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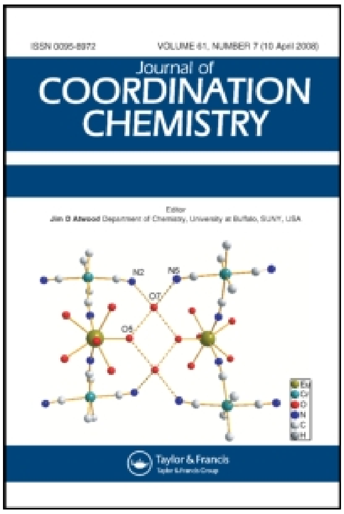

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Synthesis, spectral, and catalytic studies of ruthenium(II) unsymmetrical Schiff-base complexes

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Synthesis, spectral, and catalytic studies of ruthenium(II) unsymmetrical Schiff-base complexes

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Unsymmetrically-substituted ruthenium(II) Schiff-base complexes, $[Ru(CO)(B)(L^x)]$ [$B = PPh_3$, $AsPh_3$ or Py; L^x = dianion of tetradentate unsymmetrical Schiff-base ligand; $x = 4$–7, L^4 = salen-*o*-hyac, L^5 = valen-*o*-hyac, L^6 = salphen-*o*-hyac, L^7 = valen-2-hacn], were prepared and characterized by analytical, IR, electronic, and ^{1}H NMR spectral studies. The new complexes were tested for their catalytic activity towards the oxidation of benzylalcohol to benzaldehyde.

Keywords: Unsymmetrical Schiff bases; Ruthenium(II) complexes; Spectral studies; Catalytic activity

1. Introduction

Chemistry of ruthenium [1] holds sizeable because of electron-transfer, photochemical, and catalytic properties. Synthesis and characterization of tetradentate unsymmetrical Schiff-base complexes offers advantages in modeling binding sites in bio-molecules and in duplication of enzymatic efficiency and selectivity of natural systems with synthetic materials [2, 3]. Unsymmetrical Schiff-base complexes have been used in certain chemical processes as catalysts [4, 5]. Ruthenium complexes of phosphines have applications in hydrogenation, isomerization, oxidation, epoxidation, cyclopropanation [6], etc. The hemilabile character of the O, N, and P or As donors should enhance catalytic activity [7] prompting us to explore the catalytic properties of complexes of this type. Herein, we report the synthesis, characterization, and oxidation of alcohols catalyzed by ruthenium(II) unsymmetrical Schiff-base [ONNO] complexes in the presence of *N*-methylmorpholine-*N*-oxide.

2. Experimental

All reagents were of Analar or chemically pure grade. IR spectra of the complexes were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer in the

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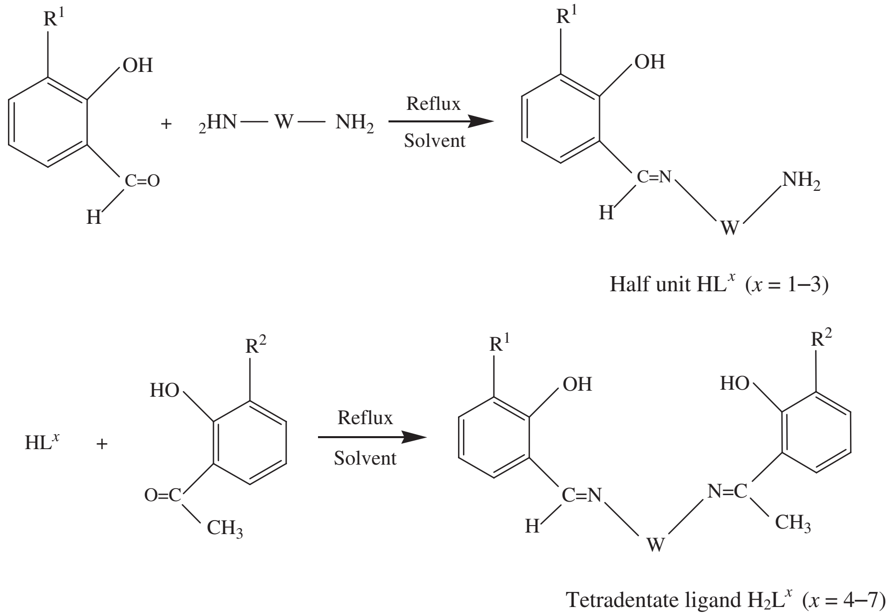


