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Synthesis, luminescent, redox and catalytic properties of Ru(II) carbonyl complexes containing 2N2O donors

K. Naresh Kumar, R. Ramesh *

School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India

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Abstract

Diamagentic ruthenium(II) complexes [Ru(CO)(B)(L)] (where B = PPh_3, $AsPh_3$, py (or) pip; L = dianion of tetradentate Schiff bases) were synthesized from the reaction of tetradentate Schiff bases derived from 2-hydroxy-1-naphthaldehyde and the appropriate diamines with monomeric metal precursors $[RuHCl(CO)(EPh_3)_2(B)]$ (where E = As, B = $AsPh_3$; E = P, B = PPh_3, py (or) pip). Elemental analyses and spectral (FT-IR, UV–Vis and ^1H NMR) studies of all the new synthesized complexes suggest the presence of an octahedral environment around the Ru(II) ion. 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. Cyclic voltammograms of all the complexes display quasireversible oxidations (Ru^{III}/Ru^{II}) in the range 0.76–1.04 V and irreversible reduction peaks (Ru^{II}/Ru^{I}) in the range −0.70 to −0.95 V. The observed redox potentials vary with respect to the size of the chelate ring of Schiff base ligands. Further, the catalytic activity of complex **1** has been found to be high towards the oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant. The formation of high valent $Ru^{IV}{=}O$ species as a catalytic intermediate is proposed for the catalytic process.

Keywords: Ruthenium(II) carbonyl complexes; 2N2O donors; Luminescence; Redox potentials; Catalytic activity

1. Introduction

The coordination chemistry of ruthenium in the oxidation state +2 is dominated by nitrogen and oxygen donors [1]. The coordination environment around ruthenium plays a key role in stabilizing its different oxidation states and hence dictates the redox properties of the central metal ion. In addition, the chemistry of chelating tetradentate Schiff base ligands with ruthenium has also been extensively studied [2]. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning metal centered electronic factors, enhancing solubility and stability, either homogenous or heterogenous catalysts [3–5]. Further, luminescent metal complexes are a fascinating class of molecules that have found applications in many areas such as light emitting devices (LED) [6], among which luminescent Ru(II) bipyridyl compounds have been extensively studied as potential sensing molecules [7–9]. Ruthenium(II) metal to ligand charge transfer (MLCT) compounds are known to display long lived luminescence life times [10] and are extremely photo stable, in particular ruthenium polypyridyl complexes have been researched extensively for decades as photochemical molecular devices due to their excellent chemical stability, facial electron transfer, strong luminescence and emission and relatively long-lived excited states [11,12]. In contrast to the considerable growth of the literature on

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* Corresponding author. Tel.: +91 431 2407053; fax: +91 431 2407045/2407020.
E-mail address: ramesh_bdu@yahoo.com (R. Ramesh).

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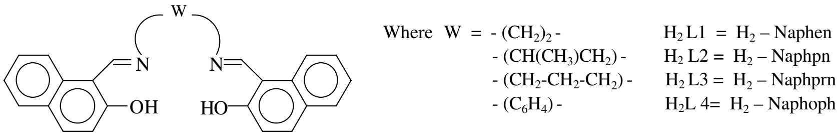


Where W = - $(CH_2)_2$ - $H_2L1 = H_2$ – Naphen
- $(CH(CH_3)CH_2)$ - $H_2L2 = H_2$ – Naphpn
- $(CH_2\text{-}CH_2\text{-}CH_2)$ - $H_2L3 = H_2$ – Naphprn
- (C_6H_4) - $H_2L4 = H_2$ – Naphoph

Scheme 1. Structure of the tetradentate Schiff bases.

the chemistry of ruthenium bi- or polypyridyl complexes, the luminescent chemistry of ruthenium(II) complexes containing Schiff bases is not well developed. Furthermore, metal complexes of ruthenium containing triphenylphosphine or arsine, nitrogen and oxygen donor ligands are found to be effective catalysts for oxidation [13,14]. In particular, the selective oxidation of alcohols into carbonyl compounds by metal complexes is well documented in the literature [15–17]. Sharpless et al. [18] carried out a yield oriented study of oxidation of cholesterol, geranial, etc., catalyzed by ruthenium complexes in the presence of *N*-methylmorpholine-*N*-oxide (NMO) and *N*-*N*-dimethylaniline-*N*-oxide, and only a very few reports are available on the oxidation chemistry using NMO as co-oxidant.

