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## New Ruthenium(III) Complexes with Tridentate Schiff Base and Their Catalytic Activity toward Oxidation of Alcohols

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## New Ruthenium(III) Complexes with Tridentate Schiff Base and Their Catalytic Activity toward Oxidation of Alcohols

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The synthesis and characterization of several hexa-coordinated ruthenium(III) complexes of the type  $[RuX_2(EPh_3)(L)]$  (E = P or As; X = Cl or Br; L = monobasic tridentate ligand derived by the condensation of *o*-phenylene diamine or ethylene diamine with salicylaldehyde or *o*-hydroxyacetophenone) are reported. Elemental analyses, IR, electronic, EPR, and cyclic voltammetric data of the complexes are discussed. An octahedral geometry has been tentatively proposed for all the complexes. The new complexes were found to be effective catalysts for the oxidation of benzyl alcohol and cyclohexanol to benzaldehyde and cyclohexanone, respectively, using N-methylmorpholine-N-oxide as a co-oxidant.

Keywords ruthenium(III), Schiff base, triphenylarsine, triphenylphosphine, catalytic oxidation

#### **INTRODUCTION**

There has been considerable interest in ruthenium complexes in recent years because of their redox stability, excited-state reactivities, and excited-state lifetimes (Balzani et al., 1996). Metal complexes of ruthenium containing nitrogen and oxygen donor ligands are found to be effective catalysts for oxidation, reduction, hydrolysis, and other organic transformations (Karvembu et al., 2003; Ramesh, 2004). In the present work, we have chosen a group of three tridentate O,N,N donor ligands (Figure 1). The ligands are abbreviated in general as HL, where H stands for the acidic proton. Each of these ligands has three potential donor sites, viz., a phenolate oxygen, an azomethine nitrogen, and an amine nitrogen. The primary objective of the present study has been to synthesize a family of ruthenium complexes containing one of these tridentate ligands and triphenylphosphine/triphenylarsine.

#### EXPERIMENTAL

RuCl<sub>3</sub> · 3H<sub>2</sub>O was purchased from Loba-Chemie Pvt. Ltd., Mumbai, India, and was used without further purification. All of the reagents used were of analytical or chemically pure grade. Solvents were purified and dried according to standard procedures. Microanalyses were performed at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. IR spectra were recorded on a Jasco FTIR-410 and Nicolet FTIR (Avatar Model) spectrophotometer using a KBr disk. The electronic spectra were recorded on a dichloromethane with a Jasco-V-530 UV/Vis spectrophotometer in the 400-200-nm range. Cyclic voltammetric studies were carried out with a BAS CV electrochemical analyzer in dichloromethane using a glassy carbon working electrode and the potentials were referenced to a silversilver chloride electrode. The supporting electrolyte used was 0.1 M tetrabutylammonium perchlorte [Bu<sub>4</sub>N]ClO<sub>4</sub> in dichloromethane solution. Melting points were recorded in a Boetius micro heating table and are uncorrected.

The starting complexes [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] (Chatt et al., 1968), [RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>3</sub>] (Poddar et al., 1974), [RuBr<sub>3</sub>(AsPh<sub>3</sub>)<sub>3</sub>] (Natarajan et al., 1977) and the ligands (Boghaei and Mohebi, 2002) were prepared according to the reported literature procedures. All of the new complexes were prepared under anhydrous conditions.



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R	W	Abbreviation
Н	$C_6H_5$	HL <sup>1</sup>
Н	$H_2C$ - $CH_2$	$HL^2$
CH <sub>3</sub>	$H_2C$ - $CH_2$	$HL^3$

FIG. 1. Structures of the ligands.

#### Preparation of Ruthenium(III) Complexes

All the new complexes were prepared by the following general procedure. To a solution of  $[RuX_3(EPh_3)_3]$  (X = Cl or Br; E = P or As) (0.099–0.126 g, 0.1 mmol) in benzene (25 mL), the appropriate Schiff base ligand (0.016–0.021 g, 0.1 mmol) was added and the mixture was heated under reflux for 5 h. The resulting solution was concentrated to ca. 3 mL, cooled to room temperature and a small quantity of petroleum ether (60–80°C) was added. The separated complexes were removed by filtration, washed with petroleum ether, recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, and dried in vacuo. Yields: 65–72%.