HL^1, W = $(CH_2)_2$, R^1 = H

HL^2, W = $(CH_2)_2$, R^1 = OCH_3

HL^3, W = C_6H_4, R^1 = H

H_2L^4, W = $(CH_2)_2$, R^1 = H, R^2 = H

H_2L^5, W = $(CH_2)_2$, R^1 = OCH_3, R^2 = H

H_2L^6, W = C_6H_4, R^1 = H, R^2 = H

H_2L^7, W = $(CH_2)_2$, R^1 = OCH_3, R^2 = C_4H_4

Scheme 1. Overall synthesis for preparation of half units and tetradentate Schiff bases.

400–4000 cm^{-1} range. Electronic spectra were recorded in CH_2Cl_2 using a Shimadzu UV-1650 PC spectrophotometer from 200 to 800 nm. ^1H NMR spectra were recorded on a Jeol GSX-400 using $CDCl_3$ as solvent. Elemental analyses were performed at the Central Drug Research Institute, Lucknow, India. Melting points were recorded on a Technico micro heating table and are uncorrected.

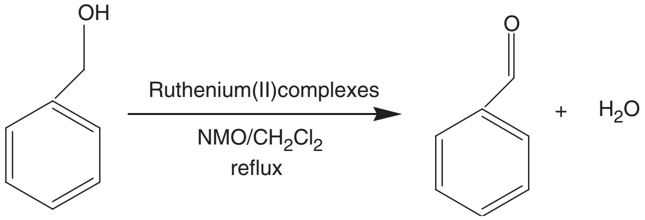
2.1. *Preparation of unsymmetrical tetradentate Schiff-base ligands*

The unsymmetrical tetradentate Schiff-base ligands were prepared by a two-stage process (Scheme 1). In the first stage, the half-unit HL^x ([$x = 1–3$] L^1 = salen, L^2 = valen, L^3 = salphen) is prepared by condensation of salicylaldehyde or *o*-vanillin with ethylenediamine or phenylenediamine in a 1 : 1 molar ratio [8]. In the second stage, to the well-stirred solution of HL^x (3 mmol) in 50 cm^3 $CHCl_3$, a solution of *o*-hydroxyacetophenone or 2′-hydroxy-1′-acetonaphthone (3 mmol) in 30 cm^3 of $CHCl_3$ was added. After the addition was complete, the mixture was stirred for 30 min and then refluxed for 2 h. The resulting solution was concentrated under vacuum. The obtained ligands (H_2L^x [$x = 4–7$] L^4 = salen-*o*-hyac, L^5 = valen-*o*-hyac, L^6 = salphen-*o*-hyac,

L^7 = valen-2-hacn) were filtered, washed with cold solvent, and recrystallized from chloroform.

2.2. *Synthesis of new ruthenium(II) Schiff-base complexes*

The new ruthenium(II) unsymmetrical Schiff-base complexes were achieved by reacting ligands with ruthenium(II) precursors $[RuHCl(CO)(PPh_3)_3]$ [9], $[RuHCl(CO)(AsPh_3)_3]$ [10], or $[RuHCl(CO)(Py)(PPh_3)_2]$ [11] in benzene (30 cm^3) under reflux for 5 h in equimolar ratio yielding $[Ru(CO)(B)(L^x)]$ (B = Py, PPh_3, or $AsPh_3$, L^x = dianion of tetradentate unsymmetrical Schiff-base ligands ([x = 4–7] L^4 = salen-*o*-hyac, L^5 = valen-*o*-hyac, L^6 = salphen-*o*-hyac, L^7 = valen-2-hacn).