In view of the rich photophysical and catalytic properties of organometallic ruthenium complexes, the introduction of Schiff bases with a 2N2O donor set to ruthenium(II) carbonyl complexes containing triphenylphosphine/triphenylarsine and heterocyclic bases has been carried out. As an extension of our preliminary communication [19–21] and to provide further insight on the catalytic and emission behaviors, an extensive series of ruthenium(II) carbonyl complexes containing tetradentate Schiff bases have been synthesized and characterized. Further, the redox and luminescent properties are also reported along with the catalytic activity of ruthenium(II) complexes towards oxidation of primary and secondary alcohols. The tetradentate Schiff bases were derived from condensation of 2-hydroxy-1-naphthaldehyde with the appropriate diamines. The following Schiff bases were used to prepare the new ruthenium(II) complexes shown in Scheme 1.

2. Experimental

2.1. Material and physical measurements

The Schiff bases were prepared in 80–90% yield by condensation of two mole equivalents of 2-hydroxy-1-naphthaldehyde and one mole equivalent of the corresponding diamine by following the reported procedure [22]. All the reagents used were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard procedures. $RuCl_3 \cdot 3H_2O$ was purchased from Loba chemie pvt Ltd. Bombay, India and was used without further purification. $[RuHCl(CO)(PPh_3)_3]$ [23], $[RuHCl(CO)(PPh_3)_2(B)]$ [24] (where B = py (or) pip) and $[RuHCl(CO)(AsPh_3)_3]$ [25] were prepared by reported literature methods.

The analysis of carbon, hydrogen and nitrogen were performed on a Carlo Erba 1160 and a model 240 Perkin–Elmer CHN analyzer at the Central Drug Research Institute, Lucknow, India. IR spectra were recorded in KBR pellets in the 4000–200 cm^{-1} region in a 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. Emission intensity measurements were carried out by using a Jasco FP-6500 spectrofluorimeter with 5 nm exit slit. Cyclic voltammetric measurements were carried out on a Bio Analytical System (BAS) model CV-50W electrochemical analyzer using acetonitrile as solvent. Melting points were recorded with a Boetius micro-heating table and are uncorrected. The catalytic yields were determined using HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness.

2.2. Synthesis of Ru(II) carbonyl Schiff base complexes

All the new complexes were prepared by the following general procedure. To a solution of $[RuHCl(CO)(EPh_3)_2(B)]$ (where E = P; B = PPh_3, py (or) pip) and $[RuHCl(CO)(AsPh_3)_3]$ (100 mg; 0.10–0.13 mmol) in benzene the appropriate Schiff base (39–53 mg; 0.10–0.13 mmol) was added and heated under reflux for 5 h. The resulting solution was concentrated to ca. 3 cm^3 and cooled. Light petroleum (60–80 °C) (5 cm^3) was then added whereupon the complex separated out. The solid was filtered off, washed and recrystallized from CH_2Cl_2/light petroleum ether mixture and dried in vacuo. The purity of the compounds were checked by TLC (yield: 65–70%).

2.3. Catalytic oxidation

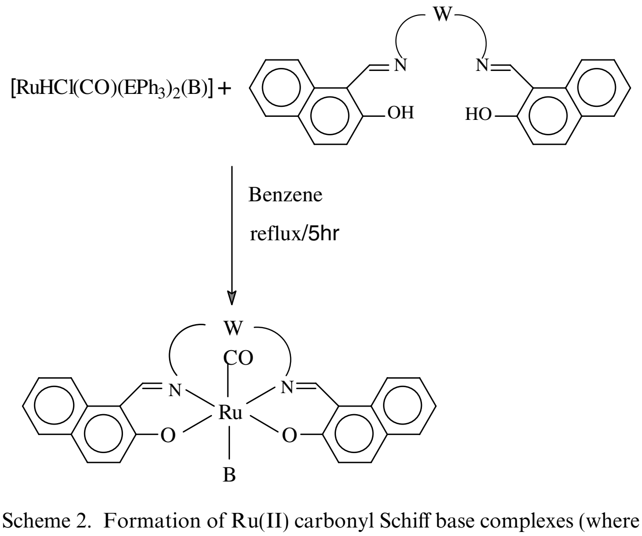
Catalytic oxidation of primary alcohols to the corresponding aldehydes and secondary alcohols to ketones by ruthenium(II) carbonyl complexes was studied in the presence of NMO as co-oxidant. A typical reaction using the complex $[Ru(CO)(PPh_3)(L1)]$ as a catalyst, and primary or secondary alcohol as substrates at a 1:100 molar ratio is described as follows. A solution of ruthenium complex **1** (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 residue was then extracted with pet. ether (60–80 °C) (20 cm^3) and was analyzed by GC. The oxidation products are known and are commercially available, and were identified by GC co-injection with authentic commercial samples.