#### **Catalytic Oxidation of Alcohols**

To a solution of alcohol (1 mmol) in dichloromethane (20 mL), N-methylmorpholine-N-oxide (3 mmol) and the ruthenium complex (0.01 mmol) were added. The solution was refluxed for 3 h. The mixture was evaporated to dryness and extracted with petroleum ether  $(60-80^{\circ}\text{C})$ . The combined petroleum ether extracts was filtered and evaporated to give the corresponding carbonyl compound, which were

#### **RESULTS AND DISCUSSION**

The tridentate Schiff bases react with the ruthenium(III) complexes of the general formula  $[RuX_3(EPh_3)_3]$  (X = Cl or Br; E = P or As) in 1 : 1 molar ratio in benzene to yield complexes of the type  $[RuX_2(EPh_3)(L)]$ .

$$[RuX_{3}(EPh_{3})_{3}] + HL \xrightarrow{Benzene}_{Reflux,5h} [RuX_{2}(EPh_{3})(L)] + 2EPh_{3} + HX$$

The analytical data obtained for the new complexes are in good agreement with the proposed molecular formulaes (Table 1). In all of the above reactions, the Schiff bases behave as uninegative tridentate ligands.

#### **IR Spectra**

In the IR spectra of Schiff bases, a strong band is observed around  $1,580-1,600 \text{ cm}^{-1}$  for the free azomethine (-CH=N-) group. In the complexes, this band is shifted to the region  $1,520-1,540 \text{ cm}^{-1}$ , indicating the coordination of the Schiff bases through the azomethine nitrogen (Khera et al., 1983). A strong band observed at  $1,280-1,300 \text{ cm}^{-1}$  in the free Schiff bases has been assigned to phenolic C-O stretching. Complexation, which shifted this band to a higher frequency region  $(1,285-1,320 \text{ cm}^{-1})$ , shows that the other coordination is through the phenolic oxygen atom (Karvembu et al., 2003). The free Schiff bases showed a very strong absorption around  $3,450-3,500 \text{ cm}^{-1}$ , which is characteristic of primary amine N-H stretching. In the spectra of the new ruthenium(III) complexes the absorptions due to the  $-NH_2$  group has been observed at a lower frequency  $3,410-3,470 \,\mathrm{cm}^{-1}$ , indicating that the other coordination site is amine nitrogen atom to the metal ion (Boghaei and Mohebi, 2002). The other characteristic bands due to triphenylphosphine/triphenylarsine were also present in the expected region.

Complex		M.p. (°C)	Elemental analysis (%) found (calc.)		
	Yield (%)		С	Н	Ν
(1)	70	103	58.25 (57.68)	4.62 (4.06)	4.46 (4.34)
(2)	68	71	56.34 (54.01)	4.10 (3.83)	4.33 (4.06)
(3)	65	72	49.15 (47.84)	3.94 (3.37)	3.71 (3.60)
(4)	70	110	56.42 (54.28)	4.95 (4.39)	4.76 (4.69)
(5)	72	85	52.63 (50.56)	4.86 (4.09)	4.45 (4.37)
(6)	69	82	47.05 (44.40)	4.59 (3.59)	3.98 (3.84)
(7)	68	123	57.21 (54.99)	4.99 (4.62)	4.67 (4.58)
(8)	71	96	53.18 (51.31)	4.89 (4.31)	4.41 (4.27)
<b>(9</b> )	67	174	47.26 (45.18)	4.06 (3.79)	3.81 (3.76)

 TABLE 1

 Analytical data for the ruthenium(III) Schiff base complexes

#### **Electronic Spectra**

The ground state of ruthenium(III) is  ${}^{2}T_{2g}$  and the first excited doublet levels in order of increasing energy are  ${}^{2}A_{2g}$  and  ${}^{2}A_{1g}$ , which arise from the  $t_{2g}{}^{4}e_{g}^{1}$  configuration (Ballhausen, 1962). In most of the ruthenium(III) complexes, the UV-visible spectra show only charge transfer bands (Lever, 1984). In a d<sup>5</sup> system, and especially in ruthenium(III), which has relatively high oxidizing properties, the charge transfer bands of type  $L_{\pi y} \rightarrow t_{2g}$  are prominent in the low-energy region. Such bands obscure the weaker bands due to d–d transition. It therefore becomes difficult to assign conclusively the bands of ruthenium(III) complexes which appear in the visible region.