2.3. *Procedure for catalytic oxidation*

Catalytic oxidation of benzylalcohol to benzaldehyde was studied in the presence of NMO as co-oxidant. A typical reaction using the complex as a catalyst and benzylalcohol as substrate 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 a solution of substrate (1 mmol) and NMO (3 mmol) and molecular sieves. The solution mixture was stirred for 3 h at room temperature and the solvent was then evaporated to dryness. The solid residue was extracted with petroleum ether (60–80°C) ($3 \times 10\,cm^3$) and the combined extracts were filtered and evaporated to give aldehyde which was quantified as the 2,4-dinitrophenylhydrazone derivative [12].

3. Results and discussion

Characterizations of these complexes were performed by elemental analysis, FT–IR, UV–Vis and ^1H NMR spectral methods. Elemental analysis (C, H, and N) of all the complexes (table 1) is consistent with the structure.

3.1. *Infrared spectral analysis*

In the IR spectra of the free Schiff bases (table 2) a strong band at 1635–1615 cm^{-1} is characteristic of the azomethine group; in the spectra of the complexes, this band is shifted to 1631–1579 cm^{-1}, indicating coordination through azomethine nitrogen [13]. A strong band at 1283–1259 cm^{-1} in the free Schiff-base assigned to phenolic C–O stretching shifts to higher frequency 1323–1303 cm^{-1} in the complexes showing coordination through the phenolic oxygen [14]. The strong absorption around

Table 1. Analytical data of the ruthenium(II) unsymmetrical Schiff-base complexes.

Complexes	Color	Yield (%)	m.p. (°C)	Calcd (found) (%)		
				C	H	N
[Ru(CO)(PPh$_3$)(L^1)]	Green	75	260	64.37(64.30)	4.65(4.64)	4.17(4.25)
[Ru(CO)(AsPh$_3$)(L^1)]	Green	68	145	60.41(60.22)	4.37(4.31)	3.91(3.78)
[Ru(CO)(py)(L^1)]	Green	73	150	56.55(56.44)	4.33(4.42)	8.60(8.53)
[Ru(CO)(PPh$_3$)(L^2)]	Green	81	146	63.33(63.12)	4.74(4.95)	3.99(3.79)
[Ru(CO)(AsPh$_3$)(L^2)]	Green	56	160	59.59(59.48)	4.46(4.40)	3.76(3.71)
[Ru(CO)(py)(L^2)]	Green	69	140	55.59(55.51)	4.47(4.52)	8.10(8.22)
[Ru(CO)(PPh$_3$)(L^3)]	Green	76	264	66.75(66.68)	4.34(4.29)	3.89(3.85)
[Ru(CO)(AsPh$_3$)(L^3)]	Brown	83	134	62.91(62.74)	4.09(4.01)	3.67(3.63)
[Ru(CO)(py)(L^3)]	Green	68	265	60.44(60.27)	3.94(3.85)	7.83(7.96)
[Ru(CO)(PPh$_3$)(L^4)]	Brown	74	175	65.50(65.34)	4.69(4.58)	3.73(3.62)
[Ru(CO)(AsPh$_3$)(L^4)]	Brown	81	155	61.89(61.72)	4.43(4.59)	3.52(3.67)
[Ru(CO)(py)(L^4)]	Brown	64	150	55.59(55.48)	4.47(4.36)	8.10(8.03)

Table 2. IR absorption frequencies (cm^{-1}) and electronic spectral data (nm) of free ligands and their ruthenium(II) unsymmetrical Schiff-base complexes.