3. Results and discussions

Complexes of the general formula [Ru(CO)(B)(L)]-(where B = PPh_3, $AsPh_3$, py (or) pip; L = dibasic tetradentate Schiff bases) were synthesized by the reactions of $[RuHCl(CO)(PPh_3)_3]$, $[RuHCl(CO)(PPh_3)_2(py)]$, $[RuHCl(CO)(PPh_3)_2(pip)]$ (or) $[RuHCl(CO)(AsPh_3)_3]$ with the respective tetradentate Schiff bases in a 1:1 molar ratio in benzene as shown in Scheme 2.

The analytical data for the new complexes agree well with the proposed molecular formula (Table 1). In all the reactions it has been observed that the Schiff bases behave as dibasic tetradentate ligands by substituting for the chloride ion, hydride ion and two triphenylphosphine/arsine ligands from each mole of the starting complexes to form the mononuclear complexes. These observations do indicate a more labile nature of the Ru–P bond compared to the Ru–N bond of the heterocyclic nitrogen bases in these complexes. The difference in the strength of Ru–P/As and R–N bonds may be explained as being due to the better σ donating ability of the nitrogen bases compared to that of triphenylphosphine/arsine. The Schiff base ruthenium(II) complexes are highly colored, stable to air and light, and soluble in chloroform, methylene chloride, benzene, DMF and DMSO.



Scheme 2. Formation of Ru(II) carbonyl Schiff base complexes (where E = P; B = PPh_3, py or pip; E = As, B = $AsPh_3$ W = $–(CH_2)_2–$, $–(CH_2)_3–$, $–(CH(CH_3)CH_2)–$, $–(C_6H_4)–$).

3.1. Spectroscopic characterization

The important IR absorption bands for the synthesized complexes are shown in (Table 2). The observed bands may be classified into those originating from the ligands and those arising from the bonds formed between Ru(II) and the coordinating sites. The free Schiff base ligands showed a strong band in the region 1628–1640 cm^{-1}, which is characteristic of the azomethine (>C=N) group [19]. Coordination of the Schiff bases to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the $\gamma_{C=N}$ absorption frequency. The band due to $\gamma_{C=N}$ is shifted to lower frequencies and appears around 1615–1625 cm^{-1}, indicating coordination of the azomethine nitrogen to the ruthenium metal [26]. A strong band observed at 1310–1330 cm^{-1} in the free Schiff bases has been assigned to phenolic C–O stretching. On complexation this band is shifted to a higher frequency range 1321–1360 cm^{-1}, indicating coordination through the phenolic oxygen. This has been further supported by the disappearance of the broad γ_{OH} band around 3395–3410 cm^{-1} in the complexes, indicating deprotonation of the phenolic proton prior to coordination [27]. The coordination of the azomethine nitrogen and phenolic oxygen are further supported by the appearance of two bands at 510–540 and 400–460 cm^{-1} due to γ_{M-O} [27] and γ_{M-N} [28], respectively. The spectra of all the complexes are dominated by a sharp band between 1925 and 1950 cm^{-1} due to a terminal $\gamma_{C\equiv O}$ group. In addition, other characteristic bands due to PPh_3 and $AsPh_3$ are also present around 1435 cm^{-1} in the spectra of all the Schiff base complexes. A medium intensity band is observed in the 1020 cm^{-1} region, characteristic of the coordinated pyridine or piperidine [28].