The electronic spectra of all the complexes in dichloromethane showed two to three bands in the 360–240-nm region (Table 2). These bands have been assigned to charge transfer transitions. Similar observations have been made for other ruthenium(III) octahedral complexes (Prabhakaran et al., 2004).

#### EPR Spectra

The solid-state EPR spectra at X-band frequencies for several of the ruthenium(III) complexes have been recorded at room temperature. All the complexes showed a single isotropic line with g value in the 2.36-2.45 range (Figure 2). Such isotropic lines are usually observed either due to intramolecular spin exchange that can broaden the lines or to the occupancy of the unpaired electron in a degenerate orbital. The nature and pattern of the EPR spectra suggest an almost octahedral environment around ruthenium ion in the complexes (Khan et al., 1990; Medhi and Agarwala, 1980).

TABLE 2 IR and electronic spectral data for ruthenium(III) Schiff base complexes

Ligand/ complex	ν(C-O)	ν(C==N)	ν(N-H)	$\lambda_{ m max}$
$HL^1$	1,283	1,591	3,500	_
(1)	1,290	1,532	3,464	345, 291, 241
(2)	1,290	1,532	3,459	343, 295, 240
(3)	1,307	1,532	3,452	339, 298, 241
$HL^2$	1,284	1,583	3,500	_
(4)	1,294	1,524	3,420	356, 241
(5)	1,293	1,528	3,417	349, 241
(6)	1,292	1,529	3,458	353, 241
$HL^3$	1,292	1,581	3,484	_
(7)	1,314	1,532	3,471	335, 241
(8)	1,317	1,539	3,450	345, 241
(9)	1,317	1,532	3,466	338, 241

 $\nu$  in cm<sup>-1</sup>;  $\lambda$  in nm.



#### **Redox Behavior**

The redox behavior of the complexes has been examined in dichloromethane at a glassy carbon working electrode using cyclic voltammetry (Table 3). The redox potentials of the Schiff base complexes are characterized by well-defined waves in the range 0.81-1.03 V (oxidation) and -0.32 V to -0.73 V (reduction) versus SCE (Figure 3). As the ligands are inactive in the potential range concerned (+2.0 V to)-2.0 V), the redox waves are assigned to the metal-centered Ru<sup>III</sup>-Ru<sup>III</sup> and Ru<sup>IV</sup>-Ru<sup>III</sup> couples. In this, the oxidation is quasi-reversible in nature, with a peak-to-peak separation  $(\Delta E_{\rm p})$  of 150–400 mV (Heinze, 1984). This is attributed to slow electron transfer and adsorption of the complexes onto the electrode surface (Wallace et al., 1989). In general, these complexes show one quasi-reversible oxidation couple and an irreversible reduction peak. The reduction processes (Ru<sup>III</sup>-Ru<sup>II</sup>) for the complexes show an irreversible cyclic voltammograms. These observations indicate that the charge transfer process for the Ru<sup>III</sup>-Ru<sup>II</sup> couple is not in general as rapid as in the case for Ru<sup>IV</sup>-Ru<sup>III</sup>. The reason for the irreversibility for these complexes may be due to reductive degradation or short-lived reduced state of the metal ion (Bond et al., 1990). It has also been observed that there is not much variation in the redox potentials due to the substitution of triphenylphosphine by triphenylarsine in the complexes. Similar behavior has been recently observed for other ruthenium(III) complexes (Ramesh and Maheswaran, 2003; Ramesh, 2004).

Analytical, spectroscopic (IR, electronic, EPR), and electrochemical data reveal that the complexes are hexa-coordinated, with the donor atoms distributed about the metal center in an octahedral manner (Figure 4).