Compound	$\nu_{\mathrm{C=N}}$	$\nu_{\mathrm{C–O}}$	$\nu_{\mathrm{C\equiv O}}$	$\lambda_{\max}$ (ε) (dm^3 mol^{-1} cm^{-1})
L^1	1635	1283	–	–
L^2	1634	1268	–	–
L^3	1630	1259	–	–
L^4	1615	1277	–	–
[Ru(CO)(PPh$_3$)(L^1)]	1601	1312	1932	233(31162), 222(29240)
[Ru(CO)(AsPh$_3$)(L^1)]	1631	1303	1920	232(31065), 224(29958), 369(21476)
[Ru(CO)(py)(L^1)]	1603	1313	1938	216(28360), 234(31940), 371(20849)
[Ru(CO)(PPh$_3$)(L^2)]	1605	1327	1934	236(32570), 367(20936)
[Ru(CO)(AsPh$_3$)(L^2)]	1606	1307	1923	232(31060), 215(28190), 340(23960)
[Ru(CO)(py)(L^2)]	1602	1316	1933	220(28974), 234(31572), 379(19485)
[Ru(CO)(PPh$_3$)(L^3)]	1601	1323	1933	233(31162), 268(33561), 334(24894)
[Ru(CO)(AsPh$_3$)(L^3)]	1599	1314	1962	262(32698), 272(33978), 333(24956)
[Ru(CO)(py)(L^3)]	1600	1322	1938	232(31065), 333(24956)
[Ru(CO)(PPh$_3$)(L^4)]	1596	1316	1943	233(31162), 219(28674), 312(28190)
[Ru(CO)(AsPh$_3$)(L^4)]	1579	1311	1960	217(28847), 234(31940)
[Ru(CO)(py)(L^4)]	1602	1320	1935	224(29958), 236(32570), 360(22374)

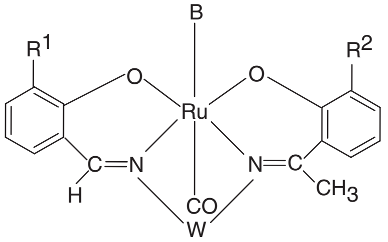
1962–1920 cm^{-1} is assigned to the terminally coordinated carbonyl in the complexes. Complexes containing coordinated heterocyclic nitrogen [11] have a medium intensity band in the region 1000–1025 cm^{-1}. Characteristic bands due to triphenylphosphine and arsine are also present in the expected regions.

3.2. *Electronic spectral analysis*

The electronic spectra of all the complexes in CH$_2$Cl$_2$ show three bands in the region 215–379 nm (table 2). Bands at 379–312 nm are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$; bands from 265 to 230 nm have been assigned as charge transfer transitions in conformity with the assignment for similar complexes [15].

Table 3. ^{1}H NMR data (δ in ppm) of ruthenium(II) complexes.

Complexes	^{1}H NMR (ppm)
[Ru(CO)(AsPh$_3$)(L^1)]	1.31 (s, CH$_3$); 3.90 (s, (CH$_2$)$_2$; 7.9–7.05 (m, phenyl))
[Ru(CO)(py)(L^2)]	4.10 (s, OCH$_3$); 3.90 (s, (CH$_2$)$_2$; 7.9–7.20 (m, phenyl))
[Ru(CO)(PPh$_3$)(L^4)]	4.21 (s, OCH$_3$); 3.92 (s, (CH$_2$)$_2$; 7.5–7.15 (m, phenyl))
[Ru(CO)(AsPh$_3$)(L^3)]	1.35 (s, CH$_3$); 7.9–7.05 (m, phenyl)



(B=AsPh$_3$ or PPh$_3$; R^1=H or OCH$_3$; R^2=H or C$_4$H$_4$; W=(CH$_2$)$_2$ or C$_6$H$_4$)

Figure 1. Proposed structure of ruthenium(II) unsymmetrical Schiff-base complexes.

3.3. *^{1}H NMR spectral analysis*

Coordination of the Schiff bases in the ruthenium(II) complexes is confirmed by ^{1}H NMR spectra (table 3). In NMR spectra of complexes, the peak at 1.76 ppm is assigned to the methyl protons of the Schiff-base. The signal for aromatic protons are multiplets in the 7.91–7.00 ppm region. Methylene protons appear as a singlet at 3.9 ppm [16] and a sharp singlet at 4.10–4.21 ppm indicates the presence of methoxy in the complexes [17].