The ^1H NMR spectra of all the complexes were recorded to confirm the binding of the Schiff base to the ruthenium ion (Table 3). The spectra of all the complexes showed a singlet in the region δ 8.90–9.54 ppm, which has been assigned to the azomethine proton (>C=N). The position of the azomethine signal in the complexes is downfield in comparison with that of the free ligands, suggesting deshielding of the azomethine proton due to its coordination to ruthenium through the azomethine nitrogen. Multiplets are observed around δ 6.45–8.50 ppm in all the complexes and have been assigned to the aromatic protons of triphenylphosphine, triphenylarsine, pyridine and naphthalene Schiff base ligands [29]. Two methylene protons appear as one triplet in the region δ 3.53–3.83 ppm in **1**, **5**, **9** and **13**. For the complexes **3**, **7**, **11** and **15**, the signal for the methylene protons appear as one triplet and one quintet in the region 3.65–3.85 ppm and δ 2.17–2.44 ppm, respectively [30]. A broad singlet appears in the region δ 1.2–1.4 ppm for the methylene protons

Table 1
Physico-chemical and analytical data of Ru(II) carbonyl Schiff base complexes

S. No.	Complex	Formula	Colour	M.p. (°C)	Found (calculated) (%)		
					C	H	N
1	[Ru(CO)(PPh$_3$)(L1)]	$C_{43}H_{33}N_2O_3PRu$	Green	202	67.95(68.12)	3.97(4.39)	3.47(3.70)
2	[Ru(CO)(PPh$_3$)(L2)]	$C_{44}H_{35}N_2O_3PRu$	Green	185	69.90(70.30)	1.87(2.02)	3.53(3.72)
3	[Ru(CO)(PPh$_3$)(L3)]	$C_{44}H_{35}N_2O_3PRu$	Green	164	69.98(70.30)	2.45(2.02)	3.87(3.72)
4	[Ru(CO)(PPh$_3$)(L4)]	$C_{47}H_{33}N_2O_3PRu$	Brown	215	71.10(71.30)	3.87(4.20)	1.54(1.77)
5	[Ru(CO)(py)(L1)]	$C_{30}H_{23}N_3O_3Ru$	Green	235	62.47(62.70)	3.90(4.20)	7.02(7.37)
6	[Ru(CO)(py)(L2)]	$C_{31}H_{25}N_3O_3Ru$	Green	195	63.01(63.26)	3.89(4.28)	6.98(7.14)
7	[Ru(CO)(py)(L3)]	$C_{31}H_{25}N_3O_3Ru$	Green	157	62.94(63.26)	4.03(4.28)	7.34(7.14)
8	[Ru(CO)(py)(L4)]	$C_{34}H_{24}N_3O_3Ru$	Brown	216	65.74(65.48)	3.57(3.88)	6.42(6.74)
9	[Ru(CO)(pip)(L1)]	$C_{30}H_{28}N_3O_3Ru$	Green	217	61.84(62.16)	4.55(4.89)	7.57(7.25)
10	[Ru(CO)(pip)(L2)]	$C_{31}H_{30}N_3O_3Ru$	Green	182	60.42(60.70)	4.87(5.12)	7.29(7.07)
11	[Ru(CO)(pip)(L3)]	$C_{31}H_{30}N_3O_3Ru$	Green	150	60.51(60.70)	4.95(5.12)	6.87(7.07)
12	[Ru(CO)(pip)(L4)]	$C_{34}H_{34}N_3O_3Ru$	Brown	185	64.46(64.96)	4.26(4.65)	6.28(6.68)
13	[Ru(CO)(AsPh$_3$)(L1)]	$C_{43}H_{33}N_2O_3AsRu$	Green	182	64.65(64.42)	3.89(4.15)	3.05(3.49)
14	[Ru(CO)(AsPh$_3$)(L2)]	$C_{44}H_{35}N_2O_3AsRu$	Green	164	64.38(64.78)	4.45(4.33)	2.07(1.72)
15	[Ru(CO)(AsPh$_3$)(L3)]	$C_{44}H_{35}N_2O_3AsRu$	Green	162	64.47(64.78)	4.04(4.33)	1.53(1.72)
16	[Ru(CO)(AsPh$_3$)(L4)]	$C_{47}H_{33}N_2O_3AsRu$	Brown	152	66.62(66.43)	3.71(3.91)	3.12(3.30)

