ruthenium complexes/NMO

Complex	Substrate	Product	Yield[a] (%)	TON[b]
2	Benzyl alcohol	A	55.8[c]	55.8
	Cinnamyl alcohol	A	91.0[c]	91.0
	Cyclohexanol	K	30.0[c]	30.0
	Benzoin	K	32.3[d]	32.3
5	Benzyl alcohol	A	59.6[c]	59.6
	Cinnamyl alcohol	A	85.4[c]	85.4
	Cyclohexanol	K	35.3[c]	35.3
	Benzoin	K	37.1[d]	37.1
12	Benzyl alcohol	A	52.7[c]	52.7
	Cinnamyl alcohol	A	90.3[c]	90.3
	Cyclohexanol	K	33.6[c]	33.6
	Benzoin	K	40.0[d]	40.0
15	Benzyl alcohol	A	60.9[c]	60.9
	Cinnamyl alcohol	A	93.5[c]	93.5
	Cyclohexanol	K	28.5[c]	28.5
	Benzoin	K	35.0[d]	35.0

A or K, corresponding aldehyde or ketone.

[a] Yield based on substrate: alcohol (1 mmol); NMO (3 mmol); catalyst (0.01 mmol).

[b] Ratio of moles of product obtained to the moles of the catalyst used.

[c] Isolated as 2,4-dinitrophenylhydrazone derivative, characterized by ^{1}H NMR and IR.

[d] Isolated yield, characterized by melting point, ^{1}H NMR and IR.

The relatively higher product yield obtained for oxidation of cinnamyl alcohol is due to the presence of α-CH unit in cinnamyl alcohol, which is more acidic than in benzyl alcohol, cyclohexanol or benzoin. Also, the oxidation of cinnamyl alcohol to cinnamaldehyde takes place with retention of C=C double bond, which is an important characteristic of ruthenium/NMO system. In the case of oxidation of secondary alcohols, it has been observed that the oxidation of cyclohexanol is substantially lower than that of benzoin. This may be due to the fact that the saturated cyclic ketones are generally prone to undergo dehydrogenation faster than acyclic ketones [40]. These ruthenium(II) Schiff base complexes have better catalytic activity compared to similar other ruthenium complexes as catalyst in the presence of NMO/*t*-BuOOH [41–43].

Results of the present investigation suggest that the ruthenium complexes are able to react efficiently with NMO to yield a high valent ruthenium–oxo species [17,44] capable of oxygen atom transfer to alcohols. The formation of ruthenium–oxo species were supported by spectral changes that occur by the addition of NMO to a dichloromethane solution of the ruthenium(II) complexes. The appearance of a peak at 390 nm is attributed to the formation of high-valent Ru(IV)–oxo species which is in conformity with other oxo–ruthenium (IV) complexes [42,44]. However, compelling evidence in favor of the formation of Ru(IV)–oxo species came from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness) which showed a band at 859 cm^{-1}, characteristic of Ru(IV)–oxo species, which is absent in the ruthenium catalyst. Except for the above difference noted, the IR spectra of the catalyst and solid mass appear quite similar, which suggests that the coordinated ligands remain intact in the oxidation process. Hence, it had been suggested that catalytic oxidation proceeds through metal–oxo intermediate. Furthermore, it is relevant from the cyclic voltammetric data that the oxidation effected by catalysts is likely to occur via higher ruthenium oxidation states, which is easily accessible through chemical oxidation with co-oxidatants like NMO, *t*-BuOOH, PhIO, etc. [17,42].

4. Conclusion

The synthesis, characterization and redox properties of new ruthenium(II) Schiff base complexes of the type [Ru(Cl)(CO)(EPh$_3$)(B)(L)] are described. These complexes are found to have luminescent properties and attempts will be made for further investigation on this study. The results of the present studies demonstrate the catalytic ability of the ruthenium(II) complexes to oxidize primary and secondary alcohols efficiently to their corresponding carbonyl compounds. A high-valent Ru(IV)–oxo species is proposed as the active intermediate in the catalytic process.

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