Based on the analytical and spectral data, an octahedral structure (figure 1) has been proposed for the ruthenium(II) unsymmetrical Schiff-base complexes.

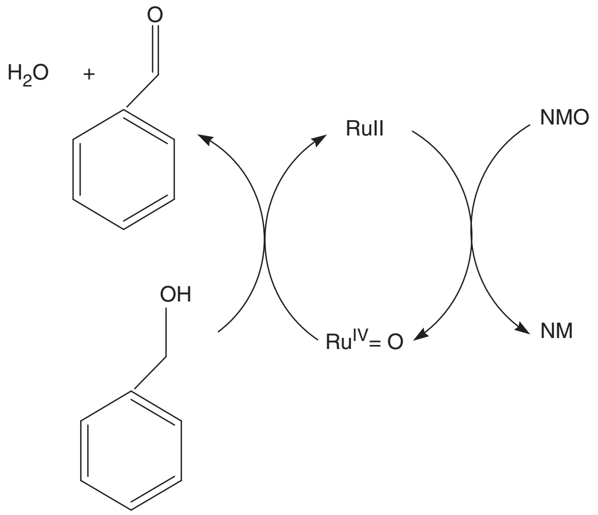
3.4. *Catalytic activity of the complexes*

Catalytic oxidation of benzylalcohol by all the synthesized ruthenium(II) unsymmetrical Schiff-base complexes was carried out in CH_2Cl_2 in the presence of *N*-methylmorpholine-*N*-oxide and the by-product water was removed using molecular sieves. The results are summarized in table 4. A series of control experiments suggest that $RuCl_3 \cdot 3H_2O$, Ru(II) precursors, ligands and *N*-methylmorpholine-*N*-oxide, alone or as a mixture, causes these transformations under identical reaction conditions, confirming necessity of ruthenium(II) complex for catalysis.

Benzaldehyde was formed from benzylalcohol after 3 h under reflux. The aldehyde was quantified as the 2,4-dinitrophenylhydrazone derivative. The complexes react efficiently with *N*-methylmorpholine-*N*-oxide to yield a ruthenium-oxo species [18, 19] capable of oxygen transfer to alcohols. This was further supported by changes that occur on addition of *N*-methylmorpholine-*N*-oxide to a dichloromethane solution of

Table 4. Catalytic activity of ruthenium(II) unsymmetrical Schiff-base complexes for conversion of benzylalcohol to benzaldehyde.

Complex	Yield (%)
[Ru(CO)(PPh$_3$)(L^1)]	39.20
[Ru(CO)(AsPh$_3$)(L^1)]	32.60
[Ru(CO)(py)(L^1)]	35.35
[Ru(CO)(PPh$_3$)(L^2)]	35.39
[Ru(CO)(AsPh$_3$)(L^2)]	39.49
[Ru(CO)(py)(L^2)]	32.23
[Ru(CO)(PPh$_3$)(L^3)]	38.90
[Ru(CO)(AsPh$_3$)(L^3)]	38.07
[Ru(CO)(py)(L^3)]	38.64
[Ru(CO)(PPh$_3$)(L^4)]	38.36
[Ru(CO)(AsPh$_3$)(L^4)]	36.13
[Ru(CO)(py)(L^4)]	37.59



Scheme 2. Proposed catalytic cycle for oxidation of alcohol by Ru(II) unsymmetrical Schiff-base complexes.

the ruthenium(II) complexes. The appearance of the peak at 380 nm is attributed to the formation of Ru(IV) = O species, in conformity with other ruthenium(IV)-oxo complexes [19–21]. The ruthenium(II) unsymmetrical Schiff-base complexes have moderate catalytic efficiency for oxidation of benzylalcohol (Scheme 2).

4. Conclusions

We have synthesized and characterized a series of ruthenium(II) unsymmetrical Schiff-base complexes and studied their catalytic properties towards the oxidation of alcohol. The new complexes exhibit promising catalytic activity.

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