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

Complex	$\gamma_{C=N}$ (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	1351	1934	751(515)[a], 415(16688)[b], 324(27680)[d], 281(39040)[c]	474
2	1620	1338	1931	718(166)[a], 409(14170)[b], 332(26190)[d], 280(34830)[c]	474
3	1617	1360	1933	680(112)[a], 419(9880)[b], 331(19010)[d], 263(38940)[c]	499
4	1617	1321	1935	673(227)[a], 487(15000)[b], 341(21890)[d], 271(39040)[c]	552
5	1615	1349	1936	429(13820)[b], 335(14080)[d], 291(17510)[c]	471
6	1617	1339	1933	671(210)[a], 436(37480)[b], 342(41730)[d], 283(55390)[c]	516
7	1625	1335	1935	658(107)[a], 413(37690)[b], 344(41880)[d], 281(43130)[c]	
8	1619	1321	1942	779(118)[a], 454(10630)[b], 329(20200)[d], 270(36900)[c]	534
9	1616	1327	1941	589(248)[a], 406(909)[b], 325(16890)[d], 287(21120)[c]	466
10	1617	1358	1937	718(276)[a], 426(35860)[b], 343(40840)[d], 297(49310)[c]	490
11	1617	1360	1931	716(212)[a], 408(13670)[b], 334(29390)[d], 270(37790)[c]	502
12	1617	1325	1950	485(6210)[b], 335(11510)[d], 269(31360)[c]	542
13	1616	1321	1925	669(148)[a], 419(4280)[b], 318(11190)[d], 269(23680)[c]	
14	1617	1321	1918	691(196)[a], 439(14250)[b], 334(20340)[d], 272(38080)[c]	
15	1617	1338	1924	688(606)[a], 428(35520)[b], 344(40090)[d], 290(49940)[c]	478
16	1625	1321	1947	457(5720)[b], 336(8560)[d], 270(30100)[c]	527

[a] $^1A_{1g} \rightarrow {}^1T_{1g}$.

[b] Charge transfer.

[c] π–π*.

[d] *n*–π*.

[e] Solvent – dichloromethane.

[f] Excitation at the higher wavelength absorption peak.

and another singlet in the region δ 10.10–10.30 ppm for the NH protons in **9**, **11** and **12**. A sharp singlet observed for the OH protons of all the ligands in the region δ 14.0 ppm disappeared in all the complexes. A representative spectrum of the complex [Ru(CO)(PPh$_3$)(L4)] is shown in Fig. 1.

The electronic absorption spectra of all the complexes in dichloromethane showed three to four bands in the region 263–779 nm. All the Schiff base ruthenium 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, and the excited states corresponding to the $t_{2g}^5e_g^1$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in order of the increasing energy.

The bands around 779–589 nm and 485–406 nm are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ [20,31] and charge transfer (CT) transitions respectively are listed in Table 2. The charge transfer bands observed in all the complexes due to M → L transitions are possible in the visible region [31–33]. Moreover, the presence of carbonyl, triphenylphospine/arsine and heterocyclic bases as ligands, which are capable of producing strong ligand field e_g^*

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

Complex	^{1}H NMR data (ppm)
1	6.80–8.10(Ar, m), 8.9(CH=N, s), 3.73(N–$(CH_2)_2$, t)
3	6.95–8.10(Ar, m), 9.15(CH=N, s), 3.85(CH_2, t), 2.34(CH_2, q)
4	6.85–8.15(Ar, m), 9.34(CH=N, s).
5	6.75–8.15(Ar, m), 8.85(CH=N, s), 3.83(N–$(CH_2)_2$, t).
7	6.84–8.1(Ar, m), 9.25(CH=N, s), 3.83(CH_2, t), 2.17(CH_2, q)
8	6.81–8.30(Ar, m), 9.42(CH=N, s).
9	6.90–7.90(Ar, m), 9.34(CH=N, s), 3.65(N–$(CH_2)_2$, t), 1.24(CH_2, s), 10.13(NH, s).
11	6.70–8.10(Ar, m), 9.3(CH=N, s), 3.84(CH_2, t), 2.30(CH_2, q), 1.40(CH_2, s), 10.30(NH, s)
12	6.57–8.40(Ar, m), 9.14(CH=N, s), 1.35(CH_2, s), 10.1(NH, s)
13	6.70–8.35(Ar, m), 9.15(CH=N, s), 3.53(N–$(CH_2)_2$, t)
15	6.95–8.45(Ar, m), 9.21(CH=N, s), 3.65(CH_2, t), 2.44(CH_2, q)
16	6.45–8.32(Ar, m), 9.0(CH=N, s)