	Ru <sup>III</sup> -Ru <sup>IV</sup>			Ru <sup>III</sup> –Ru <sup>II</sup>				
Complex	$E_{\rm pa}\left({ m V} ight)$	$E_{\rm pc}$ (V)	$\Delta E_{\rm p}~({\rm mV})$	$E_{1/2}(V)$	$E_{\rm pa}\left({\rm V}\right)$	$E_{\rm pc}$ (V)	$\Delta E_{\rm p}~({\rm mV})$	$E_{1/2}$ (V)
(1)	1.0	0.79	210	0.895	_	-0.36		_
(3)	1.13	0.73	400	0.930	_	-0.73	_	
(5)	1.03	0.87	160	0.950	_	-0.50		
(8)	1.08	0.85	230	0.965	—	-0.65	—	—

 TABLE 3

 Cyclic voltammetric data<sup>a</sup> for ruthenium(III) Schiff base complexes

<sup>a</sup>Supporting electrolyte: [NBu<sub>4</sub>]ClO<sub>4</sub> (0.1 M). Scan rate: 100 mV s<sup>-1</sup>. Reference electrode: Ag/AgCl.

$$\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$$
$$E_{1/2} = 0.5(E_{\rm pa} + E_{\rm pc})$$

where  $E_{pa}$  and  $E_{pc}$  are the anodic and cathodic peak potentials in V, respectively.



FIG. 3. Cyclic voltammogram of 3.



Complexes	R	W	Е	х
(1)	Н	$C_6H_4$	Р	Cl
(2)	Н	$C_6H_4$	As	Cl
(3)	Н	$C_6H_4$	As	Br
(4)	Н	$C_2H_4$	Р	Cl
(5)	Н	$C_2H_4$	As	Cl
(6)	Н	$C_2H_4$	As	Br
(7)	$CH_3$	$C_2H_4$	Р	Cl
(8)	$CH_3$	$C_2H_4$	As	Cl
(9)	CH <sub>3</sub>	$C_2H_4$	As	Br

FIG. 4. Proposed structures of the new complexes.

#### **Catalytic Oxidation**

The oxidation of benzyl alcohol and cyclohexanol was carried out with different ruthenium complexes as catalysts in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant in dichloromethane (Table 4). Benzaldehyde was formed from benzyl alcohol and cyclohexanol was converted into cyclohexanone after 3h of stirring at room temperature. The aldehydes/ketones formed were quantified as their 2,4-dinitrophenylhydrazone derivatives. In no case was there any detectable oxidation of alcohols/ketones in the presence of N-methylmorpholine-N-oxide alone and without the ruthenium complex. All of the synthesized ruthenium complexes were found to catalyze the oxidation of alcohols to aldehydes/ ketones, but the yields and the turnover were found to vary with different catalysts. The ruthenium(III) complexes were found to exhibit yields and turnover comparable to those reported for similar ruthenium(III) complexes (El-Hendaway et al., 1997). The relatively high product yield obtained for the oxidation of benzyl alcohol as compared to cyclohexanol is due to the fact that the  $\alpha$ -CH moiety of benzyl alcohol is

 TABLE 4

 Catalytic oxidation of alcohols<sup>a</sup> by ruthenium(III) Schiff base complexes in the presence of N-methylmorpholine-N-oxide

Complex	Substrate	Product	Yield <sup>b</sup>	Turnover <sup>c</sup>
(1)	Benzyl alcohol	А	55	76
	Cyclohexanol	Κ	39	57
(4)	Benzyl alcohol	А	51	70
	Cylohexanol	Κ	23	34
(7)	Benzyl alcohol	А	42	57
	Cylohexanol	Κ	34	49

 ${}^{a}A =$  benzaldehyde, K = cyclohexanone, reaction time = 3 h.  ${}^{b}$ Yields based on substrate.

<sup>c</sup>Moles of product per mole of catalyst.

more acidic than the moiety in cyclohexanol (Chatterjee et al., 2000).

#### CONCLUSION

Mononuclear complexes of the type  $[RuX_2(EPh_3)(L)]$ (where X = Cl or Br; E = P or As; L = monobasic tridentate ligand) were synthesized by a simple procedure. Elemental analysis (C, H, and N) of the complexes agrees well with the molecular formula proposed. IR spectral data confirm the coordination of Schiff base through the azomethine nitrogen, phenolic oxygen, and amine nitrogen to the metal. Electronic spectra reveal the charge transfer transitions in the complexes. EPR studies suggest an octahedral geometry around ruthenium(III). Cyclic voltammetric data shows that the complexes are redox-active. Moreover, the complexes exhibit catalytic activity for the oxidation of alcohols in the presence of N-methylmorpholine-N-oxide as co-oxidant.

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