levels place these levels relatively high in energy. Therefore, the lowest charge bands due to excitation of an electron from the metal t_{2g} level to an unfilled molecular orbital derived from the π* level of the ligands should appear in the relatively high energy region compared to those due to $t_{2g} \rightarrow e_g^*$ transitions [32–34]. The other high intensity bands in the 344–269 nm region were characterized by ligand-centered (LC) bands and have been designated as π–π* and *n*–π* transitions for the electrons localized on the azomethine group of the Schiff bases [33]. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around the ruthenium(II) ion, similar to that of other ruthenium(II) octahedral complexes [21].

Emission properties of the ruthenium(II) Schiff base complexes were examined in dichloromethane solution at room temperature, and excitation and emission maxima are listed in Table 2. In the present series, the excitation of all the complexes was made at their charge transfer bands and the emission maxima of the complexes have experienced a positive shift of the order of 50–90 nm. The emission maxima fall in the range 471–552 nm and a representative spectrum is shown in Fig. 2. The observed CT luminescence in these complexes may be due to the presence of di-imine functions. It is likely that the emission originates from the lowest energy metal to ligand charge transfer (MLCT) state, probably derived from the excitation involving a dπ(Ru) → π* (di-imine) MLCT transition, and similar MLCT transitions are observed in ruthenium(II) bipyridyl complexes [34,35]. The slightly lower MLCT transition energy is probably due to the chelate ring of the complexes. In the complexes **4**, **8**, **12** and **16** it is observed that an increase in the rigidity of the ligand results in an increase in the emission maxima. If increased rigidity of the complexes is solely responsible for potential emission changes then it would be expected that this is because of the ligands present in the complexes [36].

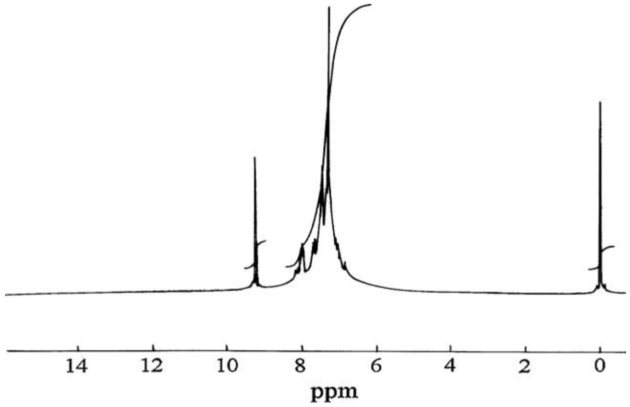


Fig. 1. ^{1}H NMR spectrum of $[Ru(CO)(PPh_3)(L4)]$.

3.2. Electrochemistry of the complexes

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 cyclic voltammograms of all the complexes (1×10^{-3}) display one quasi-reversible oxidation with $E_{1/2}$ values 0.76–1.04 V and one irreversible reduction, with respect to the SCE. In general, the changes in oxidation and reduction potential are probably due to the relative stabilization of the ruthenium(II) state over ruthenium(III) by a combination of σ and π effects exhibited by the ligand. A representative voltammogram of $[Ru(CO)(AsPh_3)(L4)]$ is shown in Fig. 3 and voltammetric data are presented in Table 4. The oxidation observed is quasi-reversible in nature, characterized by a rather

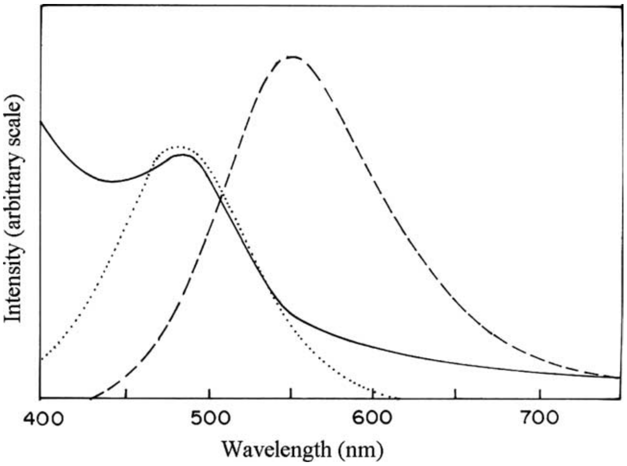


Fig. 2. Absorption (—), fluorescence (–––) and excitation (· · ·) spectra of [Ru (CO)(pip)(L4)] in dichloromethane.

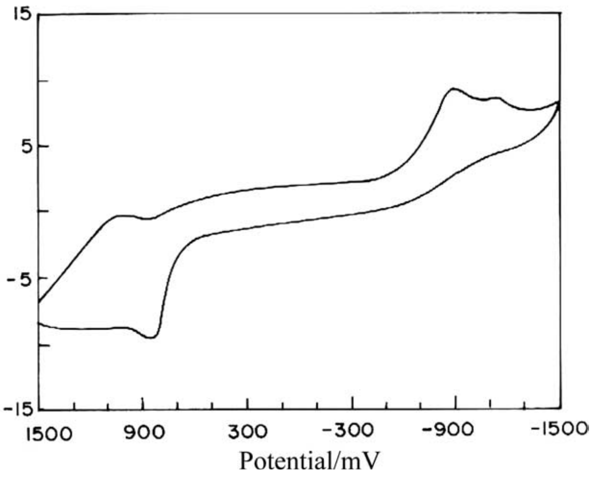


Fig. 3. Cyclic voltammogram of [Ru(CO)(AsPh$_3$)(L4)].

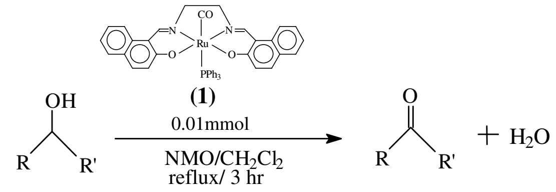
large peak-to-peak separation (ΔE_p) of 110–220 mV and the cathodic peak current (i_{pc}) is less than the anodic peak current(i_{pa}). The one electron nature of this oxidation has been verified by comparing its current height (i_{pa}) with that of the standard ferrocene–ferrocenium couple under identical experimental conditions [37].

The reason for the irreversibility observed for reductive response of all the complexes may be due to a short lived reduced state of the metal ion [38] or due to oxidative degradation of the ligands [39]. The reduction potential of Ru(II) complexes are affected by chelate rings of the ligands and it is observed that the reduction potential of complexes with a larger chelate ring is more than that of complexes with a smaller chelate ring. Further, an irreversible ligand based reduction peak is observed in the range −0.96 to −1.18 V, which corresponds to reduction of the azomethine(—C=N) moiety of the Schiff base ligands, and the reduction occurred at more negative values.

It has also been observed from the electrochemical data that there is not much variation in the redox potential due to triphenylphosphine, triphenylarsine, pyridine or piperidine [21]. Hence, it is inferred from the electrochemical data that the present ligand system is ideally suitable for stabilizing the higher oxidation state of ruthenium.

3.3. Catalytic activity of the complexes

Catalytic oxidation of primary alcohols and secondary alcohols by the synthesized ruthenium(II) carbonyl Schiff base complex [Ru(CO)(PPh$_3$)(L1)] was carried out in CH$_2$Cl$_2$ in the presence of NMO, and the by product water was removed by using molecular sieves. Complex **1** oxidizes primary alcohols to the corresponding aldehydes and secondary alcohols to ketones with high yield and the results are listed in Table 5 (entries 1–8). The aldehydes or ketones formed after 3 h of refluxing were determined by GC and there was no detectable oxidation in the absence of ruthenium complex.



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

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

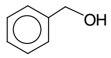
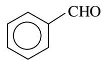
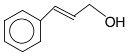
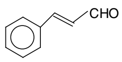
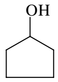
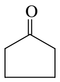
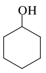
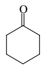
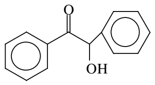
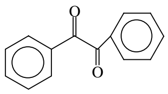
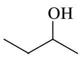
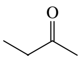
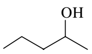
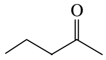
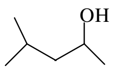
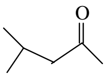
Complex	Metal based oxidation					Ligand based reduction
	Ru^{III}/Ru^{II}				Ru^{II}/Ru^{I}	
	E_{pa}(V)	E_{pc}(V)	ΔE_p(mV)	$E_{1/2}$(V)	E_{pc}(V)	E_{pc}(V)
1	0.90	0.70	200	0.80	−0.95	
2	0.88	0.71	170	0.80	−0.70	−0.98
3	0.86	0.69	170	0.76	−0.73	−0.96
4	0.83	0.70	130	0.77	−0.88	−1.18
5	0.86	1.02	160	0.94	−0.91	
6	1.06	0.93	130	1.00	−0.86	
7	0.89	0.70	190	0.80	−0.83	−1.01
8	0.86	0.96	100	0.91	−0.79	−1.12
9	0.85	0.97	120	0.91	−0.94	
10	0.89	0.67	220	0.78	−0.85	−0.98
11	0.96	0.76	200	0.86	−0.77	−1.06
12	0.85	0.98	130	0.92	−0.70	−0.97
13	0.96	1.07	110	1.01	−0.94	
14	1.09	0.98	110	1.04	−0.85	−1.02
15	0.90	1.08	180	0.99	−0.79	−0.97
16	0.87	1.01	140	0.94	−0.88	−1.11

Supporting electrolyte: NBu$_4$ClO$_4$ (0.005 M); complex: 0.001 M; solvent: CH$_3$CN; $\Delta E_p = E_{pa} - E_{pc}$ 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}.

Results of the present investigation suggest that the complexes are able to react efficiently with NMO to yield a high valent ruthenium-oxo species [2,40] capable of oxygen atom transfer to alcohols. This was further supported by spectral changes that occur by 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 $Ru^{IV}{=}O$ species, which is in conformity with other oxo ruthenium(IV) complexes [2,41,42]. Further support in favor of the formation of such species was identified from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness), which showed a band at 860 cm^{-1}, characteristic of $Ru^{IV}{=}O$ species [2,40,41].

The oxidation of benzylalcohol to benzaldehyde resulted in 89% conversion. Unsaturated cinnamylalcohol was oxidized to cinannamaldehyde with 95% conversion, without cleavage of carbon–carbon double bonds. This is an important characteristic of the ruthenium/NMO system. Further, the complex effectively catalyzes the oxidation of aliphatic alcohols such as butane-2-ol, methylpropylcarbinol and isobutylmethylcarbinol to the corresponding ketones with high conversions. In the case of benzoin the oxidation product was isolated and characterized by melting point, IR and ^{1}H NMR. Moreover, the complex efficiently catalyzes the oxidation of five and six membered cyclic alcohols to the corresponding ketones with conversions of 99% and 92%, respectively. This reaction provides a new environmentally friendly route to the conversion of alcoholic functions to carbonyl group and water is the only by product during the course of the reaction. It has been observed that complex **1** has a better catalytic efficiency in the case of oxidation of primary and secondary alcohols when compared to an earlier report [42–44] on similar ruthenium complexes as catalysts in the presence of NMO/*t*-BuOOH. Hence, it is relevant from the cyclic voltammetric data that the oxidation effected by catalysts is likely to occur via higher ruthenium oxidation states, which are easily accessible through chemical oxidation with co-oxidants like NMO, *t*-BuOOH, PhIO etc. [42].

Table 5
Catalytic oxidation of alcohols to the corresponding aldehydes and ketones with complex **1** in the presence of NMO

Entry	Substrate	Product	Conversion (%)[b]	Turnover[c]
1			89	89
2			95	95
3			99	99
4			92.2	92.2
5			46[a]	46
6			88	88
7			99	99
8			99	99

Substrate (1 mmol); NMO (3 mmol); complex (0.01 mmol): solvent dichloromethane.

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

[b] Yield determined by GC and comparing with the analyses of authentic samples.

[c] Moles of product per mole of catalyst.

4. Conclusion

A new family of ruthenium(II) carbonyl complexes containing tetradentate Schiff bases were synthesized and characterized. These complexes are found to have luminescent properties and attempts will be made for further investigation on this study. The oxidation of alcohols to carbonyl compounds has been studied with NMO in the presence of catalyst **1** and high yields were obtained.

Acknowledgment

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